Ammonia at sea:

Studying the potential impact of ammonia as a shipping fuel on marine ecosystems

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Ammonia as a Shipping Fuel: Impacts of large spill scenarios

Environmental Assessment Report

November 2022

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Approved by: S Coates

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S Coates, Dr. L Dawson, Dr. J Ware and L Vest

Executive Summary

Ammonia is being considered as an alternative, sustainable fuel source. The maritime industry has experience with the carriage of ammonia in gas carriers and the use of ammonia as a refrigerant. However, the introduction of ammonia as a shipping fuel creates new challenges related to safe ammonia fuel bunkering, storage, supply and consumption for different ship types, as ammonia is toxic if released into the environment. Therefore, the potential impacts of ammonia as a fuel in the shipping industry on aquatic environments need to be identified and assessed.

This study focused specifically on the impacts of acute large-event spills of ammonia used as a shipping fuel, that can occur during bunkering or in the case of a ship's collision and sinking. The report does not consider the effect of chronic low-level spills and atmospheric emissions of ammonia or its combustion by-products. The potential environmental consequences were assessed for riverine, transitional and marine habitats where a spill may occur. This included rivers, estuaries, wetlands, coastal waters, coral reefs, mangroves, polar regions and the deep sea. The impacts on ecological receptors within each aquatic habitat were also considered. This included bacteria, plankton, macrophytes, invertebrates, fish, birds, reptiles, and marine mammals. Outputs were then compared to marine gas oil (MGO) to enable an assessment of environmental impacts.

Abiotic parameters fluctuate to varying degrees within different habitat types and therefore, the sensitivity of each habitat to an ammonia spill varies. This is because abiotic parameters including temperature, pH and salinity influence the form of ammonia present and thus the toxicity.

Estuaries, mangroves and wetlands are particularly sensitive, while the polar regions and the deep sea are less so. Within these habitats, it is typically fish which are the most sensitive to an ammonia spill, with birds and mammals to a lesser degree.

Reports of the environmental impacts of oil spills (heavy fuel oil, MGO and crude oil) show high impacts on invertebrates and birds, compared to ammonia spills which have a high impact on fish. Additionally, ammonia has a medium impact on all other ecological receptors, except bacteria, while oil spills have lower impacts on plankton, fish and marine mammals.

In conclusion, the use of ammonia as a shipping fuel could impact on aquatic environments and associated ecological receptors if a spill were to occur without mitigation measures and solid spill management practices (see Table A and B). Therefore, a robust regulatory framework establishing suitable mitigation measures needs to be developed for ammonia to be a viable low-carbon alternative for shipping.

This study does not consider all environmental and health impacts of ammonia as a shipping fuel. This is a first look at the risks of using ammonia in this context. Additional research is needed to evaluate the full range of ecological and health implications of ammonia used as a shipping fuel, including the increased nitrogen deposition from chronic ammonia spills and combustion by-products. Due to a lack of real-world data for ammonia fuel spills in aquatic environments, the impacts of ammonia on habitats and ecological receptors have been discussed using available literature in relation to natural or run-off ammonia sources. These are more ambient or chronic inputs of ammonia, dissimilar to episodic releases of ammonia fuel. A knowledge gap identified in this report pertains to the potential impacts of an ammonia spill on ecological receptors in the deep sea and on birds (specifically seabirds, waders and wildfowl), marine mammals and aquatic reptiles.

Future studies should investigate the full risk profile of ammonia as a shipping fuel, introduced at a large scale and what feasible and effective mitigation measures should be implemented to manage these risks.

Table A High-level summary of potential impacts of an ammonia spill on aquatic habitats.

Habitat	Key impacts of ammonia
Rivers	Increase in algal growth and biochemical oxygen demand could lead to eutrophication. Toxicity to fauna could have implications on food chain dynamics.
Estuaries	Increase in algal growth and biochemical oxygen demand could lead to eutrophication. Toxicity to fauna could have implications on food chain dynamics.
Wetlands	Increase in algal growth and biochemical oxygen demand could lead to eutrophication. Toxicity to fauna could have implications on food chain dynamics.
Coastal Waters	Increase in algal growth and biochemical oxygen demand could lead to eutrophication and smothering of intertidal habitats. Toxicity to fauna could have implications on food chain dynamics.
Coral Reefs	Increase in algal growth and biochemical oxygen demand could lead to eutrophication and smothering of intertidal habitats. Toxicity to fauna could have implications on food chain dynamics.
Polar regions	Changes in phytoplankton and ammonia oxidising organism population abundance. Toxicity to fauna could have implications on food chain dynamics.
Mangroves	Potential beneficial effects on mangrove growth and ecosystem health as nutrient limited systems. However, could result in stunted growth, increased sensitivity to drought and hypersalinity. Toxicity to fauna could have implications on food chain dynamics.
Deep Sea	Unknown impacts.

Table B High-level summary of potential impacts of an ammonia spill on ecological receptors.

Ecological receptors	Key impacts of ammonia
Bacteria	Elevated growth until tolerance threshold exceeded, causing a reduction in reproductive success via slower cell growth and mortality at toxic levels.
Plankton	Elevated growth until tolerance threshold exceeded which alters the ionic equilibrium, causing inhibited growth and photosynthesis and mortality at toxic levels.

Macrophytes	Elevated growth until tolerance threshold exceeded which alters the ionic equilibrium, causing inhibited growth and photosynthesis and mortality at toxic levels.
Invertebrates	Reduction in growth and reproductive rate and mortality at toxic levels.
Reptiles	Physiological damage and mortality at toxic levels, impacts on habitat quality and prey availability.
Fish	Physiological damage and mortality at toxic levels, impacts on habitat quality and prey availability.
Birds	Physiological damage and mortality at toxic levels, impacts on habitat quality and prey availability.
Marine mammals	Physiological damage and mortality at toxic levels, impacts on habitat quality and prey availability.

Key Words

Ammonia, toxicity, shipping fuel, aquatic environments, habitats, ecological receptors, PHAST modelling and marine gas oil comparison.

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Contents

List of Abbreviations

ABS	American Shipping Bureau
AOA	Archaea
AOB	Ammonia-oxidising Bacteria
CH4	Methane
CO2	Carbon Dioxide
EDF	Environmental Defense Fund
EPA	Environmental Protection Agency
EQS	Environmental Quality Standards
ESAS	European Seabird at Sea
HFO	Heavy Fuel Oil
ITOPF	International Tanker Owners Pollution Federation
JNCC	Joint Nature Conservation Committee
LNG	Liquid Natural Gas
LRMDH	Lloyds' Register Maritime Decarbonisation Hub
MGO	Marine Gas Oil
NH3	Ammonia (unionised), NH4 – Ammonium cation
NO2	Nitrogen Dioxide
NOEC	No Observed Effect Concentration
NOx	Nitrogen Oxide
PHAST	Process Hazard Analysis Software Tool

Ammonia as a Shipping Fuel

1. Introduction

The Environmental Defense Fund (EDF) is seeking to understand the potential environmental risks of using ammonia (NH_3)[1] as an alternative marine fuel. It is well understood that global energy production needs to transition from fossil fuels to less environmentally damaging sources, to reduce pollutant release and meet the Paris Agreement/countries' climate goals. This includes the shipping sector, which is under increasing pressure to decarbonise via a shift from fossil fuels and the identification and application of sustainable alternative fuels. It is estimated that maritime shipping emits approximately 1,056 million tonnes of carbon dioxide per annum and is responsible for an estimated 2.89 % of all greenhouse gas emissions[2]. The International Maritime Organisation has set targets of reducing carbon dioxide emissions from shipping by at least 50% by 2050, in comparison with the 2008 baseline[3].

Ammonia produced with renewable energy is being considered as an alternative, sustainable fuel source. Therefore, the potential impacts of ammonia as a fuel in the shipping industry on aquatic environments need to be identified and assessed. Although the toxicity of ammonia in the aquatic environment is well understood[4,5] there is currently a lack of literature investigating the impacts of ammonia release when being used as a shipping fuel and the safety regulations, training and emissions mitigations that will be required to prevent significant impacts to aquatic ecosystems and associated species[6,7]. This report aims to investigate the potential environmental risks of an ammonia spill from different fuel

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[1] 'Ammonia' in text should be taken to refer to NH_3, unless otherwise stated

[2] International Maritime Organization (2020) Fourth International Maritime Organization Greenhouse Gas Study 2020. Accessed from: [Greenhouse Gas Emissions (imo.org)]

[3] Mallouppas, G., Ioannou, C and Yfantis, E. A. (2022). A Review of the Latest Trends in the Use of Green Ammonia as an Energy Carrier in Maritime Industry. *Energies*, **15**, 1453.

[4] Constable, M., Charlton, M., Jensen, F., McDonald, K., Craig, G. and Taylor, K. W. (2010). An Ecological Risk Assessment of Ammonia in the Aquatic Environment. *Human and Ecological Risk Assessment: An International Journal*, **2**, 527-548.

[5] Randall, D. J. and Tsui, T. K. N. (2002). Ammonia toxicity in fish. *Marine Pollution Bulletin*, **1 – 12**, 17 – 23.

[6] Cames, M., Wissner, N. and Sutter, J. (2021). Ammonia as a marine fuel, risks and perspectives. Öko-Institute.

[7] Green Shipping Programme (2020). Ammonia as a marine fuel, safety handbook. 1 – 25.

storage types under varying abiotic conditions. The assessment will consider potential impacts on freshwater, brackish and marine habitats and associated ecological receptors. The outcomes of the assessment will be compared to spills of marine gas oil (MGO), to set the level of environmental risks in context.

1.1. Ammonia as a Fuel

The basis for using ammonia as a fuel has been investigated since the early 20th century. An example of the application of ammonia as a fuel was when, in 1943, Emeric Kroch developed ammonia/coal gas hybrid motors to keep public transportation in operation, despite diesel shortages during World War II[8]. Once the shortages ceased in 1945, hydrocarbon-based fuels became the main fuel source due to comparatively low prices. However, the use of ammonia as a sustainable fuel has gained global traction in recent years, particularly in the shipping industry[9]. Research into the applications of ammonia as a marine fuel date back to 2018 and in 2022, the 'world's' first ammonia-ready ship' was produced by China's New Times Shipbuilding Co., Ltd. The American Bureau of Shipping (ABS) classed, the Suezmax tanker Kriti Future conformed to the requirements outlined in the ABS Guide for Gas and Other Low-Flashpoint Fuel Ready Vessels; though it is noted that the Kriti Future is currently conventionally fuelled and that it complies with the ABS Ammonia Ready Level 1 requirements, indicating it is designed to be converted to run on ammonia in the future. Other ammonia-related projects in the maritime sector include the Global Maritime Forum that launched 'Nordic Green Ammonia Powered Ship' which aims to deploy the first ammonia-powered deep sea vessel by 2025 and MAN Energy Solutions, which aims to have two commercially available two-stroke ammonia engines by 2024[10]. Such projects will aid in understanding of the efficiency of using ammonia as a fuel, economical viability and appropriate safety regulations.

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[8] Zamfirescu, C, Dincer, I. (2008). Using ammonia as a sustainable fuel. Journal of Power Sources, 185. Pp 459–465

[9] Mærsk Mc Kinney Møller Center for Zero Carbon Shipping (2021). Position Paper Fuel Option Scenarios, October 2021.

[10] Landstrand, N. (2022). Unlocking ammonia's potential for shipping. MAN Energy Solutions. Accessed from: The case for two-stroke ammonia engines (man-es.com).

The global interest in ammonia as a shipping fuel is because it can potentially be combusted in an environmentally benign way, exhausting only water and nitrogen[11] which means zero tank-to-wake carbon dioxide emission. Moreover, so-called ‘green’ ammonia (made with renewable energy) means zero emission can be achieved on a well-to-wake basis. However, when ammonia is combusted in large, internal combustion engines, nitrogen oxide (NO_x) emissions are produced. Additionally, ‘ammonia slip’ can be produced during combustion, where the ammonia is subsequently catalysed to nitrogen dioxide (NO_2); a potent pollutant which causes respiratory issues and reacts in the atmosphere to form secondary pollutants including ozone and acid rain. These emissions of ammonia and NOx can affect ecological systems when they deposit onto surface water.

In addition, the process of making ammonia is currently not a “green” process as it is commonly made from fossil-derived methane (CH_4), water and air, using steam methane reforming (to produce the hydrogen (H_2)) and the Haber process (also known as Haber-Bosch)[12]. This produces carbon dioxide, ~90 % of which is produced from the steam methane reforming process. This process consumes a lot of energy and produces around 1.8 % of global carbon dioxide emissions[13].

‘Green ammonia’ production is where the process of making ammonia can be 100 % renewable and carbon-free. One method of making ammonia is by using hydrogen from water electrolysis and nitrogen (N) separated from the air, where the electricity for the electrolysis is derived from renewable resources. These are then fed into the Haber process which is also powered by renewable electricity. In the Haber process, hydrogen and nitrogen are reacted together at high temperatures and pressures to produce ammonia. As ammonia is a globally traded commodity with existing global logistics transport infrastructure, it does not require cryogenic storage, is relatively energy-dense as a liquid and is less flammable, it is considered advantageous in comparison to other fuels such as hydrogen and battery storage[14].

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[11] Strickland, G. (1980). Ammonia as a hydrogen energy storage medium, in Proceedings of the 5th Annual Thermal Storage Meeting, Paper 8010555-2, 10th October 1980, McLean, VA, USA.
[12] Ash, N., and Scarbrough, T. (2019). Sailing on solar: Could green ammonia decarbonize shipping? Environmental Defense Fund. 1 – 62.
[13] The Royal Society. (2020). Ammonia: zero-carbon fertiliser, fuel and energy store.
[14] Barrios, K. (2020). Ammonia: Another Maritime Fuel of the Future? Xeneta.

Although the potential use of ammonia as a shipping fuel is gaining traction[15], there are potential risks to human health and welfare and the receiving environment from ammonia spills and combustion by-products. These risks must be well characterized and fully addressed for ammonia to become a viable fuel for shipping. There are currently no health, safety or environmental guidelines for ammonia as a shipping fuel, although in discussion[16]. The implications of its application and potential risk factors must be well understood to inform these future guidelines and ensure the safety of both humans and the environment.

1.2. Advantages of Ammonia as a Fuel

There are several advantages of using ammonia as a fuel which have been identified from a practical and environmental perspective. These include (and are not limited to) the following:

There is existing distribution infrastructure for ammonia as the second most commercialised chemical in the world to deliver it in large quantities (approximately 100 million tons per annum[17]). However, it is noted that this is not the case for use of ammonia as an energy carrier[18].

Ammonia is stored as a pressurised liquefied gas (like propane), at around 8 bar vapour pressure at room temperature1, or alternatively as a refrigerated liquefied gas (like LNG) at 1 bar vapour pressure and at < -33 °C. In contrast, hydrogen must be cooled to -253 °C or pressurised to between 35 MPa to 70 MPa (350 bar to 700 bar) to be stored as a liquid[19]

Ammonia can be transported as a liquid with significantly higher energy density than as a gas. As a fuel, it has a narrow flammability range (when not mixed with air) and therefore, flammability is less of a concern during most storage and transportation.

If released into the atmosphere from atmospheric refrigerated storage, ammonia's density is lighter than that of air, which aids in dissipation. Though it should be noted that

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15 Mærsk Mc-Kinney Møller Center. (2021). Position Paper Fuel Option Scenarios.
16 Green Shipping Programme (2020). Ammonia as a marine fuel, safety handbook. 1 – 25.
17 J.O. Jensen, A.P. Vestbo, Q. Li, N.J. Bjerrum, J. (2007.) Alloys Compd. 446-447. Pp 723–728
18 Razon, L. F. and Valera-Medina, A. (2021). A Comparative Environmental Life Cycle Assessment of the Combustion of Ammonia/ Methane Fuels in a Tangential Swirl Burner. Frontiers in Chemical Engineering. 1 – 13.
19 Vries, N. de (2018). Ammonia: a new way of fuelling the marine industry. Cruise & Ferry. Accessed from: http://www.cruiseandferry.net/articles/ammonia-a-new-way-of-fuellingthe-marine-industry.

refrigerated ammonia is liquefied under pressure, which upon release to the atmosphere will aerosolize and forms a dense, visible white cloud of ammonium hydroxide (NH_4OH).

Ammonia is synthesized either from fossil fuels, from any kind of renewable energy, or from waste heat including that from nuclear reactors[18]. Ammonia can be produced with untapped renewable energy in many parts of the world without causing any upstream emissions ('green ammonia') aiding decarbonisation efforts.

1.3. Disadvantages of Ammonia as a Fuel

There are several disadvantages to using ammonia as a fuel which have been identified from a human welfare and environmental perspective. These include (and are not limited to) the following:

Ammonia is toxic to humans. In the context of being used as a shipping fuel for passenger-carrying vessels, environmental release of ammonia during bunkering and operation would be a public health concern.

Ammonia can be toxic to terrestrial and aquatic environments and associated species if exposed. As ecosystems are currently under stress from the increasing prevalence of reactive nitrogen, the use of ammonia as a shipping fuel could exacerbate environmental degradation occurring as a result of nutrient loading in aquatic environments.

There can also be adverse effects from chronic "small" spills of ammonia as, through the nitrogen cycle, nutrients stimulate aquatic plant production, disrupting the functioning of the aquatic ecosystem through algal blooms, that can cause eutrophication and anoxia. Excess nitrogen pollution is a global phenomenon which has been linked to fertilizer overuse, sewage treatment discharge, manure management and atmospheric deposition from various sources. Global warming in aquatic environments is also accelerating these impacts. Therefore, ammonia spills from the use of ammonia as a shipping fuel could also contribute to algal blooms and their associated impacts. In addition, the combustion of ammonia produces by-products such as nitrogen oxides that contribute to air pollution and nitrogen deposition into aquatic systems.

Ammonia is more flammable when mixed with air (15 – 28 % by volume of ammonia). Ammonia canisters which are exposed to heat may expand and fracture, causing an initial primary explosion and then, potentially, the ammonia released from the canister might ignite and explode and cause a secondary explosion.

Ammonia's low energy density compared to existing maritime fuels (see Section 1.2 above), thus requiring more space.

The narrow flammability range of ammonia means it requires a pilot fuel for use in combustion engines, typically marine diesel, leading to the continued release of carbon dioxide and other pollutants. With low-speed two-stroke engines where ammonia intake is optimized, there will remain a need for a more flammable substance to ignite the fuel.

1.4. Environmental Chemistry of Ammonia

1.4.1. Chemistry of Ammonia

Ammonia consists of hydrogen (H) and nitrogen (N), with the formula NH3 (unionised). Under typical conditions (room temperature it is a colourless gas with a distinct pungent odour. When dissolved in water the NH3 molecule undergoes self-dissociation and behaves as a weak base, combining with acids to form salts containing the ammonium cation (NH4)+. In water, ammonia forms an equilibrium as seen in **Equation 1** below.

$$NH_{3(aq)} + H_2O_{(l)} \leftrightarrow NH^+_{4(aq)} + OH^-_{(aq)}$$

Equation 1 Equilibrium between ammonia and ammonium.

Different environmental factors such as temperature, pH and salinity can influence the favourability of the ammonia or ammonium species and this is shown in **Figure 1** below.

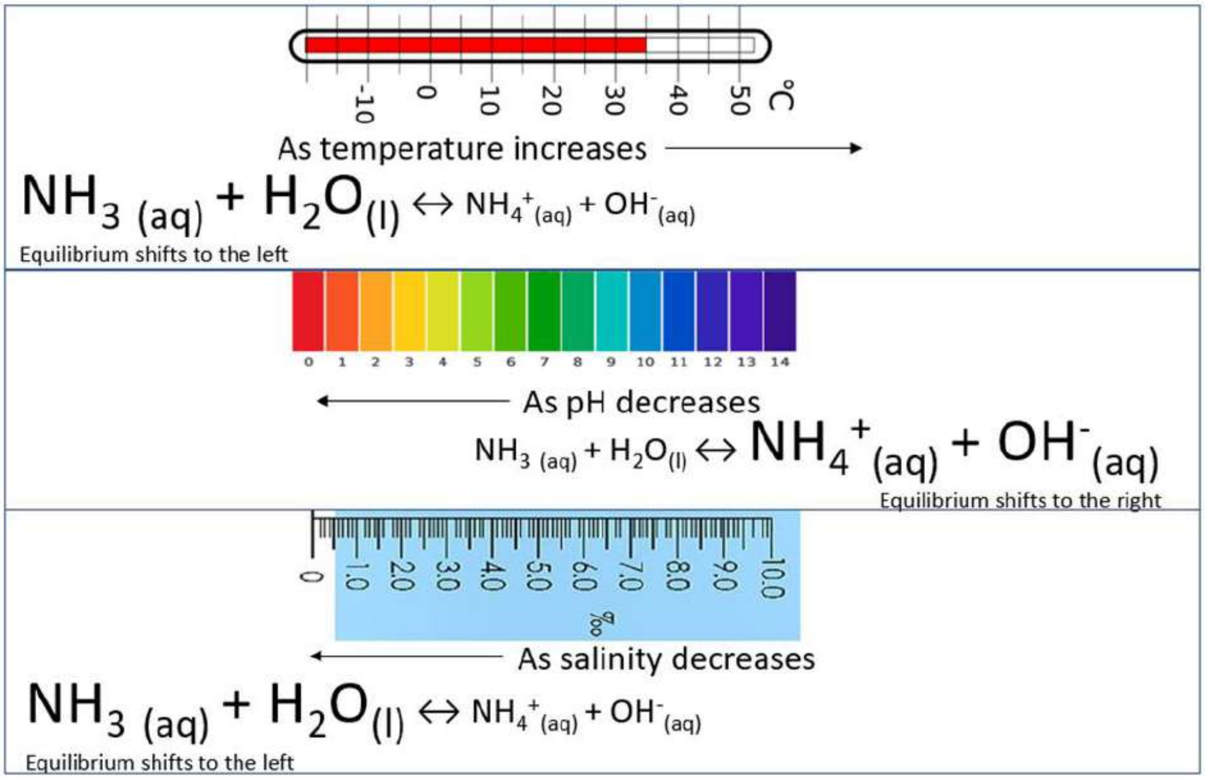

Figure 1: Chemistry of Ammonia

Further information on the chemistry of ammonia can be found in Appendix 1.

1.4.2. Ammonia within the Environment

Ammonia is a common toxicant derived from wastes, fertilizers, and natural processes. Natural sources of ammonia include the decomposition or breakdown of organic waste matter, gas exchange with the atmosphere, forest fires, animal, and human waste and nitrogen fixation processes.

As with all chemicals, ammonia behaves differently depending on its environment. Gaseous ammonia multiple complex phenomena can take place however, in general, ammonia can either be converted to (NH4)+ or subjected to dry or wet deposition. In aquatic environments, ammonia exists in equilibrium as described above and is therefore a function of temperature, pH and salinity. Further detail on the influences on ammonia species in freshwater, marine and estuarine environments can be found in Appendix 1.

1.4.3. Fate of Ammonia

While the concentration of a chemical released into the environment, as well as the habitat (air, water, or soil) into which it is released, are important factors, the environmental fate is determined by processes after the chemical has been released.

The fate of ammonia (and all chemical species) is determined by three factors: the partitioning of the chemical between environmental media, the transportation propertied of that media and the transformation rate of the chemical substance.

The nitrification cycle is an important microbial process by which nitrogen compounds are sequentially oxidised to nitrite and nitrate. This is a key environmental process and governs much of the aquatic and soil/sedimentary fate of ammonia. It is important to note that this report does not detail the environmental impact of the fate of ammonia (such as nitrate and nitrite) but the potential impact of ammonia in multiple scenarios involving large spills from individual vessels. Further detail on the fate of ammonia can be found in Appendix 1.

2. Aims and Objectives

The broad aim of this report is to assess one of the potential environmental risks of using ammonia as a shipping fuel. We examine the environmental impacts of multiple scenarios involving large spills of ammonia from individual vessels (assessed based on likelihood) and compare those to spills of MGO. The report consists of the following objectives:

- A review of the literature base and qualitative assessment of the potential environmental impacts of large ammonia spills within rivers, estuaries, wetlands, coastal waters, coral reefs, mangroves, polar regions and deep sea habitats.
- To assess the potential environmental effects within each habitat of an ammonia spill from a bulker ship, container ship and tanker ship during three-hole size scenarios (2 mm, 23 mm and 200 mm), under different weather scenarios[20].
- To assess the potential environmental effects within each habitat of a storage tank ammonia spill caused by a collision on a containership (assuming a 1200 mm hole).
- To undertake a comparison of the environmental effects of such ammonia spills and MGO.

[20] It should be noted that the effects assessed are those directly caused by a spill of ammonia and that other species of nitrogen are not considered here. Therefore, effects is assessed primarily as toxicity and does not address wider impacts such as altered ecosystems or ecological cascades.

3. Methodology

3.1. Literature Review

A literature review was produced by the Lloyds' Register Maritime Decarbonisation Hub (LRMDH) and shared with Ricardo Energy and Environment. This reviewed the relevant physical, chemical and eco-toxicological properties of ammonia as a fuel, examples of ammonia spills in the aquatic environment and recommendations for mitigating the potential impacts of ammonia spills in the aquatic environment[21]. This literature review will inform the environmental assessment provided in the report. In addition, during the completion of this report by Ricardo Energy and Environment, literature was sought on the impacts of ammonia spills in aquatic habitats and on associated ecological receptors. This was done via a 'keywords' online search and examination of publicly available literature such as peer-reviewed scientific papers, regulatory reports and guidance, and private sector published articles.

3.2. Environmental Assessment

To assess the potential environmental risks of using ammonia as a shipping fuel, aquatic habitats were identified where a spill of ammonia may occur. Ecological receptors present within each habitat were then identified and potential effects were considered (as shown in **Table 1**). To assess potential effects, a literature search was performed for each habitat and ecological receptor identified. This was then repeated for each habitat and ecological receptor for potential effects of oil spills to enable a comparison to be drawn.

[21] Lloyd's Register (2022). Environmental Safety of Ammonia as a Marine Fuel: Literature Review for EDF, pp 23.

Table 1 Habitats and ecological receptors included in the environmental assessment.

Habitat	Ecological Receptors
Rivers	Plankton, Invertebrates, Macrophytes, Fish, Reptiles, Birds and Mammals
Estuaries	Plankton, Invertebrates, Macrophytes, Reptiles, Fish, Birds and Mammals
Wetlands	Plankton, Invertebrates, Macrophytes, Fish, Birds and Mammals
Coastal Waters	Plankton, Invertebrates, Macrophytes, Reptiles Fish, Birds and Mammals
Coral Reefs	Plankton, Invertebrates, Macrophytes, Reptiles, Fish, Birds and Mammals
Polar regions	Plankton, Invertebrates, Macrophytes, Fish, Birds and Mammals
Mangroves	Plankton, Invertebrates, Macrophytes, Reptiles, Fish, Birds and Mammals
Deep Sea	Plankton, Invertebrates, Fish and Mammals

3.3. Modelling

3.3.1. Scenarios modelled

The modelling of potential ammonia spill scenarios was carried out by LRMDH using the consequence modelling package PHAST (Process Hazard Analysis Software Tool). PHAST examines the progress of a potential incident from the initial release to the far-field dispersion, including the modelling of rainout and subsequent vaporisation[22].

The model set up by LRMDH was for three different ship types each with different fuel storage types[23]:

- Containership – fully refrigerated storage conditions in a Panamax (comparatively small ship operating in regional trade);
- Bulker – pressurised storage conditions in a Post-Panamax (common size engaging in oceanic trade); and
- Tanker – semi refrigerated storage conditions of an unknown size.

[22] Witlox, H. W. M., Harper, M., Oke, A. (2012). PHAST Validation of Discharge and Atmospheric Dispersion for Pressurised Carbon Dioxide Releases. SYMPOSIUM SERIES NO. 158. Hazards XXIII.
[23] It must be noted that the selection of cases are fictive; and that, for example, the preferred storage system for a tanker could be pressurized if the design footprint would benefit from that.

These vessels have various storage conditions for liquid ammonia ($NH_{3(l)}$). The vessel and storage parameters, alongside abiotic parameters, are described in Appendix 2. Throughout this report, ‘Containership’, ‘Bulker’ and ‘Tanker’ represent the storage conditions assigned to each vessel type.

The abiotic parameters of pH and salinity were fixed within the model and so, temperature was examined for each of the above habitats (Appendix).

For each scenario described below the spill of $NH_{3(l)}$ is assumed to be above the water line.

This modelling was also conducted for an oil spill, under the same parameters, but for only a bunkering scenario.

3.3.1.1. Bunkering spills

For each vessel, three hole size scenarios were run (2 mm, 23 mm, 200 mm), and each hole scenario was run at day and at night and at various weather conditions. Appendix 2 describes the weather conditions used. The modelled holes are set in the bunker line of the vessel during the loading of fuel.

The oil spill modelling was conducted for the same hole size scenarios (though with a 219 mm hole size rather than 200 mm), day and night and for the same weather scenarios. Though it also includes the storage tank spill hole size as described below.

3.3.1.2. Collision – storage tank spill

The storage tank spill from a collision is only applicable to the containership due to the ship design. This scenario assumes a 1200 mm hole in the below-deck tank and was run at the same day/ night weather conditions as with the bunkering spills. The collision is also assessed on the basis that the ship consequently sinks.

3.3.1.3. Summary of Conditions Modelled

Various conditions were modelled for each bunkering type and these include the following conditions shown in **Table 2** and **Table 3**.

Table 2 Modelled Conditions

Condition Modelled	Description		
Ammonia Storage Type and Hole Size	Bunker 2mm, 23 mm, 200 mm	Tanker 2mm, 23 mm, 200 mm	Container Ship 2mm, 23 mm, 200 mm, 1200 mm (collision)
Day/Night (based on Rotterdam due to high rank on list of world ports for containers)	Parameter	Day	Night
	Ambient temp	12 °C	8 °C
	Water temp	9.8 °C	9.8 °C
	Humidity	76.5 %	86.3%
	Solar radiation flux	0.25 kW/m^2	0 kW/m^2
	Fraction of 24 hr period	0.44	0.56
Weather Condition	Weather conditions within the PHAST model use reference conditions for Rotterdam as it is ranked highly on the lists of world's ports for containers. Weather descriptions are composed of two parts, the Pasquill Stability Class and a wind speed full details can be found in the Table below.		

Table 3 Weather Conditions Index

Pasquill Stability Class	Wind speed (m/s)	Percentage Day	Percentage Night
B	3.0	24.50	0.00
D	1.5	11.19	15.19
D	5.0	30.76	26.06
D	9.0	33.55	21.87
E	5.0	0.00	10.85
F	1.5	0.00	26.04

The letter scale on the Pasquill Stability Test is as follows;

- A=Extremely Unstable
- B=Unstable
- C=Slightly Unstable
- D=Neutral Unstable
- E=Slightly Stable
- F=Stable

3.3.2. Output parameters

For every scenario the outputs from nine parameters were produced and defined below:

- Pool vaporisation rate - Rate at which the ammonia pool converts from liquid to gaseous phase;
- Pool temperature - Ammonia pool temperature on the water surface;
- Mass spilt - Total mass of ammonia spill;
- Mass remaining - Mass of ammonia remaining after vaporisation and dissolution has occurred;
- Mass dissolved - Mass of ammonia as a solute in liquid phase that has passed through a solvent to form a solution;
- Pool radius - distance from the centre of the ammonia pool to its perimeter;
- Pool depth - distance from the water surface to water column where ammonia is present in liquid phase;
- Mass vaporised - Mass of ammonia that has converted from liquid to gaseous phase; and
- Solution rate - time taken for ammonia as a solute in liquid phase to pass through a solvent to form a solution.

3.3.3. Gas cloud dispersion

In addition to the immediate vaporisation from the potential ammonia spill scenarios, the subsequent atmospheric dispersion of the resulting gas cloud is assessed. In the absence of specific ecological thresholds for atmospheric ammonia, predicted concentrations are compared with workplace exposure limits[24], (**Table 4**) and the areas exceeding the thresholds are quantified.

Table 4 Workplace Exposure Limits – Ammonia

Substance	Long-term exposure limit (8-hr TWA reference period)	Short-term exposure limit (15-minute reference period)
Ammonia, anhydrous	25 ppm (18 mg m^{-3})	35 (25 mg m^{-3})

EH40/2005 Workplace Exposure Limits- ammonia

The assessment is undertaken at a number of heights that follow the Joint Nature Conservation Committee (JNCC) European Seabird At Sea (ESAS) flight height bands (**Table 5**) which are used for recording bird flight[25]. The results are presented in Appendix 4.

The duration of the ammonia spill scenarios and the time taken for the spillage pools to completely evaporate, or dissolve is estimated to be a few minutes. As such, the short-term exposure limit is deemed to be more appropriate. However, due to uncertainties surrounding the use of human health thresholds for ecological assessments, both limits have been used in the comparisons.

Initial calculations suggest that deposition of ammonia for the gas cloud is negligible.

[24] EH40/2005 Workplace exposure limits (2020). Health and Safety Executive on behalf of the Controller of Her Majesty's Stationery Office.

[25] Camphuysen, K.J., Fox, A.D., Leopold, M.F. & Petersen, I.K. 2004. Towards standardised seabirds at sea census techniques in connection with environmental impact assessments for offshore wind farms in the U.K.: a comparison of ship and aerial sampling methods for marine birds, and their applicability to offshore wind farm assessments (PDF, 2.7 mb), NIOZ report to COWRIE (BAM – 02-2002), Texel, 37pp.

Table 5 Seabird Flight Height

Flight height band	Flight height
H0	0 – 5m
H1	5 – 10m
H2	10 – 20m
H3	20 – 25m
H4	25 – 180m
H5	> 180m

ESAS seabird flight height bands.

4. Results

4.1. PHAST Modelling Analysis

The range of parameters within the modelling allowed for many comparisons to be drawn both between and within the produced data. The main comparisons considered are as follows:

- Between fuel storage types (refrigerated (container), pressurised (bulker) and semi-refrigerated (tanker);
- Day and night;
- Hole sizes; and
- Between weather conditions.

However, these interact with each other to produce a multitude of comparison scenarios. A summary of the main comparisons are presented below and relevant interactions discussed. See Appendix 3 for full graphical results.

For each fuel storage type and hole size scenario, a 'scenario likelihood' was produced (**Table 6**). For each fuel storage type, the likelihood of a spill from each hole size decreases with increasing hole size. Therefore, a 2 mm hole in a Containership bunker line was the most likely spill scenario (1.15E-03 per year) and a 1200 mm hole in the storage tank of a Containership was the least likely spill scenario (7.73E-0.5 per year).

Table 6 Scenario Likelihood

Vessel	Hole size (mm)	Scenario likelihood (frequency per year)	Notes
Containership	2	1.15E-03	This information is applicable to day/night and all weather conditions.
	23	1.82E-04	
	200	1.28E-05	
	1200 (storage tank)	7.73E-05	
Bulker	2	1.23E-03	
	23	1.77E-04	

	200	1.16E-05
Tanker	2	1.20E-03
	23	1.77E-04
	200	1.16E-05

The above table describes the likelihood of each scenario with reference to each fuel storage type and hole size with a 2 mm hole on a containership most likely and a 1200 mm on a containership least likely.

4.1.1. General trends

This section describes the general trends which were noted in the PHAST modelling outputs. Each output variable is described and an example is displayed. The example figures do not show all of the scenarios and are presented for a Bulker, day and 23 mm hole scenario only.

Some general trends for each output are described below:

- Pool Vaporisation rate described in Section 4.1.1.1
- Pool Radius described in Section 4.1.1.2
- Pool Temperature described in Section 4.1.1.3
- Pool Depth described in Section 4.1.1.4
- Mass Spilt described in Section 4.1.1.5
- Mass Vaporised described in Section 4.1.1.6
- Mass Remaining described in Section 4.1.1.7
- Mass Dissolved described in Section 4.1.1.8

4.1.1.1. Pool Vaporisation Rate

Pool vaporisation rate exhibited a similar trend under the 2 mm and 23 mm scenarios in which there is an initial sharp increase followed by a sharp to steady decrease, to an eventual plateau. Under the 200 mm scenario, pool vaporisation rate showed a different pattern in which there is an initial sharp increase and decrease, followed by a steady decrease or plateau, a smaller increase and decrease and then a final steady decrease or plateau. Under the 1200 mm scenario, pool vaporisation rate follows a sharp increase which slows slightly before decreasing sharply to 0 kg/s.

In refrigeration systems, ammonia is liquefied under pressure. Any liquid ammonia released to the atmosphere will aerosolize rapidly producing a mixture of liquid and vapour. This rapid vaporisation is observed within the modelling.

During the Bulker, day and 23 mm hole scenario, peak pool vaporisation rate is reached during Category 1.5/D at approximately 5.5 kg/s after 60 seconds (shown in **Figure 2**).

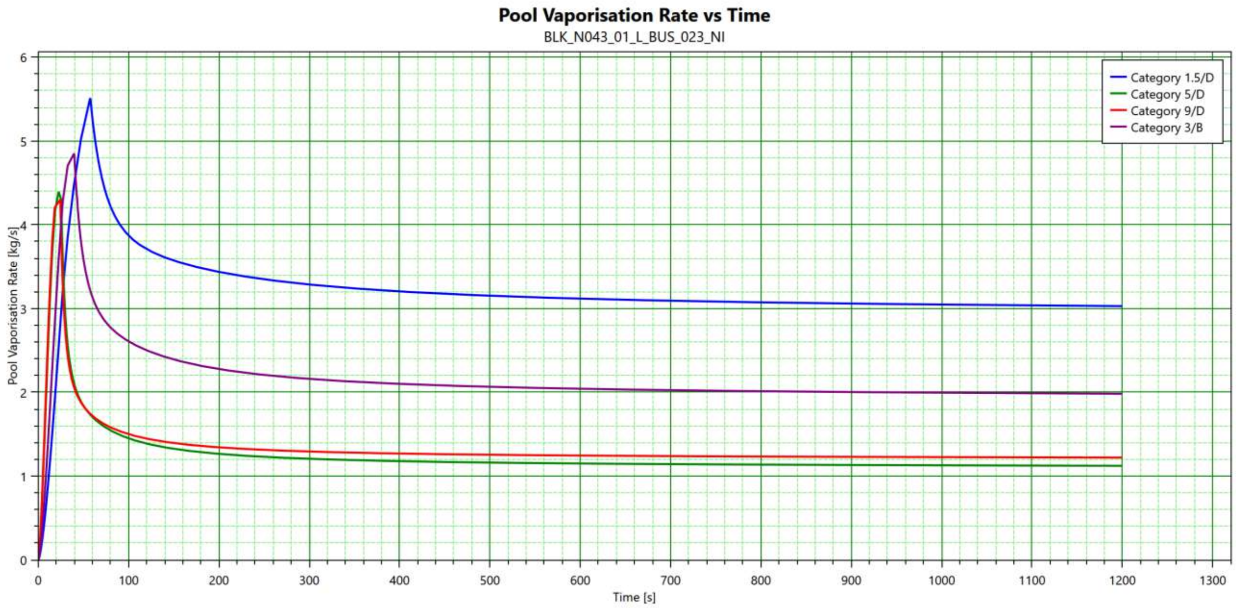

Figure 2 Pool Vaporisation Rate vs Time - Shows the Pool Vaporisation Rate for a Bulker, day and 23 mm hole scenario.

4.1.1.2. Pool radius

The pool radius results showed a general trend in which there is an initial sharp increase, followed by a steadier increase and then a plateau. This trend is generally consistent across hole size scenarios, although the gradient of the initial increase in pool radius varies considerably.

It is likely that the pool radius is limited by the size of the spill hole, with larger holes producing larger pool radii. The pool of ammonia will also be limited by the volume of ammonia which aerosolizes, see above.

During the Bulker, day and 23 mm hole scenario, peak pool radius is reached during Category 1.5/D at approximately 11.3 m after 700 seconds (shown in **Figure 3**).

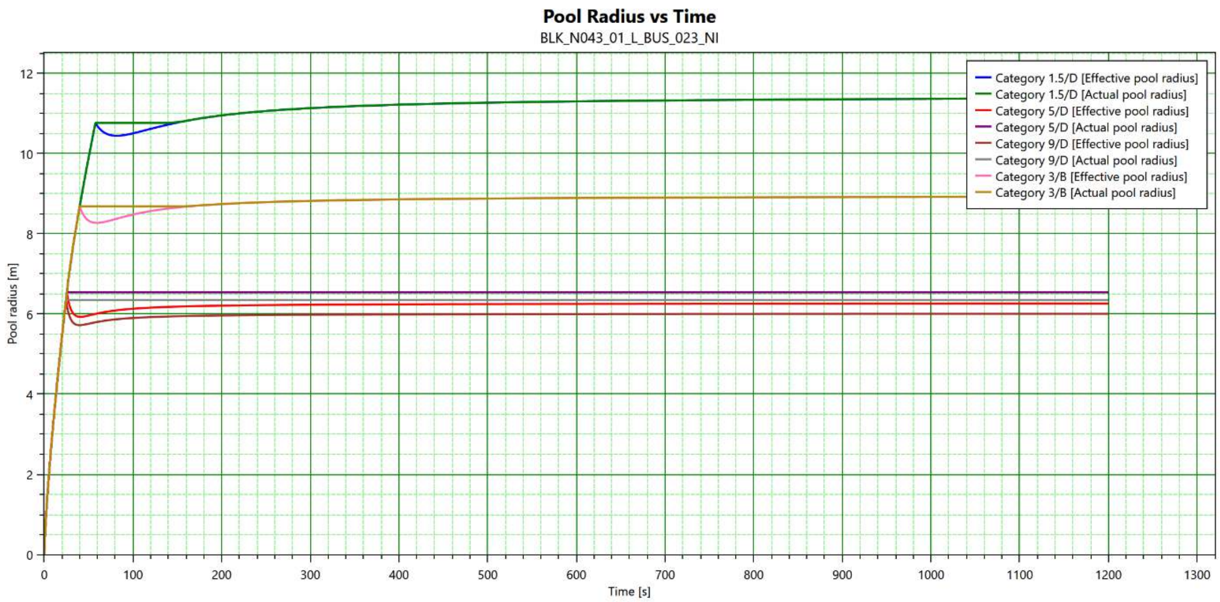

Figure 3 Pool Radius vs Time - For a bulker, day and 23 mm hole scenario

4.1.1.3. Pool temperature

The pool temperature results differ according to hole size scenario. Pool temperature under both the 2 mm and 23 mm scenarios showed an initial sharp decrease followed by a very steady decrease, eventually reaching a plateau. Under the 200 mm scenario, pool temperature showed a very sharp initial increase followed by a steady decrease, small increase and then very steady decrease or plateau depending on weather scenario. Under the 1200 mm scenario, pool temperature remains stable for at least 150 seconds before decreasing and then exhibiting either small fluctuations or a plateau.

A spill of liquid ammonia onto the water surface will cause it to evaporate. As it evaporates, heat is extracted from the surroundings and the ammonia temperature decreases as observed within the modelling results.

During Category 1.5/D, pool temperature remains at approximately -34.4 to -34.6 °C over the 1200-second period for Bunker, day and 23 mm scenario (as shown in **Figure 4**).

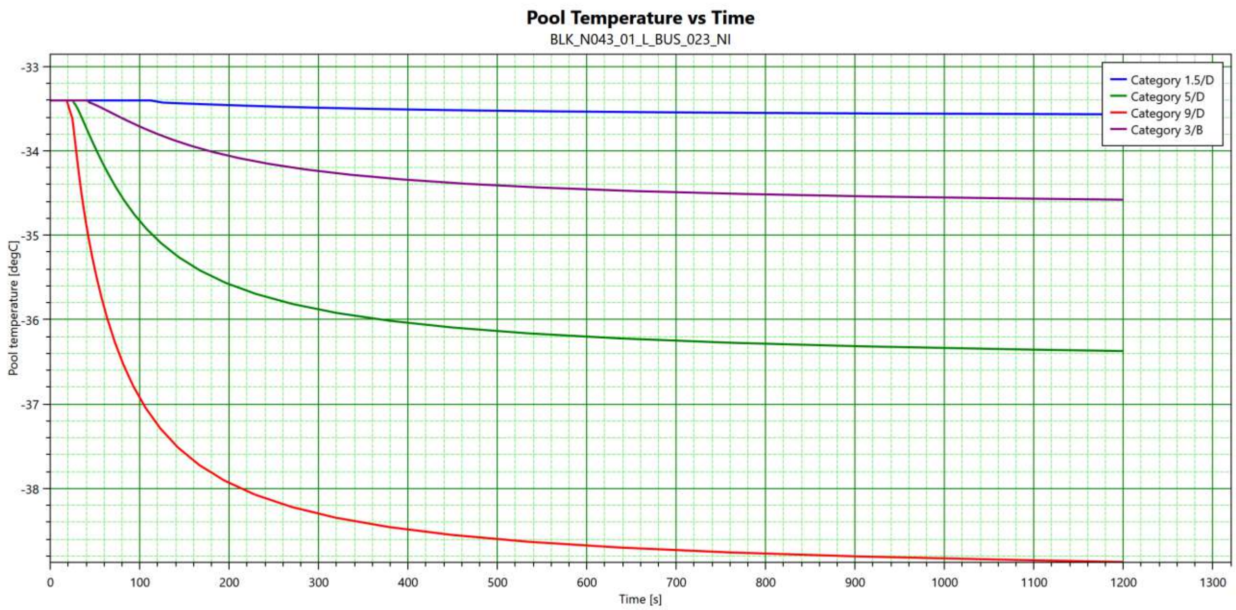

Figure 4 Pool Temperature vs Time - Pool temperature vs time for the Bunker, day and 23 mm hole scenario

4.1.1.4. Pool depth

The pool depth results showed a linear trend in which pool depth remains constant over time as shown in **Figure 5**. In the 23 mm, 200 mm and 1200 mm hole size scenarios, there is an initial increase and then steady decrease in pool depth before stabilising. Therefore, hole size, weather and time did not impact on the pool depth dynamics in the model.

It is considered that a spill of ammonia would not remain for long on the surface of the water as a pool as evaporation and dissolution would occur quickly rapidly reducing the depth of any pool (as shown in **Figure 5**).

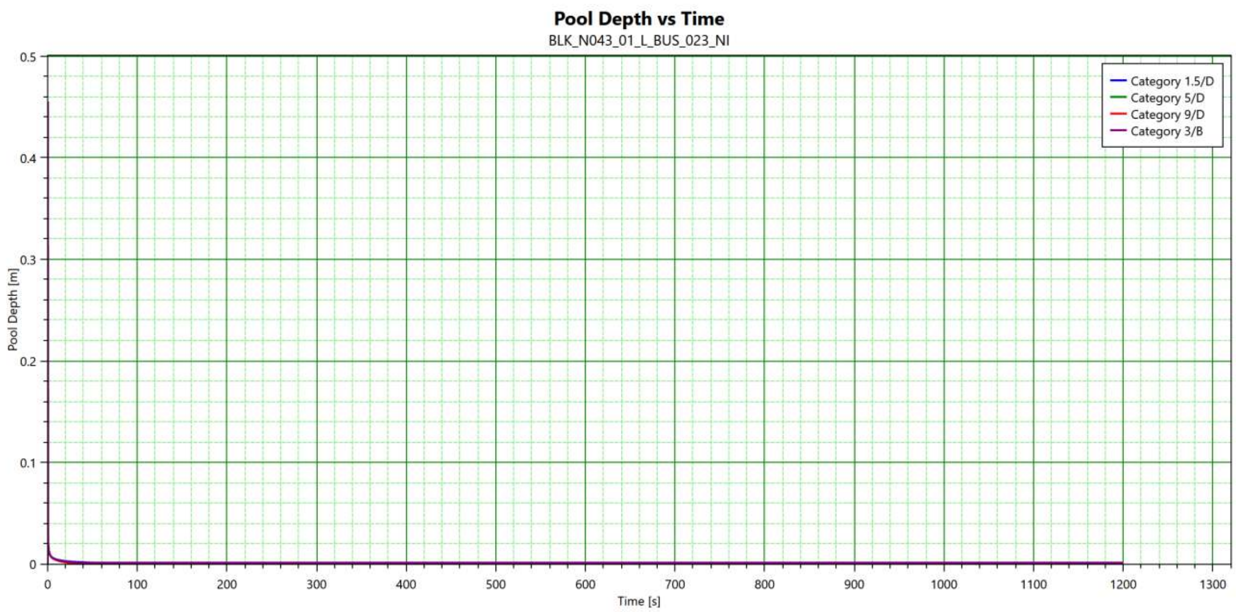

Figure 5 Pool Depth vs Time – for bunker, day and 23 mm hole scenario

4.1.1.5. Mass spilt

Under the 2 mm and 23 mm hole size scenarios, mass spilt followed a linear increase over time with little to no difference between weather scenarios (as shown in **Figure 6**). Mass spilt showed a slightly different trend under the 200 mm and 1200 mm scenarios with an initial linear increase followed by an immediate plateau.

Mass spilt is likely related primarily to the size of the hole from which the spill occurs (in the absence of mitigation measures).

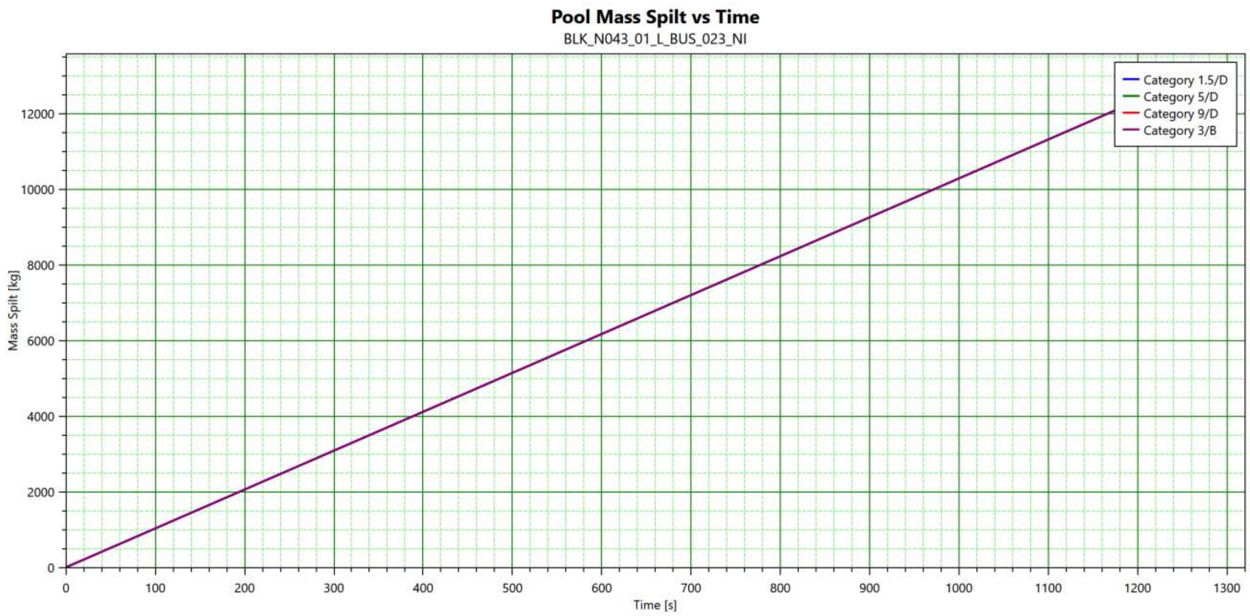

Figure 6 Pool Mass Spilt vs Time for Bunker, day and 23 mm scenario

4.1.1.6. Mass vaporised

The mass vaporised modelled results, under the 2 mm and 23 mm scenarios, showed a linear increase with slightly different gradients between weather scenarios (as shown in **Figure 7**). Under the 200 mm and 1200 mm scenarios, mass vaporised shows a general trend of a slightly delayed (~40 seconds) sharp increase which slows slightly before reaching a plateau.

The vaporisation of ammonia would likely be rapid, and the modelling indicates that this is quicker under warmer, milder weather conditions.

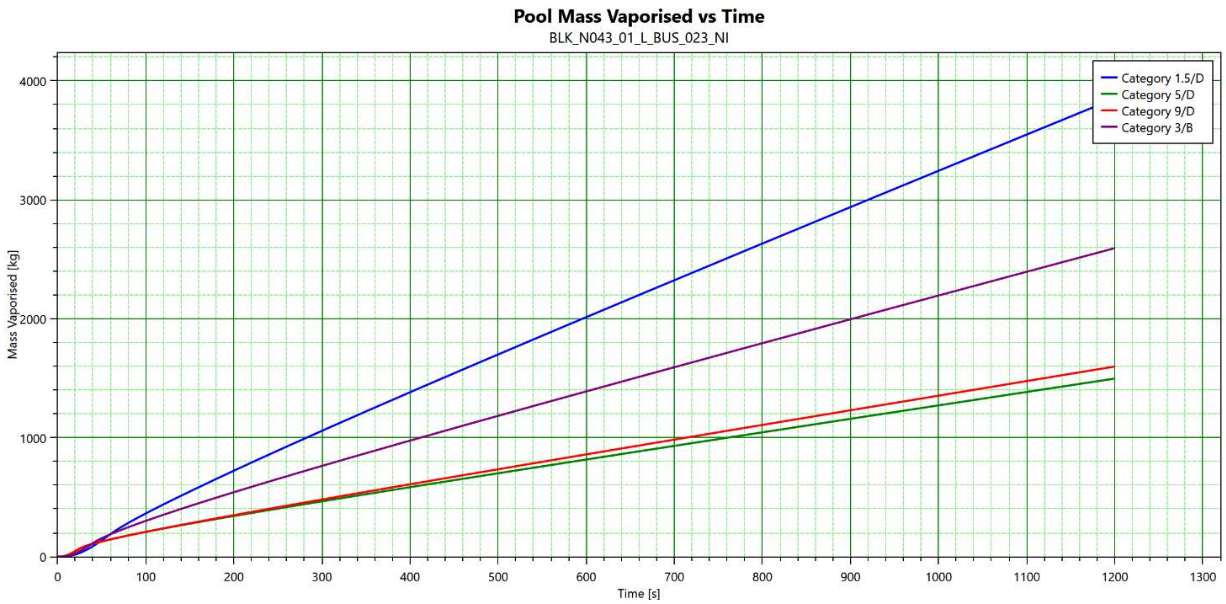

Figure 7 Pool Mass Vaporised Over Time – for bunker, day and 23 mm hole scenario

4.1.1.7.Mass remaining

The mass remaining results differ between hole size scenarios. Under the 2 mm scenario, mass remaining exhibited an initial sharp increase followed by a plateau. Under the 1200 mm scenario, mass remaining exhibited a sharp increase followed immediately by a sharp decrease to 0 kg.

Under the 23 mm scenario, mass remaining showed an initial sharp increase followed by a small decrease and then increases very steadily to a plateau over time (**Figure 8**). The results from the 200 mm scenario show a similar pattern to 23 mm but after reaching a plateau, mass remaining decreases rapidly to 0 kg.

Based on the low mass remaining as a solute in liquid phase (maximum of 275 kg in the Bunker, day and 23 mm scenario) in comparison to mass spilt (maximum of 12000 kg), a high proportion of the ammonia mass spilt has been lost via vaporisation and dissolution.

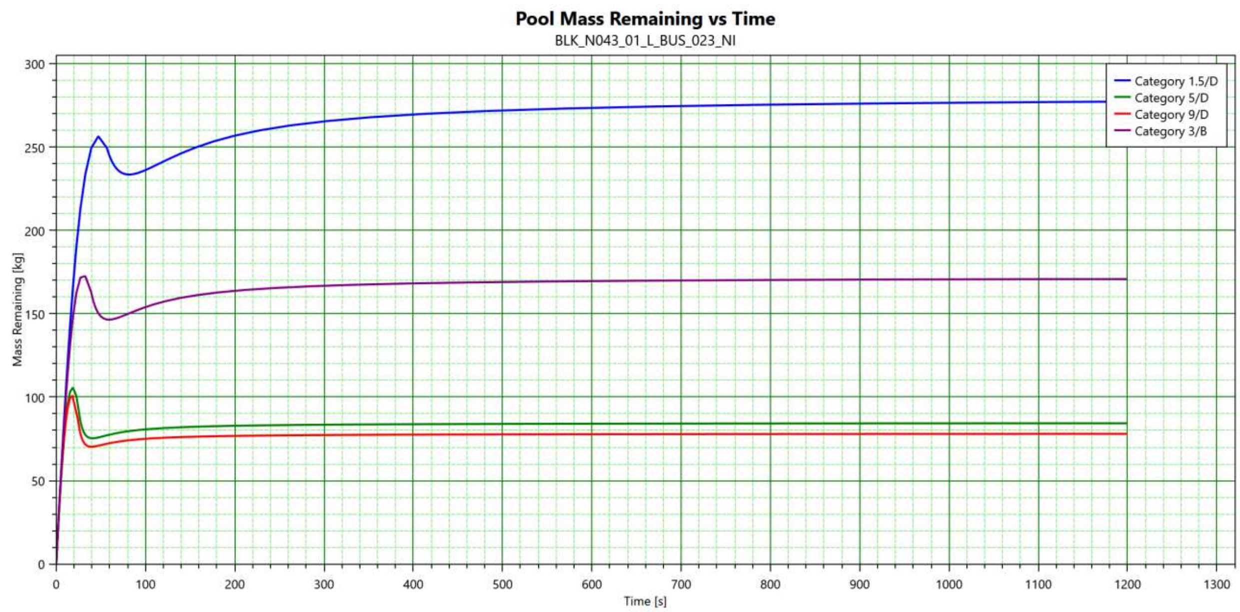

Figure 8 Pool Mass Remaining vs Time – bunker, day, 23 mm hole scenario

4.1.1.8. Solution rate

The solution rate results differ between hole-size scenarios. Under the 2 mm scenario, the solution rate exhibited an initial sharp increase followed by a plateau. The 23 mm scenario shows a largely similar trend except for a small sharp decrease after the initial increase in solution rate (**Figure 9**).

Under the 200 mm scenario, the solution rate showed an initial increase followed by a decrease and levelling out before decreasing again, until reaching 0 kg/s. Under the 1200 mm scenario, the solution rate shows an initial increase followed by a sharp decrease to 0 kg/s.

The solution rate is initially rapid as ammonia is very water soluble, it is then considered likely that the optimum rate is reached as shown by the plateau.

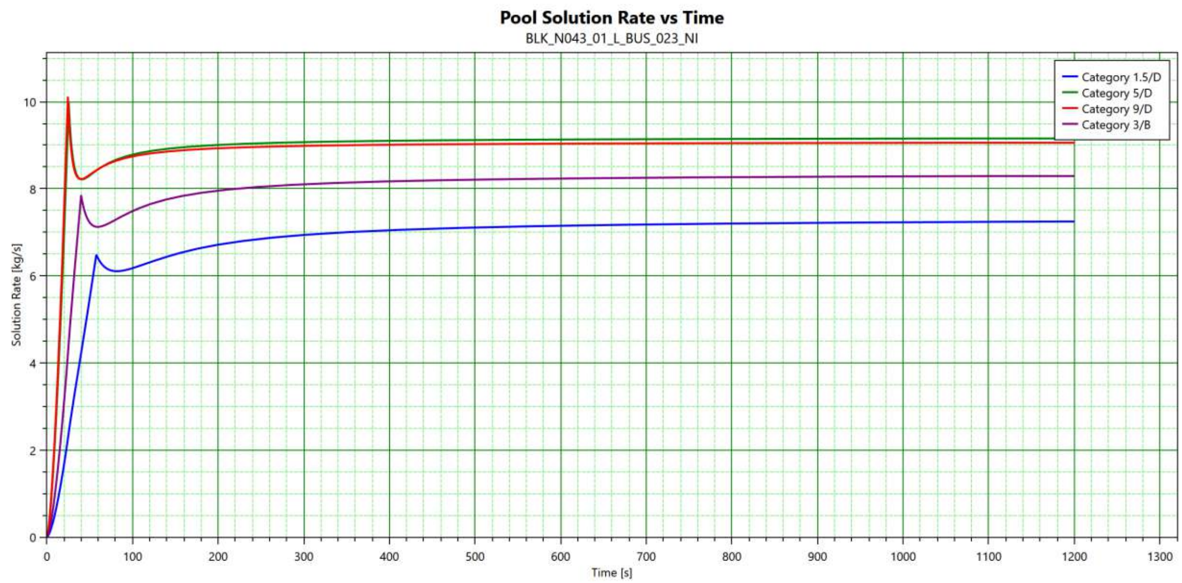

Figure 9 Pool Solution Rate vs Time – bunker, day and 23 mm scenario

4.1.1.9. Mass dissolved

The mass dissolved results generally follow a linear increase over time with little difference between weather scenarios, with the exception of the 200 mm and 1200 mm scenarios. Mass dissolved for 200 mm scenarios followed an initial linear increase which plateaus at around 100 seconds. Under the 1200 mm scenario, mass dissolved exhibits a delayed increase, beginning at around 50 seconds and increasing steadily, before reaching a plateau.

As above for the solution rate, ammonia readily dissolves in water, as observed in the modelling by the rapid increase in mass dissolved (as shown in **Figure 10**).

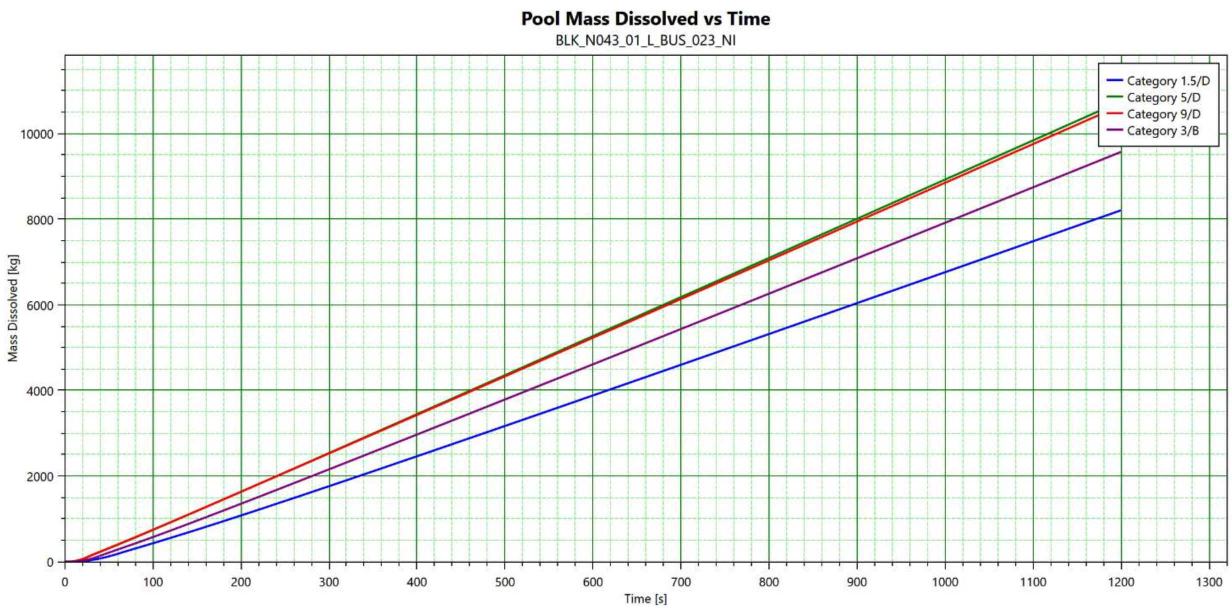

Figure 10 Pool Mass Dissolved vs Time – bunker, day and 23 mm hole scenario

4.1.2. Impact of Ammonia storage types

The main difference between the fuel storage type conditions is that the Bulker is pressurised and the Tanker and containership are refrigerated[26]. Full specifications of storage types modelled can be found in Appendix 2 and **Table 7.2**. However, when comparing the modelled ammonia spills, the fuel storage type accounted for a small number of variations between trends and results.

For example, comparing the Bulker and Tanker, the mass of ammonia spilt followed a similar linear increase with time under the 2 mm and 23 mm hole scenarios but differed under the 200 mm hole scenario. However, the Containership mass of ammonia spilt displayed a linear increase with time for each hole scenario (2 mm, 23 mm and 200 mm). The mass spilt variation is likely related to the storage conditions, as the Containership storage is both fully refrigerated and therefore, at the least pressure, suggesting less variation in the mass spilt due to the lower pressure and the dynamic viscosity of the ammonia as it is released.

The pool radius differed for the Bulker in comparison to the Tanker and Containership. This was also observed for the solution rate and mass dissolved. Though the Containership also had some trend variation for solution rate and mass dissolved.

[26] The Containership is fully refrigerated and the Tanker is semi refrigerated.

The Bulker further showed some trend variation for mass vaporised and mass remaining. Differences observed between the mass vaporised may be due to the increased pressure at which the ammonia is stored within the Bulker compared to the other vessels and the solution rate and thereby mass dissolved and remaining, may be related to the increased storage temperature. Full graphical results can be seen in Appendix 3.

4.1.3. Between day and night

Within the modelling set up the differences between day and night account for a 4 °C decrease in ambient temperature, an ~10 % increase in humidity, a 0.25 kW/m^2 reduction in solar radiation flux and an increase of 11 in a fraction of a 24-hour period from day to night (full details found in Appendix 2). Whether an ammonia spill occurs during the day or night does not impact directly on trends observed in the results. However, masses vaporised, dissolved and remaining and solution rates are indirectly impacted by higher temperatures during the day and variations between weather conditions (see Section 4.1.5). One notable exception is a slight trend variation for the collision scenario (1200 mm hole size) during the day but not the night.

Ammonia spilled at night remains for longer on the surface compared to in the day. This may suggest that water temperature and evaporation could influence the rate of ammonia remaining after a spill, or it may be related to the occurrence of wind speeds at night. The mass remaining also has diurnal influences; ammonia that is spilt at night remains on the surface for approximately 600 seconds longer compared to the day. Further, there is a longer duration of time for the mass to vaporise in all wind speeds during the night vs day, it is considered likely that the temperature of the water will have an influence on this. Full graphical results are seen in Appendix 3.

4.1.4. Between hole sizes

The modelled hole sizes for each fuel storage type are 2 mm, 23 mm and 200 mm with the Containership having an additional collision scenario with a 1200 mm hole size. For each fuel storage type, there was limited variation in trends of results for hole sizes 2 mm and 23 mm. However, the 200 mm hole size showed increased variation from established trends, particularly for the Bulker, but also noticeably for the Tanker and Containership, for all results (except for pool temperature, for which trends appear to be unaffected by any modelled variable). This is most noticeably observed in mass spilt and pool depth.

As an ammonia spill would occur from a finite, defined volume mass spilt and pool depth were unaffected by hole size, with linear increases over time under all scenarios and no noticeable difference for each weather scenario. At 200 mm for both the Tanker and Bulker (under day and night), variation between scenarios was observed. In contrast, variation for 200 m Containership (both day and night) was limited for mass spilt. This suggests that the size of the spill limits the depth range of the spill into the water as it remains mainly on the surface.

The 1200 mm hole size scenario showed significant variations, particularly for, the vaporisation rate, indicating that the vaporisation rate may be linked to pool radius as the radii at 1200 mm was significantly larger than those at other hole sizes and therefore, a larger surface area is vaporising.

4.1.5. Between weather conditions

The weather conditions within the PHAST model (**Table 7** and Appendix 2) are composed of two parts, the Pasquill stability class and wind speed. The Pasquill stability class within the model ranges from B[27] to F[28] ('unstable' to 'stable' conditions), while the wind speed ranges from 1.5 to 9 m/s (light to strong wind speeds). Weather conditions 5E and 1.5F were not modelled during day and 5B were not modelled during night due to the stability class not being applicable.

The weather conditions appear to be the most significant parameter within the modelling and drive many of the trends observed within the results (Appendix 3). **Table 8** shows a high-level summary of those trends[29].

Table 7 Summary of Pasquill Stability Class and Wind Speed

Pasquill Stability Class	Wind speed (m/s)	Percentage Day	Percentage Night
B	3.0	24.50	0.00
D	1.5	11.19	15.19
D	5.0	30.76	26.06

[27] A bright sunny day
[28] A clear night with little wind
[29] The RAG colour scale shown is indicating value only

D	9.0	33.55	21.87
E	5.0	0.00	10.85
F	1.5	0.00	26.04

Table 7 Representative environmental conditions assumed for the purposes of consequence modelling.

Table 8 General Summary for Model Outputs with Weather Conditions*

Model output	Weather conditions					
	1.5D	5D	9D	3B	5E	1.5F
Mass spilt						
Pool depth						
Pool radius						
Pool temperature						
Solution rate						
Mass dissolved						
Pool vaporisation rate						
Mass vaporised						
Mass remaining						

Scale	
	Lowest
	Highest

* This presentation shows the graphical outputs for each weather scenario (as shown **Table 7** and Appendix 2) ranked (according to the scale) lowest to highest in terms of the greatest value displayed by the parameter. Note that the scaling does not take into account whether the 'highest' or 'lowest' values are a relative positive or a negative for that output and further, that the greatest value refers to the greatest value achieved over the time modelled and is not necessarily a start or end value. Day and night variations are considered together.

The lowest wind speeds (1.5 m/s) parameterised in the model have the highest number of modelled outcomes which describe the highest values for parameters modelled (5 out of 9 for 1.5D weather conditions and 7 out of 9 for 1.5F weather conditions). The mid-level wind speeds (3 and 5 m/s) generally fall in the middle and the highest wind speed (9 m/s) typically has the highest number of modelled outcomes which describe the lowest values for parameters modelled (see **Table 8**).

For example, the mass of liquid ammonia that is dissolved increases when there are higher wind speeds- the gas transfer velocity is frequently parameterised as a function of wind speed. Air speed is an important variable because it affects both the velocity at which the components evaporate and the way that the ammonia cloud evolves and moves[30].

Solution rate and mass dissolved fall outside of these observed trends and have the highest rate/mass observed during mid-level weather and the lowest during stable weather with little wind. However, it may be that this deviation from the trends actually does fit, as higher rates and mass vaporised to the atmosphere would leave less mass remaining for dissolution.

These observable trends may also suggest that it is the wind speed rather than the atmospheric turbulence stability which is the significant driver in the modelled outcomes.

4.1.6. 'Worst case' spill scenario

This section attempts to synthesise the above results and describe what could be considered as the 'worst case' spill scenario. For example, the higher the ammonia mass spilt, pool depth, pool radius and mass remaining, the greater extent of potential impact on habitats and ecological receptors and increased prevelance in the aquatic environment. This will then aid in the environmental assessment below.

However, it should be noted that this synthesis may not consider a single scenario as 'worst case' as, for example, a high solution rate may be considered 'worst case'' for some receptors and a high vaporisation for others and these factors would be unlikely to both be high during a single scenario. **Table 9** summarises the below sections.

[30] Corruchaga, A., Casal, O., Palacios, A., Casal, J. (2022). Influence of wind speed and ammonia concentration on its evaporation rate from aqueous solution leaks. Journal of Loss Prevention in the Process Industries. 76. 104750, ISSN 0950-4230.

Table 9 Summary of 'Worst Case' Scenario31

Model output	Vessel type	Hole size (mm)	Day/Night	Weather condition
Mass spilt	Containership	1200	Night	-
Pool depth	-	-	-	-
Pool radius	Containership	1200	Night	1.5/D and 1.5/F
Pool temperature	-	-	-	-
Solution rate	Containership	1200	Day	5/E and 5/D
Mass dissolved	Containership	1200	Day and Night	5/E and 5/D
Pool vaporisation rate	Containership	1200	Day	1.5/D and 1.5/F
Mass vaporised	Containership	1200	Day and Night	1.5/D and 1.5/F
Mass remaining	Containership	1200	Night	1.5/D and 1.5/F

4.1.6.1. Mass spilt

The greatest mass (kg) of ammonia spilt occurs during the 1200 mm hole scenario for the Containership at >1.3 million kg during both the day and the night, with little variation observed during the various weather scenarios.

The mass spilt increases with hole size, from 2 mm to 200 mm, except for the Bulker, where 200 mm spills less ammonia than 23 mm under day and night scenarios. Slightly more ammonia is also spilt during the night than during the day. The Containership (200 mm hole size) spills the second highest mass of ammonia and overall, the 2 mm hole for the Tanker the least mass of ammonia.

Therefore, a spill from the Containership at 1200 mm/ 200 mm at night is considered to be the 'worst case' scenario for mass spilt.

[31] The RAG colour scale shown is indicating value only, red as greatest value refers to the greatest value achieved over the time modelled and is not necessarily a start or end value

4.1.6.2. Pool depth

Overall, pool depth shows little variation between the scenarios and ranges from 0 m to 0.002 m within seconds of the ammonia spill. Therefore, this is not considered to be a useful parameter in determining a ‘worst case’ scenario.

4.1.6.3. Pool radius

Pool radii were determined to reach the largest size during the weather conditions of 1.5 D (day) and 1.5 F (night).

The largest pool radii occurred during the 1200 mm hole scenario for the Containership at night with >240m. The Containership (200 mm hole size, during the night) the second highest pool radii of ammonia, and overall, the 2 mm hole for the Bulker the smallest.

4.1.6.4. Pool temperature

Overall, the pool temperatures of ammonia follow the pattern, as described in Box 3. Due to evaporation rates, under modelling scenarios the ammonia does not reach the required temperature to boil, and typically temperature decreases over time. Temperature is therefore not considered to be a useful parameter in determining a ‘worst case’ scenario.

4.1.6.5. Solution rate

Solution rates were determined to reach the highest rate during the weather conditions of 5E and 5D.

The highest solution rate occurred during the 1200 mm hole scenario for the Containership during the day with >7,000 kg/s. The solution rate also increases with hole size, from 2 mm to 200 mm, related to being a function of pool size, and the Containership (200 mm hole size, during the day) has the second highest solution rate of ammonia, and overall, the 2 mm hole for the Tanker the lowest.

4.1.6.6. Mass dissolved

Mass dissolved was determined to be the highest during the weather conditions of 5E and 5D.

The highest mass dissolved occurred during the 1200 mm hole scenario for the Containership during both the day and night with >800,000 kg. For the Containership and Tanker the mass dissolved increases with hole size, but this is not the case for the Bulker where the 23 mm hole size spill has a greater mass dissolved than the 200 mm hole size.

The Containership also has the second largest mass dissolved at >820,500 kg during the night from a 200 mm hole.

4.1.6.7. Pool vaporisation rate

Pool vaporisation rates were determined to reach the highest rate during the weather conditions of 1.5 D (day) and 1.5 F (night).

The highest pool vaporisation rate occurred during the 1200 mm hole scenario for the Containership during the day with 3,300 kg/s. The solution rate also increases with hole size, from 2 mm to 200 mm and the Containership (200 mm hole size, during the night) has the second highest pool vaporisation rate of ammonia, and overall, the 2 mm hole for the Containership the lowest.

4.1.6.8. Mass vaporised

Mass vaporised was determined to be the highest during the weather conditions of 1.5 D (day) and 1.5 F (night).

The highest mass vaporised occurred during the 1200 mm hole scenario for the Containership during both the day and night with 610,000 kg. Similarly, to mass dissolved, for the Containership and Tanker the mass vaporised increases with hole size, but this is not the case for the Bulker where the 23 mm hole size spill has a greater mass vaporised than the 200 mm hole size. The Tanker has the second largest mass vaporised at 7,100 kg during both the day and night from a 200 mm hole.

4.1.6.9. Mass remaining

Mass remaining was determined to be the highest during the weather conditions of 1.5 D (day) and 1.5 F (night).

The largest mass remaining occurred during the 1200 mm hole scenario for the Containership at night with >1.2 million kg. The Containership (200 mm hole size, during the night) had the second highest mass remaining of ammonia, and overall, the 2 mm hole for the Containership was the smallest.

Overall, the 'worst case' occurs during the 1200 mm hole scenario for the Containership, however, this scenario is also considered to be the least likely to occur (**Table 9**). Therefore, the next overall 'worst case' scenario is also considered.

This is considered to be the Containership, with a 200 mm hole and a spill of ammonia occurring during the night with low wind and stable conditions (1.5F).

4.2. Air Dispersion Modelling Analysis

This section analyses the results from the air dispersion modelling by looking at the trends at each of the ESAS flight height bands (see **Table 5**) for each of the fuel storage types.

4.2.1. General trends

- The size of the footprint increases based on hole size.
- For a given hole size, generally, the footprint of the bulker is greater than the tanker. The footprint for the containership is generally the smallest of the three vessels[32] except for the 200mm hole size scenario where it is the greatest.
- Generally, the modelling shows that weather category 1.5/D produces the greatest cloud footprint in the daytime and weather category 1.5/F produces the greatest cloud footprint in the night-time.
- Generally, the modelling shows that weather category 3/B produces the smallest cloud footprint in the daytime and weather category 5/E produces the smallest cloud footprint in the night-time.
- Generally, the modelling shows that the cloud footprint shrinks with height.
- Generally, the modelling shows that weather category 1.5/F which is present in night-time travels furthest downwind and weather category 1.5/D for both day and night tends to produce the widest cloud footprints.

4.2.2. Exposure limits

4.2.2.1. Short-term exposure limit (35 ppm/ 25 mg m-3)

Overall, this follows a similar pattern as described above for the PHAST modelling, where the greatest areas of exceedance occur during the weather conditions of 1.5D (daytime) and 1.5F (night-time). With exceedance areas being greater during the night-time. Appendix 5 shows the area (km^2) with ground level concentrations which exceed the short-term exposure limit of 35 ppm (25 mg m^{-3}) for each scenario.

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32 Within this study

The exceedances are also greatest during the 1200 mm hole scenario for the Containership and for the 200 mm hole size for the three ship types, ranging from 1.4 km^2 (200 mm hole for a Containership during the Day at 3B) to 19 km^2 (200 mm hole for a Containership during the Day at 1.5D).

4.2.2.2. Long-term exposure limit (25 ppm/ 18 mg m-3)

As above, overall, a similar pattern to the PHAST modelling emerges, where the greatest areas of exceedance occur during the weather conditions of 1.5D (daytime) and 1.5F (night-time). Again, with exceedance areas being greater during the night-time. Appendix 5 shows the area (km^2) with ground-level concentrations which exceed the short-term exposure limit of 25 ppm (18 mg m^{-3}) for each scenario.

The exceedances are also greatest during the 1200 mm hole scenario for the Containership, and for the 200 mm hole size for the three ship types, ranging from 1.7 km^2 (200 mm hole for a Containership during the Day at 3B) to 23 km^2 (200 mm hole for a Containership during the Day at 1.5D).

In general, the area with ground-level concentrations which exceed the exposure limits are greater for the long-term limit than for the short-term limit. It is also noted that the area with exceedances increases with hole size, but that ship type does not appear to make significant contributions to observed trends.

4.2.3. Bulker

The infographic below describes the 'worst case' for bulker storage types where the greatest cloud footprint could be found. The worst case is seen as a function of night or day, hole type and weather conditions. This resulted in different widths and downwind distances as seen in the summary **Figure 11**. It should be noted that each flight band was modelled separately so conditions for each 'worst case' may differ per fight band.

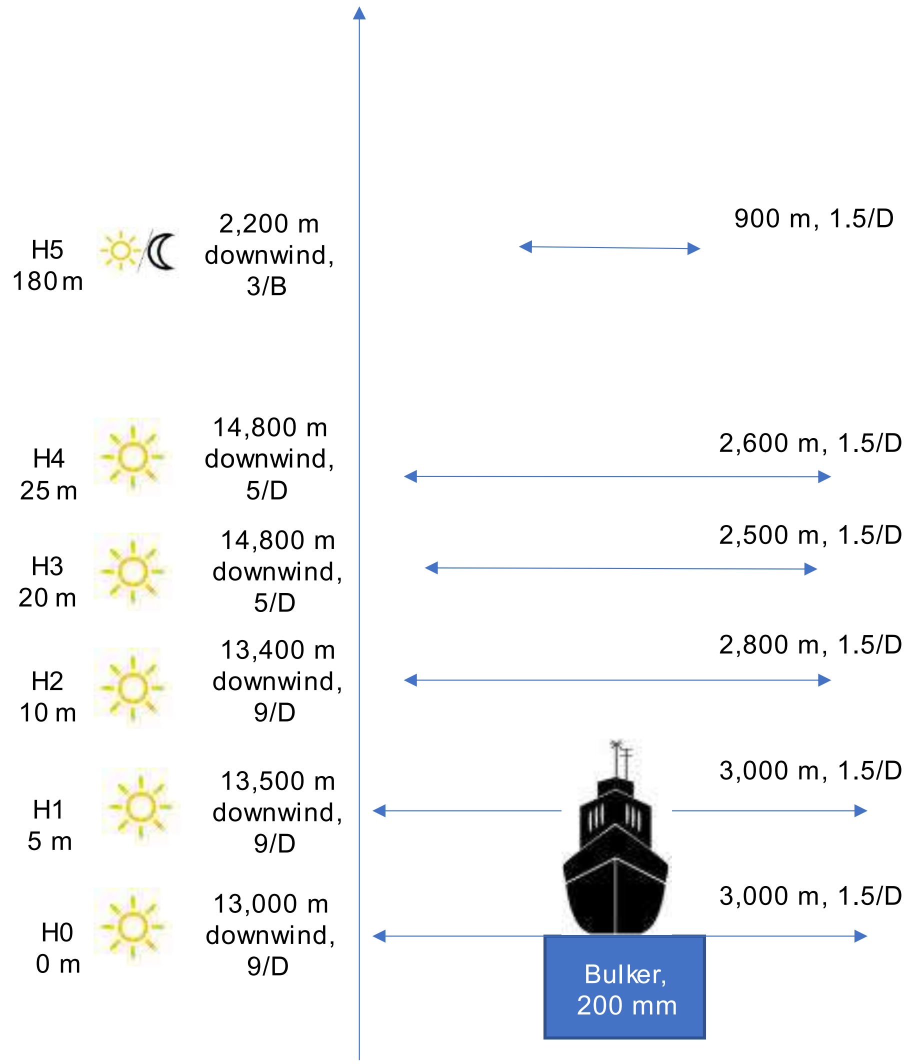

Figure 11 Dispersion of ammonia at different flight heights and which scenarios resulted in the 'worst case' for a bulker

4.2.4. Tanker

The infographic below describes the 'worst case' for tanker storage types where the greatest cloud footprint could be found. The worst case is seen as a function of night or day, hole type and weather conditions as seen in the summary **Figure 12**. This resulted in different widths and downwind distances. It should be noted that each flight band was modelled separately so conditions for each 'worst case' may differ per fight band.

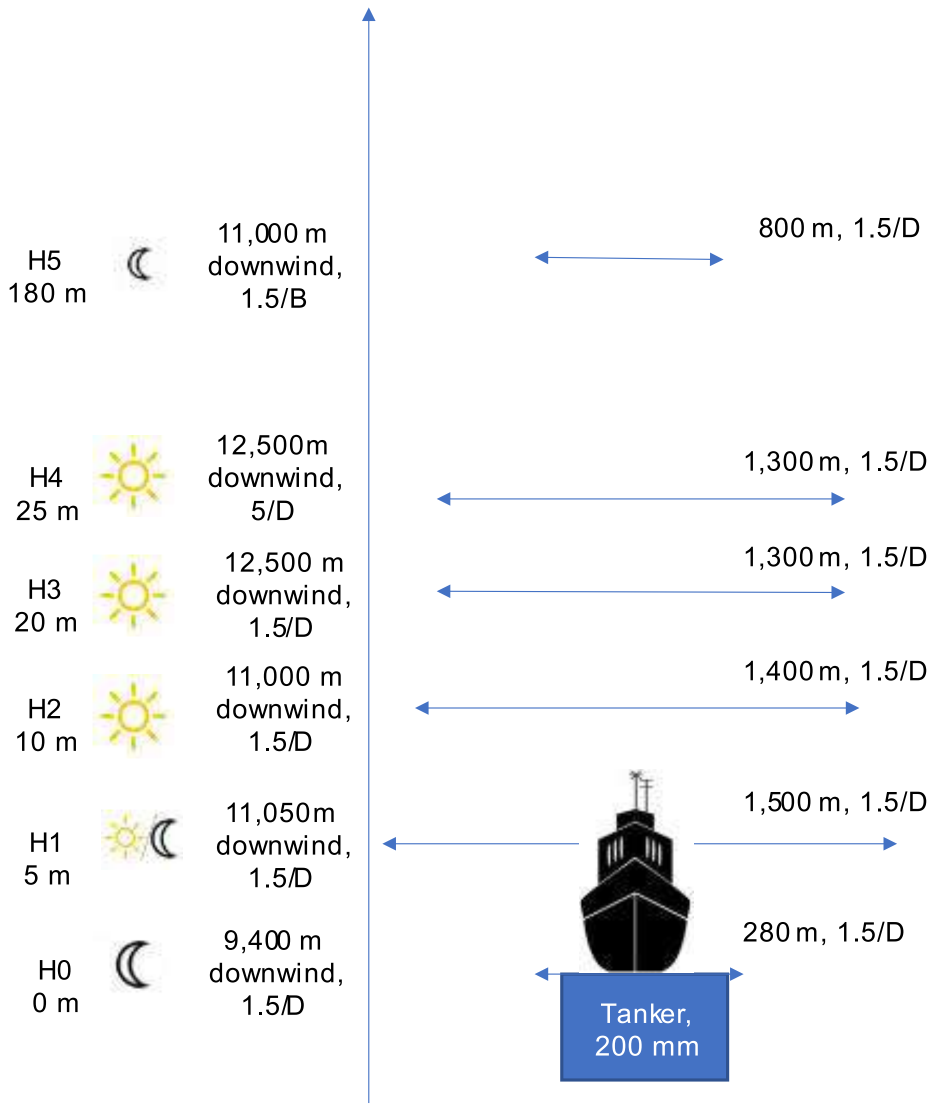

Figure 12 Summary for Tanker 'worst case' air dispersion model

4.2.5. Containership

The infographic below describes the 'worst case' for containership storage types where the greatest cloud footprint could be found. The worst case is seen as a function of night or day, hole type and weather conditions as seen in **Figure 13**. This resulted in different width and downwind distance. It should be noted that each flight band was modelled separately so conditions for each 'worst case' may differ per fight band.

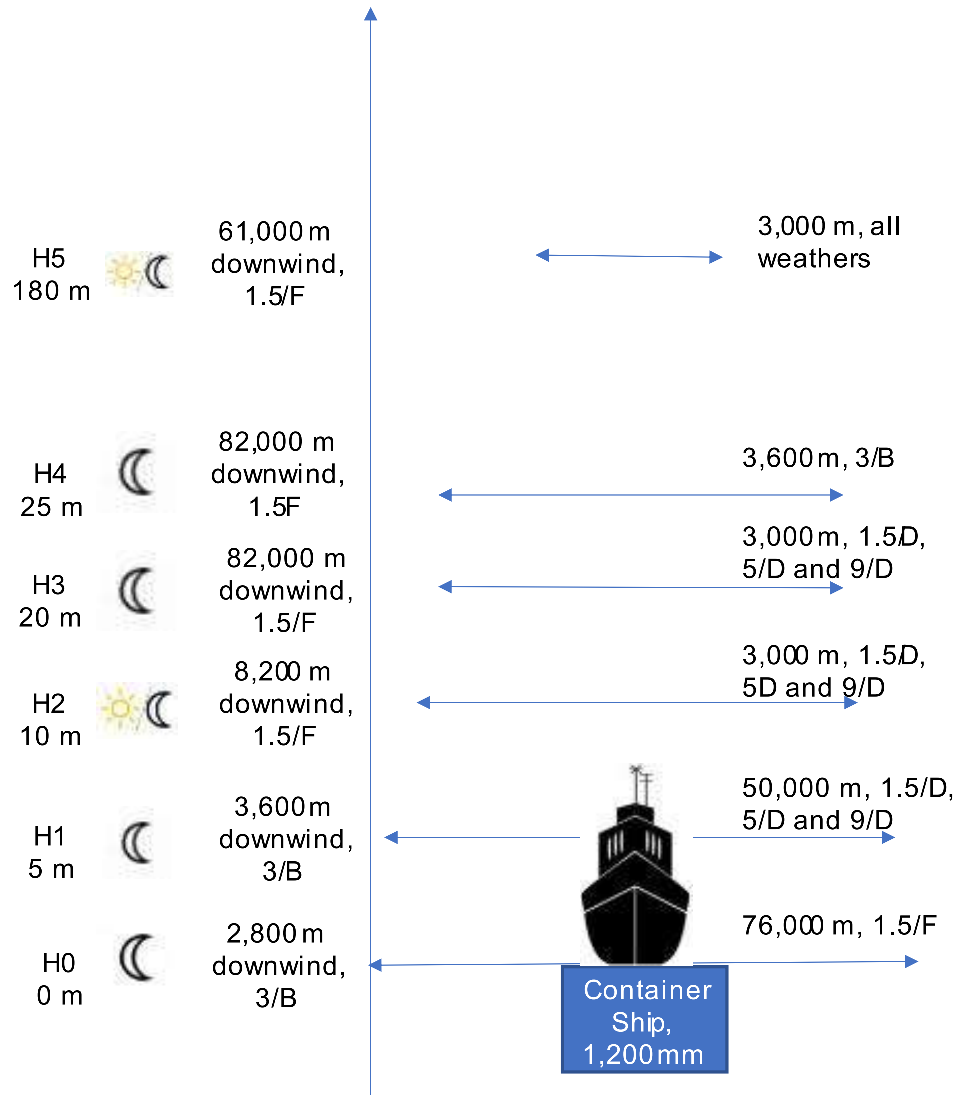

Figure 13 Summary of containership 'worst case' dispersion model

4.3. Environmental Assessment

Section 4.3.1 provides an overview of ammonia naturally present, abiotic processes that govern the fate of ammonia and the potential impacts of elevated ammonia concentrations in each habitat. Section 4.3.2 assesses the potential impact of elevated ammonia concentrations on each ecological receptor and relates to each habitat, with case studies from available literature. The potential impact of the ‘worst case’ spill scenario on ecological receptors and associated habitats is then assessed to contextualise to the modelling that has been undertaken.

4.3.1. Habitats

4.3.1.1. Rivers

Ammonia concentrations in surface waters are typically low (<0.1 mgL^{-1}). For example, in a river system where surface water temperatures are 20 °C and pH 7 – 8, ammonia (NH_3) concentrations range from 0.0004 – 0.004 mgL^{-1} [33]. Discharge from wastewater treatment works, industry and agriculture all contribute to increases in ammonia concentrations in rivers. The concentration of unionised ammonia and longevity within the environment is governed by localised abiotic parameters, including water temperature, pH and water flow. From the point of discharge, ammonia will be transported via water flow downstream. If mixing occurs, the discharge pool will disperse both horizontally on the surface and at depth. Ammonia particles can also be retained in the water when there is turbulence from rapids or tidal actions, due to mixing within the upstream base flow of the river[34]. The concentration of unionised ammonia in a river, spatial extent and time present in the system all contribute to the overall impact on the ecological function of a river.

It is also important to consider the impact of elevated ammonium concentrations on rivers. Ammonium is typically transformed to nitrate and nitrite by oxidising bacteria, increasing the biochemical oxygen demand of the environment and causing an increase in algal growth; which in slow-flowing systems could lead to eutrophication. This could have severe impacts on the ecological function of a river if ammonium concentrations were elevated for a long period. For example, submerged macrophytes reliant on light penetration for photosynthesis would deteriorate and potentially deplete in extent, reducing the habitat available for invertebrates and fish. In addition, habitat suitability for fish would be reduced by the decreased availability of dissolved oxygen required for respiration.

4.3.1.2. Wetlands

Ammonia concentrations in natural wetlands are typically below 2 mgL^{-1} [35]. Wetlands are defined as ecosystems 'whether natural or artificial, permanent or temporary, with water

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[33] Constable, M., Charlton, M., Jensen, F., McDonald, K., Craig, G., Taylor, K. W. (2003). An Ecological Risk Assessment of Ammonia in the Aquatic Environment. Human and Ecological Risk Assessment: An International Journal, 9, pp 1 – 104.

[34] Little, A.D. (1974). Prediction of hazards of spills of anhydrous ammonia on water, NTIS.

[35] Kadlec, R.H., Knight, R.L. (1996.) *Treatment Wetlands*. Lewis Publishers, Boca Raton, FL.

that is static or flowing, fresh, brackish or saline[36]. In the context of this report, wetlands will consider an assessment of reed *Phragmites*-dominated habitats and tidal marshes. Due to the high rate of primary production and sedimentation, wetlands present in estuarine environments (tidal freshwater wetlands) are likely to be net sinks for nutrients, with a net accumulation of nutrients during the growing season and net release in autumn and winter[37]. Therefore, tidal freshwater wetlands are sites of nutrient transformation under normal conditions, with nutrients in particulate form largely present during the flood tide and dissolved nutrients during the ebb tide. The exchange of ammonium between wetlands and floodwaters is dependent on the diffusive gradient between the soil pore waters and tidal waters, which is also influenced by microbial assimilation[38]. A study conducted on a freshwater marsh in Belgium discovered that a higher percentage of ammonium available in the water column was removed via microbial assimilation than was sequestered by marsh plants (approximately 4 %)[39]. Due to the dynamic nature of wetland systems (particularly in estuarine and coastal environments), it is anticipated that variations in water temperature, pH and salinity will cause the equilibrium between unionised ammonia and ammonium to fluctuate more rapidly during a spill scenario than other more stable environments. Localised abiotic parameters will, therefore, govern the potential impact on ecological receptors associated with wetlands.

4.3.1.3. Estuaries

Estuaries are individual and complex environments, with daily and seasonal fluctuations in nutrient levels, water quality, salinity, productivity, and turbidity, that support diverse ecosystems. In comparison to marine and freshwater environments, estuaries are more susceptible to the effects of nutrient pollution, due to their location at the mouths of large watersheds and adjacent to dense population centres[40]. Stresses from fuel spills, such as oil or liquid ammonia, will therefore intensify these challenges[41].

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[36] Ramsar Convention on Wetlands (1971). What are wetlands? Ramsar Information Paper no. 1. Pp 1 – 2.

[37] Odum, W. E., Smith III, T. J., Hoover, J. K., McIvor, C. C. (1984). *The Ecology of Tidal Freshwater Marshes of the United States East Coast*: A Community Profile. FWS OBS-83-17, US Fish and Wildlife Service, Washington, DC, pp 177.

[38] Perillo, G. M. E., Wolanski, E., Cahoon, D. R., Brinson, M. M. (2009). *Coastal Wetlands an Integrated Ecosystem Approach*. Elsevier.

[39] Gribsholt, B., Struyf, E., Tramper, A., Andersson, M. G. I., Brion, N., De Brabandere, L., *et al.* (2006). Ammonium transformation in a nitrogen-rich tidal freshwater marsh. *Biogeochemistry* 80, pp 289–298.

40 Bricker, S. B., Longstaff, B., Dennison, W., Jones, A., Boicourt, K., Wicks, C., Woerner, J. (2008). Effects of nutrient enrichment in the nation's estuaries: a decade of change. Harmful Algae, 8, pp 21 – 32.

41 Eddy, F. B., (2005). Ammonia in estuaries and effects on fish, Journal of Fish biology, 67, pp 1495-1513.

Naturally in an estuarine system, ammonium concentrations fluctuate in the upper and lower reaches. For example, in the Schelde estuary (located north of Belgium), ammonium concentrations ranged from 200 - 500 µM (3,608 – 9,020 $\mu g L^{-1}$) in the upper estuary to 10 µM (180.4 $\mu g L^{-1}$) in the lower estuary[42]. This is associated with peaks in nitrification activity where chemoautotrophic bacteria oxidise ammonia to nitrite in the upstream reaches. The nitrification process is affected by salinity, with peak activity recorded at intermediate salinities[43], oxygen and ammonium limitations and turbidity (influenced by the tidal cycle). For example, in the Elbe estuary, 50 – 100 % of nitrifying bacteria were attached to flocks formed by particulate matter[44]. Therefore, the ability of an estuarine system to process excess ammonia will be dependent on the location of the ammonia spill and abiotic conditions at the time of the spill. It is noted that in the lower estuary, the habitat is ammonium limited and therefore, with an increase in ammonium concentration, nitrification activity increases[46]. Ammonia-oxidising microorganisms also vary within the upper and lower estuary. In the Douro River estuary on the north-west coast of Portugal, upper estuarine sediments were dominated by nitrite-oxidising bacteria (*Nitrospira* genus) and lower estuarine sediments were dominated by ammonia oxidising archaea (*Nitrosomonas* genus)[45].

Due to the dynamic nature of estuarine systems and the complex water chemistry associated, the concentration and therefore, the impact of unionised ammonia on ecological receptors will be difficult to predict. A degree of mixing will occur particularly in the brackish zone of the estuary. As diverse ecosystems provide key migration pathways for anadromous fish to spawning grounds and nursery habitats in the upper reaches, exposure to unionised ammonia could have significant impacts on population trends. In addition, it may impact the composition of plankton, macrophyte and macroinvertebrate assemblages depending on the tolerance threshold of each species and fate of ammonia in the system.

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[42] De Bie, M. J. M., Starink, M., Boschker, H. T. S., Peene, J. J., Laanbroek, H. J. (2002). Nitrification in the Schelde estuary: methodological aspects and factors influencing its activity. FEMS Microbiology Ecology, 42, pp 99 – 107.

[43] Helder W. de Vries R.T.P. (1983) Estuarine nitrite maxima and nitrifying bacteria (Ems-Dollard estuary). Neth. J. Sea Res.17 (1), 1–18.

[44] Stehr G., Böttcher B., Dittberner P., Rath G., Koops H.-P. (1995) The ammonia-oxidizing nitrifying population of the River Elbe estuary. FEMS Microbiology Ecology.17, 177–186.

[45] Santos, J. P., Sousa, A. G. G., Ribeiro, H., Magalhães, C. (2020). The Response of Estuarine Ammonia-Oxidising Communities to Constant and Fluctuating Salinity Regimes. Front Microbiology, 11.

4.3.1.4. Coastal waters

In the context of this report, coastal waters will include an assessment of seagrass, coastal lagoons, tidal flats and rocky shore. Such habitats provide feeding, breeding and nursery grounds for a multitude of species including invertebrates, fish, birds and marine mammals. As dynamic environments (similar to wetlands and estuaries), coastal ecosystems exhibit high rates of nutrient recycling and filtering, primary productivity and pollutant transportation and transformation in sediments[46]. Typically, ammonium oxidation within the water column from the shore to shelf increases with distance from the shore, with oxidation rates significantly higher at water depths >20 m in comparison to <20 m[47]. In addition, approximately 50% of marine nitrogen removal occurs within the substrate by ammonia-oxidising archaea and bacteria[48].

When considering the potential impact of excess ammonia in coastal waters, ammonia is more toxic in seawater compared to freshwater. However, it has been reported that ammonia toxicity is higher when the pH of seawater is lowered to ~7. Depending on the location and timing of the ammonia spill, intertidal habitats could be exposed to both gaseous ammonia at low tide (influenced by atmospheric conditions) and dissolved ammonia at high tide. Seagrass for example is present in intertidal and shallow sub-tidal habitats, with dwarf eelgrass Zostera noltii and eelgrass Zostera marina present in temperate regions and shoal grass Halodule wrightii and paddle weed Halophila ovalis in tropical regions[49]. Uptake of ammonium by seagrass is influenced by water movement around the leaf surface, caused by waves and the ability of the canopy to remain upright with an open leaf surface, which is influenced by currents. Maximum uptake of ammonium has been recorded in conditions with low currents and wave exposure to maintain water movement[53]. However, high ammonium concentrations (> 25 μM/> 451 μgL-1) are toxic to seagrass as it causes slower growth via the uncoupling of ATP production from

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[46] Zang, X., Agogue, H., Depuy, C., Gong, J. (2014). Relative abundance of ammonia oxidizers, denitrifiers and anammox bacteria in sediments of hyper-nutrified estuarine tidal flats and in relation to environmental conditions. Soil, Air, Water, 1 – 21.

[47] Heiss, E. M., Fulweiler, R. W. (2019). Coastal Water Column Ammonium and Nitrite Oxidation are Decoupled in Summer. Estuarine, Coastal and Shelf Science: Volume 178: 110-119.

[48] Codispoti, A., Brandes, J. A., Christensen, J. P., Devol, A. H., Naqvi, S. W. A., Pearl, H. W., Yoshinari, T. (2001). The oceanic fixed nitrogen and nitrous oxide budgets: moving targets as we enter the Anthropocene?. Science Marine, 65 pp 85 – 105.

[49] Gillis, L. G., Paul, M., Bouma, T. (2017). Ammonium uptake rates in a seagrass bed under combined waves and currents. Frontiers in Marine Science. https://doi.org/10.3389/fmars.2017.00207

photosynthetic electron transport, changes in intracellular pH and increased respiratory demand50.

Elevated ammonium concentrations also cause excessive algae growth, resulting in blooms that reduce light penetration and impact on the photosynthetic rate of macrophytes. For example, some toxigenic species of pennate diatom *Pseudo-nitzschia* have been shown to increase in number to form a bloom (>100,000 cells L^{-1}) in coastal waters rich in ammonium. *Pseudo-nitzschia* can produce domoic acid, a neurotoxin responsible for amnesic shellfish poisoning (ASP) which can affect fish and other organisms[51]. Algal blooms can lead to hypoxic and anoxic conditions which can have severe effects on local ecosystems and cause many different poisoning syndromes and impacts. These include paralytic shellfish poisoning, neurotoxic shellfish poisoning, amnesic shellfish poisoning, ciguatera fish poisoning and various other harmful algal bloom phenomena such as fish kills, loss of submerged vegetation, shellfish mortalities and widespread marine mammal mortalities[52]. For example, a mass fish kill event occurred in the Chunnambar backwater of Puducherry, India in September 2019 where around 1.5 metric tonnes of fish were found. This coincided with a Pseudo-nitzschia bloom. High ammonia (and phosphate) levels attributed to eutrophic conditions in the water column and hypoxemia due to low dissolved oxygen. Therefore, the algal bloom was the proximate cause of the sudden fish kills[53].

Algal mats also can smother other habitats associated with coastal waters such as honeycomb worm *Sabellaria alveolata* and blue mussel *Mytilus edulis* beds. Based on peak nitrification activity at depths > 20m, shallow water habitats may be more vulnerable to increases in ammonia concentration and associated algal blooms.

Depending on the extent of freshwater inputs into the coastal environment and tidal regime, the stability of abiotic parameters will vary on a site-specific basis. These site-specific

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[50] Moreno-Marin, F., Vergara, J. J., Perez-Llorens, L., Pedersen, M. F., Brun, F. G. (2016). Interaction between ammonium toxicity and green tide development over seagrass meadows: a laboratory study. PLOS ONE. https://doi.org/10.1371/journal.pone.0152971

[51] Van Meerssche, W, Greenfield, D. I., Pickney, J. L., (2018), Coastal eutrophication and freshening: Impacts on Pseudo-nitzschia abundance and domoic acid allelopathy, *Estuarine, Coastal and Shelf Science,* 209, pp 70-79, https://doi.org/10.1016/j.ecss.2018.05.013

[52] Anderson, D, *et al.,* (2008) Harmful Algal Blooms and Eutrophication: Examining linkages from select coastal regions of the United States, *Harmful Algae,* 1(8), pp 39-53, https://doi.org/10.1016/j.hal.2008.08.017

[53] Mishra, P., *et al.,* (2022) Algal bloom, hypoxia, and mass fish kill events in the backwaters of Puducherry, Southeast coast of India, *Oceanologia,* 64(2), pp 396-403, https://doi.org/10.1016/j.oceano.2021.11.003

conditions will determine the concentration of unionised ammonia, degree of mixing and longevity within the system.

4.3.1.5. Coral reefs

Most large coral reef systems are present in shallow waters within the tropical zone (30°N and 30°S), where light can penetrate 50 m through the water column and deposition of suspended sediment is low. Cold water and deep-water coral reefs are also present (to a lesser extent) in coastal waters and ocean basins of temperate, cold and polar regions. Corals (hosts) mutually exchange nutrients with symbiotic algae (dinoflagellates), with the corals themselves providing inorganic nutrients and the algae providing organic nutrients[54]. Symbiotic algal growth is inorganic nitrogen-limited (reliant on inorganic ammonium and nitrate for photosynthesis) and limited ammonium is the main source of nitrogen. Approximately 0.6 μM (10.8 μgL^{-1}) of ammonia can sustain symbiotic dinoflagellate populations[55]. This symbiotic relationship and mutual exchange of nutrients determines the stability and maintenance of coral populations. Increases in nutrient concentrations within the environment can cause excessive algal growth, resulting in blooms and creating oxygen-limited conditions. More specifically in corals, elevated nutrient concentrations could lead to an increase in symbiotic algae density, a decrease in coral calcification or growth and a decrease in photosynthetic rate per algal cell[56]. Alteration of the symbiotic relationship between the coral and algae can inevitably result in the expulsion of symbiotic algae (known as coral bleaching). Bleached corals exhibit high mortality, reduced productivity and increased risk of diseases. Any impact on the algae can lead to reef degradation and the breakdown of coral reef systems. They can also be impacted by reduced light penetration due to nutrient-stimulated phytoplankton growth. This can lead to an increase in the growth of seaweed which can rapidly outgrow, smother and replace corals. Other fast-growing organisms can gain a competitive edge over corals with an increased nutrient supply (such

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[54] Tang, J., Ni, X., Wen, J., Wang, L., Luo, J., Zhou, Z. (2020). Increased Ammonium Assimilation Activity in the Scleractinian Coral *Pocillopora damicornis* but Not Its Symbiont After Acute Heat Stress. *Frontiers in Marine Science*, https://doi.org/10.3389/fmars.2020.565068

[55] Grover, R., Maguer, J-F., Reynaud-Vaganay S., Ferrier-Pagès, C. (2002). Uptake of ammonium by the scleractinian coral *Stylophora pistillata*: Effect of feeding, light and ammonium concentrations. *American Society of Limnology and Oceanography*, 47 pp 782 – 790.

[56] Dubinsky, Z., Stambler, N., Ben-Zion, M., McCloskey, R., Muscatine, L., Falkowsky, P. G. (1990). The effect of external nutrient resources on the optical properties and photosynthetic efficiency of Stylophora pistillata. *Proc. R. Soc.* 239, pp 231 – 246.

as an increase in ammonia)[57]. The stress susceptibilities vary between coral species and therefore, coral bleaching can occur when exposed to varied concentrations of ammonia[59]. Limited research has been undertaken on the direct impacts of unionised ammonia on coral reefs.

4.3.1.6. Mangroves

Mangroves are salt-tolerant evergreen forests, covering approximately 240 x 10^3 km^2 of sheltered subtropical and tropical coastlines[58], acting as a buffer between land and sea. Although this is a small portion of the world's coastline and forested landscape, mangroves are deemed vitally important for the productivity of tropical estuaries and global biochemical processes[59]. In addition, mangrove prob roots support diverse ecological communities of >100 species of fauna and >40 algal species[60].

Net primary productivity and nutrient biochemistry vary across different ecological types of mangroves and geomorphological settings, due to nutrient, sediment and freshwater inputs[61]. Mangroves grow in anaerobic and nutrient-limited soils (oligotrophic) exposed to high tidal interference, high winds and fluctuating salinities. As a result, ammonium is the primary form of nitrogen in mangrove soils supporting tree growth. At a mangrove forest in the Tio Coco Solo, Panama ammonia concentrations ranged from 0 – 0.2 mgL^{-1} [62]. As mangrove ecosystems are nutrient-limited, it has been suggested that they are more resistant to nutrient enrichment and eutrophication in comparison to neighbouring coastal lagoons and coral reefs, with potential beneficial effects on mangrove growth and ecosystem health[63]. However, high levels of sewage pollution can result in stunted growth

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[57] Costa, O. S., Nimmo, M, Attrill, M, (2008), Coastal nutrification in Brazil: A review of the role of nutrient excess on coral reef demise, *Journal of South American Earth Science,* 2(25), pp 257-270, https://doi.org/10.1016/j.jsames.2007.10.002

[58] Lugo, A. E. (1990). *Fringe wetlands*: In Ecosystems of the World. Elsevier, Amsterdam. Pp 143 – 169.

[59] Twilley, R. R., Chen, R. H., Hargis, T. (1992). Carbon sinks in mangrove forests and implications to the carbon budget of tropical coastal ecosystems. *Water Air Soil Pollution.* 64, pp 265 – 288.

[60] Cubit, J.D., Getter, C.D., Jackson, J.B.C., Garrity, S.D., Caffey, H.M., Thompson, R.C., Weil, E. and Marshall, M.J. (1987), "An oil spill affecting coral reefs and mangroves on the Caribbean coast of Panama", in STRI (Ed.), The 1987 Oil Spill Conference, STRI, Panama City, pp. 401-6.

[61] Twilley, R. R. (1997). *Mangrove wetlands*: In Southern Forested Wetlands: Ecology and Management. CRC Press, Boca Raton, FL, pp 445 – 473.

[62] Lin, B. B., Dushoff, J. (2004). Mangrove filtration of anthropogenic nutrients in the Rio Coco Solo, Panama. *Management of Environmental Quality: An International Journal*, 15, pp 131 – 142.

[63] Clough, B. F., Boto, K. G., Attiwill, P. M. (1983). Mangroves and sewage: a re-evaluation, Chapter 17 In: Tasks for vegetation science. Dr W. Junk Publishers, The Hague, pp 151 – 152.

and increased sensitivity to drought and hypersalinity[64]. In addition, nutrient enrichment may change the community assemblage of macroinvertebrates associated with mangrove forests.

4.3.1.7. Deep sea

The deep sea, defined as the part of the ocean at depths below 1000 m, covers 60 % of the Earth's surface, making it the planet's largest biome (homogeneous ecological formation). The geological, geochemical and physical conditions of the seabed and water column define varied habitats, sheltering specific biological communities. The ocean floor is composed of several distinct environments, including continental margins, abyssal plains, oceanic trenches, mid-ocean ridges and seamounts. Over 90 % of the deep seabed is covered with fine sediments composed of particles of biogenic, terrigenous, volcanic and authigenic origin[65].

This environment is globally characterised by an absence of sunlight, high pressure (increasing by 1 atmosphere of pressure every 10 m), low and relatively constant temperatures and salinities, low levels of water movement and an oxygen content generally sufficient for animal life to develop; but unlikely to allow for aerobic processes.

Ammonia is globally produced on an industrial scale, primarily by the Haber-Bosch process where N_2 and H_2 gases are allowed to react at pressures of 200 bar (≈ 2000m depth). However, ammonia (NH_3) is also produced naturally at hydrothermal vent sites in the deep sea. Here, iron-bearing minerals act as catalysts and nitrogen, both as N_2 and as its oxidized forms, NO_2 and NO_3, react with iron oxides, iron sulphides and basalt at high temperatures and pressures, resulting in high (relative to non-hydrothermal vent deep sea habitats) concentrations of ammonia. This ammonia in the hydrothermal vent plumes is estimated to be removed in 8-28 days[66]. Ammonium may be removed from deep sea seawater via two likely pathways: anaerobic ammonia oxidation to dinitrogen gas or assimilation into organic matter[67].

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[64] Mandura, A. S. (1997). A mangrove stand under sewage pollution stress: Red Sea. *Mangroves Salt Marshes*, 1, pp 255-262.
[65] Galéron, J. (2014). Deep-sea Environment. In: Fouquet, Y., Lacroix, D. (eds) Deep Marine Mineral Resources. Springer, Dordrecht.
[66] Cowen J.P Wen X Jones R.D Thomson R.E (1998) Elevated NH_4^+ in a neutrally buoyant hydrothermal plume. Deep-Sea Res. I45, 1891–1902.
[67] Lam, P., Cowen, J. P., Jones, R. D. (2004). Autotrophic ammonia oxidation in a deep-sea hydrothermal plume, FEMS Microbiology Ecology, 47, 2, Pp 191–206

If an ammonia spill were to occur in surface waters, it is unlikely that spilled ammonia would reach the deep sea. As liquid ammonia is less dense than water, liquid or aqueous ammonia would reach the deep sea only after being transformed or degraded.

Therefore, ammonia from a spill may reach the deep sea in one of two ways: as an allochthonous input related to a spill or via a vessel sinking and rupturing the fuel tank in the deep sea environment.

At the temperatures and pressures present within the deep sea, it is understood that ammonia would be as a compressible liquid. A compressible liquid is one in which the fluid density changes when it is subjected to high pressure-gradients. Ammonia is a non-newtonian fluid and therefore, is subject to deformation with shear stress. Viscosity is consequently changed as a function of that pressure and for compressible liquids, it is the kinematic viscosity which varies as the density increases. It is considered that if an ammonia spill were to reach the deep sea upon a vessel sinking and rupturing the fuel tank in the deep sea environment, the imposition of force upon the ammonia would need to be sufficient and directed to cause motion among the contents of the fuel tank. In a compressible fluid, the imposition of a force at one end of a system does not result in an immediate flow throughout the system. Instead, the fluid compresses near where the force was applied; that is, its density increases locally in response to the force. The compressed fluid expands against neighbouring fluid particles causing the neighbouring fluid itself to compress and setting in motion a wave pulse that travels throughout the system[68]. Water is considered a non-compressible fluid and may limit the motion of the wave pulse. Therefore, the rupturing of a fuel tank in the deep sea environment may not release ammonia to the surrounding water in the same manner as a spill at the ocean's surface and would likely contain the ammonia through the characteristics of fluids at extreme pressures. However, it may be assumed, though it is not completely known due to the variation in the forces involved, that the ammonia would still dissolve in the water. This may be a slower action than at the surface and once dissolved, dispersal may also be slower due to a lack of currents and wind-related ocean surface movement.

[68] Morrison, F. A. (2004.) Compressible Fluids. Michigan Technological University.

4.3.1.8. Polar regions

The polar regions are characterised by extreme environmental conditions induced by cold temperatures and extensive snow and ice cover. Polar freshwater and marine ecosystems have concentrated periods of primary productivity due to fluctuations in temperature, solar radiation and dissolved nutrient concentrations. Open ocean present in polar regions comprises of unique ecosystems, with nutrients sourced predominantly from ice algae, atmospheric input and riverine sources. Chemical processes such as dissolution, biodegradation and volatilization will occur at a slower rate in the polar regions, resulting in increased persistence of ammonia spills in the water column.

Nitrification rates in surface waters (0–6.5 m) of the Arctic Ocean (Chukci Shelf region) have been recorded at ~1 nmol N L^{-1} day^{-1}. The turnover time of ammonium in surface water is generally less than 1 day, implying that ammonium resource competition between ammonia-oxidising organisms and phytoplankton is intense in polar regions[69].

4.3.1. Summary of the impact of ammonia on habitats

Table 10 High-level summary of potential impacts from ammonia spills on aquatic habitats

Habitat	Key impacts of ammonia
Rivers	Increase in algal growth and biochemical oxygen demand could lead to eutrophication. Toxicity to fauna could have implications on food chain dynamics.
Estuaries	Increase in algal growth and biochemical oxygen demand could lead to eutrophication. Toxicity to fauna could have implications on food chain dynamics.
Wetlands	Increase in algal growth and biochemical oxygen demand could lead to eutrophication. Toxicity to fauna could have implications on food chain dynamics.
Coastal Waters	Increase in algal growth and biochemical oxygen demand could lead to eutrophication and smothering of intertidal habitats. Toxicity to fauna could have implications on food chain dynamics.
Coral Reefs	Increase in algal growth and biochemical oxygen demand could lead to eutrophication and smothering of intertidal habitats. Toxicity to fauna could have implications on food chain dynamics.

[69] Shiozaki, T., Ijichi, M., Fujiwara, A., Makabe, A., Nishino, S., Yoshikawa, C. & Harada, N. (2019). Factors regulating Nitrification in the Arctic Ocean: Potential impact of sea ice reduction and ocean acidification. Global Biochemical Cyles, 33, 1085 – 1099.

Polar regions	Changes in phytoplankton and ammonia oxidising organism population abundance. Toxicity to fauna could have implications on food chain dynamics.
Mangroves	Potential beneficial effects on mangrove growth and ecosystem health as nutrient limited systems. However, could result in stunted growth, increased sensitivity to drought and hypersalinity. Toxicity to fauna could have implications on food chain dynamics.
Deep Sea	Unknown impacts.

4.3.2. Ecological Receptors

Case studies for ecological receptors within each habitat are presented below. It should be noted that literature is limited in some instances on the ecotoxicology of ammonia to each ecological receptor and the impact of ammonia on each relevant environment. Therefore, Section 4.3.2 represents a selection of literature based on data availability for each habitat.

4.3.2.1. Bacteria

Chemolitho-autotrophic ammonia-oxidizing bacteria (AOB) and AOA are responsible for the rate-limiting step of nitrification in a wide variety of environments from hydrothermal vents to wetlands[70], making them important in the global cycling of nitrogen. These organisms are unique in their ability to use the conversion of ammonia to nitrite as their sole energy source.

Ammonia concentrations contribute to the composition of soil microorganisms, with AOB growth highest at elevated concentrations of 200 µg NH_{4+}-N per gram of soil, whereas AOA growth continues from 20 - 200 µg NH_{4+}-N per gram of soil[71]. However, ammonia is also toxic at certain concentrations to bacteria. More specifically, *Peptostreptococcus russellii* which is an anaerobe mesophilic bacterium was grown under ammonia-stressed conditions (0.29 M NH_{4+}, 74 mM NH_3) and compared with unstressed growth to determine physiological responses. When exposed to high concentrations of ammonia, the bacterium shifted its energy conservation systems to the upregulation of glycogen synthesis rather than major amino acid fermentation pathways[72]. This resulted in a decrease in cell growth of 0.54 ± 0.08 in the unstressed growth scenario, to 0.35 ± 0.03 in the ammonia-stressed scenario.

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[70] Kowalchuk, G. A., & Stephen, J. R. (2001). Ammonia-oxidizing bacteria: a model for molecular microbial ecology. Annual review of microbiology, 55, 485–529.

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No mortality of bacteria cells was recorded. Therefore, ammonia exposure may reduce the reproductive success of bacteria via slower cell growth.

For freshwater macrophytes, plant-specific differences in the composition and abundance of AOB and AOA have been described both in the rhizosphere[73] and on the epiphyton of submerged shoots[74], with the AOA generally outcompeting AOB at low ammonia concentrations. However, the addition of ammonia to the soil stimulated the growth of AOB but not AOA. The mortality of AOA increased upon the addition of ammonia to soil; however, the variance in these measurements was high[75]. Therefore, exposure to elevated ammonia may change the species composition of bacteria within the substrate based on tolerance.

4.3.2.2. Plankton

Ammonium is used as a nitrogen source by planktonic algae. However, unionised ammonia is highly lipo-soluble and easily absorbed into biological membranes[76]. As a result, unionised ammonia can replace sodium ions (Na^+) in certain cellular processes, altering the ionic equilibrium and causing inhibited growth and photosynthesis[77]. This can result in a reduction in the extent and potential mortality of plankton populations. For example, in a deep waste treatment pond under natural conditions, a significant decrease in zooplankton community biomass (mix of protozoa (ciliata), rotifera and crustacea) was recorded at un-ionised ammonia concentrations of > 2.5 mg L^{-1}. When exposed to unionised ammonia < 2.5 mg L^{-1}, zooplankton biomass was 743 ± 449 mgC m^{-3}, in comparison to 71 ± 23 mgC m^{-3} when exposed to >2.5 mg L^{-1} of unionised ammonia. Rotifera was the most affected biological group within the zooplankton community. This varied from phytoplankton biomass, which significantly increased when exposed to unionised ammonia concentrations > 2.5 mg L^{-1} [78].

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[78] Arauzo, M. (2003). Harmful effects of un-ionised ammonia on the zooplankton community in a deep waste treatment pond. *Water Research*, **37** 1048 - 1054

Estuaries

Unionised ammonia concentrations and the effects on estuarine plankton were examined in a study by Livingston et al.79. Field data indicated that ammonia concentrations in the receiving system (Amelia Estuary; range, 0.19–0.43 mgL–1) were significantly higher than those taken in the reference system (Nassau Estuary; range, 0.09–0.11 mgL–1). Significantly reduced chlorophyll α concentrations were noted in the Amelia system and these varied inversely with ammonia concentrations. Field surveys also indicated that net phytoplankton abundance and species richness were significantly lower in the Amelia system. Although zooplankton abundance was also significantly lower at various Amelia stations, no significant differences in zooplankton species richness between the two study areas were recorded. This study showed that elevated ammonia concentrations in estuarine systems have an overall negative impact on zooplankton populations, with less defined tolerance thresholds than phytoplankton where the abundance and species richness were both affected.

Coastal waters

The uptake of nitrogen (including ammonia) and the growth of phytoplankton has been described by Michaelis-Menton kinetics, meaning that the growth rate is likely to increase hyperbolically with ammonia concentrations[80,81]. A study investigating elevated nutrient concentrations in coastal sewage-enriched areas found that sewage with ammonia concentrations three to five times greater than in unenriched areas, resulted in a 10-fold increase in phytoplankton biomass[82]. However, it was noted that other nutrients, including phosphate, were also at elevated concentrations. Abiotic parameters such as nitrogen availability can also impact the growth response of phytoplankton to increased ammonia concentrations, with the more rapid growth of phytoplankton recorded in tropical areas compared to temperate areas. This is due to phytoplankton populations in tropical areas

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[82] Hardy, J. and Jubayli, Z. (1976) Phytoplankton standing crop and sewage nutrient enrichment along the central coast of Lebanon. *Environmental Science*.

being adapted to lower nitrogen levels[83]. Photosynthetic production may also be inhibited at high ammonia concentrations. A study on sea lettuce *Ulva lactuca* found that photosynthetic production was stimulated at ammonia concentrations of 30 - 60 μM (542.4 - 1,084.8 μgL^{-1}) and inhibited at concentrations of >60 μM (>1,084.8 μgL^{-1})[84]. Moreover, a study on dinoflagellate phytoplankton found that growth and photosynthesis were inhibited at concentrations of 100 - 200 μM (1,808-3,616 μgL^{-1}) of ammonia[85]. Therefore, elevated ammonia can have both a positive and negative impact on phytoplankton populations depending on the concentration present in the medium.

In addition to changes in growth and biomass, low levels of ammonia enrichment in the marine environment could lead to significant shifts in species composition of phytoplankton and near-shore benthic macroalgae populations. A study on coastal sewage enrichment found that increased concentrations of ammonia reduced phytoplankton species diversity and shifted species dominance from diatoms to blue-green algae and dinoflagellates[86]. This could have impacts on pelagic and benthic ecosystem functioning via changes in the biogeochemical cycling of key elements and input of organic matter to sediment. For example, diatoms sink quickly out of the epipelagic zone, whereas dinoflagellates sink as inert resting cysts or lyse in the water column contributing to slow-settling phytodetritus[87]. In diatom-dominated communities, the stoichiometry of sinking material has a higher C:N:P ratio than in dinoflagellate-dominated communities. Diatoms also synthesis large quantities of dissolved silicate, nitrogen and phosphate. On a large scale, this could have consequences on food quality for primary consumers and remineralisation in the pelagic and benthic systems[88]. Another study found that the diversity of macroalgae also decreased with increasing proximity to coastal sewage effluents[89].

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Polar regions

Nitrogen is the primary limiting nutrient in the growth of phytoplankton in the Polar regions Ocean[90],[91] and thus, it plays a critical role in controlling the biological carbon cycle and influencing the nitrogen inventory in the Atlantic Ocean. Nitrification is mediated by specialized prokaryotes that convert ammonia into nitrite and then to nitrate. Ammonia oxidation, the first rate-limiting step in nitrification, is known to be susceptible to changes in ammonium concentration, pH and light[92]. Ammonia is the substrate for ammonia oxidation and, thus, its availability limits nitrification. In the upper ocean of the polar regions, AOB and AOA compete with phytoplankton for ammonium. Wan *et al.*[93] recently showed that ambient nitrate levels could determine the outcome of this competition. Namely, nitrifiers are outcompeted for ammonium resources by phytoplankton in nitrate-depleted waters while they have higher ammonium affinity than phytoplankton in nitrate-rich waters. There is limited literature on the impact of ammonia on plankton present in the polar regions, however, polar zooplankton have been recorded with elevated lipid/ trimethylamine oxide which is hypothesized to be an adaptive trait to enhance ammonia tolerance[94].

4.3.2.3. Macrophytes

Macrophytes are aquatic plants that can be seen with the naked eye ("large plants"[95]) such as large filamentous algae, mosses and liverworts, encrusting lichens, bryophytes and vascular flowering plants. They can be categorised based on their lifeform which includes emergent, floating-leaved, submerged and free-floating plants[96]. Macrophytes have multiple functioning roles within an ecosystem which include the uptake of nutrients, oxygenating the substrate, attenuating water flow and providing surfaces for microbial

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[90] Tremblay, J. É., Anderson, L. G., Matrai, P., Coupel, P., Bélanger, S., Michel, C., & Reigstad, M. (2015). Global and regional drivers of nutrient supply, primary production and CO2 drawdown in the changing arctic regions Ocean. Progress in Oceanography, 139, 171–196.

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colonisation[97]. This is referred to as habitat provisioning. At low to moderate concentrations, ammonia stimulates biomass production. However, elevated concentrations of ammonia (NH_3 and NH_4^+) that exceed specific tolerance levels can directly inhibit photosynthesis via penetration through the cell membrane, altering biochemical and physiological processes. This can lead to a reduction in growth rate and biomass reduction, chlorosis of leaves, deterioration of species extent and potential population mortality. Toxicity, as previously mentioned, is predominantly caused by unionised ammonia, which is two orders of magnitude more toxic than ammonium ion. The sensitivity and the toxic threshold of macrophytes to high concentrations of ammonia vary per species. The cause of toxicity is due to the elevated energy consumption caused by ammonium ion transport costs[98] which can reduce the activity of nitrate reductase and glutamine synthetase[99], decreasing soluble protein and sugar content[100] and causing oxidative stress or an imbalance in reactive oxygen species[101].

Rivers

Ammonia toxicity in duckweed species has been examined due to interest in the application of duckweed for nutrient recovery of wastewater. Duckweed also preferentially sequesters ammonium, rather than other nitrogen sources. For example, the common duckweed *Lemna minor* was reviewed when exposed to unionised ammonia. At 3.0 mg L^{-1}, duckweed growth was significantly depressed by ≥ 20%[102]. A similar result was also recorded in an alternative experiment, where 7.2 mg L^{-1} of unionised ammonia caused 50% duckweed growth inhibition[103]. However, it is difficult to directly compare studies due to differences in water temperature, pH, the composition of the wastewater and duckweed species used in the experiment.

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97 Surrency, D. (1993.) Evaluation of aquatic plants for constructed wetlands. In: Moshiri, G.A. (Ed.), Constructed Wetlands for Water Quality Improvement. Lewis Publishers, Boca Raton, FL, pp. 349–357.

98 Britto, D.T., Siddiqi, M.Y., Glass, A.D.M. and Kronzucker, H.J. (2001). Futile transmembrane NHþ4 cycling: A cellular hypothesis to explain ammonium toxicity in plants. P. Natl. Acad. Sci. USA 98, pp 4255–4258.

99 Gao, J., Li, L., Hu, Z., Yue, H., Zhang, R. and Xiong Z. (2016). Effect of ammonia stress on nitrogen metabolism of Ceratophyllum demersum. Environ Toxicol Chem, 1 pp 205 – 211.

100 Cao, T., Ni, L.Y. and Xie, P. (2004). Acute biochemical responses of a submersed macrophyte, Potamogeton crispus L., to high ammonium in an aquarium experiment. J. Freshwater Ecol. 19, pp 279–284.

101 Nimptsch, J and Pflugmacher, S. (2007). Ammonia triggers the promotion of oxidative stress in the aquatic macrophyte Myriophyllum mattogrossense. Chemosphere, 66, pp 708 – 714.

102 Wang, W. (1991). Ammonia toxicity to macrophytes (common duckweed and rice) using static and renewal methods. Environmental Toxicology and Chemistry. 10, pp 1173 – 1177.

103 Caicedo, J. R., Van der Steen, N. P., Arce, O., Gijzen, H. J. (2000). Effect of total ammonia nitrogen concentration and pH on growth rates of duckweed (Spirodela polyrrhiza). Water Resources. 34, pp 3829 – 3835.

Estuaries

Due to ammonia's frequent presence and potential toxicity in sediments, it is one of three classes[104] of toxicants suspected of causing the majority of observed sediment toxic effects[105]. However, *Ulva lactuca* removes ammonia from the aqueous phase by consuming it as a nutrient, thus reducing its' exposure to organisms, particularly epibenthic species[106].

Wetlands

One study reviewed the impact of elevated ammonia (defined as $NH_3 + NH_4OH + NH_4^+$) concentrations during flooded and unflooded conditions on the growth of common rush *Juncus effusus*, *Sagittaria latifolia*, common cattail *Typha latifolia*, narrow-leaved cattail *Typha angustifolia* and great bulrush *Schoenoplectus tabernaemontani*[107]. These species are characteristic of temperate wetlands. At ammonia concentrations >200 mg/l, growth was inhibited for the common rush, *S. latifolia* and common cattail and ammonia concentrations >100 mgL^{-1} inhibited the growth of great bulrush, after a month. Note that shorter periods of exposure did not seem to effect growth. Flooding the plants with 10 cm of water did not significantly increase the ammonia toxicity for common cattail and great bulrush. The concentration of ammonia that stimulates biomass production varied from 45 mg L^{-1} in great bulrush to 110 mg L^{-1} in common cattail[110]. In contrast, characteristic macrophytes of tropical wetlands have also been reviewed in relation to growth rate and physiological response to elevated concentrations of ammonium chloride (NH_4Cl). This included bulrush *Typha orientalis*, *Scirpus validus*, Indian shot *Canna indica* and Japanese roof iris *Iris tectorum*[108]. Results showed that *S. validus* and Japanese roof iris were more sensitive to ammonium chloride concentrations above 100 mgL^{-1} in comparison to Indian shot and bulrush, that showed stimulated growth at 100 – 200 mgL^{-1}. Physiological responses of the plants to elevated ammonium chloride included oxidative stress, and

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[104] The other two classes are metals and organic toxicants.

[105] Ho, K.T., Burgess, R.M., Pelletier, M.C., Serbst, J.R., Ryba, S.A., Cantwell, M.G., Kuhn, A. & Raczelowski P. (2002).An overview of toxicant identification in sediments and dredged materials. Marine Pollution Bulletin, 44, pp. 286-293

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[108] Wang, Y., Wang J., Zhao, X., Song, X., Gong J. (2016). The inhibition and adaptability of four wetland plant species to high concentration of ammonia wastewater and nitrogen removal in constructed wetlands. *Bioresource Technology*, 202, pp 198 – 205.

increased proline and malondialdehyde contents[110]. Based on the interaction of ammonia with abiotic parameters such as temperature, pH and salinity, wetlands in tropical climates with high freshwater inputs (present in rivers and upper estuaries) are deemed most vulnerable to an ammonia spill scenario.

Coral reefs

Elevated concentrations of ammonium can cause the expulsion of symbiotic algae associated with coral bleaching. However, the stress threshold varies for different coral species. For example, at ≥ 0.001 mmol/L (≥ 0.00018 μgL^{-1}) of ammonium chloride solution, *Acropora nobilis* continued to expel symbiotic algae while in *Palythoa* species and *Alveopora verrilliana* the expulsion of symbiotic algae decreased with increasing ammonia concentrations[109]. This is due to algae requiring inorganic nitrogen for photosynthesis and growth.

Polar regions

Alpha macrophyte diversity declines at high latitude polar regions and one of the most common taxa is alternate water-milfoil *Myriophyllum alterniflorum*.

In one study[110], nitrate reductase activity was measured in three alternate water-milfoil populations (upstream, median and downstream populations) after experimental enrichment with ammonium. Ammonium enrichment decreased activity starting at very low concentrations. However, inhibition levels depended on tested populations, with upstream populations being less sensitive due to the natural ammonium content in water.

Mangroves

Mangrove forests dominate the world's tropical and subtropical coastlines. Similar to other plant communities, nutrient availability is one of the major factors influencing mangrove forest structure and productivity. Many mangrove soils have extremely low nutrient availability, although nutrient availability can vary greatly among and within mangrove forests. A complex range of interacting abiotic and biotic factors controls the availability of

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[109] Baohua, Z., Guangce, W., Bo, H., Tseng, C. K. (2004). Effects of temperature, hypoxia, ammonia and nitrate on the bleaching among three coral species. *Chinese Science Bulletin*, 49, pp 1923 – 1928.

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nutrients to mangrove trees. Due to the low nutrient availability, mangroves are characteristically plastic in their ability to opportunistically use nutrients when available. Nitrogen and phosphorus have been implicated as the nutrients most likely to limit growth in mangroves. Ammonium is the primary form of nitrogen in mangrove soils supporting tree growth, in part, as a result of anoxic soil conditions.

There is evidence that nutrient additions can stimulate mangrove growth[111,112] as sediment microbial communities are capable of depurating large amounts of inorganic nitrogen, however, eutrophication can also have negative consequences for mangrove growth.

A Red Sea study[113] demonstrated that grey mangrove *Avicennia marina* grown under eutrophication stress showed stunted morphology and that mortality rates within the effected mangrove strand were high, probably due to the loss of pneumatophores and soil anoxia. However, this was observed over a prolonged period and not within the context of an ammonia spill.

Nutrient enrichment can also increase sensitivity to drought and hypersalinity due to energy allocation to the canopy rather than the root system indirectly increasing mortality rates due to enhanced susceptibility to water deficits[114]. Eutrophication can also increase herbivory rates via the increase in abundance of marine wood-borers[115] and bark-mining moths impacting the health of the mangrove forest[116].

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[116] Feller I.C., Chamberlain A. (2007). Herbivore responses to nutrient enrichment and landscape heterogeneity in a mangrove ecosystem, Oecologia, vol. 153 Pp 607-616

4.3.2.4. Invertebrates

Rivers

Relatively few toxicity studies with freshwater invertebrates have made the distinction between the ionised and unionised forms of ammonia. Tabata in 1962 concluded that the ionised ammonia fraction was responsible for only 2 % of total ammonia toxicity to the water flea *Daphnia pulex*[117]. Williams *et al* attempted to determine whether the ammonium ion was acutely toxic to 11 species of freshwater invertebrates or whether mortalities recorded in the concentration-response test were due predominantly to unionised ammonia[118]. This study indicated that median lethal threshold limits range from 0.25 to 1.6 mgL^{-1} NH_3. Another study investigated the long-term effects of ammonia exposure in the large water flea *Daphnia magna* and found a no observed effect concentration (NOEC) of 0.79 mgL^{-1} [119]. In addition, it was found that at higher test concentrations of 1.3 mgL^{-1}, daphnid growth was significantly reduced and reproduction was also affected.

Fingernail clam *Musculium transversum*, a species of freshwater clam, exhibits inhibited ciliary beating at 0.08 - 0.09 mgL^{-1} of ammoniacal nitrogen when in conditions of 7 - 15 °C and pH 7.8 - 8.3[120].

A study on the toxicity of unionised ammonia to nine freshwater invertebrate species native to New Zealand found 96 h effective concentration (EC50) values of 0.18 - 0.8 mgL^{-1}[121]. The least sensitive species was the shrimp *Paratya curvirostris* and the most sensitive was the crustacean *Paracalliope fluviatilis*. Species that were most sensitive to ammonia were those usually associated with lowland streams.

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[117] Tabata, K. (1962). Toxicity of ammonia to aquatic animals with reference to the effect of pH and carbon dioxide. Bull Tokai Reg Fish Research Laboratory, 34, pp 67-74.

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[120] Anderson, K.B. (1978) Rapid assessment of water quality using the fingernail clam, Musculium transversum. *Illinois University Water Resource Centre.*

[121] Hickey, C.W. and Vickers, M.L. (1993) Toxicity of ammonia to nine native New Zealand freshwater invertebrate species. Archives of Environmental *Contamination and Toxicology*, 26, pp. 292-298.

Estuaries

A study on the species distribution of benthic diatoms on estuarine mudflats found that a shift in species occurred at 2 - 10mM (36.2 - 28.1 mgL^{-1}) of ammonium, with some species being inhibited and others tolerating the increased concentrations[122].

Wetlands

Species such as midge flies *Chironomus tentans* which are present within northern hemisphere wetlands indicate that unionised ammonia: lethal concentration (LC50) was 0.72 mgL^{-1} at a pH of 6.3 and total ammonia: LC50 was 82.4 mgL^{-1} at a pH of 8.53[123].

Coastal waters

Bivalves are highly sensitive to ammonia, despite being naturally low in seawater. A study found that the mortality of bay scallops increased when both the pH and ammonia increased. Unionised ammonia concentrations above 1.0 mg $N\text{-}NH_3$ L^{-1} resulted in 100 % scallop mortality within 72 h. Studies on juvenile life stages of the blue swimmer crab *Portunus pelagicus* have shown a 96 h LC50 of 1.65 - 3.62 mgL^{-1} ammoniacal nitrogen, with tolerance increasing with ontogenetic development[124]. Further investigation on the blue swimmer crab showed that even at sub-lethal concentrations of ammoniacal nitrogen, the gills of juvenile crabs showed drastic histopathological changes within a short period of exposure[125]. These changes included epithelial damage/ thickening, pillar cell necrosis and distortion, constriction and collapse of lamellae. Lamellae collapse occurred within 1 hour of exposure to 0.706 mM (12.8 mgL^{-1}) ammoniacal nitrogen and within 3 hours of exposure to 2.798 mM (50.6 mgL^{-1}).

A study on the exposure of California blackworm *Lumbriculus variegatus* to varying concentrations of ammonium chloride found that the LC50 for unionised ammonia was 0.455 mgL^{-1} at a pH of 6.52 and for total ammonia was 6.6 mgL-1 at a pH of 8.59.

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[122] Admiraal, W. and Peletier, H. (1980) Distribution of diatom species on an estuarine mud flat and experimental analysis of the selective effect of stress. *Journal of Experimental Marine Biology and Ecology*.

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[125] Romano, N. and Zeng, C. (2010) Changes to the histological gill structure and haemolymph composition of early blue swimmer crab Portunus pelagicus juveniles during elevated ammonia-N exposure and the post-exposure recovery. *Aquaculture Research*, 41, pp. 468-480.

Larvae of American lobster *Homarus americanus*, under 25 °C conditions, exhibited significant mortality at 0.05 mgL^{-1} residual chloramine and had an acute LC50 of 0.32 mgL^{-1} [126]. Under 35 °C conditions, the lobster larvae exhibited respiratory stress at <0.01 mg/l residual chloramine.

A study on finger plough shell *Bullia digitalis*, an African marine gastropod, investigated tolerance to solutions of ammonium nitrate in natural sea water under 12 – 13 °C conditions[127]. Inhibited burrowing activity was recorded at 50 mgL^{-1}, reversible paralysis at 300 - 400 mgL^{-1} and irreversible paralysis at 500-1500 mgL^{-1}.

Brine shrimp *Artemia salina* reduced their feeding rate to 50 – 66 % of the 'normal' feeding rate at ammoniacal nitrogen concentrations of >100 μM (>1,808 μgL^{-1})[128].

Coral reefs

High ammonia concentrations are considered a stress factor for corals, although evidence has demonstrated that tolerance is variable depending on species. A study investigating the impacts of ammonia concentration on the bleaching of three species of coral (*Acropora nobilis, Palythoa* sp. and *Alveopora verrilliana*) found that a concentration of 0.001 mmol/L ammonia could significantly increase the expulsion of symbiotic algae from the coral species and therefore, increase bleaching[129]. Moreover, another study investigated the acute toxicity of ammonia to the *Acropora* sp. and *Porites* sp. corals and found 48 h LC50 values of 0.043 mgL^{-1} and 0.054 mg/L^{-1} respectively at a temperature of 33 °C[130]. In addition, Disc coral *Turbinaria peltata* has been shown to have a 48 h LC50 of 0.075 mgL^{-1} ammonia, also at 33 °C[131]. Both studies looking at the LC50 of coral species found that mortality was below 50 % at 24h and 48h under 30 °C conditions and at 24h under 33 °C conditions. A study in

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127 Brown, A.C. and Currie, A.B. (1973) Tolerance of Bullia digitalis to solutions of ammonium nitrate in natural sea water. *South African Journal of Science*.
128 Hanaoka, H. (1977) Harmful effect of ammonia on growth of the brine shrimp Artemia salina and inhibition of ammonia accumulation with an alga Chlorella. *Bulletin of Plankton Society of Japan.*
129 Zhu, B., Wang, G., Huang, B. and Tseng, C.K. (2004) Effects of temperature, hypoxia, ammonia and nitrate on the bleaching among three coral species. *Chinese Science Bulletin*, 49, pp. 1923-1928.
130 Chawakitchareon, P., Udomsap, B. and Rungsupa, S. (2018) The effect of temperature and ammonia on species-dependent coral health status: A comparative case study of Acropora sp and Porites sp. *New Biotechnology*, 44, pp. 149-150.
131 Udomsap, B., Chawakitchareon, P. and Rungsupa, S. (2018) Effects of temperature and ammonia on coral health status: a case study of disc coral. *Journal of Engineering, Management and Applied Sciences and Technologies*, Vol. 9, 1.

2009[132] recorded the impact of ammonia supplements (NH_3 gas and NH_4^+ ion) on starved giant sea anemone hosts *Entacmaea quadricolor* and their endosymbiotic zooxanthellae *Symbiodinium spp.*, under laboratory conditions. It found that the zooxanthellae within host anemones increased in abundance (173 % and 139 % respectively) and provided the hosts with energy that minimized host body size loss.

Deep sea

A study looking at the exposure of four marine benthic amphipod species to ammonia in seawater found 96-hour LC50 values in the range of 49.8 - 148.3 mgL^{-1} of total ammonia and 0.83 - 3.35 mgL^{-1} of unionised ammonia. In order from least to most sensitive to ammonia, the species studied were the amphipods *Grandidierella japonica, Eohaustorius estuaries, Rhepozynius abronius* and *Ampelisca abdita*[133].

4.3.2.5. Reptiles

Literature on the potential impacts of elevated concentrations of ammonia on reptiles is limited. However, research has been undertaken on the toxic effects of ammonia on freshwater turtles (native to tropical climates). Therefore, the following section will focus on case studies identified on freshwater turtles, which may also relate to other reptile groups including alligators, crocodiles, sea iguanas *Amblyrhynchus cristatus* and sea turtles.

Rivers

The potential impacts of ammonia were examined on the intestinal health and microbiota composition of red-eared sliders *Trachemys scripta elegans,* which are native freshwater turtles in eastern America and adjacent regions of Mexico. The species occupies multiple habitats including rivers, ditches, swamps and lakes. When exposed to ammonia at 1.418 mg $NH_3\ L^{-1}$ for 30 days, the thickness of the intestinal wall decreased and the length of the intestinal villus decreased. In addition, ammonia changed the bacterial composition of the turtles[134]. This was similarly echoed by a study investigating the impact of ammonia on Chinese striped-neck turtles *Mauremys sinensis* which are native to China, Taiwan and

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[132] Roopin, M., Chadwick, N. E. (2009). Benefits to host sea anemones from ammonia contributions of resident anemonefish, Journal of Experimental Marine Biology and Ecology, Volume 370, Issues 1–2, Pp 27-34

[133] Kohn, N.P., Word, J.Q., Niyogi, D.K., Dillon, T. and Moore, D.W. (1994) Acute toxicity of ammonia to four species of marine amphipod. Marine Environmental Research.

[134] Ding, L., Huang, Z., Lu, Y., Liang, L., Li, N., Xu, Z., Zhang, J., Shi, H., Meiling, H. (2021). Toxic effects of ammonia on intestinal health and microbiota in red-eared slider (*Trachemys scripta elegans*). *Chemosphere.* 280.

northern and central Vietnam. At 100 – 200 mgL^{-1}, the length of the intestinal villus decreased causing mucosal membrane damage and altering the bacteria composition of the intestines. This experiment was also undertaken over a 30-day period[135].

Based on the results above, there is potential for an ammonia spill to cause physiological damage to freshwater turtles if present within the river system. However, the degree of damage will be determined by the concentration of liquified ammonia in solution and length of time the freshwater turtles were exposed.

Within a wider context, ammonia spills may impact on habitat quality and availability of prey, as reptiles are typically omnivores. This could have implications on local population dynamics.

4.3.2.6. Fish

Literature on the potential impacts of elevated concentrations of ammonia on fish is extensive, though most of the research is focussed on freshwater species. Fish excrete ammonia via the gills as the product of protein metabolism and high concentrations of ammonia in the surrounding environment can prevent ammonia excretion in fish or cause a net increase in the uptake of ammonia, resulting in an imbalance of ionic regulation. This can cause hyper-excitability and alternations in the behaviour of the individual such as reduced feeding, slower growth (long-term exposure), convulsions and mortality, if at toxic levels[136]. In addition, if fish are not feeding, if they are active, or if they are swimming, they will be further at risk from ammonia toxicity. The permeability of biological membranes increases by a factor of 2 – 3 for every 10 °C increase in water temperature; therefore, in tropical environments ammonia is more toxic due to the higher proportion of unionised ammonia created by the abiotic conditions and increased permeability into biological membranes[138]. The potential modes of toxic action of ammonia within fish include gill damage (eventually causing suffocation), alteration of biochemical mechanisms, osmoregulatory disturbance, severe electrolyte imbalance, reduction in cellular K^+ levels,

[135] Khan, I., Huang, Z., Liang, L., Li, N., Ali, Z., Ding, L., Hong, M., Shi, H. (2021). Ammonia stress influences intestinal histomorphology, immune status and microbiota of Chinese striped-neck turtle (*Mauremys sinensis*). *Ecotoxicology and Environmental Safety*. 222

[136] Eddy F. B. (2005). Ammonia in estuaries and effects on fish. *Journal of Fish Biology*, 67, pp 1495 - 1513

inhibition of ATP production and an increase in cerebral glutamine levels leading to a decrease in the neuro-inhibitor GABA[137].

Rivers

The toxicity of unionised ammonia to freshwater fish is approximately 0.068 – 2.0 mgL^{-1} [138]. In freshwater habitats, fish can be divided into two main groups: cyprinid fish including members of the carp family and salmonid fish which include trout species[139]. These groups of fish have been used to establish Environmental Quality Standards (EQS) to protect rivers within Europe and an unionised ammonia standard was proposed in 1978 of 0.021 mgL^{-1} to protect both salmonid and cyprinid waters[140]. Toxicity trials with rainbow trout *Oncorhynchus mykiss* and roach *Rutilus rutilus* have indicated that both are similarly sensitive to ammonia, though rainbow trout responded faster than roach and some studies have also shown that the early life-stages of fish (eggs and fry) are more sensitive than older free-swimming stages of fish [77].

Estuaries

As discussed in Section 4.3 the upper oligohaline reach of an estuary can be equivalent to riverine systems, whereas the lower reaches of an estuary are polyhaline and similar to coastal waters. The impact of ammonia spills on estuaries and the ecosystems within in is dependent on several factors. When estuarine fish are exposed to ammonia, they are likely to be most at risk when they are larvae or juveniles; if the temperature is elevated; if salinity is near the sea water value; and if the pH value decreases below pH 7. Conditions such as these will favour a transfer of ammonia from the water into the fish, with retention of ammonia by fish being likely. This can be both ionised and unionised ammonia.

Successful navigation of the estuary by migrating species could involve changes in physiological and behavioural systems so that there is less vulnerability to the stressful effects of ammonia and other pollutants. This could result in a shift in the behaviour of fish with such a spill.

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[137] National Rivers Authority (1992). Predicting the toxicity of ammonia to freshwater fish. Water Research Council R&D Report 83.

[138] Seager, J., Wolff, E., Cooper, V. A. (1988). Proposed environmental quality standards for list II substances in water. Ammonia. WRC Technical Report TR 260.

[139] Nelson, J.S, (2006). Fishes of the world (4th edition). John Wiley & Sons, pp 601.

[140] National Rivers Authority (1990). Determination of Ecotoxicological effects – A review of the toxicity of common pollutants to fish. Water Research Council R&D Report P-104.

Wetlands

Section 4.3.1.2 indicates a range of habitats available to fish along with the water environment (static, freshwater, brackish or saline). Within temperate wetlands, the habitats present are more likely to favour cyprinid species of fish and species belonging to catfish and eel families. However, in more tropical ecosystems the fish species composition is likely to be more diverse. Wetland habitats are likely to naturally exhibit seasonal and even diurnal variations in salinity and dissolved oxygen concentrations. Research undertaken by Alabaster & Lloyd[141] indicated that the toxicity of ammonia increases at low levels of dissolved oxygen. In contrast, similar experiments undertaken with American fathead minnow *Pimephales promelas*[142] showed that there was no difference in toxicity between dissolved oxygen at 2.6 to 8.9 mgL^{-1}. Studies undertaken within recreated tidal wetlands[143] have also shown the importance of wetland areas to marine juvenile fish at and around high water, though these juvenile fish are only present on site for short periods per tidal cycle.

Coastal waters

The acute toxicity of unionised ammonia to marine fish is approximately 0.09 – 3.35 mgL^{-1} depending on the species, temperature and pH[144]. Marine fish have much lower ion concentrations within their body fluids than seawater and to overcome osmotic water loss, they drink seawater[145].

Coral reefs

Red drum *Sciaenops ocellatus* are a species present in coral reefs of south Florida, the Gulf of Mexico and the Caribbean.[146]. Ambient water quality criteria for ammonia developed by the United States Environmental Protection Agency (EPA)[147] have indicated that red drums have a mean LC_{50} value of 0.55 mgL^{-1} of unionised ammonia. Planehead filefish *Stephanolepis hispida* were also considered within the EPA review, which are found within

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[141] Alabaster, J.S. & Lloyd, R. (1982). Water quality for European freshwater fish. Butt

[142] Thurston, R.V., Russo, R.C. & Phillips, G.R. (1983). Acute toxicity of ammonia to fathead minnows. Transactions of the American Fisheries Society, 112, pp.696-704

[143] Colclough, S., Fonseca, L. Astley, T. & Watts, W. (2005). Fish utilisation of managed realignments Fisheries Management and Ecology, 2005, 12, 351–360

[144] Eddy F. B. (2005). Ammonia in estuaries and effects on fish. *Journal of Fish Biology*, 67, pp 1495 - 1513

[145] Bone, Q., Marshall, N.B., & Blaxter, J.H.S. (1995). Biology of fisheries (2nd Edition). Chapman & Hall, pp 332.

[146] https://www.marinespecies.org/aphia.php?p=taxdetails&id=159335#distributions.

[147] United States Environmental Protection Agency (1989). Ambient Water Quality Criteria for Ammonia (Saltwater). Office of Water Criteria and Standards Division, Washington, DC 20460.

similar tropical coral reef habitats as well as extending its range to Eastern Atlantic and North Africa[148]. A mean LC_{50} value of 0.83 mgL^{-1} of NH_3 was reported for planehead filefish within the EPA study.

Polar regions

Ammonia toxicity research for polar regions' specific species is limited, though work has been undertaken for salmonid species which are present within southern polar regions. Such species include Atlantic salmon *Salmo salar*, rainbow trout *Oncorhynchus mykiss* and brown trout *Salmo trutta*. It should be noted that both rainbow and brown trout are catadromous species that migrate to the sea to spawn ('at sea' life-strategy adaptation). Once at sea, the species are referred to as steelhead trout and sea trout respectively. Rainbow/ steelhead trout are native to coldwater tributaries of the Pacific Ocean in Asia and North America and brown/ sea trout are native to coldwater tributaries of the Atlantic. Atlantic salmon overwinter at sea, off the coast of Greenland during the marine phase of their life. Ecotoxicological studies undertaken by the National Rivers Authority in 1990 have indicated that LC_{50} values between 0.28 of 0.41 mgL^{-1} of unionised ammonia were reported for all three salmonid species.

The 1989 EPA research also provided toxicity values for winter flounder *Pseudopleuronectes americanus* which reside in the sub-polar regions waters of north-east America and Canada[149]. A mean LC_{50} value of 0.45 mgL^{-1} of unionised ammonia was recorded for winter flounder.

Mangroves

Due to the structural complexity of mangrove forests, they trap and store disproportionate amounts of suspended particles, nutrient-rich organic matter and pollutants from catchment runoff in comparison to other adjacent habitats. As a result, mangroves have formed key nursery grounds for a diversity of fish including rainbow parrotfish *Scarus guacamaia* (near threatened) and Atlantic goliath grouper *Epinephelus itajara* (critically endangered) due to the provision of shelter and food (bacteria and mangrove tree detritus). The productivity of mangroves can cause an increase in adult fish and invertebrate biomass

[148] https://www.marinespecies.org/aphia.php?p=taxdetails&id=307126.
[149] https://www.fishbase.se/summary/Pseudopleuronectes-americanus.html#

within adjacent reefs[150]. Due to the similarity in fish community composition of mangroves to tropical reefs, a mean LC_{50} value of 0.55 - 0.83 mgL^{-1} of unionised ammonia is considered appropriate for fish species associated with mangrove habitats, as determined by EPA

Deep sea

Given the depths associated with the deep sea (>1000 m), there are no ecotoxicological studies have been undertaken on deep sea fish.

However, it is noted that the Pacific hagfish *Eptatretus stoutii* can both withstand and recover from exposure to high external ammonia concentrations. This tolerance is likely due to the feeding behaviour of Pacific hagfish. As scavengers, they feed on intermittent food falls of carrion (e.g. fish, large marine mammals), which during decomposition contain high concentrations of total ammonia[151].

4.3.2.7. Birds

Thus far, there has been limited research on the impact of gaseous or liquified ammonia on the physiology of wild birds. Therefore, the following assessment focussed on the literature available on the impact of gaseous ammonia associated with poultry farming on bird welfare and condition. Although this does not consider impacts in an open/ unconfined environment, the literature indicated the potential physiological effects of gaseous ammonia on birds. In poultry houses, gaseous ammonia >25 mgL^{-1} adversely affects bird performance[152]. At high concentrations, ammonia irritates the conjunctiva and corneas of the eyes, which can lead to conjunctivitis and even partial or complete blindness under long-term exposure. It can also impact the mucous membranes of the respiratory tract. Cilia that form the mucociliary blanket in the respiratory tract can become paralysed or even lost, causing mucus present on the surface of the trachea to not be cleared. This leaves birds more susceptible to respiratory infection as bacteria and dust particles remain trapped[154].

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[150] Jupiter, S. D., Pots D. C., Phinn S. R., Duke, N. C. (2007). Natural and anthropogenic changes to mangrove distributions in the Pioneer River Estuary (QLD, Australia), *Wetland and Ecol Manage,* 15: 51-62.

[151] Clifford, A. M., Goss, G. G., Wilkie, M. P. (2015). Adaptations of a deep sea scavenger: High ammonia tolerance and active NH4+ excretion by the Pacific hagfish (*Eptatretus stoutii*), Comparative Biochemistry and Physiology Part A: Molecular & Integrative Physiology, Volume 182, Pp 64-74.

[152] Sheikh, I. U., Nissa, S. S., Zaffer, B., Bulbul, K. H., Akand, A. H., Ahmend, H. A., Hasin, D., Hussain., Hussain, S. A. (2018). Ammonia production in poultry houses and its harmful effects. *International journal of veterinary sciences and animal husbandry.* 3, pp 30 – 33.

In addition to the physiological effects of gaseous ammonia, there is potential for ammonia to impact on migration pathways of procellariform seabirds such as petrels, albatrosses and shearwaters, that use olfactory cues to navigate to both foraging and nesting locations[153]. As both the prey of seabirds and chicks produce nitrogen waste products including unionised ammonia, it is plausible that seabirds use the scent of ammonia to return to foraging and nesting grounds. This was examined for blue petrel *Halobaena caerulea*, with results suggesting that birds were able to detect ammonia at 10^{-11} to 10^{-5} M which are concentrations they are likely to be exposed to[156].

Concerning the ammonia spill scenarios, gaseous ammonia will dissipate quickly. It is therefore anticipated that exposure to flying birds will be short-term, as they are likely to fly away in response to the odour. No long-term severe effects are anticipated, however, irritation of the eye and trachea may be experienced. There is potential for gaseous ammonia to impact the olfactory cues of seabirds causing disorientation and failure of birds to return to breeding locations.

Limited literature is available on the impact of liquified ammonia on diving seabirds (grebes, loons, cormorants and penguins).

Within a wider context, birds such as waders and wildfowl feed on macrophytes and aquatic invertebrates and diving seabirds feed on fish. Significant impacts to these key prey sources such as a reduction in extent and abundance due to exposure to unionised ammonia will have a negative effect on birds and their ability to sustain healthy populations. This will need to be considered on a case-by-case basis depending on the location of the ammonia spill and the associated habitat.

4.3.2.8. Marine mammals

In mammals, high levels of ammonia (hyperammonemia) can be highly toxic to tissues, especially in the brain. Increased absorption of ammonia by the brain leads to increased glutamine production, causing cellular swelling and metabolic dysfunction[154]. Hyperammonemia can also affect skeletal muscles in mammals, leading to muscle wasting.

[153] Nevitt, G. A., Bergstrom, D. M., Bonadonna, F. (2006). The potential role of ammonia as a signal molecule for procellariform seabirds. *Marine Ecology Progress Series*. 315, pp 271 – 277.

[154] Hill, R.W., Wyse, G.A. and Anderson, M. (2016). Animal Physiology 4th Ed. Oxford University Press. ISBN: 9781605354712. pp 828.

Excess gaseous ammonia may also lead to adverse effects on the eyes and nasal cavities and chronic liver injuries.

Limited research has been undertaken on the specific effects of liquified ammonia on marine mammals. Similarly, to birds, in the wider context, significant impacts on prey availability for marine mammals (invertebrates and fish) will have a negative effect on marine mammals and their ability to sustain healthy populations.

4.3.3. Impacts on ecological receptors with modelled 'worst case' scenario

As described within Section 4.1.6, the overall 'worst case' scenario is the collision scenario from the Containership. This is the 'worst case' scenario without consideration of other environmental parameters (weather or day/ night). With consideration of environmental parameters, the Containership with a 200 mm hole and a spill of ammonia occurring during the night, with low wind and stable conditions (1.5F) is considered the 'worst case' scenario and deemed more suitable for this assessment.

Regarding the potential impacts of the 'worst case' scenario on each habitat, it is deemed unlikely that the weather conditions and day/ night ammonia spills will result in differing impact pathways or differing magnitude of impact. Therefore, the ecological receptors are considered here only.

Bacteria

An ammonia spill occurring at night, under low wind and stable weather conditions is not considered to have different impacts, to an ammonia spill occurring under alternative conditions for bacteria. This is due to no known changes in behaviour or function in bacteria with diurnal changes or weather patterns.

Plankton

An ammonia spill during the night with low wind speeds which reduce dispersion is considered to have a more significant impact on plankton, than a spill under alternative conditions. Marine plankton typically follow a diurnal cycle, where they move closer to the water surface at night, increasing the likelihood of exposure to the ammonia spill and potential toxic impacts.

Macrophytes

As for bacteria above, a spill of ammonia occurring at night, under low wind and stable weather conditions is not considered to have different impacts to an ammonia spill occurring under any other conditions for macrophytes.

Invertebrates

It is considered unlikely that the impacts from an ammonia spill on invertebrates will be different under day/ night or differing weather conditions. This is because invertebrates are either sessile or mobile. Based on model outputs for the collision scenario (relatively small pool radius and low pool depth) the extent of the ammonia spill within an open environment would be considered as a localised area of impact. Note that in environments such as rivers, which are more contained, this would not be the case. Mobile invertebrates are likely to move away from the impacted area where possible. Sessile invertebrates may be subjected to toxic effects from exposure to high concentrations of unionised ammonia. As described in Section 1.1.1, ammonia in water is in equilibrium between NH_3 and NH_4^+ (the ammonium ion) dependant on abiotic factors. Therefore, the proportion of ammonia in its toxic form will be dependent on the environment.

Reptiles

An ammonia spill during the night, with low wind speeds which reduce dispersion, is considered to have a less significant impact on reptile species than a spill under other conditions. Marine reptiles breathe air and many reside out of the water overnight, thus reducing their proximity to the ammonia spill. Reptiles are also mobile and able to commute away if affected by the odour or irritation of the eyes from ammonia vaporised in the atmosphere. While this does not apply to marine reptiles such as sea snakes, they are a mobile species and able to leave an area of impact. Therefore, only short-term exposure is anticipated.

Fish

An ammonia spill during the night, with low wind speeds which reduce dispersion, is considered to have a more significant impact on fish than a spill under other conditions.

Many fish 'sleep' at night with reduced brain activity and metabolism[155] or remain motionless, reducing their response to stimuli. In contrast, predatory species are often nocturnal and alert during the night-time[156]. Based on this, the impact of a night time spill under low wind conditions will vary depending on the location of the spill and the species present.

Birds

An ammonia spill during the night, with low wind speeds which reduce dispersion, is considered to have a more significant impact on birds than a spill under other conditions. Most waterbirds roost overnight on waterbodies to reduce the likelihood of predation and move to feeding grounds during the daytime. However, as mobile species, it is anticipated that birds will respond to short-term impacts of odour and/ or irritation to eyes and trachea if exposed to ammonia vaporised in the atmosphere. The area at ground level which exceeds the exposure limits is modelled at a maximum of 144 km^2, however, this dispersion distance is time-dependent and birds are considered likely to continue commuting outside of the effected area until physiological effects are reduced.

Marine Mammals

An ammonia spill during low wind speeds which reduces dispersion is considered to have a more significant impact on marine mammals than a spill under alternative conditions. The lack of wind may increase the exposure time, however, as mobile species, only short-term effects are anticipated on marine mammals. Pinnipeds which include seals, sea lions and walruses, overnight both in the water and on land. Therefore, there is no difference between the impact of a day or night ammonia spill.

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[155] Bone, Q., Marshall, N.B., & Blaxter, J.H.S. (1995). Biology of fisheries (2nd Edition). Chapman & Hall, pp 332.
[156] Nelson, J.S. (2006). Fishes of the world. John Wiley & Sons, pp. 601. ISBN 0-471-25031-7.

4.3.4. Summary of the impact of ammonia on ecological receptors

Table 11 High-level summary of potential impacts of an ammonia spill on ecological receptors.

Ecological receptors	Key impacts of ammonia
Bacteria	Elevated growth until tolerance threshold exceeded, causing a reduction in reproductive success via slower cell growth and mortality at toxic levels.
Plankton	Elevated growth until tolerance threshold exceeded which alters the ionic equilibrium, causing inhibited growth and photosynthesis and mortality at toxic levels.
Macrophytes	Elevated growth until tolerance threshold exceeded which alters the ionic equilibrium, causing inhibited growth and photosynthesis and mortality at toxic levels.
Invertebrates	Reduction in growth and reproductive rate and mortality at toxic levels.
Reptiles	Physiological damage and mortality at toxic levels, impacts on habitat quality and prey availability.
Fish	Physiological damage and mortality at toxic levels, impacts on habitat quality and prey availability.
Birds	Physiological damage and mortality at toxic levels, impacts on habitat quality and prey availability.
Marine mammals	Physiological damage and mortality at toxic levels, impacts on habitat quality and prey availability.

4.4. Comparative Assessment

This section aims to provide a comparative overview of MGO, one of today's primary marine fuels, as an alternative to ammonia. MGO was used for the comparative assessment as HFO (heavy fuel oil) was not suitable for the modelling used.

4.4.1. Conventional Fuel

Since the mid-19th century, HFO has been the main fuel used by the shipping industry with HFO accounting for 86% of international shipping fuel used in 2014. This is due to the high energy output of HFO. However, since the International Maritime Organisation put a cap on the sulphur content of shipping fuel in 2020, the quantity of HFO used in shipping worldwide has decreased from 172.5 million metric tons in 2019 to 100.5 million metric tons in 2020[157]. One of the most common low sulphur alternatives to HFO is MGO and industry experts expect that MGO will be used more often in the years ahead.[158]

Oil within the environment

MGO are finite natural resources, formed from the deposition of organic material. As such, it is classed as a fossil fuel. The formation process of oil is described below:

- A mass death of marine biomass occurred, typically due to sudden changes in salinity or water temperature.
- Organic matter was deposited next to silts and sands in anoxic conditions which were then buried under heavy layers of sediment for millions of years forming sapropelic muds.
- The organic matter is converted into hydrocarbons by a fermentation process, while the sands and silts are transformed into the sedimentary rock that constitutes the 'mother rock'. This 'mother rock' is saturated with hydrocarbons.
- As oil density is low, it tends to rise to the surface and dissipate in the atmosphere leaving a solid bituminous residue. However, if as the oil begins to rise, it encounters an impermeable mass, it will accumulate and permeate the underlying porous rocks, constituting 'storage rocks'. These form the reservoir or deposit from which the oil is extracted.

4.4.1.1. Environmental toxicity of oil

There are two main environmental impacts caused by the use of MGO (and HFO); combustion of its by-products and the release of oil to the environment through a spill. Combustion generates particles such as nitrous oxides, and sulfur oxides and also releases carbon dioxide emissions into the atmosphere. Oil spills can occur in both the terrestrial and aquatic environments, however, the impacts on the aquatic environment were assessed in this report.

[157] Placek, M (2021). Annual fuel consumption by ships worldwide from 2019 to 2020, by fuel type. Statistica. Accessed from: Amount of fuel consumed by ships worldwide by fuel type 2020 | Statista

[158] ShipInsight (2019), Explaining the types of fuel used on ships, Accessed 14/10/2022 from: https://shipinsight.com/articles/explaining-the-types-of-fuel-used-on-ships

The toxicity of MGO (and HFO) and its impact on biota are primarily determined by its chemical composition. As described above, oil is derived from biological materials whose composition has been modified by diagenesis over millions of years to produce the complex mixture of hydrocarbon and non-hydrocarbon compounds that constitute these fossil fuels. The four classes of hydrocarbons in crude oil are saturated, aromatics, asphaltenes, and resins[159]; saturates and aromatics generally dominate. Saturate hydrocarbons, which contain straight-chain, branched, and cyclic structures, constitute the greatest percentage of crude oil. The majority of crude oils encountered in oil spills contain straight-chain hydrocarbon molecules, ranging from single-carbon methane to molecules that contain more than 35 carbons, with associated branched and cyclic hydrocarbon structures[160].

Unlike ammonia, when oil enters the environment from spills, ruptures, or blowouts, it undergoes continuous compositional changes associated with weathering. Weathering processes include evaporation, dissolution, emulsification, sedimentation, microbial oxidation, and photooxidation[107]. Weathering changes the oil's physical and toxic properties, whereas ammonia toxicity is determined due to environmental factors such as pH, salinity and temperature. Fresh oil is more volatile, contains more water-soluble components, floats, is not very viscous, and easily disperses from the source. Therefore, freshly spilled oil is the most environmentally significant type of oil. Weathered oil initially loses volatile components, which are also the most water-soluble components, and the oil becomes more viscous and more likely to coagulate as opposed to spreading out in a thin film. Over time, weathering continues to change the composition of oil until it degrades in the environment, leaving behind only small quantities of residue (e.g., tar balls). Typically, during weathering, much of the oil (especially heavier oil) will mix with water and emulsify, forming a viscous mixture that is resistant to rapid weathering and more difficult to remediate.

Oil can cause environmental damage through several mechanisms, including the toxicity associated with ingestion or absorption through the biota's respiratory structures or skin; coating or smothering, which affects gas exchange, temperature regulation, or other life-supporting processes; and oxygen depletion by microbial processes associated with oil

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[159] Leahy, J.G., Colwell, R. R. (1990.) Microbial degradation of hydrocarbons in the environment. Microbiological Reviews 54: Pp 305–315.

[160] Mendelssohn, I. A., Andersen, G. L., Baltz, D. M., Caffey, R. H., Carman, K. R., Fleeger, J. F., Joye, S. B., Lin, Q., Maltby, E., Overton, E. B., Rozas, L. P. (2012). Oil Impacts on Coastal Wetlands: Implications for the Mississippi River Delta Ecosystem after the Deepwater Horizon Oil Spill, BioScience, Volume 62, Issue 6. Pp 562–574.

degradation. Weathering changes the effectiveness of these mechanisms (toxicity, routes of exposure, bioavailability) for causing environmental impacts and, in general, lessens the opportunity for damage. However, exposure of crude oil to sunlight enhances the toxicity of its water-soluble fraction because this contains some hydrocarbon compounds that are phototoxic or exhibit at least photo-enhanced toxicity[161].

4.4.1.2. Oil spills to the environment

Since the 1970's the number of HFO and MGO spills globally has declined significantly. This is determined from the dataset produced by the International Tanker Owners Pollution Federation (ITOPF) which covers data on oil spills globally for the past five decades. In the 1970s, there were 24.5 large oil spills per year; by the 2010s the average number of large oil spills had decreased to 1.7 oil spills per year[162].

To achieve the modelling below n-dodecane ($C_{12}H_{26}$) was used in the PHAST model to compute the results. It has very similar properties to MGO and can allow for a direct comparative assessment.

PHAST Modelling, as above in Section 4.1, the range of parameters within the modelling allowed for many comparisons to be drawn both between and within the produced data. The main comparisons considered are as follows:

- Day and night;
- Hole sizes; and
- Between weather conditions.

However, these interact with each other to produce a multitude of comparison scenarios. A summary of the main comparisons is presented below and relevant interactions are discussed. See Appendix 6 for full graphical results and Appendix 7 for a full summary.

Pool Mass Dissolved

Pool mass dissolved remains consistently at 0 kg and is unaffected by any of the parameters.

[161] Marigomez (2014). Oil, Crude, Mechanism of Toxicity in Encyclopedia of Toxicology (Third Edition)
[162] Roser, M.,Ritchie, H. (2022) - "Oil Spills". Published online at OurWorldInData.org. Retrieved from: 'https://ourworldindata.org/oil-spills' [Online Resource]

Pool Mass Remaining

Pool mass remaining increases linearly with the time of the spill and is unaffected by any of the parameters. For the 1200 mm hole size, there is a rapid increase before a plateau.

Mass Spilt

Mass spilt increases linearly with time of spill and is unaffected by any of the parameters. For the 1200mm hole size there is a rapid increase before a plateau.

Mass Vaporised

Mass vaporised follows the same pattern under both day and night scenarios and increases in volume as hole size increases. It is primarily affected by weather conditions, with wind speed producing similar results and variations in mass over time occurring between atmospheric stability classes. An example is shown below in **Figure 14**.

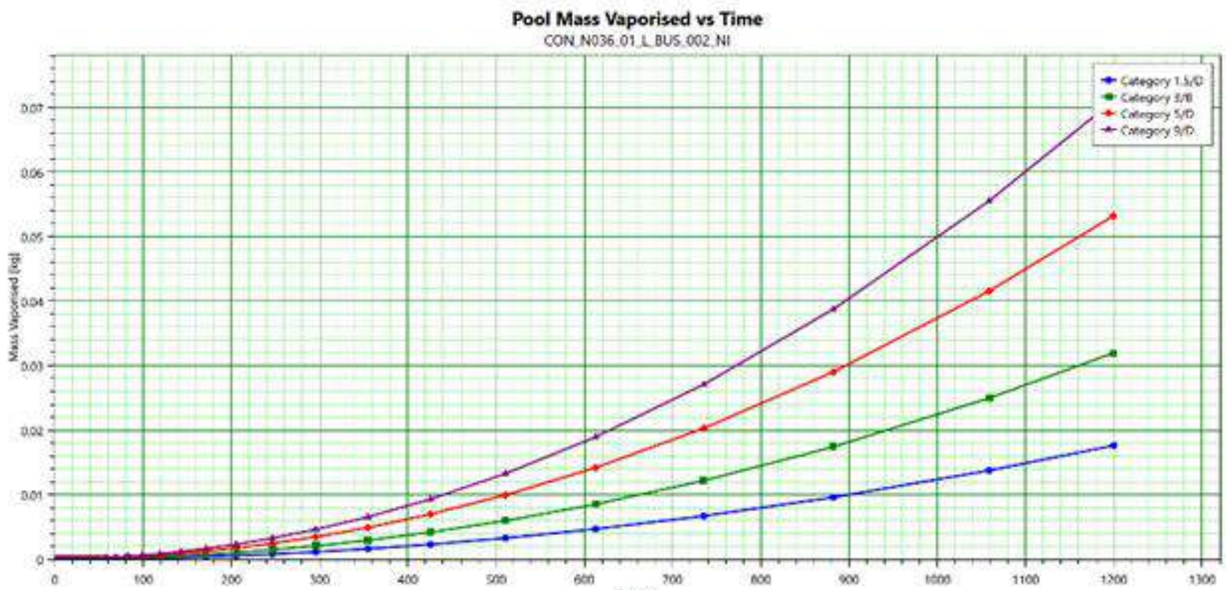


Figure 14 PHAST modelling results for pool mass vaporised over time for a bunkering spill of MGO from a 2 mm hole size during the day

Pool Depth

Pool depth remains consistently at 0 m and is unaffected by any of the parameters.

Pool Radius

Pool radius increases with time but is unaffected by any of the parameters.

Pool Temperature

Pool temperature decreases rapidly, then remains at 0°C for the 2 mm and 23 mm hole sizes and is unaffected by any of the other parameters. For the 200 mm and 1200 mm hole size, this decrease is less rapid. The 1200 mm hole size also shows some slight variation in temperature under both day and night conditions, primarily affected by the weather conditions, with wind speed producing similar results and variations in mass over time occuring between atmospheric stability classes. An example is shown below in **Figure 15.**

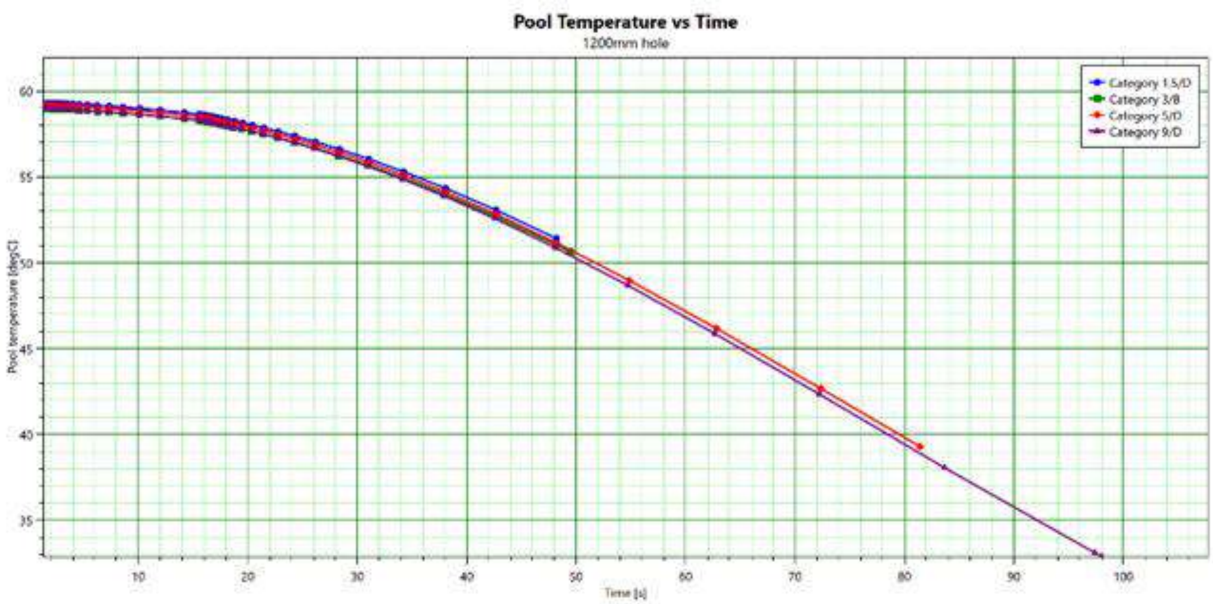


Figure 15 PHAST modelling results of pool temperature over time for a bunkering spill of MGO from a 1200 mm hole size during the day

Pool Vaporisation Rate

Pool vaporisation rate follows the same pattern under both day and night scenarios, and increases in volume as hole size increases. It is primarily affected by the weather conditions, with wind speed producing simailr results and variations in mass over time occuring between atmospheric stability classes. An example is shown below in **Figure 16.**

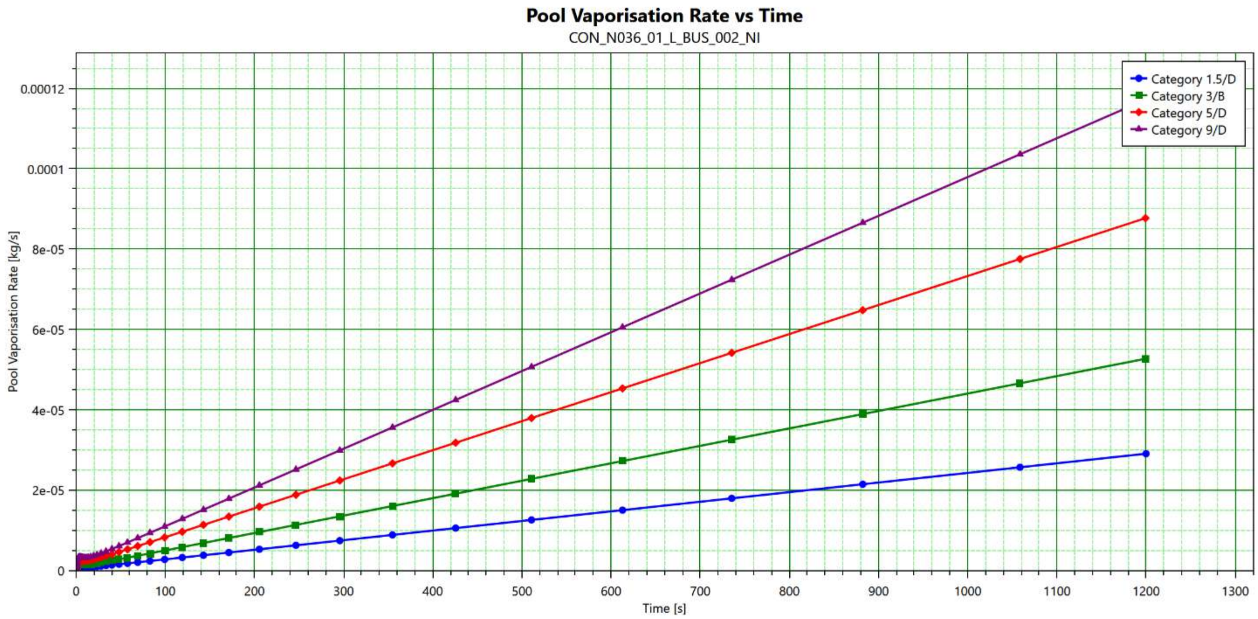


Figure 16 PHAST modelling results for pool vaporisation rate over time for a bunkering spill of MGO from a 2 mm hole size during the day.

Solution Rate

The solution rate remains consistently at 0 kg/s and is unaffected by any of the parameters. As discussed in Section 4.4.1.2, this suggests that the behaviour of an MGO spill into the aquatic environment is primarily affected by the weather conditions.

4.4.1.3. Impact of oil on habitats

This section summarises the key impacts of an MGO spill on different aquatic habitats (**Table 12**), full descriptions of these impacts can be found in Appendix 9.

Table 12 High level summary of potential impacts from MGO spills on aquatic habitats

Habitat	Key impacts of an MGO spill
Rivers	Food chain disruptions (extent and presence of macrophytes) and toxic to fauna.
Estuaries	Food chain disruptions (extent and presence of macrophytes) and toxic to fauna.
Wetlands	Reduction in oxygen levels caused by hydrocarbon degrading bacteria. Food chain disruptions (extent and presence of macrophytes) and toxic to fauna.
Coastal Waters	Food chain disruptions (extent and presence of macrophytes) and toxic to fauna.
Coral Reefs	Food chain disruptions (extent and presence of macrophytes) and toxic to fauna
Polar regions	Food chain disruptions and toxic to fauna.
Mangroves	Reduction in oxygen levels caused by hydrocarbon degrading bacteria. Food chain disruptions (extent and presence of macrophytes) and toxic to fauna.
Deep Sea	Food chain disruptions and toxic to fauna

4.4.1.4. Impact of oil on ecological receptors

This section summarises the key impacts of an oil spill on different ecological receptors (**Table 13**), full descriptions of these impacts can be found in Appendix 9.

Table 13 Key impacts of an MGO spill on different ecological receptors

Ecological Receptors	Key impacts of an MGO spill
Bacteria	Act as mediators of biodegradation and can undergo increases in abundance.
Plankton	Variable impacts dependant on life history strategies.
Macrophytes	Variable impacts, however, oil typically prevents gas exchange reducing growth rates and potentially causing mortality.

Invertebrates	Variable impacts, though typically species are highly sensitive and can lead to mortality.
Reptiles	Short term toxic effects and long term embryo deformities.
Fish	Typically unaffected in open water, though acute toxic effects in shallow or confined water can lead to a reduction in fitness and potentially mortality.
Birds	Reduces buoyancy, effectiveness of waterproof coating and insulation capacity. Also, toxic if ingested.
Marine mammals	Highly sensitive as oil is ingested impacting on ingestion of food and can bioaccumulate becoming toxic.

A case study[163] is also examined in Appendix 9 for the recorded ecological impacts from a conventional fuel spill, a summery is shown in **Table 14**.

Table 14 Key impacts of the oil spill on different ecological receptors in Milford Haven

Ecological Receptors	Key impacts of the oil spill in Milford Haven
Commercial fisheries	No attributable mortalities of commercial fin-fish, crustaceans or molluscs were recorded, and spawning and recruitment remained successful
Plankton	Few observed effects
Macrophytes	Variable impacts depending on macrophyte type
Invertebrates	Large numbers of dead or moribund molluscs
Birds	Large numbers of dead and oiled birds
Marine mammals	Few observed effects

The negative impacts of oil spills vary with the spill's location and magnitude as well as invertebrate life stage, habitat affected, sensitivity, feeding mode and ability to avoid or process contaminants. The effects of oil on the ecological receptors, in general, include

[163] Edwards, E., White, I. (1998). The Sea Empress Oil Spill: Environmental Impact and Recovery. Paper presented at The International Oil Spill Conference 1999, 7-12 March 1999, Seattle, USA.

habitat degradation; smothering; fouling of gill structures; impaired reproduction, growth, development, feeding, immune response and respiration; and disturbance of the food web.

4.4.2. Comparison with ammonia

The below **Tables 15** and **16** consider a high-level comparison between ammonia as a marine fuel and MGO. These comparisons draw upon the research presented above and in Appendices 7, 8 and 9 to present a low, medium or high impact for each habitat and ecological receptor where possible. It should be noted that the information used in the comparison is not complete, as some areas have insufficient data for ammonia impacts and therefore, more research into these areas is needed for an in-detail comparison to be made.

The impact scoring is based upon the factors of severity of impact and likelihood of occurring. Therefore, low impacts are assigned where an impact is not considered to be severe or the likelihood of that impact occurring is low. A medium impact is assigned where the effects may be severe but the likelihood of occurrence is low and high impacts are assigned where the effects are severe and they are likely to occur during a spill.

Key

Low Impact	
Medium Impact	
High Impact	

Table 15 Summary of comparison of ammonia with marine gas oil for environments

Habitat	**Ammonia**	**MGO**
Rivers		
Wetlands		
Estuaries		
Coastal Waters		
Coral reefs		
Mangroves		
Deep sea		
Polar regions		

Table 16 Summary of comparison of ammonia with marine gas oil for ecological receptors

Ecological Receptors	Ammonia	MGO
Bacteria		
Plankton		
Macrophytes		
Invertebrates		
Reptiles		
Fish		
Birds		
Marine Mammals		

5. Discussion

This report aims to assess the potential environmental risks of using ammonia as a shipping fuel due to large-event ammonia spill scenarios and to compare the effects of ammonia spills with those of MGO. This was undertaken via PHAST modelling of ammonia in the marine environment and also by air dispersion modelling, to account for the dissolution and volatilisation of the spilled ammonia under various conditions.

The following key conclusions were made from the analysis of the PHAST modelling results:

- A spill of ammonia to the aquatic environment has the greatest probability of occurring from a 2 mm hole in a Containership bunker line (0.00115 per year) due to ship and fuel storage design;
- The timing of an ammonia spill (day/ night) and wind conditions (category 1.5D and 1.5F) had the greatest impact on the spread of gaseous and liquid phase ammonia; and
- The most likely 'worst case' scenario was a night-time spill of ammonia under low wind/ stable conditions (1.5F) on a Containership[164], with a 200 mm hole in a bunker line. This considered the likelihood of the spill occurring.

The most likely 'worst case' scenario was then utilised to inform the below tables (see **Table 17 – 22**).

To further consider the environmental impact of an ammonia spill, specific habitats present in the freshwater, brackish and marine environments were considered. The toxicity of ammonia depends on abiotic conditions (temperature, salinity and pH) within each habitat. Where abiotic conditions fluctuate, habitats and associated ecological receptors/ species will be most vulnerable to negative ecological impacts due to an ammonia spill. Specific species present within each habitat were also assessed, ranging from plankton to mammals.

The following key conclusions were made from the assessment of the potential impacts of ammonia spills on habitats and ecological receptors/species:

[164] 'Containership' relating to the storage conditions

- Estuaries, mangroves, wetlands, coral reefs and their associated species are considered most vulnerable to direct and indirect ecological impacts via increased algal growth;
- Polar regions and the deep sea environments are considered least vulnerable to ecological impacts due to the stability of abiotic parameters;
- Sessile species such as benthic invertebrates and fish are considered to be particularly sensitive to ammonia spills; and
- Birds, mammals and reptiles are considered less sensitive, however, there is limited research on both ecological receptors.

The following tables (**Table 17-24**) highlight a summary of each habitat and its ecological receptors considering the most likely 'worst case' modelling scenarios. The impact level is shown in the key above the tables. The potential impacts of an ammonia spill were also compared with the impacts of conventional fossil fuels. As **Tables 15** and **16** highlight, conventional fuels are considered to have a high impact in all habitats, except the deep sea where there is a medium impact, whereas an ammonia spill is considered to have a high impact on estuaries mangroves, wetlands, coastal waters and coral reefs, a medium impact in rivers, and low impacts in the polar regions and the deep sea.

MGO is further considered to have high impact on invertebrates and birds, compared to ammonia having a high impact on fish. Ammonia has a medium impact on all other ecological receptors, except bacteria, while MGO has low impact on plankton, fish and marine mammals.

Impact level	
Low	
Moderate	
High	

Table 17 Summary table of potential impacts to rivers from an ammonia spill

Environment	Ecological Receptor	Sensitivity to abiotic conditions	Modelling scenario impacts	Case study[165] sensitivities	Overall ranking
Rivers	Plankton	Moderate	Moderate		Moderate
	Macrophytes	Moderate	Moderate	High	Moderate
	Invertebrates	Moderate	Moderate	High	Moderate
	Fish	Moderate	Moderate	High	Moderate
	Birds	Moderate	Low	High	Moderate
	Reptiles	Moderate	Low		Moderate
	Mammals	Moderate	Low	High	Moderate

Table 18 Summary table of potential impacts to estuaries from an ammonia spill

Environment	Ecological Receptor	Sensitivity to abiotic conditions	Modelling scenario likelihood	Case study sensitivities	Overall ranking
Estuaries	Plankton	High	Moderate	High	High
	Macrophytes	High	Moderate		High
	Invertebrates	High	Moderate		High
	Fish	High	Moderate	High	High
	Birds	High	Low	High	Moderate
	Reptiles	High	Low		Moderate
	Mammals	High	Low	High	Moderate

[165] Based on Milford Haven, Appendix 9

Table 19 Summary table of potential impacts to wetlands from an ammonia spill

Environment	Ecological Receptor	Sensitivity to abiotic conditions	Modelling scenario likelihood	Case study sensitivities	Overall ranking
Wetlands	Plankton				
	Macrophytes				
	Invertebrates				
	Fish				
	Birds				
	Mammals				

Table 20 Summary table of potential impacts to coastal waters from an ammonia spill

Environment	Ecological Receptor	Sensitivity to abiotic conditions	Modelling scenario likelihood	Case study sensitivities	Overall ranking
Coastal Waters	Plankton				
	Macrophytes				
	Invertebrates				
	Fish				
	Birds				
	Reptiles				
	Mammals				

Table 21 Summary table of potential impacts to coral reefs from an ammonia spill

Environment	Ecological Receptor	Sensitivity to abiotic conditions	Modelling scenario likelihood	Case study sensitivities	Overall ranking
Coral Reefs	Plankton				
	Macrophytes				
	Invertebrates				
	Fish				
	Birds				
	Reptiles				
	Mammals				

Table 22 Summary table of potential impacts to polar regions from an ammonia spill

Environment	Ecological Receptor	Sensitivity to abiotic conditions	Modelling scenario likelihood	Case study sensitivities	Overall ranking
Polar regions	Plankton				
	Macrophytes				
	Invertebrates				
	Fish				
	Birds				
	Mammals				

Table 23 Summary table of potential impacts to mangroves from an ammonia spill

Environment	Ecological Receptor	Sensitivity to abiotic conditions	Modelling scenario likelihood	Case study sensitivities	Overall ranking
Mangroves	Plankton				
	Macrophytes				
	Invertebrates				
	Fish				
	Birds				
	Reptiles				
	Mammals				

Table 24 Summary table of potential impacts to deep sea from an ammonia spill

Environment	Ecological Receptor	Sensitivity to abiotic conditions	Modelling scenario likelihood	Case study sensitivities	Overall ranking
Deep Sea	Plankton				
	Invertebrates				
	Fish				
	Mammals				

5.1. Limitations

There are several limitations and knowledge gaps within this study to evaluate spill scenarios as described below. As noted in the introduction, this study does not consider all environmental and health impacts, so further work is needed to understand the full range of environmental risks posed by the increased use of ammonia as a shipping fuel.

1. It must be noted that ammonia as discussed in the literature cited for describing these habitats is related to natural or run-off ammonia sources. These are more ambient or chronic inputs of ammonia, not similar to episodic releases of ammonia fuel (anhydrous ammonia). This is due to a lack of real-world data for ammonia shipping fuel spills covering all the habitats and ecological receptors assessed within this report.
2. Knowledge gaps have been identified while completing the literature review to assess the potential impacts of an ammonia spill on multiple habitats and species. Further research is required on the impact of an ammonia spill on ecological receptors within the deep sea and birds (particularly seabirds, waders and wildfowl), marine mammals and aquatic reptiles.
3. The aquatic environment and shipping design scope are broad and could benefit from a more in-depth review in future.
4. The PHAST model is only capable of modelling single parameters therefore, a cumulative assessment of the parameters was based on expert judgement.
5. The model utilises weather conditions as typical of the port of Rotterdam, considered to be the busiest port in the world. Therefore, the applicability of the results presented above for other regions, such as hurricane regions, tropical regions or polar regions is likely to be reduced. The likelihood or frequency of the occurrence of each weather category may also influence the applicability of the results.
6. In addition, future modelling of the dispersion and volatilisation of ammonia in aquatic environments should consider changes in salinity and pH as key parameters affecting the concentration of unionised ammonia.

6. Conclusion

In conclusion, the use of ammonia as a shipping fuel could impact aquatic environments and associated ecological receptors if a spill were to occur. The magnitude of impact would be dependent on the location of the ammonia spill, abiotic parameters and mitigation measures applied. Mitigation measures to prevent adverse impacts in the aquatic environment need to be developed for ammonia to be a viable low-carbon alternative for shipping.

Future Recommendations

Future studies should investigate the full risk profile of ammonia as a shipping fuel introduced at a large scale and what feasible and effective regulatory measures across different areas could be implemented. This is already in place for oil-based fuels, which have the advantage of longevity of use allowing for regulations to be designed and implemented.

The technology required to propel and power ships with ammonia as fuel is still immature, and extensive development and policy measures are needed for its use on a larger scale. Effective health, safety and environmental regulations for the use of ammonia as fuel onboard ships are currently not in place and must be established. Ammonia is a toxic chemical and it is important that the additional safety challenges are thoroughly addressed before considering ammonia as a shipping fuel.

In addition, future work should investigate chronic spills of ammonia and effects of nitrogen deposition, if ammonia is used as a shipping fuel at scale. This should include an evaluation of the potential exacerbation of algal blooms caused by chronic ammonia spills and regulatory measures that can be put in place to avoid chronic ammonia spills.

7. Appendices

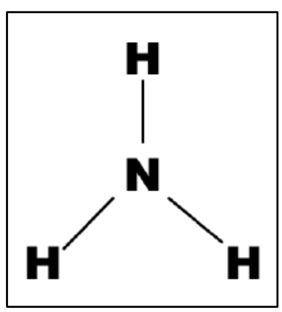
- Appendix 1 – Environmental Chemiastry of Ammonia
- Appendix 2 – PHAST model set up information
- Appendix 3 – Graphical results of PHAST modelling for ammonia
- Appendix 4 – PHAST modelling for ammonia summary
- Appendix 5 – Air dispersion modelling
- Appendix 6 - Graphical Results of PHAST Modelling for oil
- Appendix 7 - PHAST Modelling for oil Summary
- Appendix 8 - Full descriptions of the impact of oil on aquatic habitats
- Appendix 9 - Full descriptions of the impact of oil on ecological receptors

7.1. Appendix 1

Environmental Chemistry of Ammonia

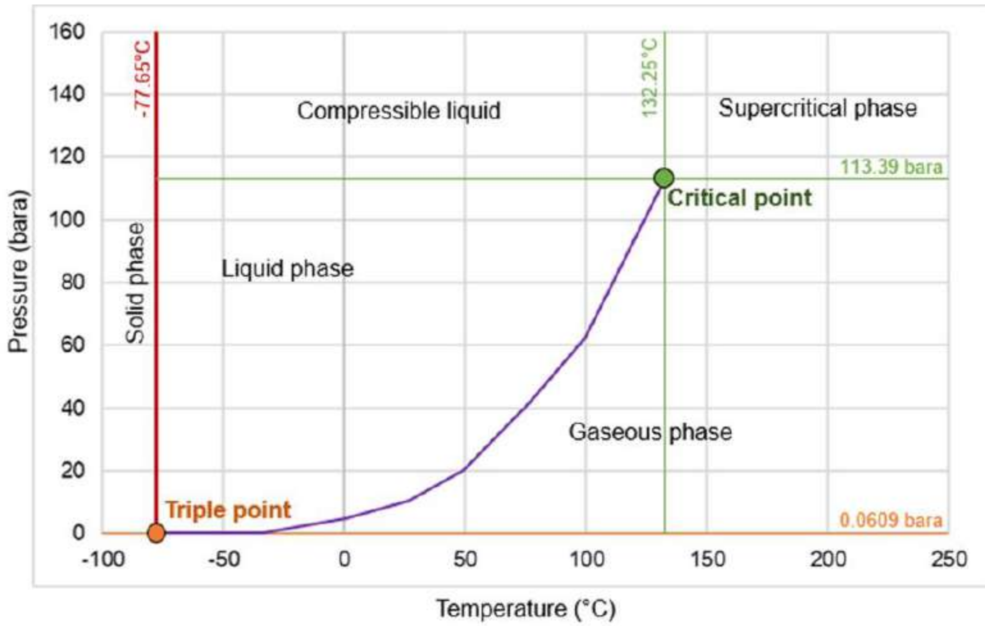
Ammonia consists of hydrogen (H) and nitrogen (N), with the formula NH3 (unionised).

Figure A.1 Structure of ammonia



Ammonia under typical conditions (room temperature and pressure) is a colourless gas with a distinct pungent odour. It has a lower density than air at room temperature and pressure, its density being 0.589 times that of air. However, under varying pressure and temperature this phase may change (Figure A2). At atmospheric pressure, ammonia is present as a liquid at temperatures below -33.6 °C. At the critical point, there is no change of state when pressure is increased or if heat is added and the triple point marks the temperature and pressure at which the three phases (gas, liquid and solid) coexist in thermodynamic equilibrium.

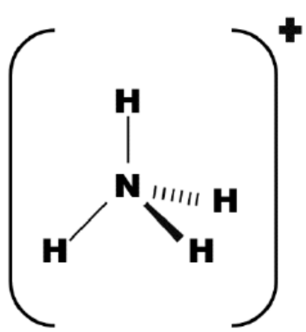
Figure A2 Ammonia (NH3) Phase Diagram17



The vapour pressure of ammonia is the pressure at which ammonia gas is in thermodynamic equilibrium with its condensed state (purple line on phase diagram, Figure A2). At higher pressures ammonia would condense. At this equilibrium condition, the vapor pressure is the saturation pressure.

The NH3 molecule undergoes self-dissociation when dissolved in water (solubility - $4.82x10^{+5}$ mgL^{-1} at 24 °C[166] , see Box 1) and behaves as a weak base, combining with acids to form salts. These acid-base reactions produce salts containing the ammonium cation

Figure A3 Structure of Ammonia Cation (NH4)



[166] Dean, J.A. (ed.). Lange's Handbook of Chemistry. 13 ed. New York, NY: McGraw-Hill Book Co., 1985., p. 10-3

($NH_{4+,}$ Figure A3). However, ammonia also exhibits weak acidic qualities and is therefore, amphoteric. These acidic qualities allow for the formation of amides via reactions with some alkali metals and earth metals.

7.1.1. Equilibrium

As previously stated, aqueous ammonia can exist as unionised ammonia (NH_3) or the ammonium cation (NH_{4+}). The major factor that determines the proportion of ammonia or ammonium in water is the water pH. The activity of ammonia is also influenced by temperature and ionic strength.

The equilibrium constant for the reaction of NH^3 with water is $1.76x10^{-5}$, and is driven by the following chemical equation:

$$NH_{3\,(aq)} + H_2O_{(l)} \leftrightarrow NH_4{}^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$$

Equation A1 The relationship between ammonia and ammonium

At more acidic (lower) pHs, the reaction is driven to the right, and at more alkaline (higher) pHs, the reaction is driven to the left (as shown in Figure A4). In general, at ~21°C, pH <6.0, the proportion of ammonia as NH_3 is lowered and ammonia as NH_{4+} is increased. At a pH ~8.0, the proportion of ammonia as NH_3 is typically <10% and at a pH ~9.0, around 50%. In an aqueous solution, therefore, the ammonia (NH_3) acts as a base, accepting hydrogen ions (H^+) from dissociating H_2O and yielding ammonium (NH_{4+}) and hydroxide ions (OH^-). This has a base ionisation constant of:

Whilst these forms of ammonia are both found ubiquitously in the water environment, they do not react with the environment in the same way. Unionised ammonia is toxic in the environment, while the ammonium cation (NH^{4+}) is less so, as the unionised ammonia can cross epithelial membranes of aquatic organisms more readily than the ammonium ion. Therefore, ammonia toxicity can be attributed to the ammonia form. Hence ammonia

$$K_b = \frac{[NH_4{}^{+}]\,[OH^{-}]}{[NH^{3}]}$$

Equation A2 Base ionisation constant

toxicity increases with water temperature and pH as the equilibrium shifts to the left of Equation A2, with a change in the ionisation constant.

However, the ionisation rate may also be affected by salinity, which varies within brackish and marine environments. In reduced salinity (brackish environments) the equilibrium favours unionised ammonia, with an increase of ~10% of unionised ammonia per reduction of 10 units of salinity[167].

Figure A4 shows which side of the equilibrium is favoured with changes in temperature, pH and salinity.

Figure A4 17Favourability of Ammonia

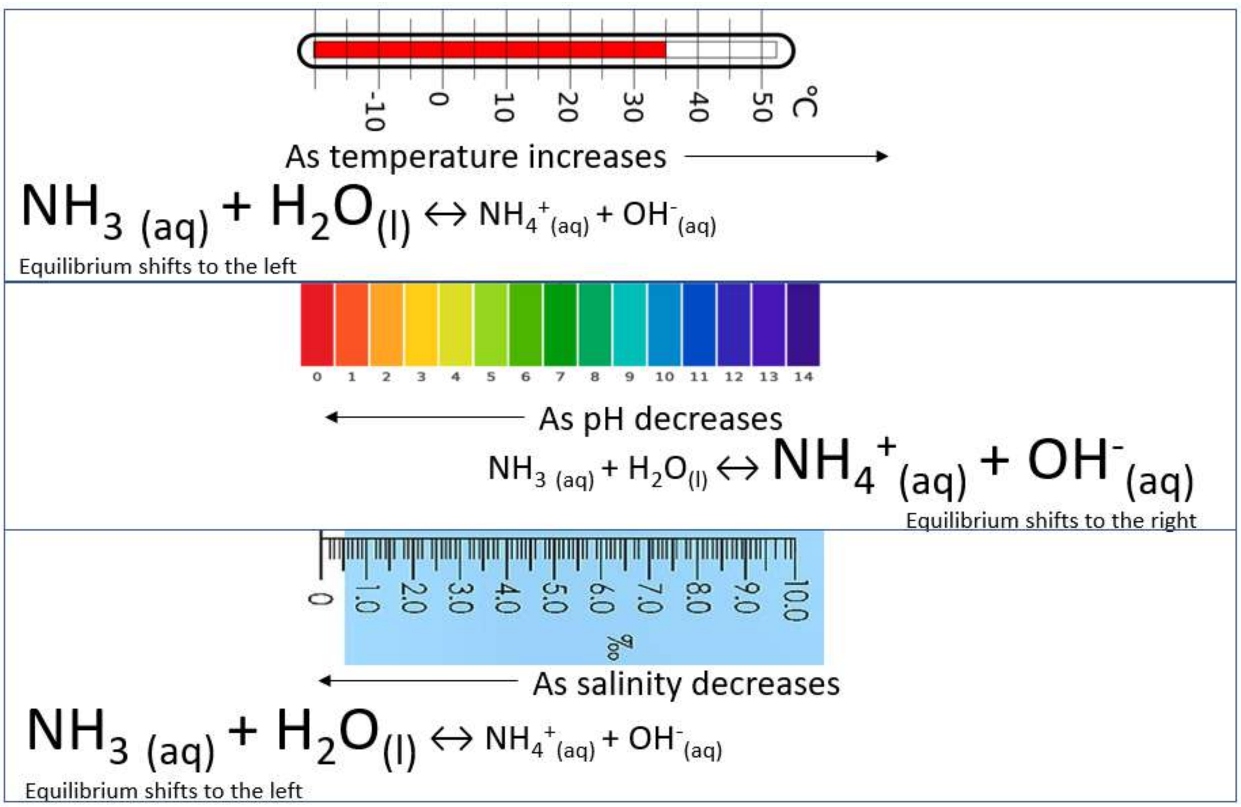


Figure A4 demonstrates what species of ammonia is favoured under a variety of conditions. The favourable form is shown in large.

[167] Khoo, K.H., Culberson, C.H. and Bates, R.G. (1977) Thermodynamics of ammonium ions in seawater from 5 to 40° C. J. Solut. Chem., 6, pp. 281-290.

7.1.2. Ammonia within the Environment

Ammonia is a common toxicant derived from wastes, fertilizers and natural processes. Natural sources of ammonia include the decomposition or breakdown of organic waste matter, gas exchange with the atmosphere, forest fires, animal, and human waste and nitrogen fixation processes.

7.1.2.1. Atmosphere

Gaseous ammonia is the most abundant alkaline gas in the atmosphere. The largest source of ammonia emissions is agriculture, including animal husbandry and NH_3-based fertilizer applications. Other sources of ammonia include industrial processes, vehicular emissions and volatilization from soils and oceans. Ammonia plays a significant role in the formation of atmospheric particulate matter, visibility degradation and atmospheric deposition of nitrogen to sensitive ecosystems.

The atmospheric chemistry of ammonia is complex (for a detailed review see Behera *et al.* 2013[168]), however, in general atmospheric phenomena, ammonia can either be converted to NH_{4+} or subjected to dry or wet deposition.

In the atmosphere, ammonia reacts with acid pollutants such as the products of sulphur dioxide (SO_2) and NO_X emissions to produce fine ammonium (NH_{4+}) containing aerosol. As the lifetime of ammonia is relatively short[169], this will impact on the transport distances of ammonia.

7.1.2.2. Aquatic

Ammonia can enter the aquatic environment directly via municipal effluent discharges and the excretion of nitrogenous wastes from animals and indirectly via nitrogen fixation, air deposition and runoff from agricultural lands.

In aquatic environments, ammonia is aqueous ammonia and therefore, exists in equilibrium, as described in Section 1.4.1, as a function of temperature, pH and salinity. As the chemistry

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[168] Behera, S. N., Sharma, M., Aneja, V. P., Balasubramanian, R. (2013) Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies. Environment Science Pollution Research, 20, 8092-8131.

[169] Fowler, D.; Sutton, M.A.; Smith, R.I.; Pitcairn, C.E.R.; Coyle, M.; Campbell, G.; Stedman, J. (1998.) Regional mass budgets of oxidized and reduced nitrogen and their relative contribution to the N inputs of sensitive ecosystems Environmental Pollution (Nitrogen Conference Special Issue) 102 337-342

of aqueous ammonia is described in Section 1.4.1, the following sections present the variances in these abiotic factors.

7.1.2.3. Freshwater

Freshwater rivers do not typically have a large input of salinity and therefore, the equilibrium phase shifts are as a function of temperature and pH changes.

Typical salinity of a freshwater river is <0.5 μgL^{-1} [170], whilst most freshwater rivers have a (natural) pH range of between 6-8, though this varies due to geology and diurnal fluctuations. The temperature of freshwater rivers varies widely by latitude. For the purposes of this report, temperature is considered to range between 1.8 and 29.2 °C (see Section 3.2), based on polar, temperate and tropical climates, seasonal and diurnal variations.

7.1.2.4. Marine

As described in Section 1.4.1, ammonia in seawater, is aqueous ammonia and therefore, exists in equilibrium in sea water as a function of temperature, pH and salinity. Though in open seawater, these abiotic factors are relatively stable.

The salinity of the ocean is on average ~35 μgL^{-1}[171] and pH ~8.1. As for freshwater the temperature of open ocean seawater varies widely by latitude. For the purposes of this report, temperature is considered to range between -1.7 and 31.6 °C (see Appendix.2), though this varies seasonally and also undergoes diurnal fluctuation at the surface.

7.1.2.5. Estuarine

Estuaries represent an ever-changing environment with respect to salinity, pH, temperature, oxygen content and if present, substances such as ammonia.

Estuarine pH levels range from 7.0 to 7.5 in the upper reaches (low salinity and 8.0 - 8.6 in the lower reaches (higher salinity)[172]. However, this is highly variable both within a specific

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[170] Montagna, P., Palmer, P., Pollack, J.(2013.) Hydrological Changes and Estuarine Dynamics. Springerbriefs in Environmental Science Volume 8. 94 pp

[171] Antonov, J.I., Locarnini, R.A., Boyer, T.P., Mishonov, A.V., Garcia, H.E., Levitus, S., (2006). World Ocean Atlas 2005 Volume 2: Salinity, in: Jolley, D.W. et al. (Ed.) (2002). The North Atlantic Igneous Province: stratigraphy, tectonic, volcanic and magmatic processes. Geological Society Special Publication, 197: pp. 253-269. NOAA Atlas NESDIS, 62(2). NOAA[S.l.]. 182 pp.

[172] https://www.epa.gov/sites/default/files/2015-09/documents/2009_03_13_estuaries_monitor_chap11.pdf

estuary and between estuaries in different locations globally. This is because the pKa[173] of pH within an estuary is dependent on the linear function of both temperature and salinity. It must also be noted that this is changeable with tidal cycles and is both seasonal and diurnal, as are both salinity and temperature.

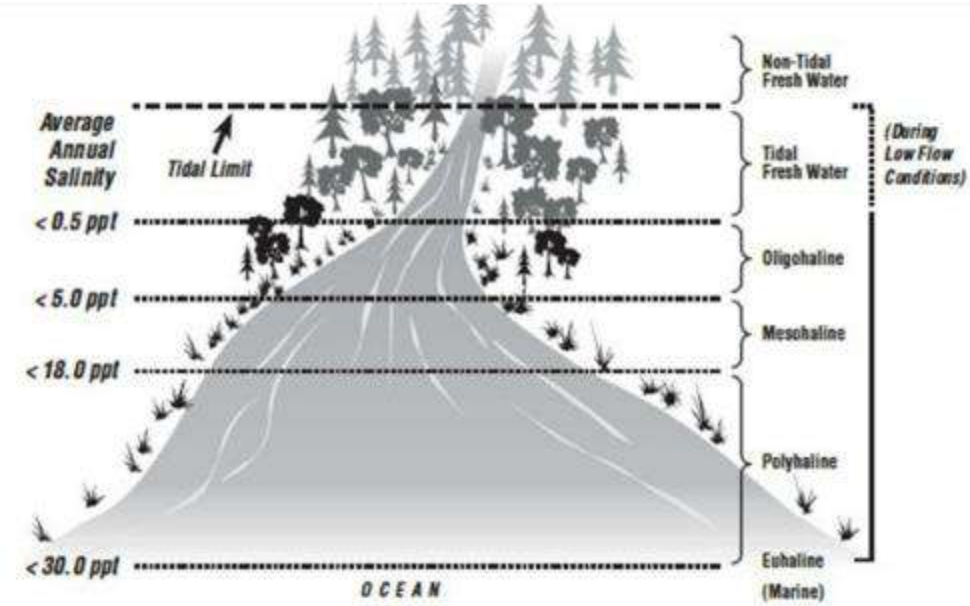
The salinity gradient generally increases from the input source of an estuary, usually a stream or river, to the output source, the sea or ocean. Within the estuary, salinity levels are referred to as oligohaline (0.5-5.0 μgL^{-1}), mesohaline (5.0-18.0 μgL^{-1}) or polyhaline (18.0 to 30.0 μgL^{-1}). Near the connection with the open sea, estuarine waters may be euhaline, where salinity levels are the same as the ocean at more than 30.0 μgL^{-1} [12] (Figure A5).

The salinity of an estuary can vary, dependent on the amount of freshwater inflows as well as the tidal movement and location within the estuary. Estuaries have a water balance that is either positive, (freshwater inputs exceed evaporation); neutral, (there is a balance between freshwater inflows and evaporation); or negative, (freshwater inflows are less than the amount of evaporation).

As with the above sections, the temperature of estuaries is highly variable, therefore, for the purposes of this report temperature is considered to range between 6.6 and 19.9 °C (see Appendix 2).

[173] pK_a is the negative base-10 logarithm of the acid dissociation constant (K_a) of a solution. pKa = $-\log_{10}K_a$. The lower the pK_a value, the stronger the acid.

Figure A5 Salinity gradients in the aquatic environment[174]



7.1.2.6. Soils/ sediments

Ammonia in sediments typically results from bacterial decomposition of organic matter that accumulates in sediment. Sediment microbiota mineralize organic nitrogen or (less commonly) produce ammonia by dissimilatory nitrate reduction. Ammonia is especially prevalent in anoxic sediments because nitrification (the oxidation of ammonia to nitrite [NO^{2-}] and nitrate [NO^{3-}]) is inhibited. Ammonia generated in sediment may be toxic to benthic or surface water biota[175].

7.1.3. Fate of Ammonia

While the concentration of a chemical released into the environment, as well as the habitat (air, water, or soil) into which it is released are important factors, the environmental fate is determined by processes after the chemical has been released.

Consequently, the fate and behaviour of a chemical is governed by its physicochemical properties (such as vapor pressure, water solubility, water–octanol partition coefficient (Kow), soil organic carbon–water partitioning coefficient (Koc), etc.). Therefore, environmental fate is based on three main factors:

[174] Source: United States Environmental Protection Agency
[175] Lapota, D., Duckworth, D., Ward, J. (2000). Confounding Factors in Sediment Toxicology - Issue Papers 1-19. Space and Naval Warfare Systems Center, San Diego CA.

1. The partitioning of the chemical between environmental media. The tendency of a substance to partition to – or concentrate in – a particular habitat can be determined from the physical and chemical properties of the substance. These properties can be measured or estimated.
2. The transport properties of the media. The tendency for environmental transport of a substance depends on the transport properties of the medium into which the substance is released or partitions. It also depends on its lifetime in the medium. Substances that migrate to environmental media responsible for transport (e.g., air and water) will be more widely distributed.
3. The transformation rate of the chemical into other substances. Environmental transformation describes a chemical's lifetime in the environment until it is converted to substances naturally found in the environment, or until its fate can be described in some other way. Environmental transformation is highly dependent on the medium. In air, transformation is by abiotic chemical reactions; in soil and water, biodegradation may also be an important contributor. Substances that persist in the environment will build to higher concentrations and may be more widely distributed.

The below sections describe the main processes which ammonia is subject to upon release into the environment.

7.1.3.1.The nitrification cycle

Nitrification is a microbial process by which reduced nitrogen compounds (primarily ammonia) are sequentially oxidized to nitrite and nitrate. The nitrification process is primarily accomplished by two groups of autotrophic nitrifying bacteria that can build organic molecules using energy obtained from inorganic sources, in this case ammonia or nitrite.

In the first step of nitrification, ammonia-oxidizing bacteria oxidize ammonia to nitrite according to Equation A3:

$$NH_3 + O^2 \longrightarrow NO_2^- + 3H^+ + 2e^-$$

Equation A3 Ammonia-oxidizing bacteria oxidize ammonia to nitrite

Nitrosomonas is the most frequently identified genus associated with this step, although other genera may be identified, including *Nitrosococcus*, and *Nitrosospira*. Some subgenera, *Nitrosolobus* and *Nitrosovibrio*, can also autotrophically oxidize ammonia[176].

In the second step of the process, nitrite-oxidizing bacteria oxidize nitrite to nitrate according to Equation 4:

$$NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-$$

Equation 4 Nitrite-oxidizing bacteria oxidize nitrite to nitrate

Nitrobacter is the most frequently identified genus associated with this second step, although other genera, including *Nitrospina*, *Nitrococcus*, and *Nitrospira* can also autotrophically oxidize nitrite[17].

Various groups of heterotrophic bacteria and fungi can also carry out nitrification, although at a slower rate than autotrophic organisms[13].

7.1.3.2. Atmospheric fate

In the ambient atmosphere, ammonia, with a vapor pressure of 9.99 bar at 25 °C[177], is expected to exist solely as a gas. Gas-phase ammonia may be degraded in the atmosphere by reactions with photochemically-produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 100 days as calculated from its rate constant of 1.60×10^{-13} cu cm/molecule-sec at 25 °C[178]. Gas-phase ammonia is also degraded in the atmosphere by reactions with nitrate radicals; the half-life for this reaction in air is estimated to be 54 days as calculated from its rate constant of 5.99×10^{-16} cu cm/molecule-sec at 25 °C[14]. Furthermore, ammonia reacts rapidly in the atmosphere with both sulphuric and nitric acids to form fine particles, with ammonia as aerosols associated with sulphate ions in

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[176] Watson, S.W., Valos , F.W. & Waterbury, J.B. (1981). The Family Nitrobacteraceae. In The Prokaryotes. Edited by M.P. Starr et al. Berlin: Springer-Verlag

[177] Daubert TE, Danner RP. (1999.) Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation. Design Institute for Physical Property Data, American Institute of Chemical Engineers. New York, NY: Hemisphere Pub Corp.

[178] NIST; NIST Chemistry WebBook. Ammonia (7664-41-7). NIST Gas Phase Kinetics Database No. 69, Sept 2013 Release. Washington, DC: US Sec Commerce. Available from: <http://webbook.nist.gov/>.

industrialised nations[179]. Ammonia does not absorb at wavelengths >290 nm[180] and, therefore, is not expected to be susceptible to direct photolysis by sunlight.

Once released into the atmosphere, ammonia is returned to the surface as either gaseous ammonia or as an ammonium ion. The ammonium ion can be associated with nitrate, sulphate, or other anions and incorporated into an aerosol or as part of the ionic mix found in clouds and raindrops[15]. Ammonia can also dissolve in the water in the atmosphere and form clouds or fog[181].

The overall half-life for ammonia in the atmosphere has been estimated to be a few days; the reaction with acidic substances in the air results in the formation of ammonium aerosols that can be removed by wet or dry deposition[17]. Vapor deposition of ammonia from air to surface (to vegetation, soil, etc) also occurs[15].

7.1.3.3. Aquatic fate

Ammonia is lost from water by volatilization[182] with volatilization being a primary fate[183] based upon a Henry's Law constant of 1.61×10^{-5} atm-cu m/mole[184] and giving volatilization half-lives for a model river and model lake of 1.4 and 12 days, respectively.

In water, ammonia is in equilibrium with the ammonium ion (NH_{4+}), and the ammonia-ammonium ion equilibrium is dependent on the pH[17] as previously discussed.

In surface water, groundwater, or sediment, ammonia can undergo sequential transformation by two processes in the nitrogen cycle: nitrification and denitrification. Both processes produce ionic nitrogen compounds and from these, elemental nitrogen[17] as discussed above.

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[179] NOAA; Atmospheric Ammonia: Sources and Fate. A Review of Ongoing Federal Research and Future Needs (June 2000). Natl Ocean Atmos Admin, Aeronomy Laboratory, Boulder, CO; Available from: <http://www.esrl.noaa.gov/csd/AQRS/reports/ammonia.pdf/>.

[180] Walsh AD, Warsop PA. (1961.) Trans Faraday Soc 57: 345-358.

[181] ATSDR. (2004.) Toxicological Profile for Ammonia. Atlanta, GA: Agency for Toxic Substances and Disease Registry, US Public Health Service. Available from: <http://www.atsdr.cdc.gov/toxprofiles/index.asp/>.

[182] Environment Agent UK; Proposed EQS for Water Framework Directive Annex VIII substances: ammonia (un-ionised). Science Report: SC040038/SR2 (Feb 2007). Bristol, England; Available from: <http://www.wfduk.org/sites/default/files/Media/ammonia.pdf/>.

[183] Lyman WJ et al. (1990.) Handbook of Chemical Property Estimation Methods. Washington, DC: Amer Chem Soc pp. 15-1 to 15-29.

[184] Betterton EA. (1992) pp. 1-50 in Gaseous Pollutants: Characterization and Cycling, Nriagu JO, Ed. John Wiley & Sons, Inc.

The ionic nitrogen compounds formed from the aerobic process of nitrification (nitrate and nitrite anions) can leach through the sediment or be taken up by aquatic plants or other organisms[17].

Removal of ammonium from water can also occur by adsorption to sediments or suspended organic material[17].

7.1.3.4. Soils/sediments

In terrestrial soils, ammonia may either volatilize to the atmosphere, adsorb to particulate matter, or undergo microbial transformation to nitrate or nitrite anions[17]. Volatilization of ammonia from moist soil surfaces is expected to be an important fate process given ammonias Henry's Law constant. However, due to ammonia's vapor pressure it would still be expected to volatilize from dry soil surfaces

In soil and sediment, ammonia can serve as a nutrient source for plants, which can be taken up by plants and microorganisms and converted to organic-nitrogen compounds[17]. Ammonia in soil can be rapidly transformed to nitrate by the microbial population through nitrification. The nitrate formed will either leach through the soil or be taken up by plants or other microorganisms[17]. Ammonia at natural concentrations in soil is not believed to have a very long half-life.

If ammonia is distributed to soil or sediments in large concentrations the natural biological transformation processes can be overwhelmed, and the environmental fate of ammonia will become dependent upon the physical and chemical properties of ammonia, until the ammonia concentration returns to background levels[17].

7.2. Appendix 2

PHAST Model Set Up Information

This section describes the various input parameters and model set up information as used to inform the PHAST modelling of potential ammonia spill scenarios.

Table A1 describes the size of the three fuel storage types assessed.

Table A1 Vessel information

Fuel storage type	Size	Length (m)	Beam (m)	Notes
Containership	3,500 TEU*	172 (estimated)	32 (estimated)	Fully refrigerated
Bulker	84,500 DWT**	235	38	Pressurised
Tanker	-	255 (estimated)	38 (estimated)	Semi refrigerated

*Twenty-foot Equivalent Unit, **Deadweight tonnage

The fuel storage types store the ammonia as shown in Table A2

Table A2 Ammonia storage conditions

	Fuel storage type	Pressure (bara)	Temperature (°C)	Storage tank volume (m^3)
Bunkering conditions	Containership	3	-33	-
	Bulker	14.4	10	-
	Tanker	7	-33	-
Storage tank conditions	Containership	0.4	-33	1,950

Although, in principle, the reference ship could operate virtually anywhere in the world, a set of conditions for Rotterdam has been selected. This is because Rotterdam is ranked high on lists of the world's ports for containers, dry bulk and bulk liquid cargoes. Table A3 shows the environmental parameters, typical of the Netherlands as a whole, which have been used in the modelling set up.

Table A3 Environmental parameters

Parameter	Daytime Value	Night-time Value
Ambient temperature:	12°C	8°C
Water temperature:	9.8°C	9.8°C
Humidity:	76.5%	86.3%
Solar radiation flux:	0.25 kW/m^2	0 kW/m^2
Fraction of 24-hour period:	0.44	0.56

The weather conditions within the model are described as a combination of a letter with a number, such as ‘F1.5 (Table A4). The letter denotes the Pasquill stability class and the number gives the wind speed in metres per second (m/s).

The Pasquill stability classes describe the amount of turbulence present in the atmosphere and range from A to F. Stability class A corresponds to ‘unstable’ weather, with a high degree of atmospheric turbulence, as would be found on a bright sunny day. Stability class D describes ‘neutral’ conditions, corresponding to an overcast sky with moderate wind. A clear night with little wind would be considered to represent ‘stable’ conditions, denoted by stability class F.

Wind speeds range from light (1-2 m/s) through moderate (around 5 m/s) to strong (6 m/s or more).

Table A4 Representative environmental conditions assumed for the purposes of consequence modelling

Pasquill Stability Class	Wind speed (m/s)	Percentage Day	Percentage Night
B	3.0	24.50	0.00
D	1.5	11.19	15.19
D	5.0	30.76	26.06
D	9.0	33.55	21.87
E	5.0	0.00	10.85
F	1.5	0.00	26.04

The PHAST model uses the partition coefficients determined by Raj and Reid[185] in laboratory tests and compared to known model applications. It is interesting to note that the principal results of the three size tests carried out in the study (small, intermediate and large,Table A5) showed constancy between the partition coefficients determined in all tests, 60-70% of the ammonia ($NH_{3(l)}$) remained in the water (Figure A6) and this was not affected by the experimental variables:

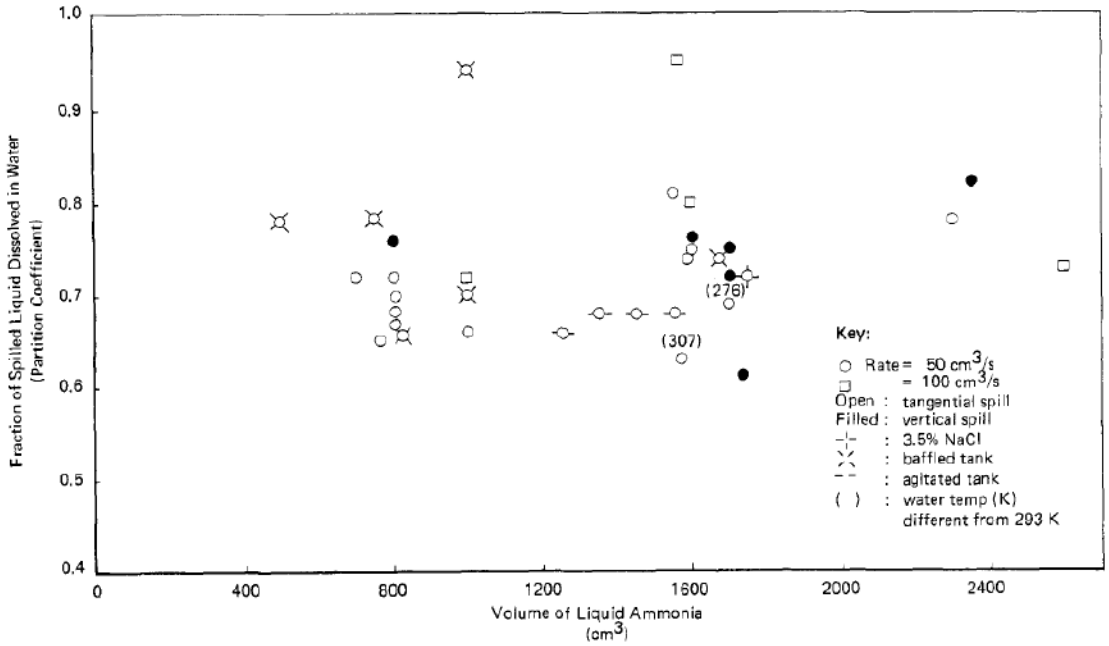
- Mode of spill
- Salinity
- Water depth,
- Spill size, etc.

Table A5 Size test parameters

Size	Tank size (m)	Water volume	Spill volume (cm^3)	Spill rate (cm^3/s)
Small/laboratory	1.8 x 0.5 x 0.5	25 cm	Up to 2,500	50-100
Intermediate	6 (diameter)	60 (depth)	2	2
Large	Natural lake	Natural lake	Up to 1,900	-

185 Raj, P. P. K., Reid, R. C. (1978.) Fate of liquid ammonia spilled onto water. Environ. Sci. Technol. 12, 13. Pp 1422–142

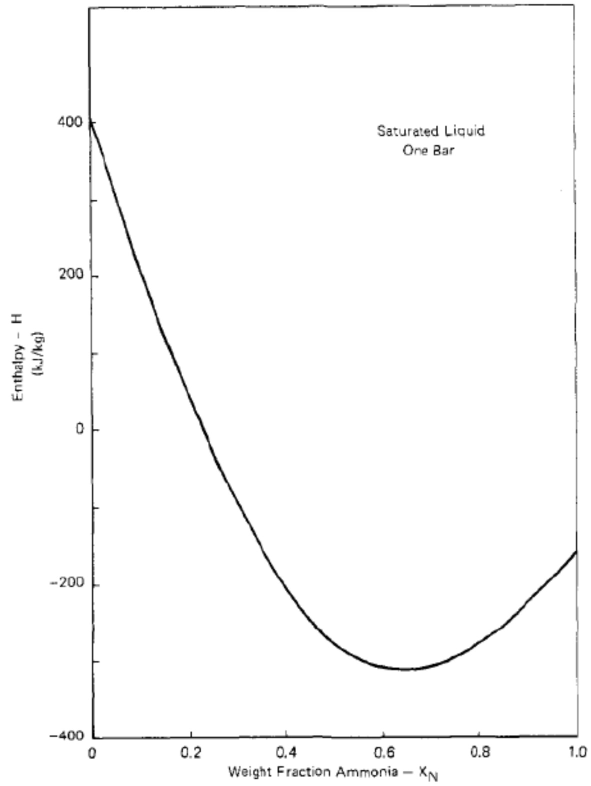
Figure A6 Partition coefficients from small-scale ammonia ($NH_{3(l)}$) spills



The modelled application[186] supported the partition coefficients, creating a physical picture from enthalpy-concentrations (Figure A7), thermodynamic analysis and utilising the phase rule:

[186] Raj, P. K., Hagopian, J., Kalelkar, A. S. (1974) "Prediction of Hazards of Spills of Anhydrous Ammonia on Water", U.S. Coast Guard Report CG-D-74-74, NTIS No. AD779400.

Figure A7 Ammonia (NH_3) – water liquid enthalpy



The results of the thermodynamic analysis, wherein dN_w^L of liquid water are added to the $NH_{3(l)}$ and dN_N^v of ammonia are vaporized, yielded:

$$dH = H_W dN_W^L - /H_N^v dN_N^V$$

Equation A5 Thermodynamic analysis of the mixing process of ammonia (NH_3) and water

Notes: H = total solution enthalpy

H_w = specific enthalpy of added water

H_N^V = specific enthalpy of the ammonia vapor

N_W^L = moles of liquid water (kmol)

N_N^V = moles of vapor ammonia (kmol)

Superscript 'L' denotes liquid phase, superscript 'V' denotes vapor phase

The phase rule dictates that for a two-component, two-phase system in equilibrium, any extensive property is a function of three other variables—at least one of which must be extensive. P (total pressure (N/m^2)), N_W^L, and N_N^L were selected as these independent variables:

$$H = f(P, N_W^L, N_N^L)$$

Equation A6 Total enthalpy as a function of independent variables

Therefore, by differentiation, at constant pressure:

$$dH = (\partial H/\partial N_W^L)_{P,N_N} dN_W^L + (\partial H/\partial N_N^L)_{P,N_W} dN_N^L$$

Equation A7 Total enthalpy modified by partial derivatives

The partial derivatives shown in Equation A7 contain the restriction that the liquid phase is in equilibrium with the vapor, as such derivatives are modified partial molar enthalpies as can be designated as per Table A6

Table A6 Designations of the modified partial molar enthalpies

Modified partial molar enthalpy	Designation (j/kmol)	Medium
$(\partial H/\partial N_W^L)_{P,N_N}$	$\overline{H}_{W'}$	Water
$(\partial H/\partial N_N^L)_{P,N_W}$	$\overline{H}_{N'}$	Ammonia (NH_3)

Euler integration[187] of Equation A5 shows that $\overline{H}W'$ and $\overline{H}N'$ are the intercepts of any tangent drawn to the 1-bar liquid saturation curve in Figure A7. Any given ammonia weight fraction $\overline{H}W'$ is read on the left-hand ordinate ($X_N = 0$) and $\overline{H}N'$ on the right-hand ordinate ($X_N = 1.0$). (X_N = mass fraction of ammonia in ammonia-water aqueous solution).

Combining EquationA5, Equation A7 and the designations in Table A6, and using the relation $(dN_N^V + dN_N^L) = 0$, yields Equation A8.

[187] Modell, M., Reid, R. C. (1974) "Thermodynamics and Its Applications", Prentice-Hall, Englewood Cliffs, N.J., Chapter 8.

The modified partial molar enthalpies were found by approximating the saturation liquid curve (Figure A7) by an analytical equation that expressed the solution enthalpy (H) as a function of composition.

Equation A8 was then integrated numerically to obtain N_N^V as a function of the quantity of water added, N_W^L.

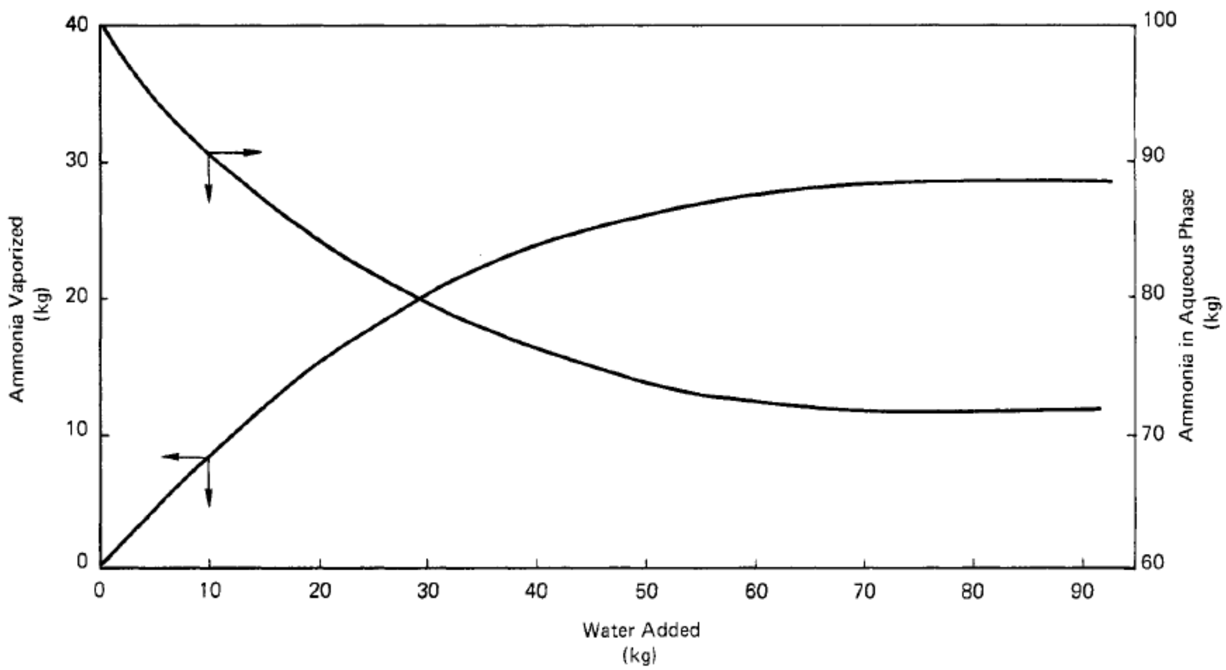
$$\frac{dN_N^V}{dN_W^L} = - \frac{(\overline{H}_{W'} - H_W)}{(H_N^V - \overline{H}_{N'})}$$

Equation A8 Relationship between moles of ammonia and enthalpy

7.2.1. 100 kg spill of $NH_{3(l)}$ case study

In a spill scenario, here a 100 kg spill of $NH_{3(l)}$ is assumed, water mixes with $NH_{3(l)}$ and vapor is evolved. Figure A8 shows the mass of ammonia evolved and that in solution as a function of added water.

Figure A8 Sample results for a 100 kg spill of liquid ammonia on 20.85°C water



This shows a plateau of ammonia in aqueous phase from ~70 kg of water added, no more ammonia evolving after ~86 kg of added water. At this point there remains ~71.5 kg of dissolved ammonia (weight fraction ammonia ~0.45).

This behaviour becomes is shown as a function of Equation A8, as the weight fraction ammonia decreases,

$\overline{H}$ W' increases. When $\overline{H}$ W' equals H_W (~83.7 kJ/kg), then the numerator in Equation A8 becomes zero and, after this point, further addition of water simply dilutes further the solution with no additional vapor evolution.

The partition coefficient found and taken forward to the PHAST modelling is 0.715. Notably varying the water temperature ± 10 °C will only slightly affect the calculated partition coefficient.

7.2.2. Temperature for the analysed environments

Using freely available information from World sea temperature 2022[188] and a literature search (deep sea environment[189]) a range of seasonal (depth for deep sea) temperatures was determined for each environment (*Table A7*).

[188] https://www.seatemperature.org/

[189] Joyce, T.M., Wunsch, C. and Pierce, S.D. (1986). Synoptic Gulf Stream velocity profiles through simultaneous inversion of hydrographic and acoustic Doppler data. Journal of Geophysical Research 91: doi: 10.1029/JC091iC06p07573. issn: 0148-0227.

Table A7 Temperature ranges for analyzed environments

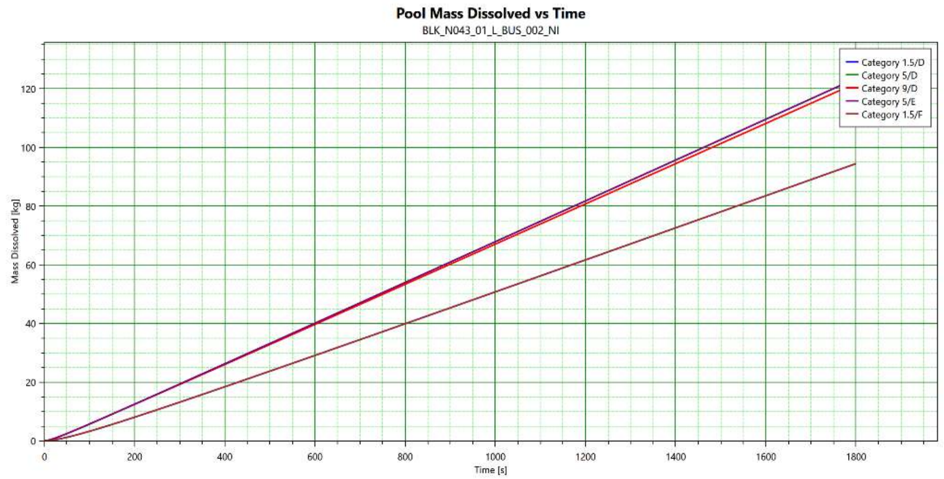
Environment	Season or Depth	Temp Range ºC
Rivers	Winter	1.8 to 27.6
	Spring	3.1 to 29.2
	Summer	12.6 to 29.2
	Autumn	9.2 to 29
Estuaries	Winter	6.6 to 15.7
	Spring	7.3 to 16.2
	Summer	11.3 to 19.9
	Autumn	10.1 to 19.8
Wetlands	Winter	-1.7 to 30.6
	Spring	-0.7 to 30
	Summer	11.9 to 29
	Autumn	2.6 to 29.3
Coastal Waters	Winter	7.8 to 28.2
	Spring	7.1 to 28.4
	Summer	11.3 to 28.6
	Autumn	9.7 to 29
Coral Reefs	Winter	21.8 to 28.3
	Spring	23.4 to 29.8
	Summer	26.2 to 31.6
	Autumn	26.5 to 32.1
Polar regions	Winter	-1.7 to 5.9
	Spring	-1.6 to 6
	Summer	0.6 to 11.3
	Autumn	-0.9 to 8.8
Mangroves	Winter	19.4 to 28.3
	Spring	26.3 to 29.8
	Summer	26.2 to 30.4
	Autumn	27.8 to 29.2
Deep Sea	1000m	5
	2000m	4
	3000m	3
	4000m	2 to 3
	5000m	1 to 3

7.3. Appendix 3

Graphical Results of PHAST Modelling for ammonia

This section presents and describes the graphical results of the PHAST modelling for ammonia. The results are presented by ship type, hole size and by a day/night comparison.

Table A8 Results for Bulker, 2mm hole, day/night

	DAY	NIGHT
Pool Mass Dissolved		

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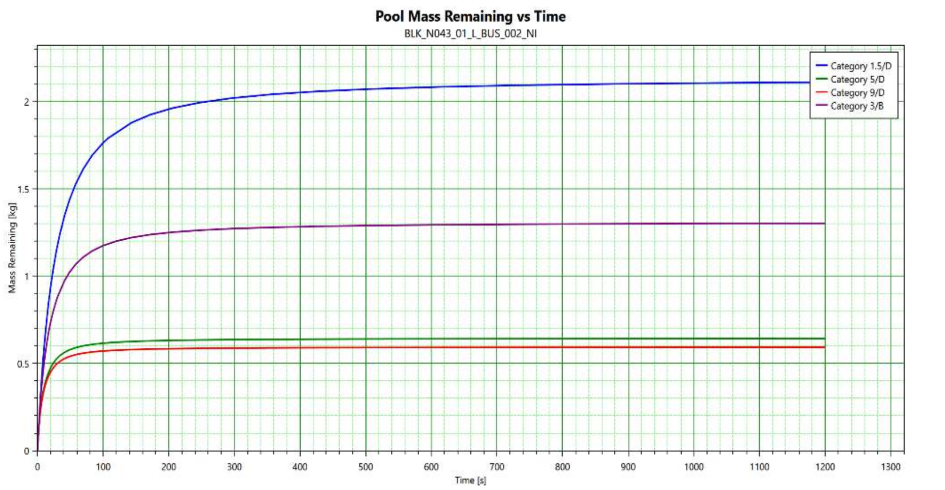
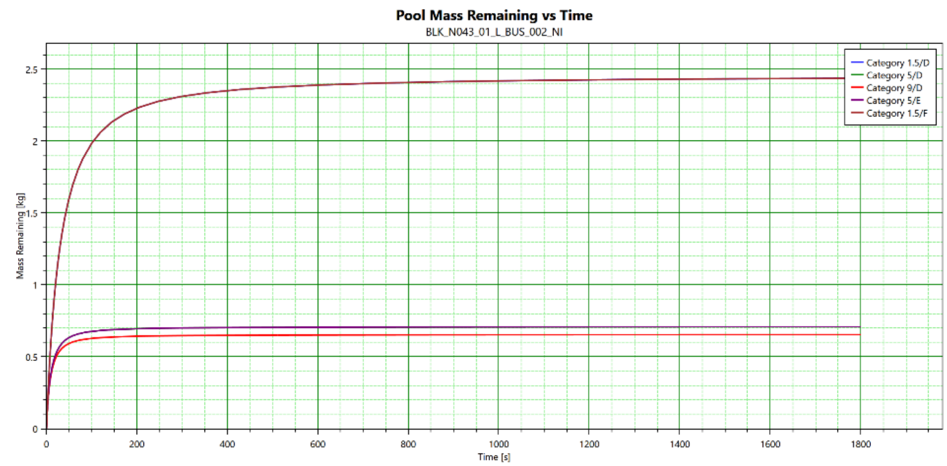
<tr><td>Pool Mass Remaining</td><td>
</td><td>
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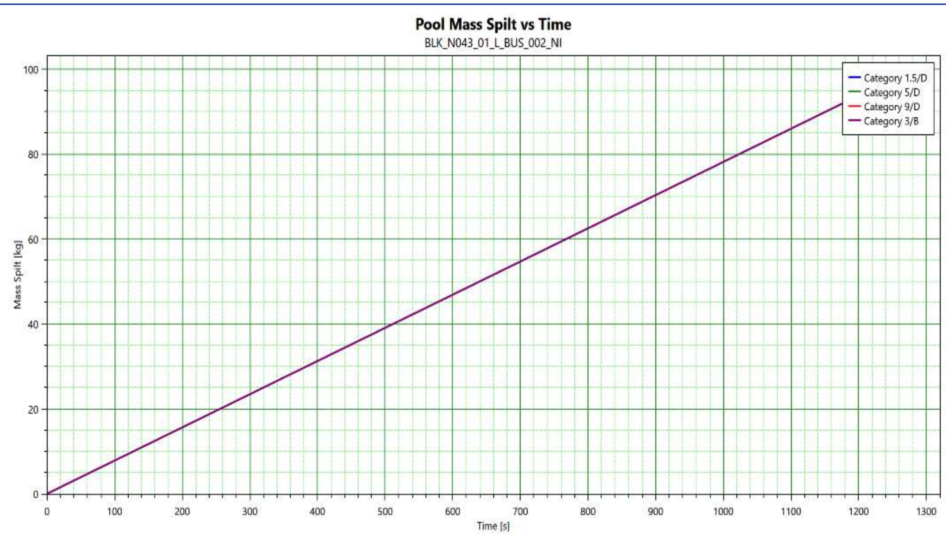
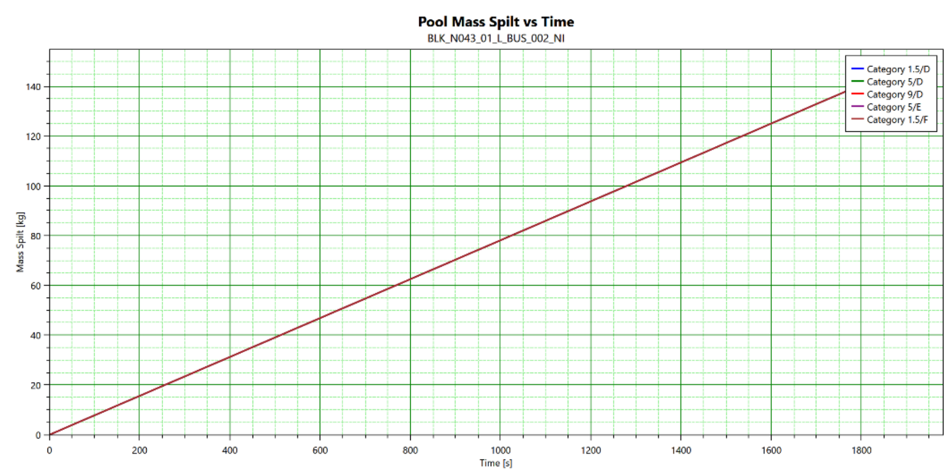
<tr><td>Mass Spilt</td><td>
</td><td>
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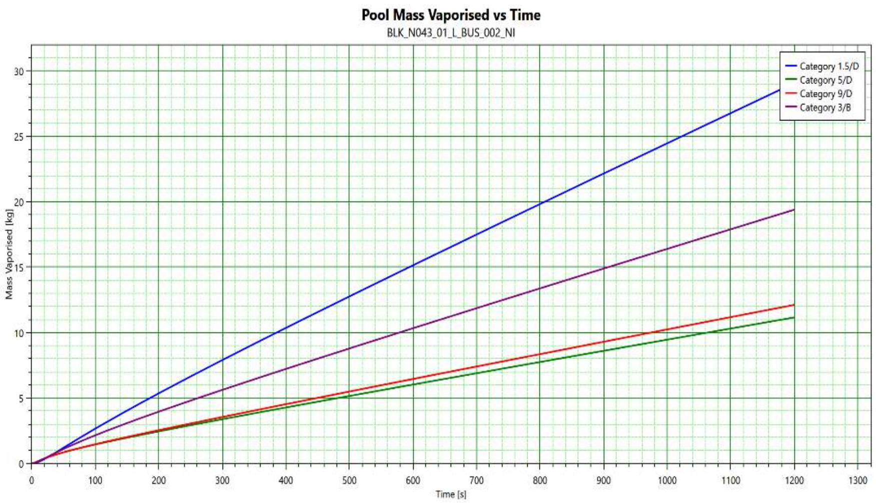
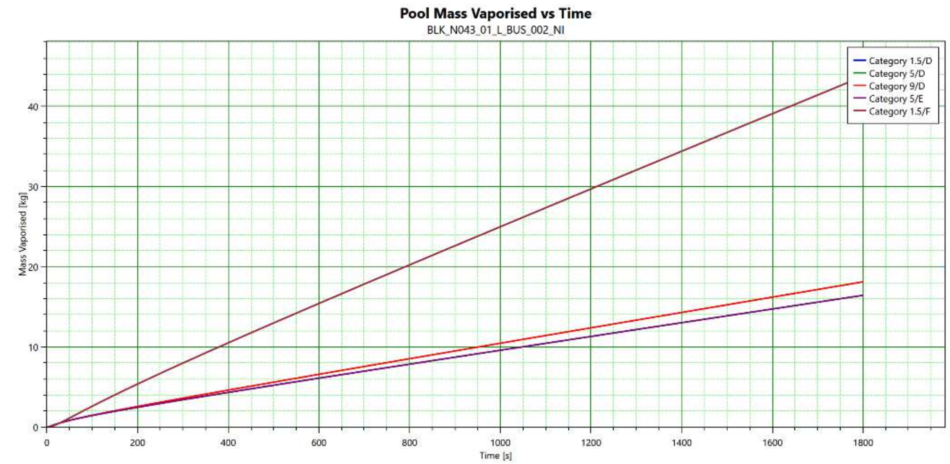
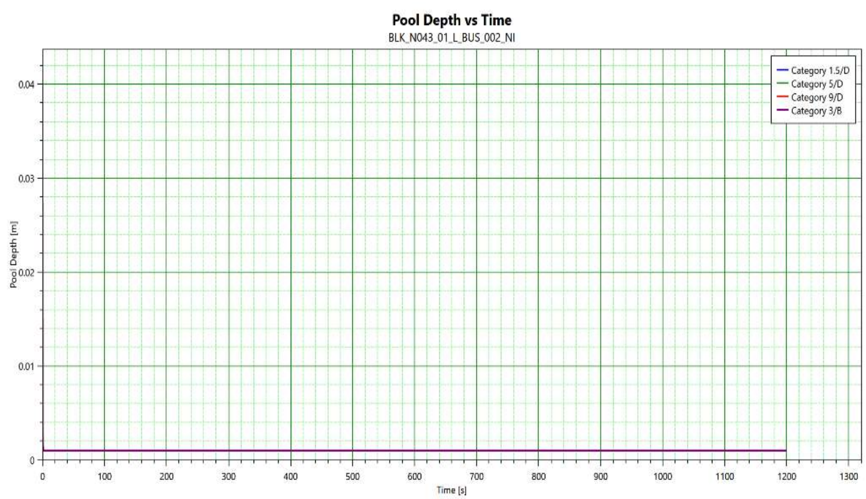
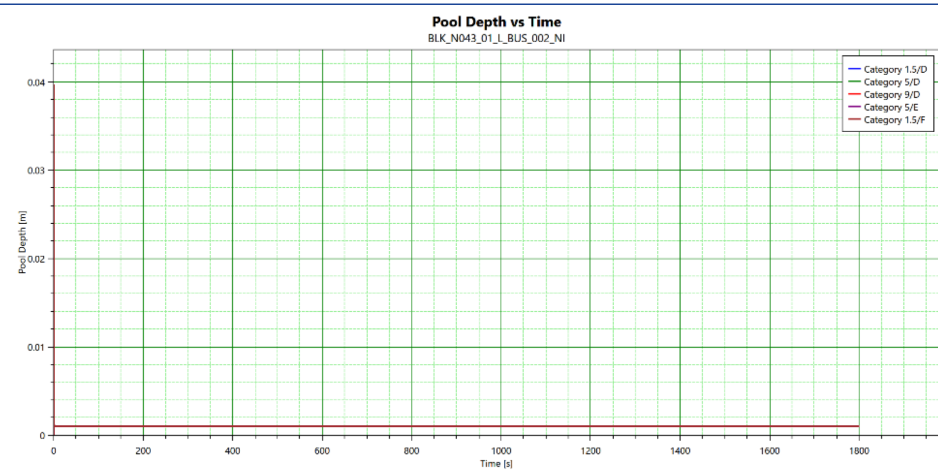
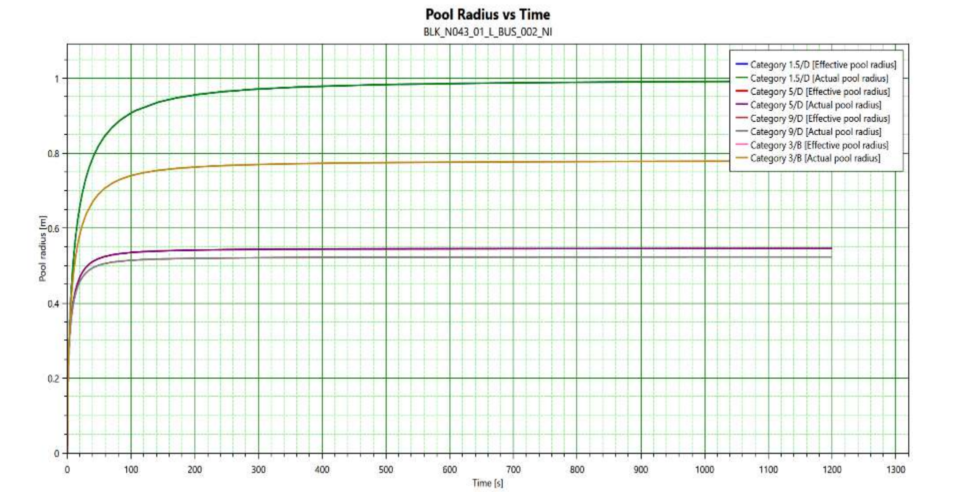
	DAY	NIGHT
Mass Vaporised		
Pool Depth		

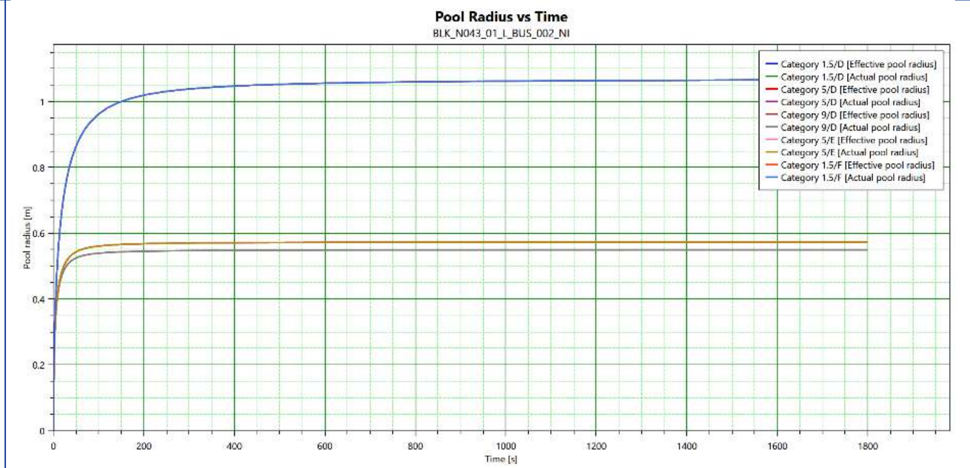
	DAY	NIGHT

Pool Radius

DAY

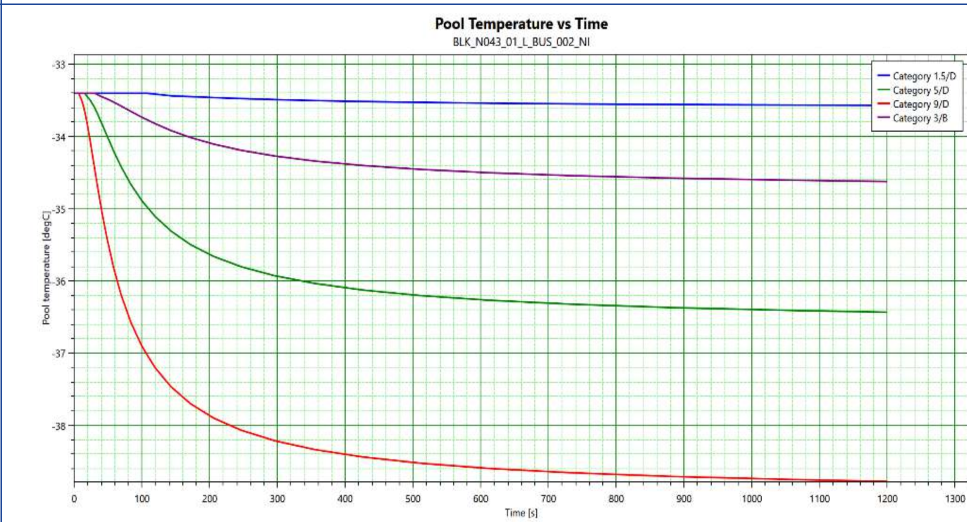


NIGHT



Pool Temp

DAY



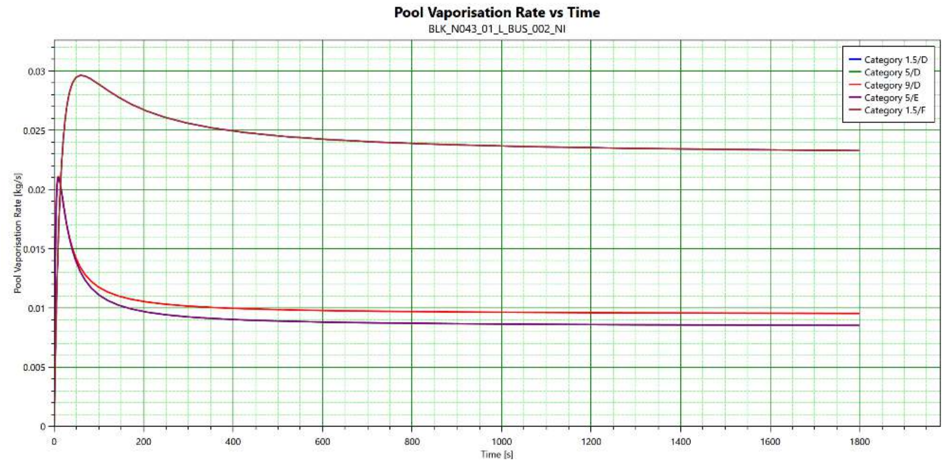
NIGHT

	DAY	NIGHT

Pool Vaporisation Rate

DAY

NIGHT



Solution Rate

DAY

NIGHT

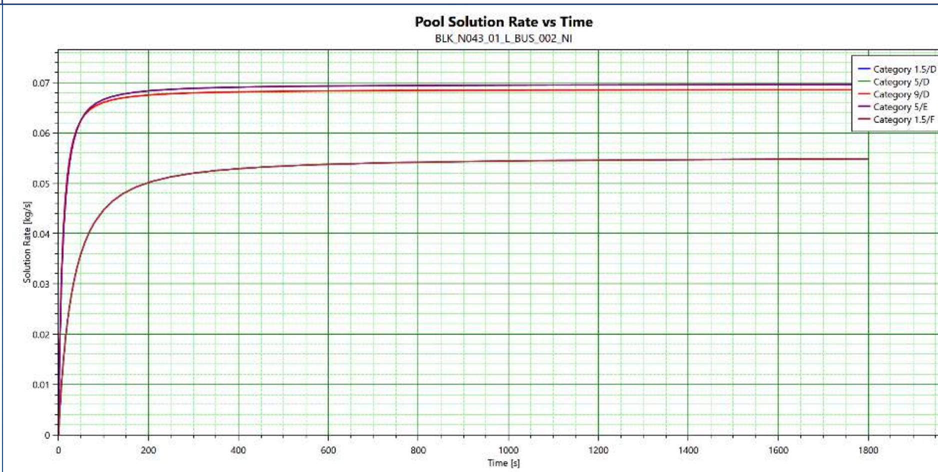


Table A9 Results for Bulker, 23mm hole, day/night

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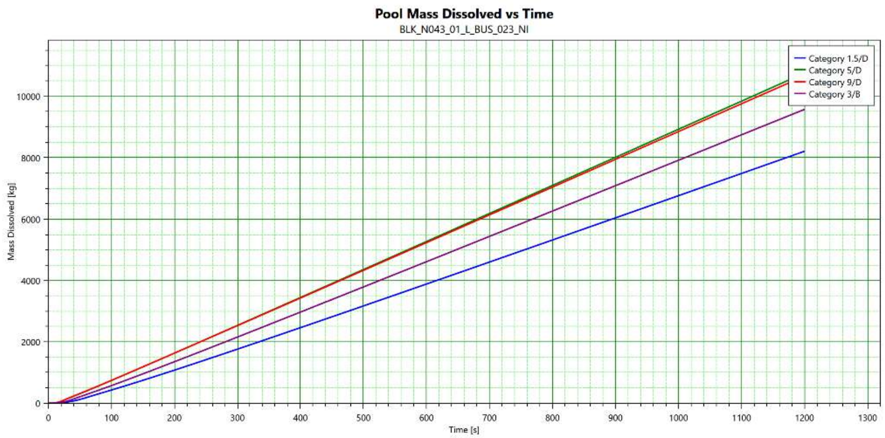

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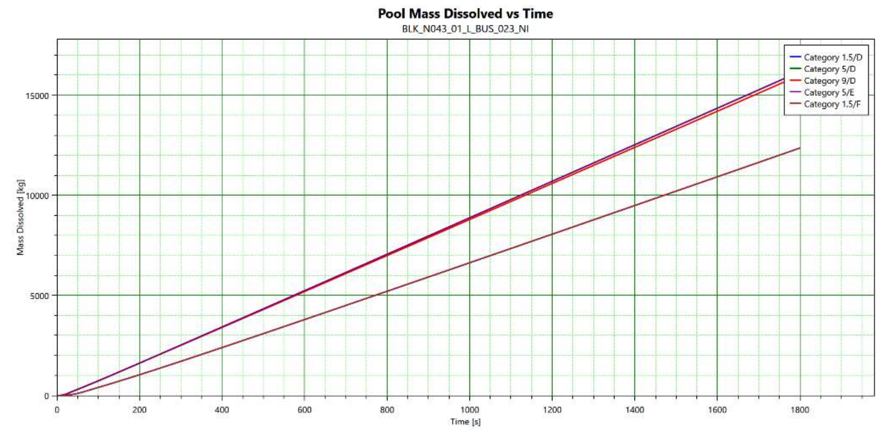

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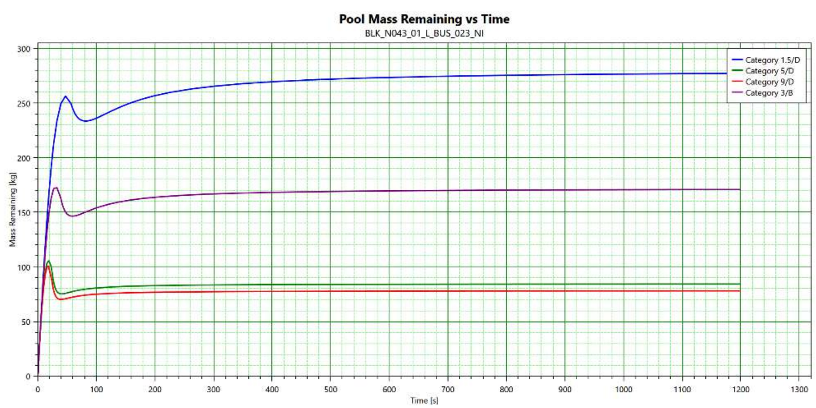

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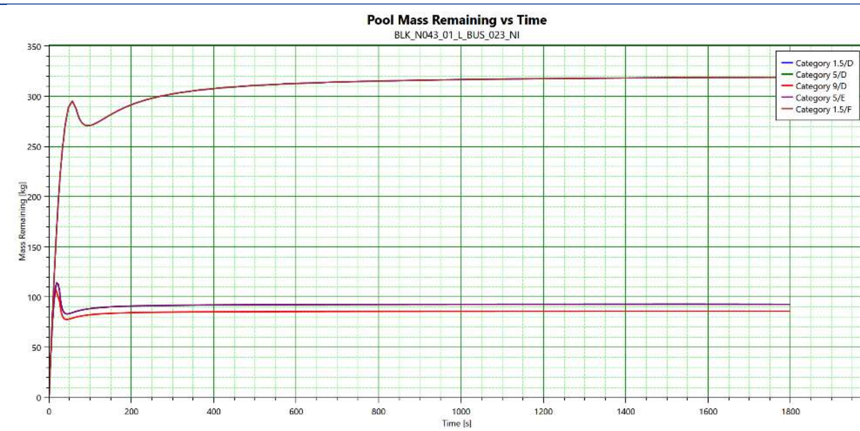

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<table>
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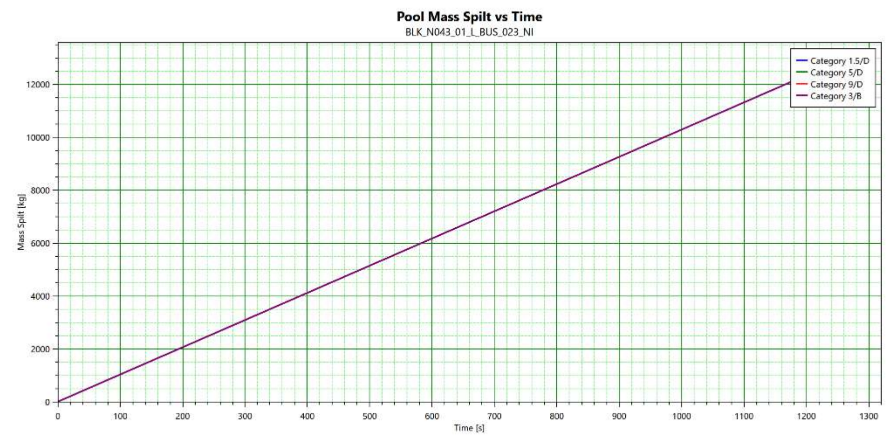
<tr><td>Mass Spilt</td><td>


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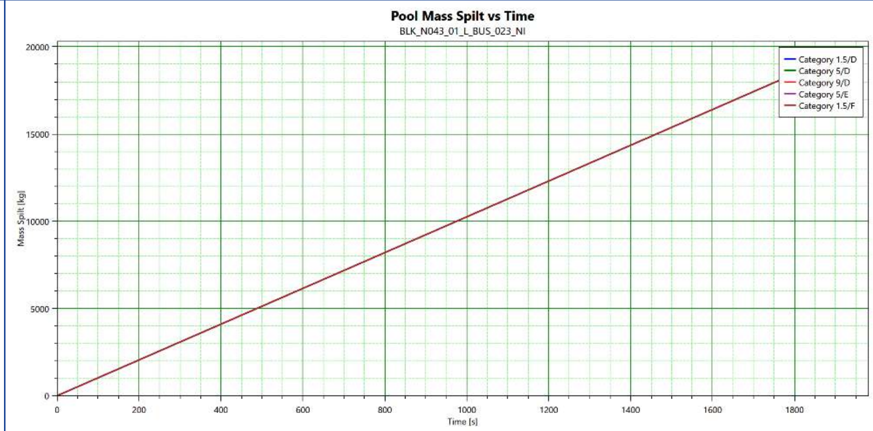

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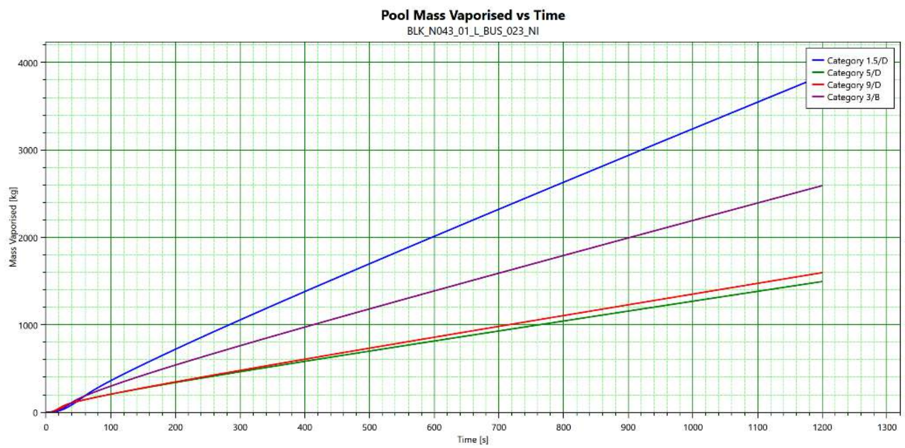

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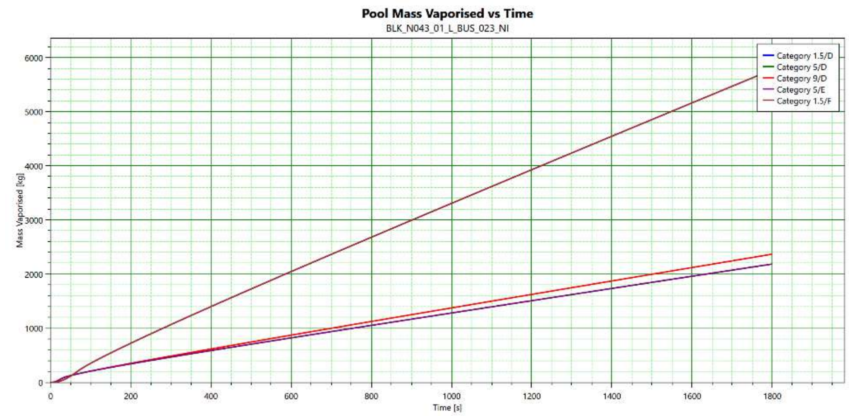
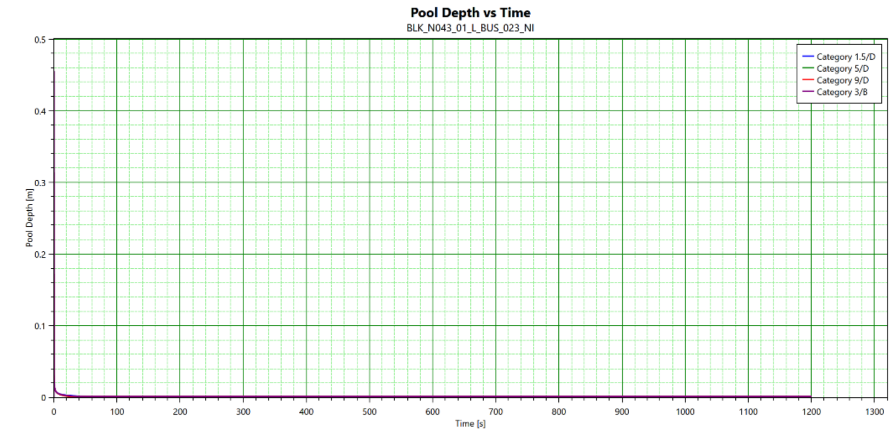


</td></tr>
</table>

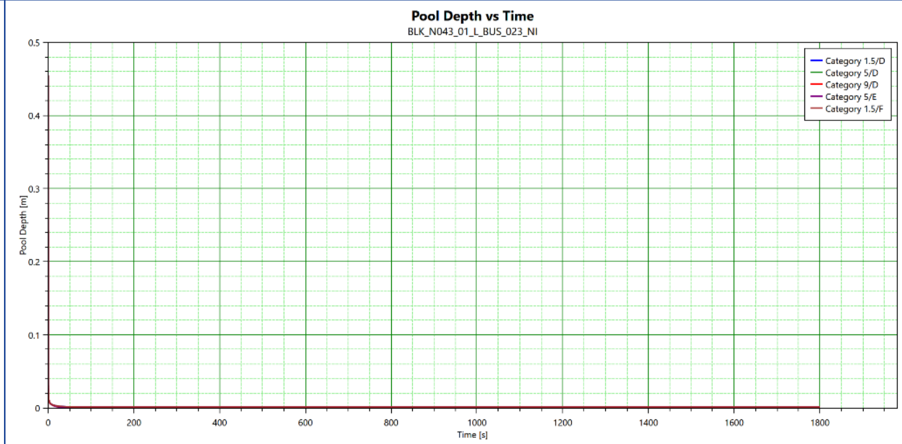
	DAY	NIGHT

Pool Depth

DAY

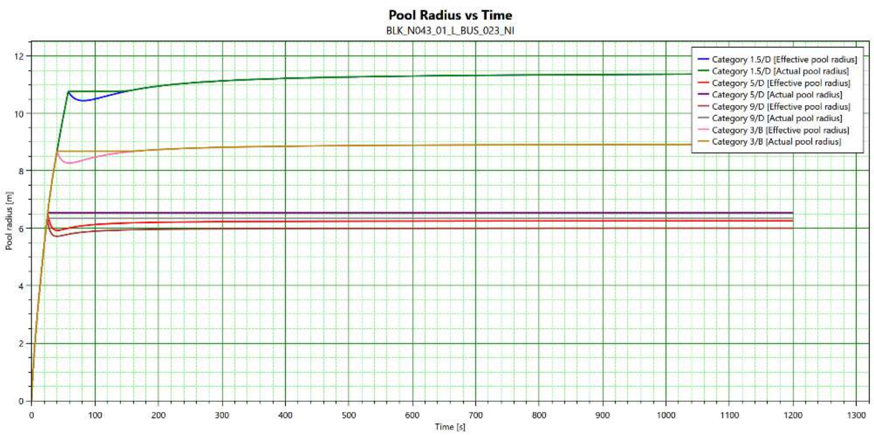


NIGHT

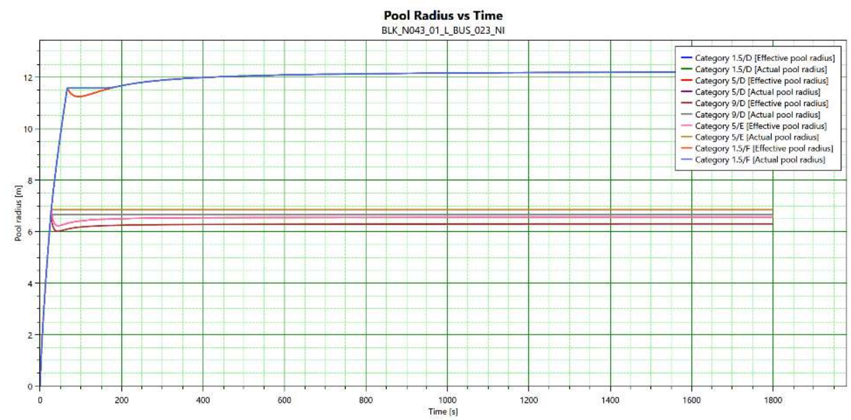


Pool Radius

DAY



NIGHT



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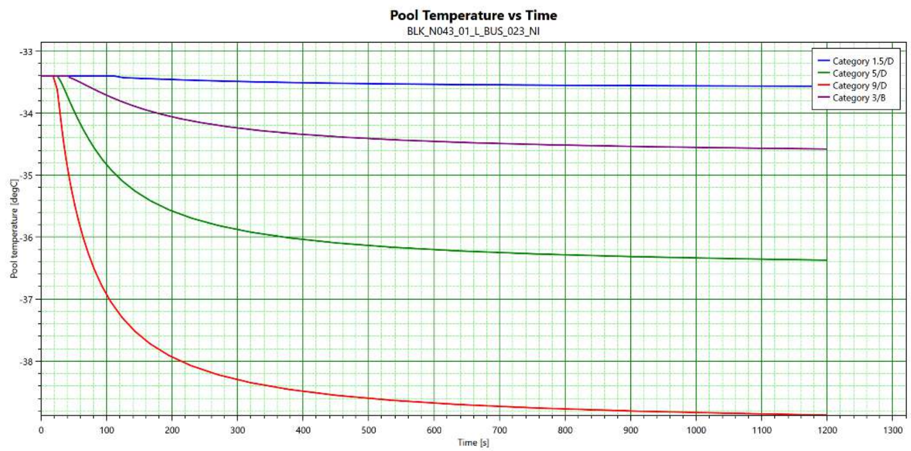
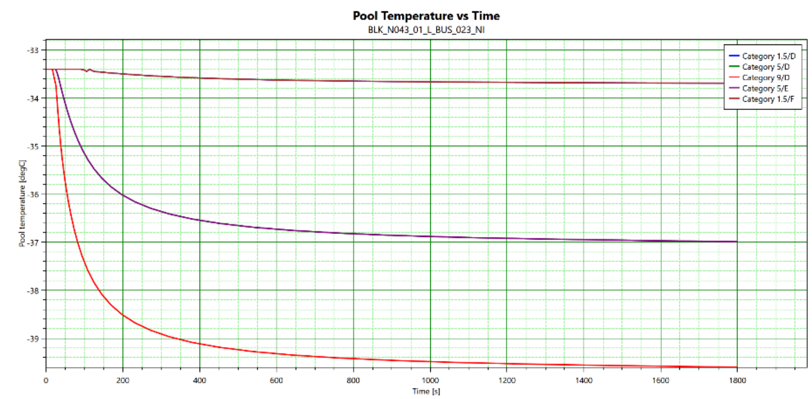
<tr><td>Pool Temp</td><td>
</td><td>
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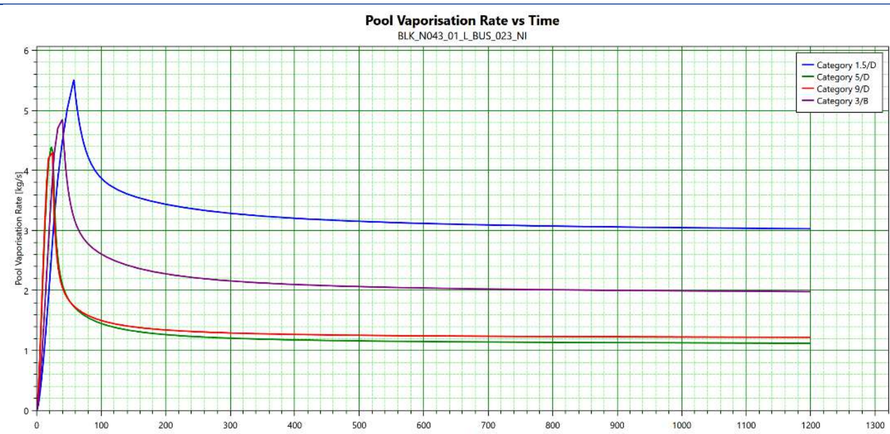
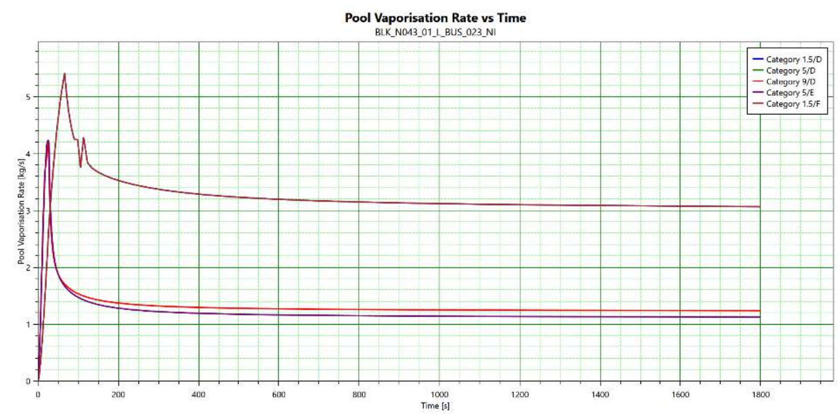
<tr><td>Pool Vaporisation Rate</td><td>
</td><td>
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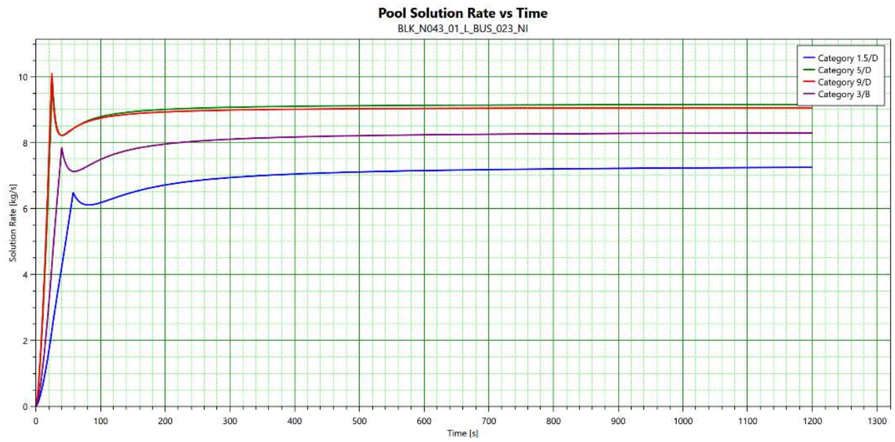
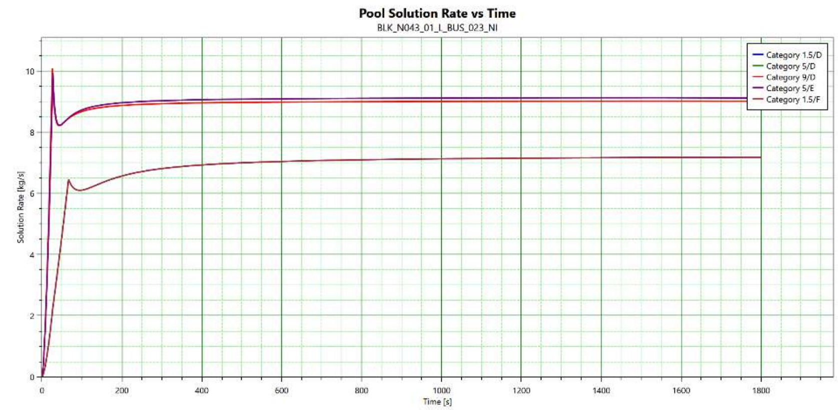
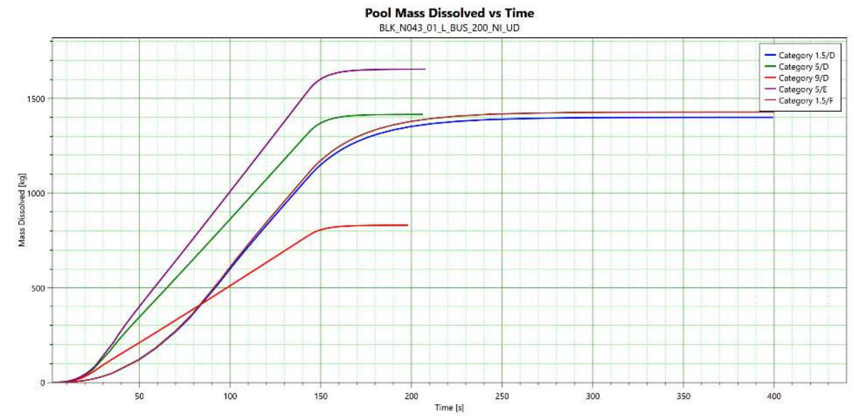
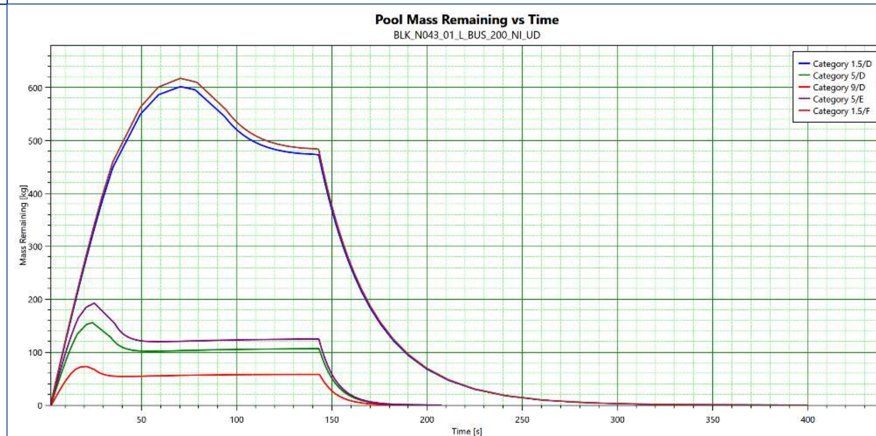
	DAY	NIGHT
Solution Rate		

Table A10 Results for Bulker, 200mm hole, day/night

	DAY	NIGHT
Pool Mass Dissolved		
Pool Mass Remaining		

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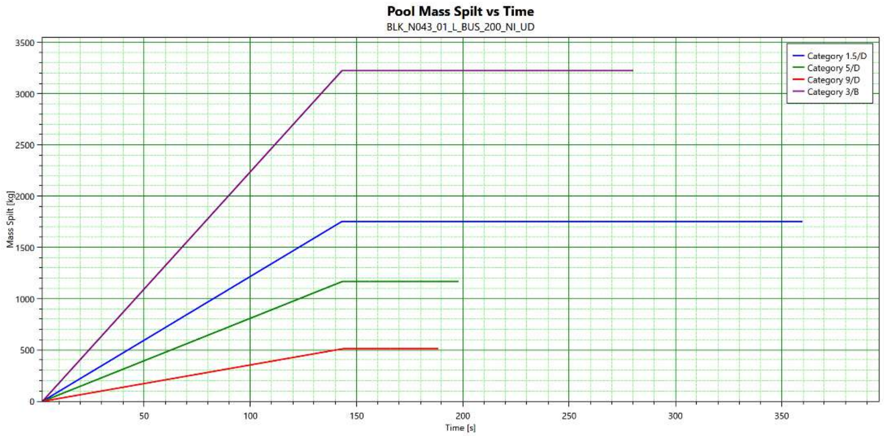
<tr><td>Mass Spilt</td><td>
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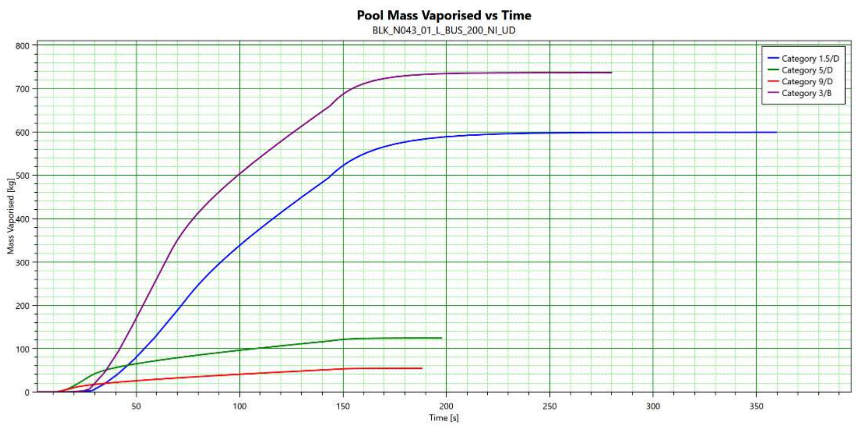
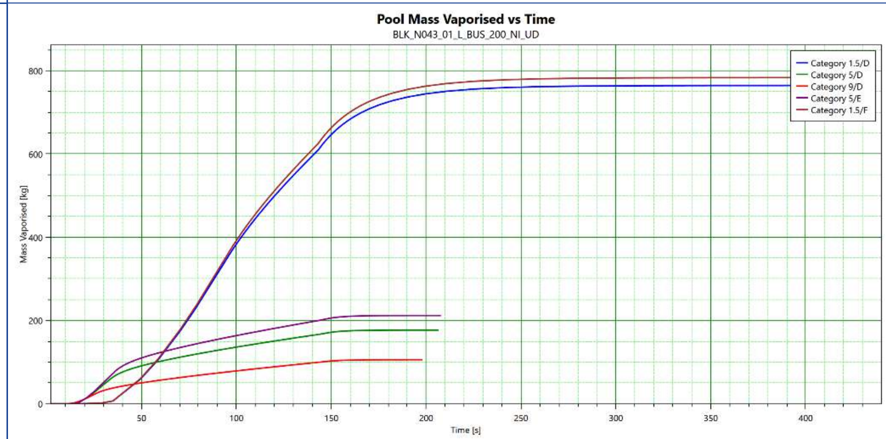
<tr><td>Mass Vaporised</td><td>
</td><td>
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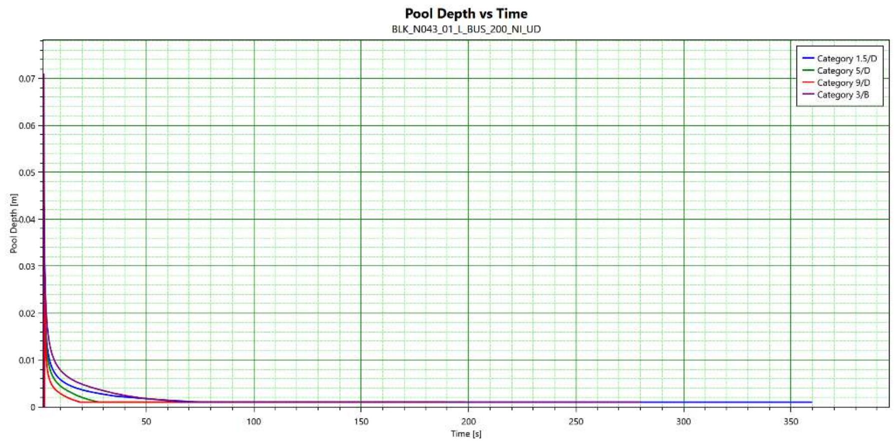
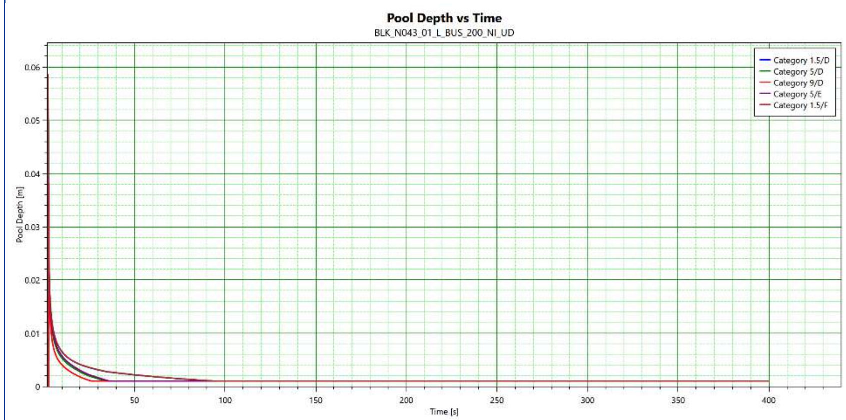
	DAY	NIGHT
Pool Depth	see below	see below
Pool Radius	see below	see below

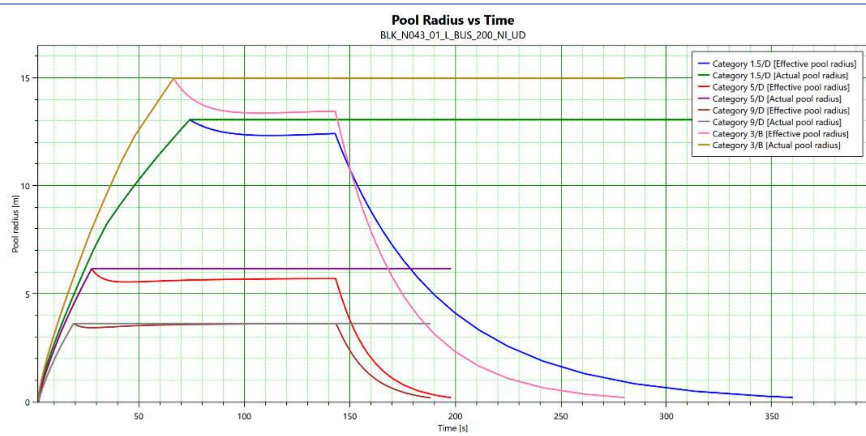
DAY – Pool Depth



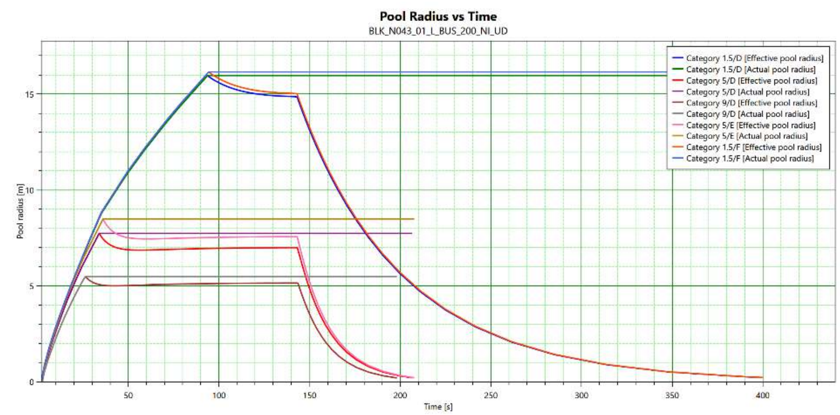
NIGHT – Pool Depth



DAY – Pool Radius



NIGHT – Pool Radius



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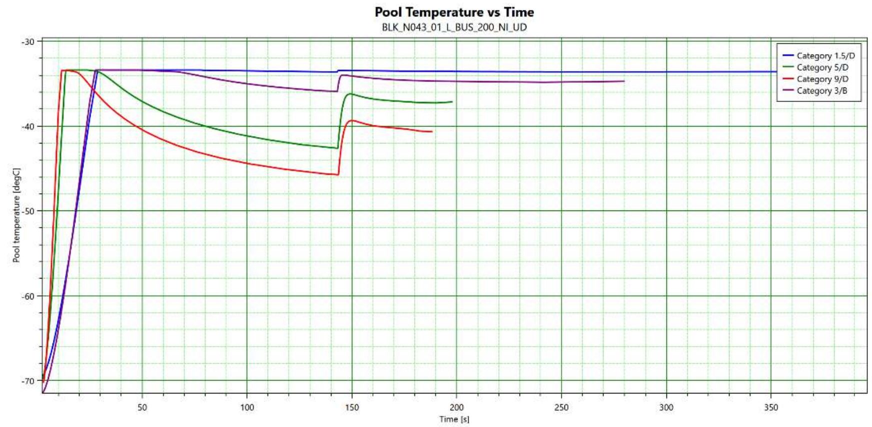
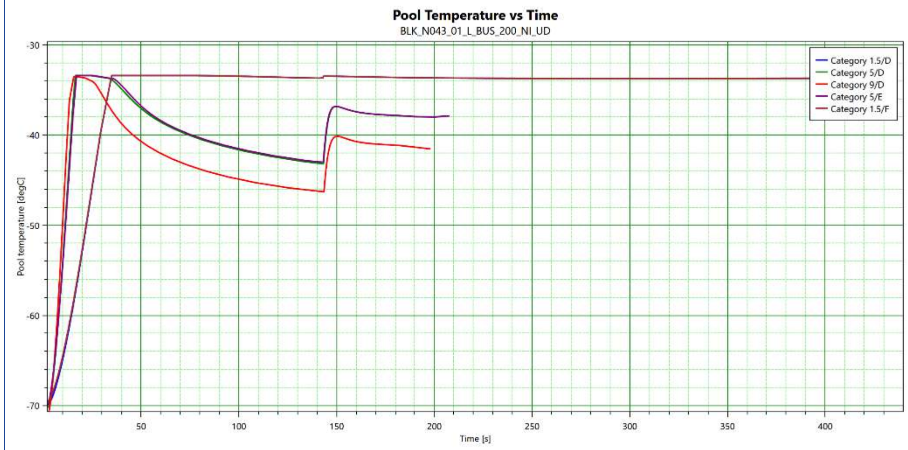
<tr><td>Pool Temp</td><td>
</td><td>
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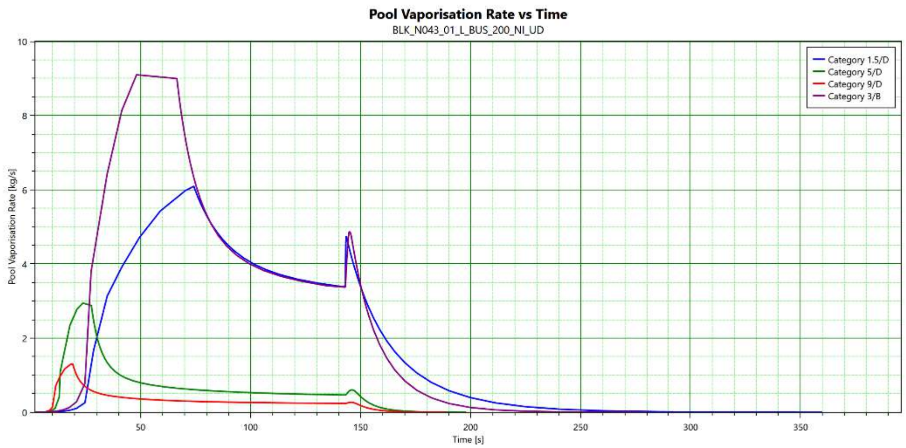
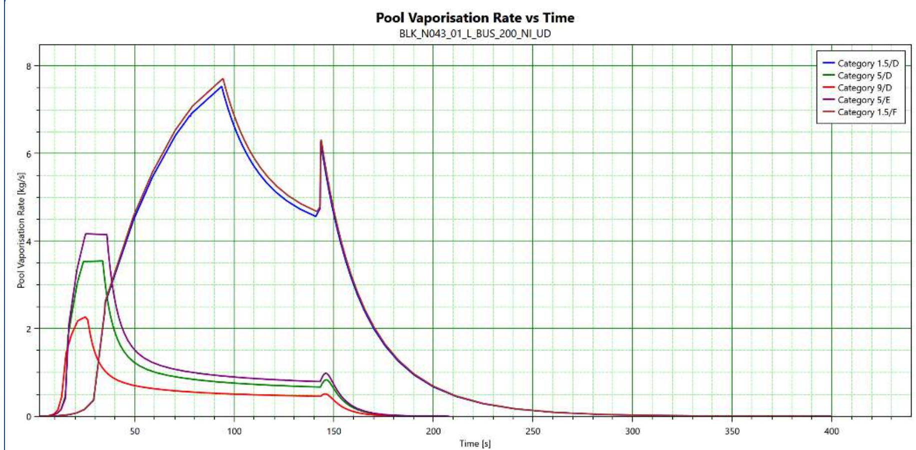
<tr><td>Pool Vaporisation Rate</td><td>
</td><td>
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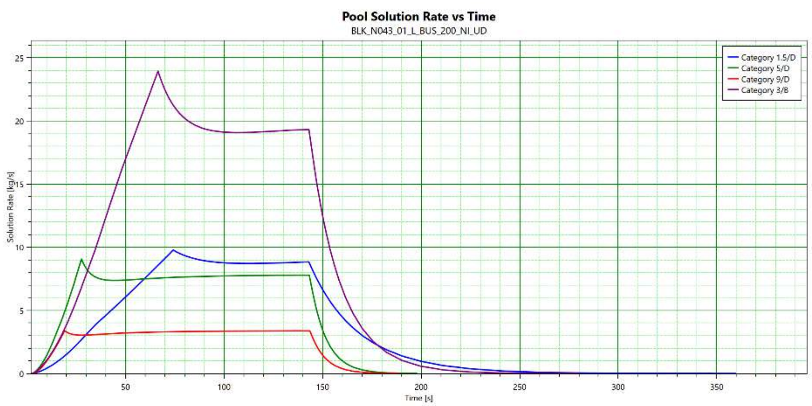
	DAY	NIGHT
Solution Rate		

Table A11 Results for Containership, 2mm hole, day/night

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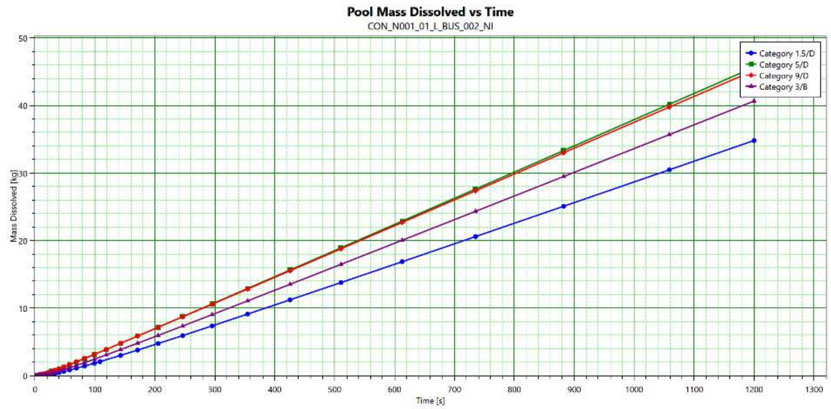

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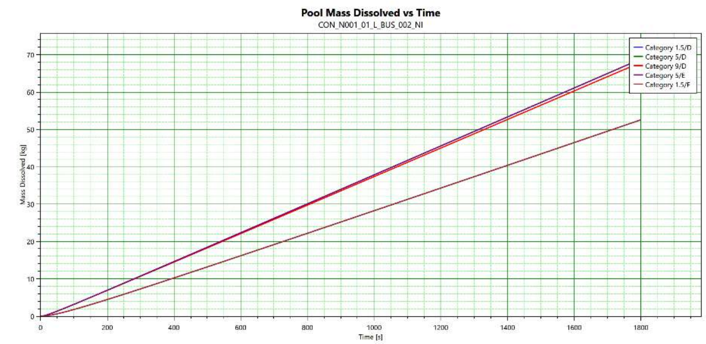

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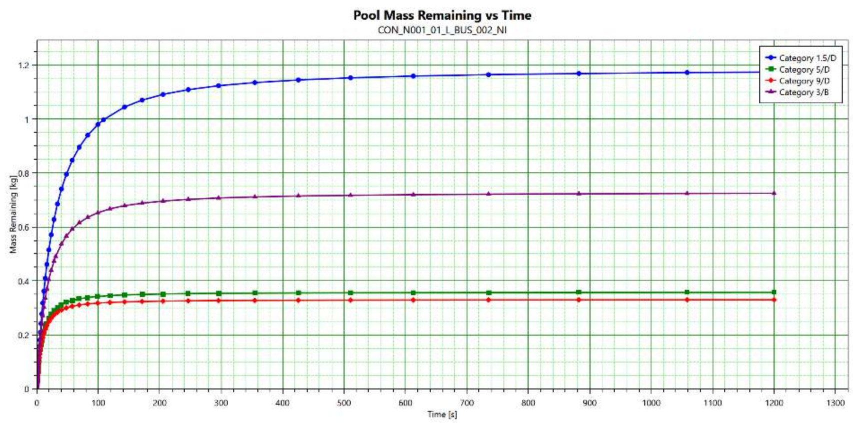

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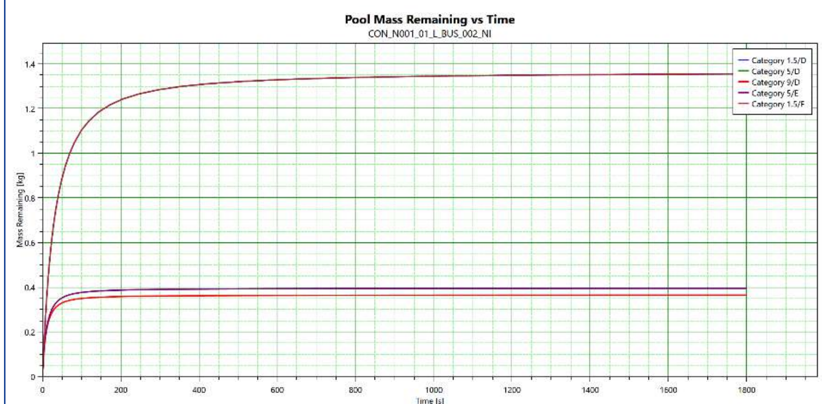

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<table>
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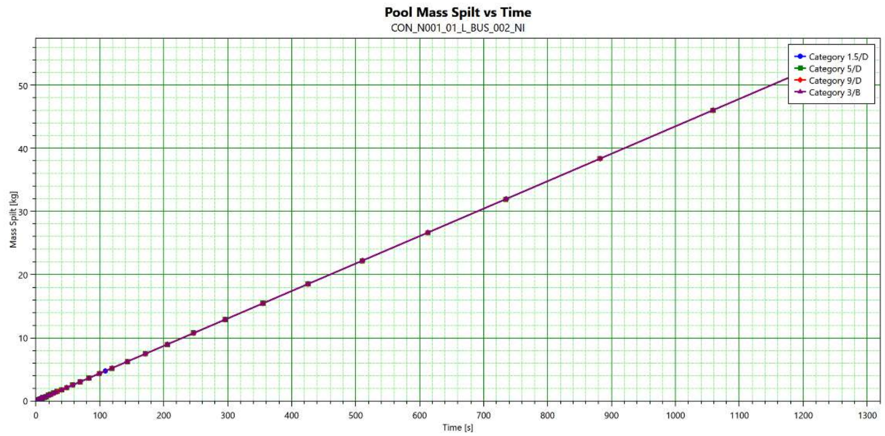
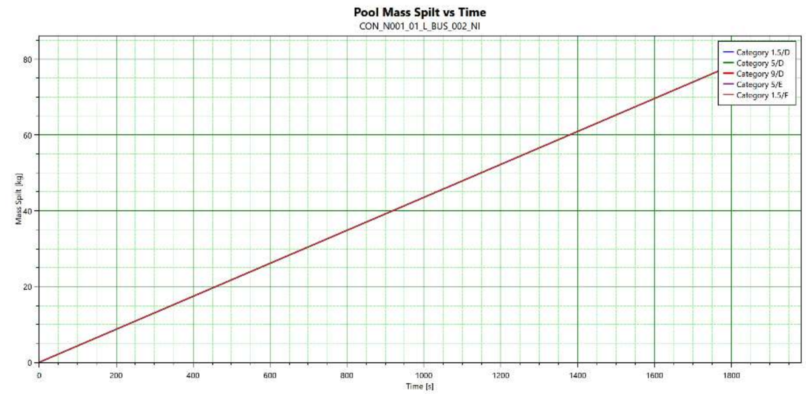
<tr><td>Mass Spilt</td><td>
</td><td>
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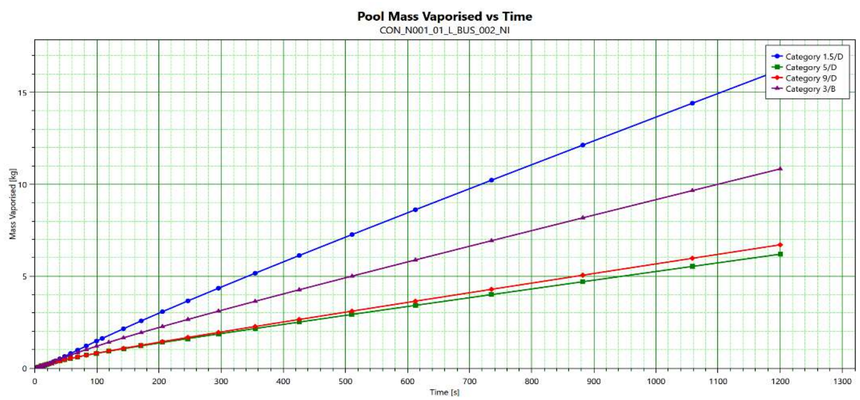
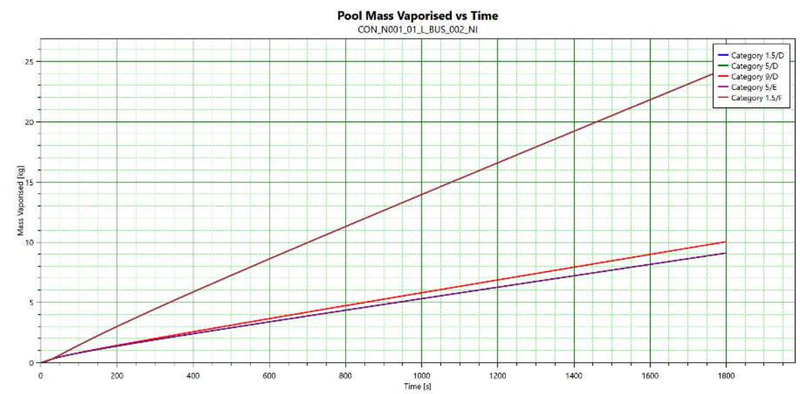
<tr><td>Mass Vaporised</td><td>
</td><td>
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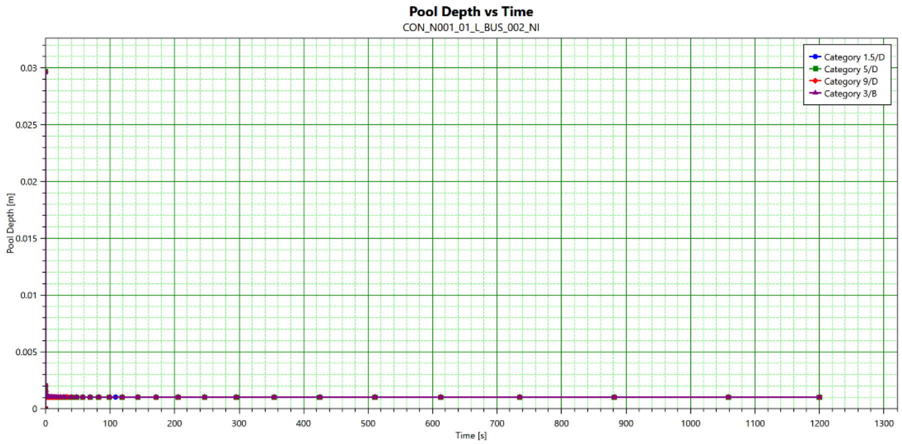
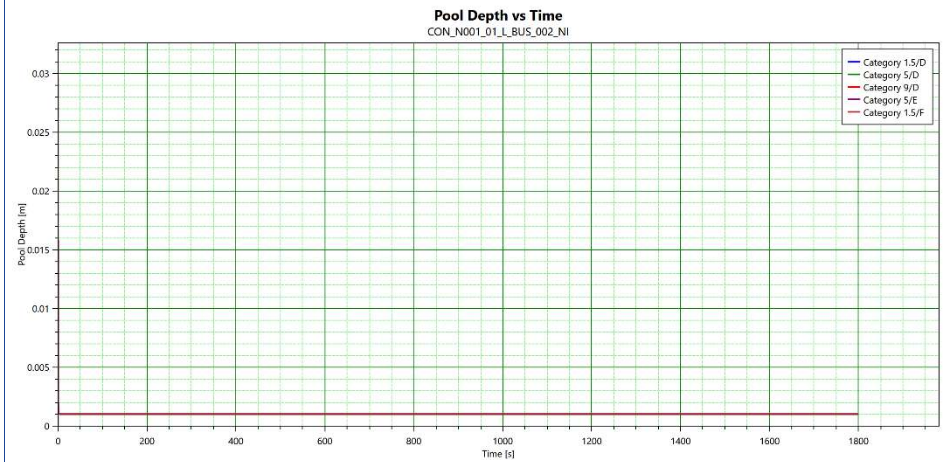
<tr><td>Pool Depth</td><td>
</td><td>
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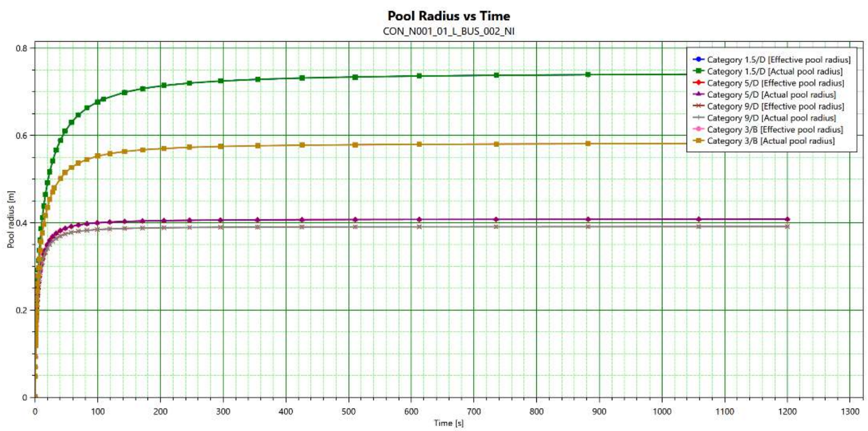
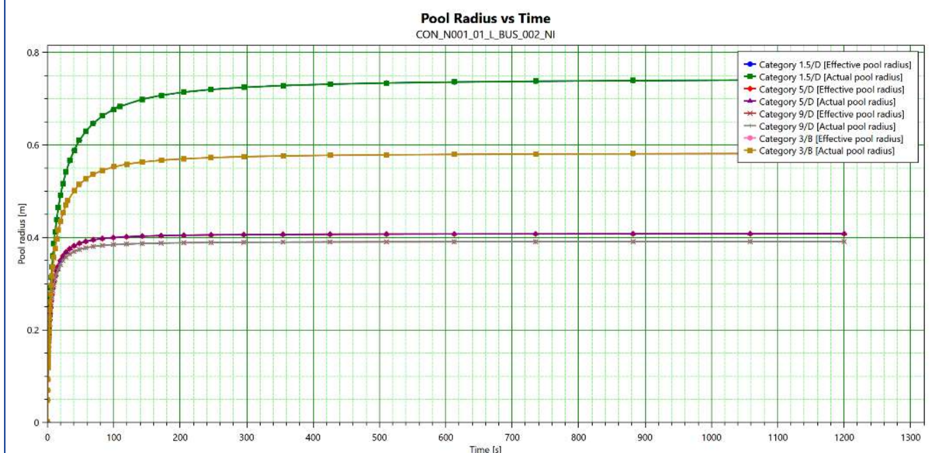
<tr><td>Pool Radius</td><td>
</td><td>
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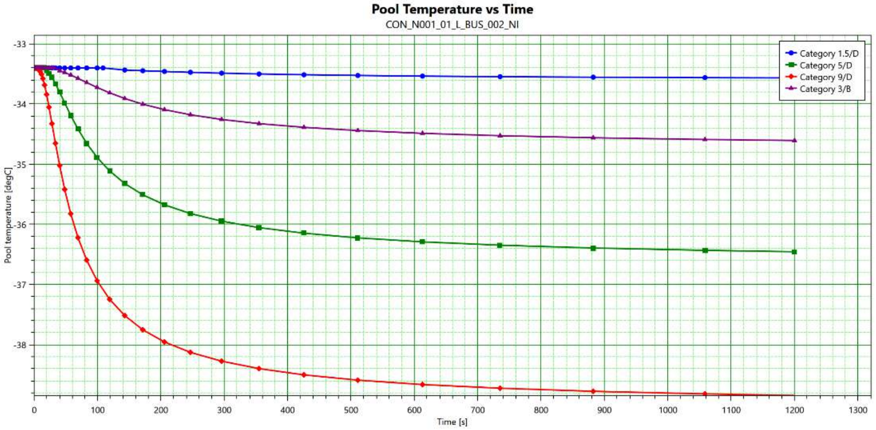
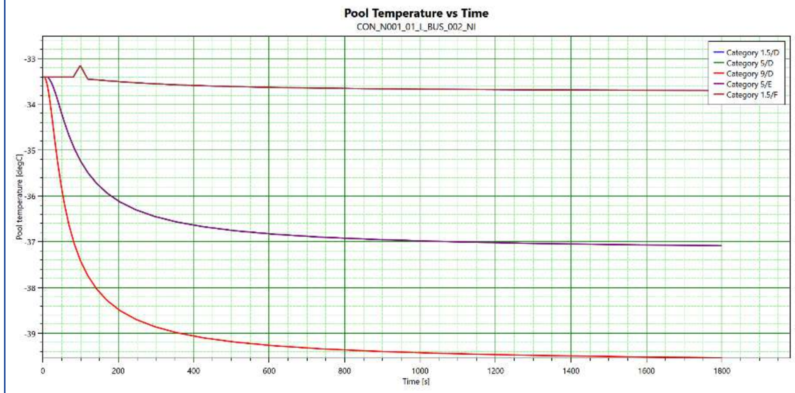
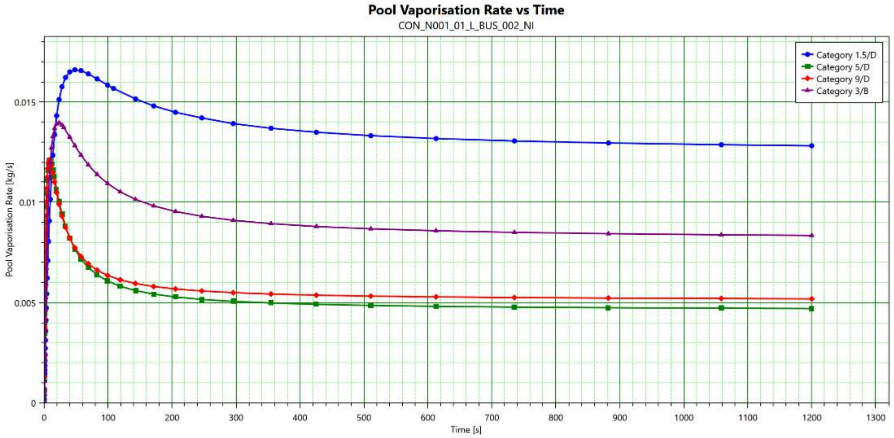
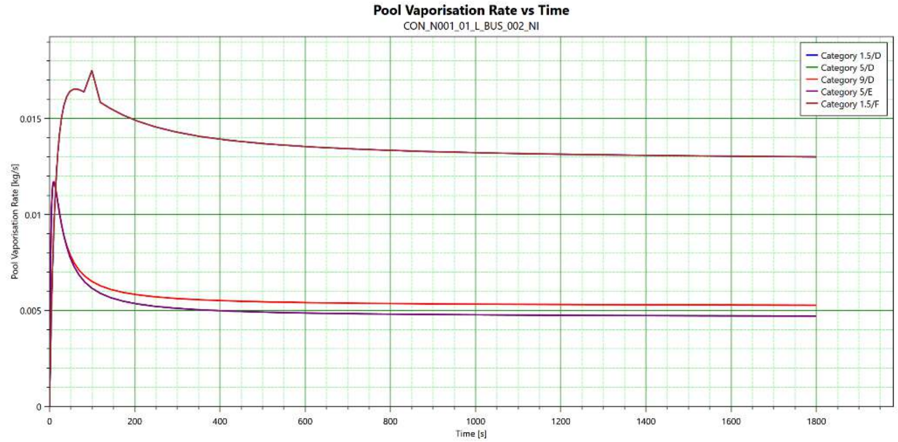
	DAY	NIGHT
Pool Temp		
Pool Vaporisation Rate		

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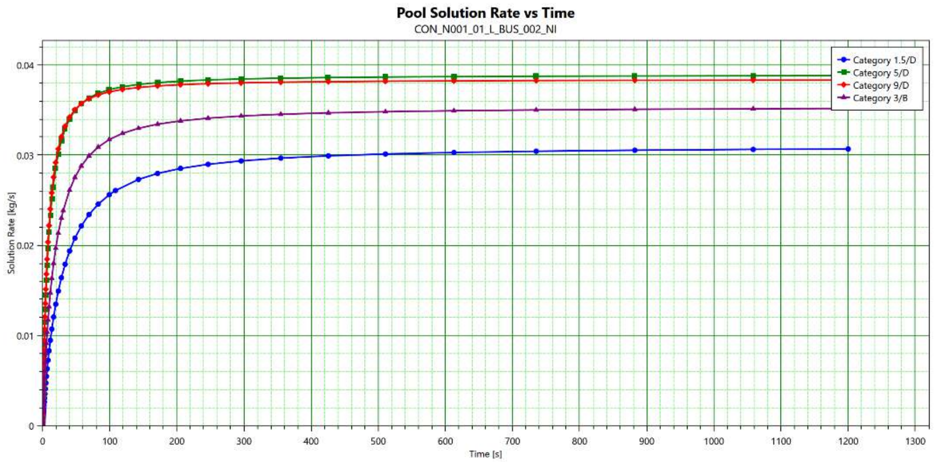
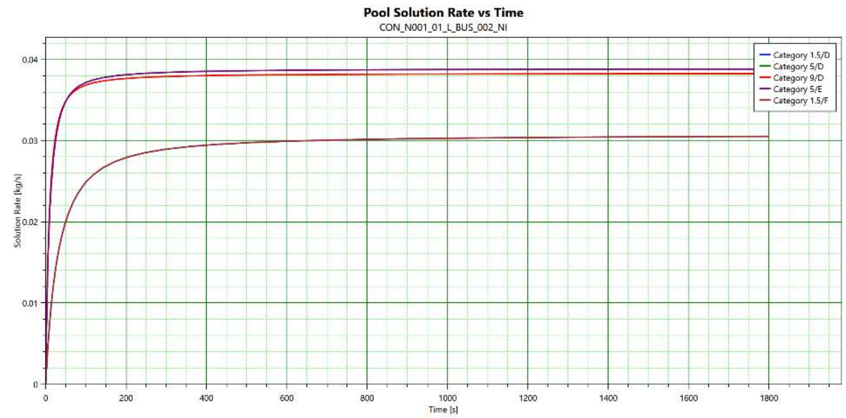
<tr><td>Solution Rate</td><td>
</td><td>
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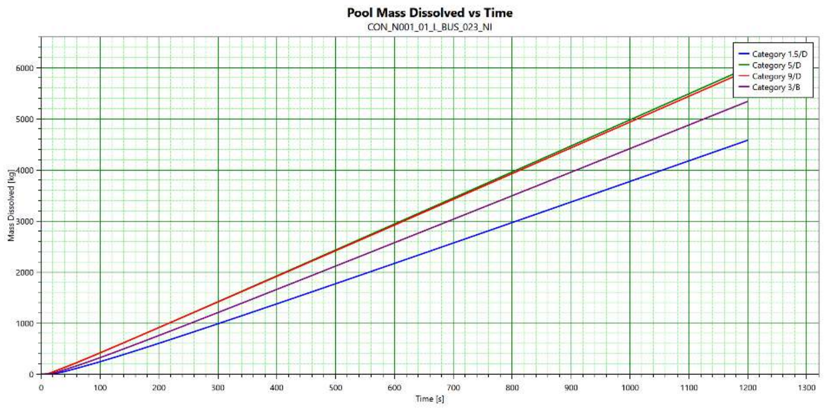
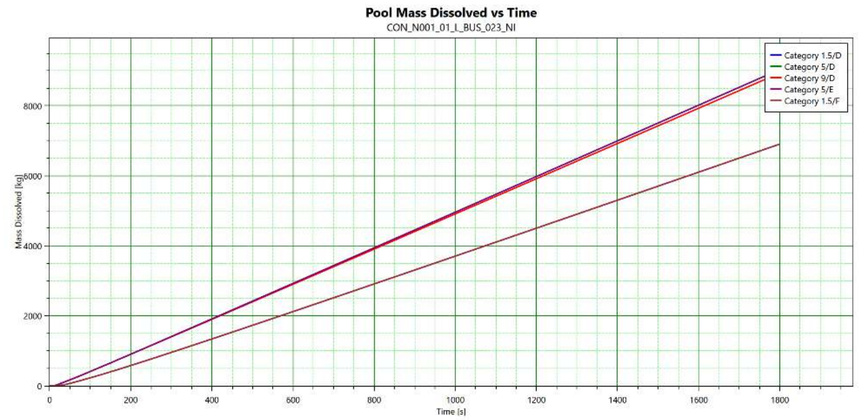
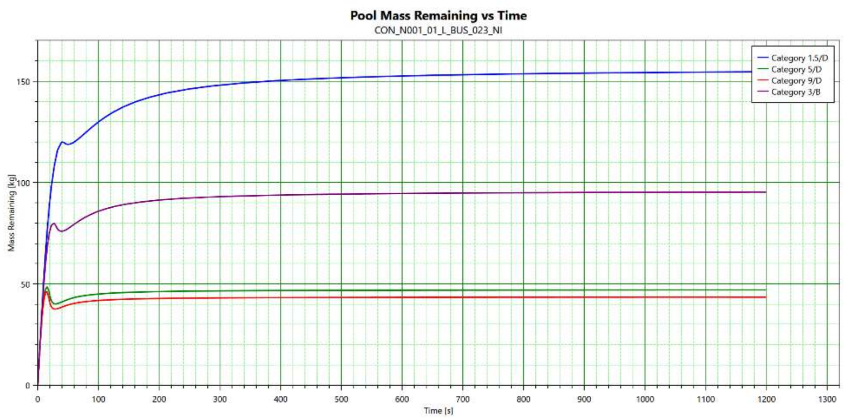
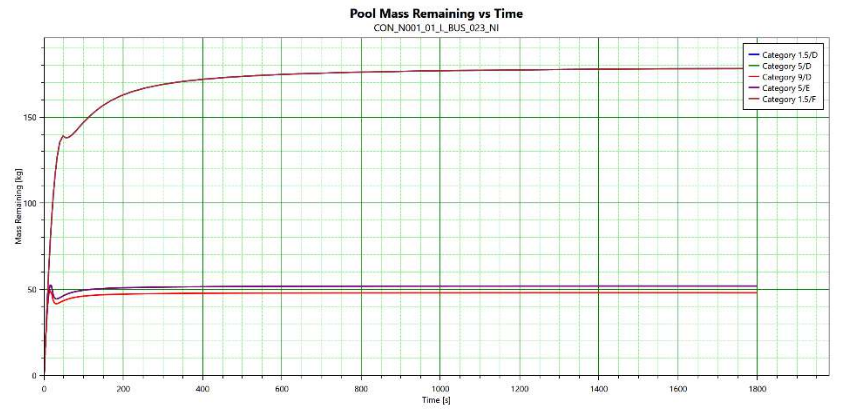
Table A12 Results for Containership, 23mm hole, day/night

	DAY	NIGHT
Pool Mass Dissolved		
Pool Mass Remaining		

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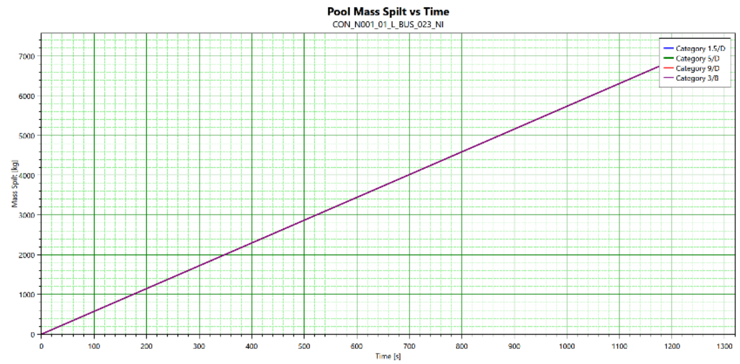
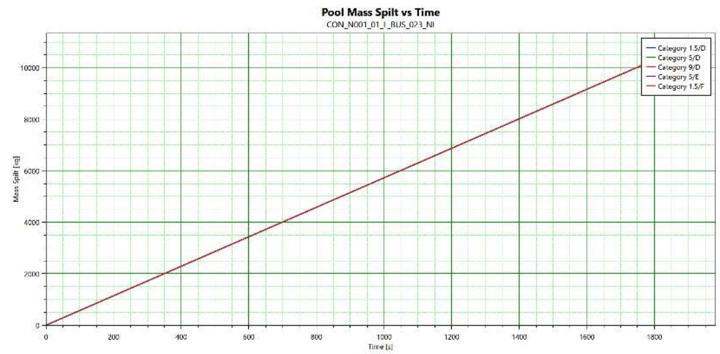
<tr><td>Mass Spilt</td><td>
</td><td>
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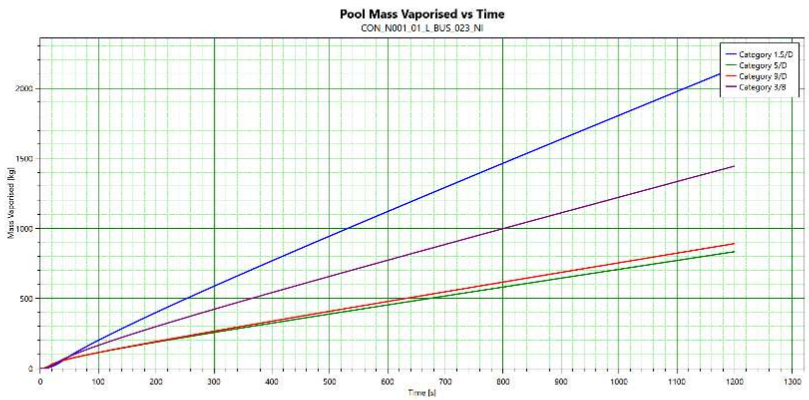
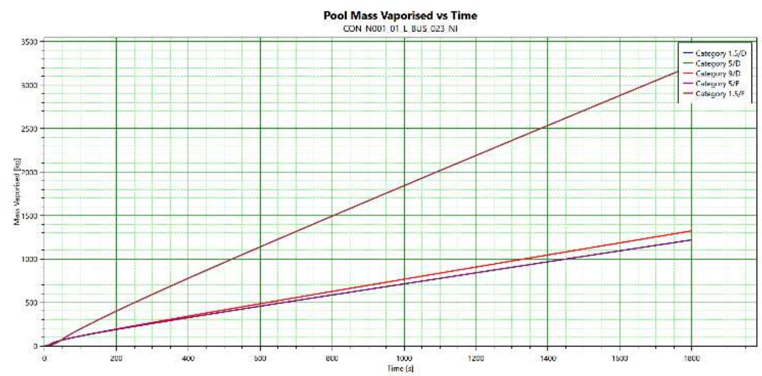
<tr><td>Mass Vaporised</td><td>
</td><td>
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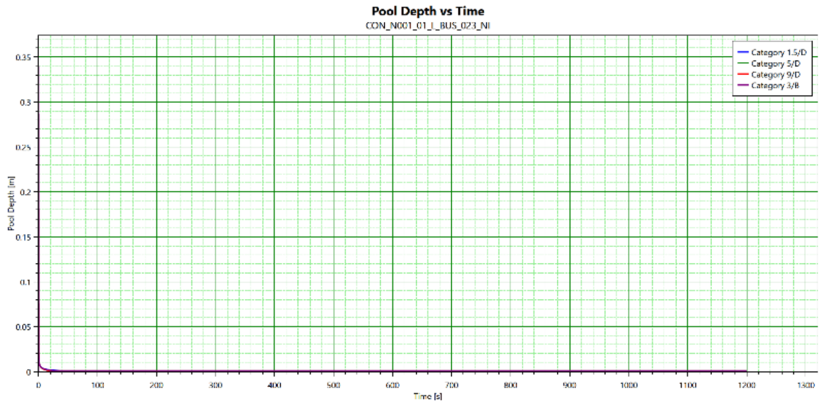
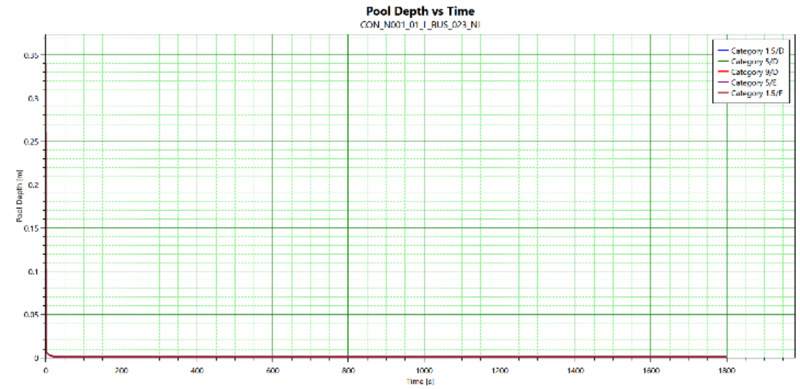
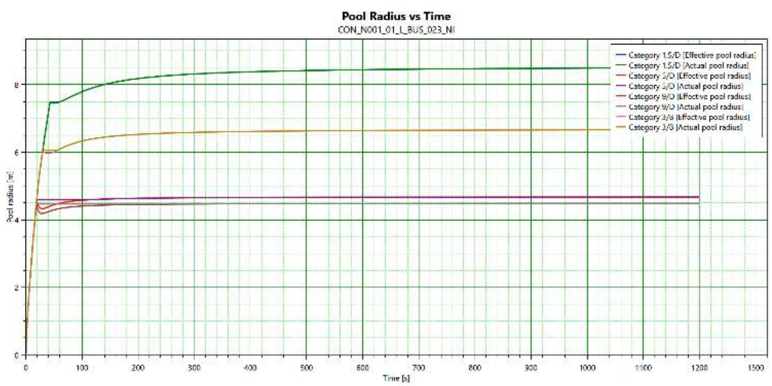
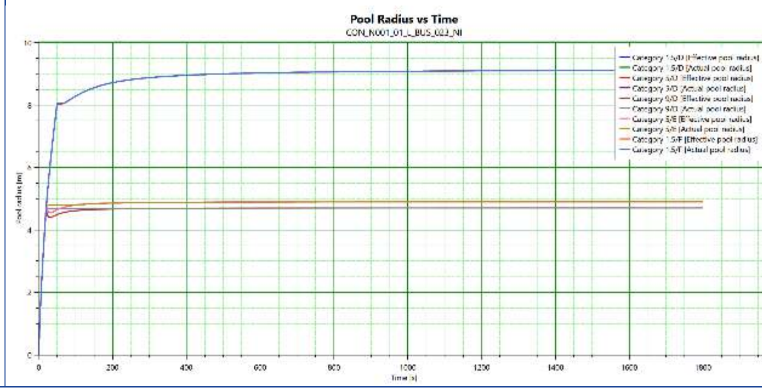
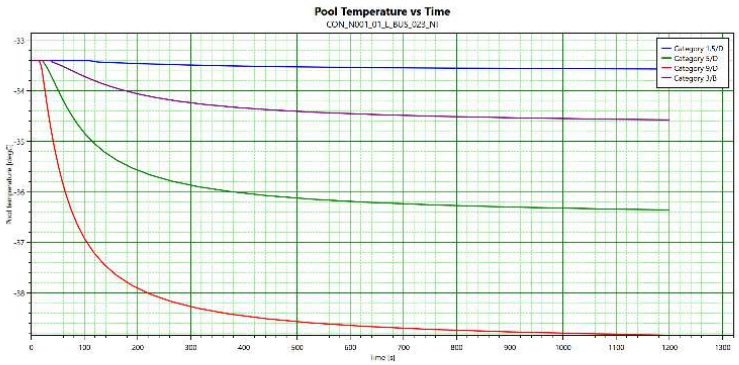
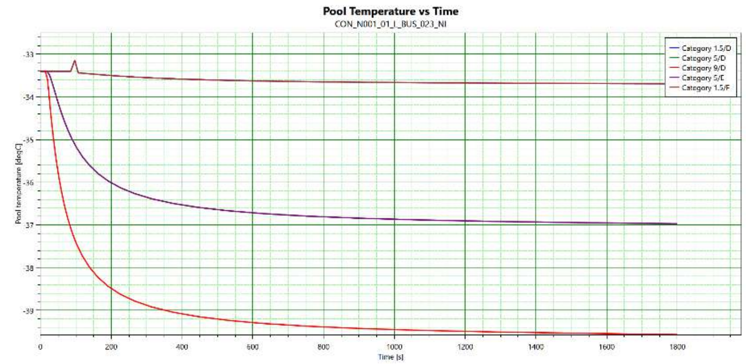
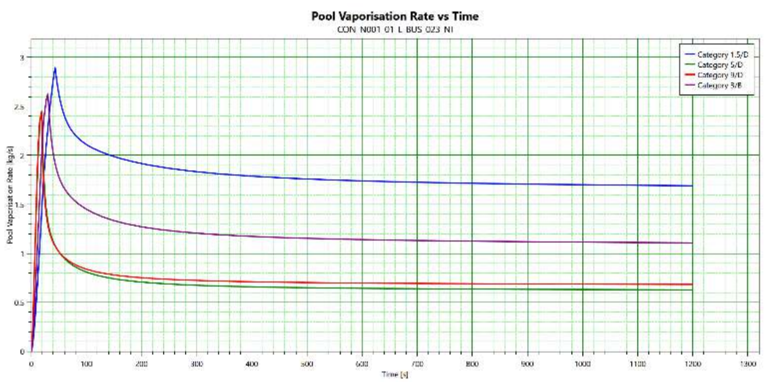
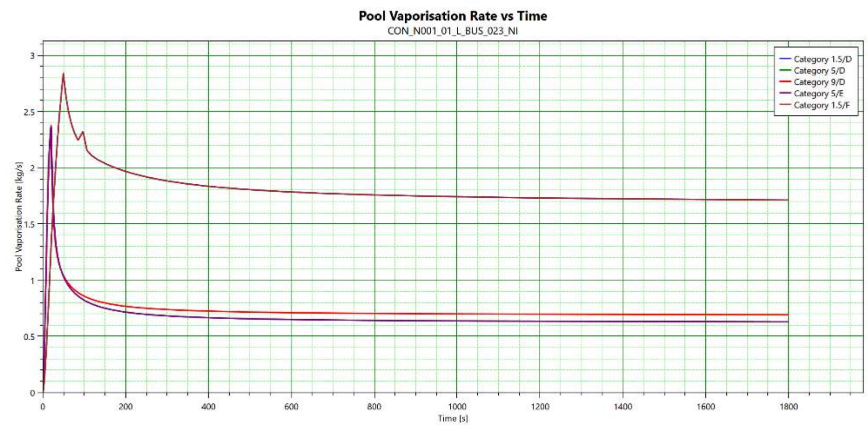
	DAY	NIGHT
Pool Depth		
Pool Radius		









	DAY	NIGHT
Pool Temp		
Pool Vaporisation Rate		

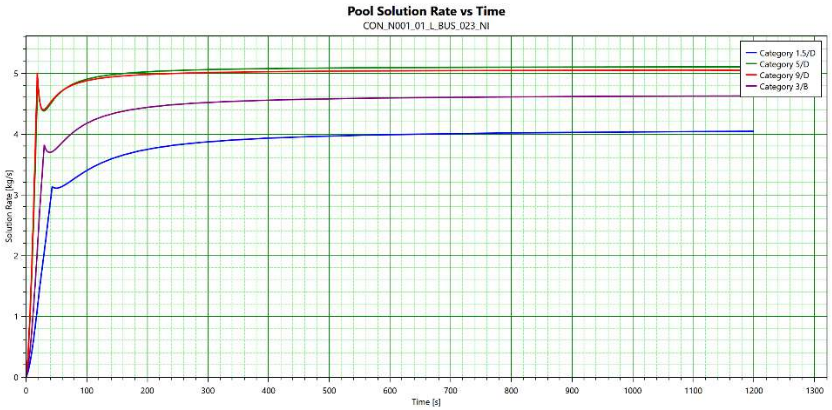
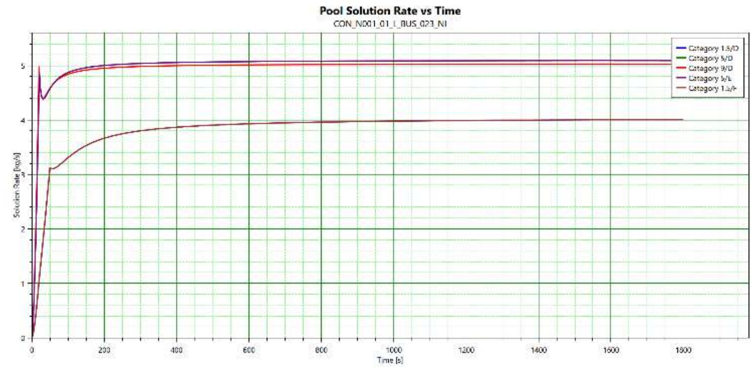
	DAY	NIGHT
Solution Rate		

Table A12 Results for Containership, 200mm hole, day/night

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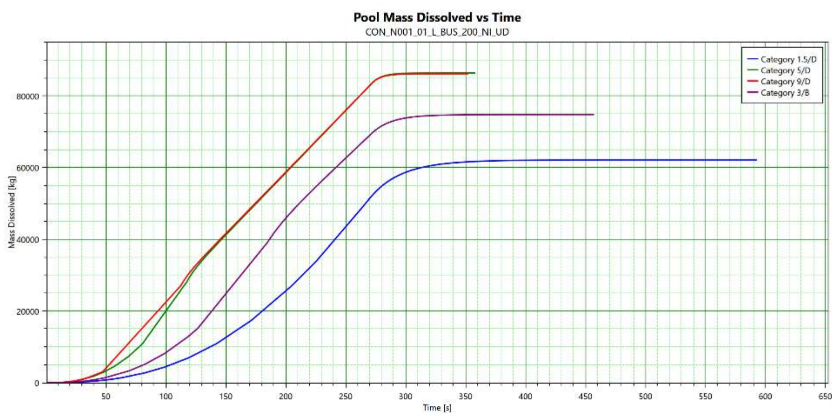
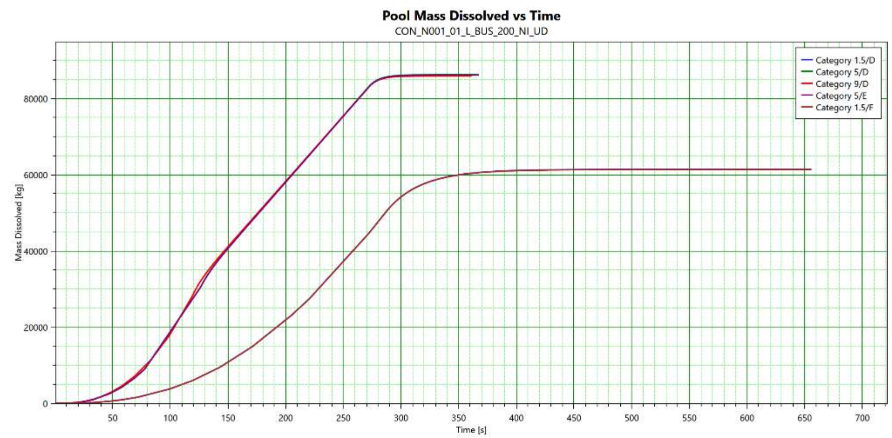
<tr><td>Pool Mass Dissolved</td><td>
</td><td>
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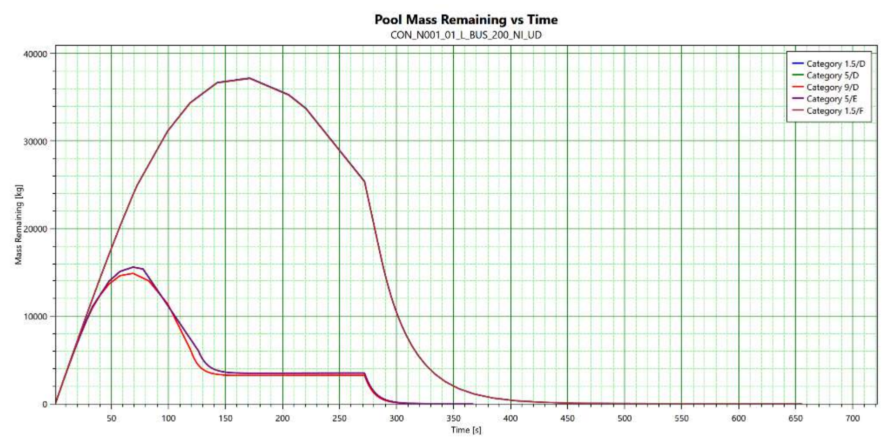
</td><td>
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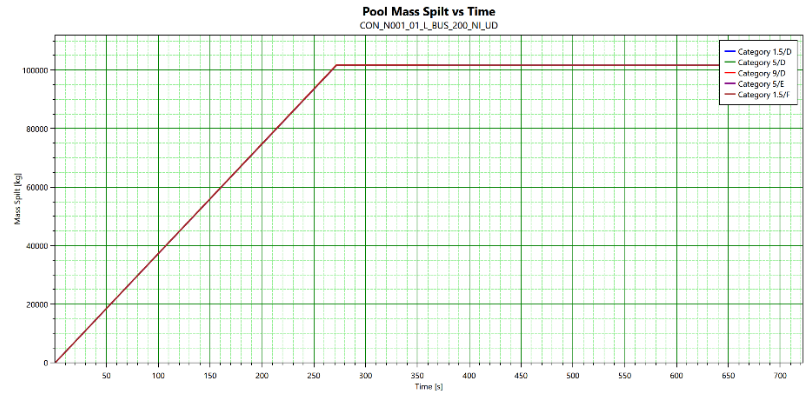
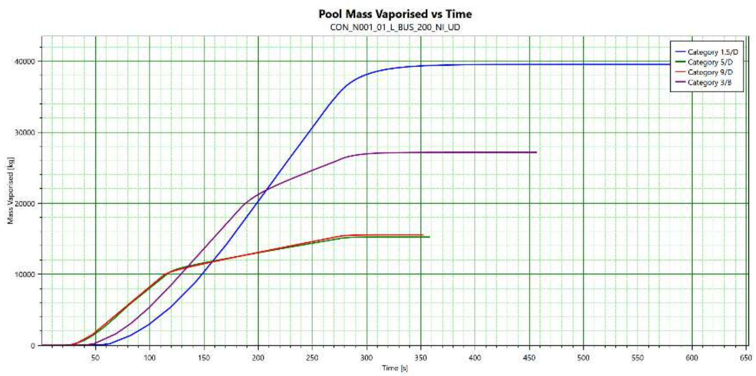
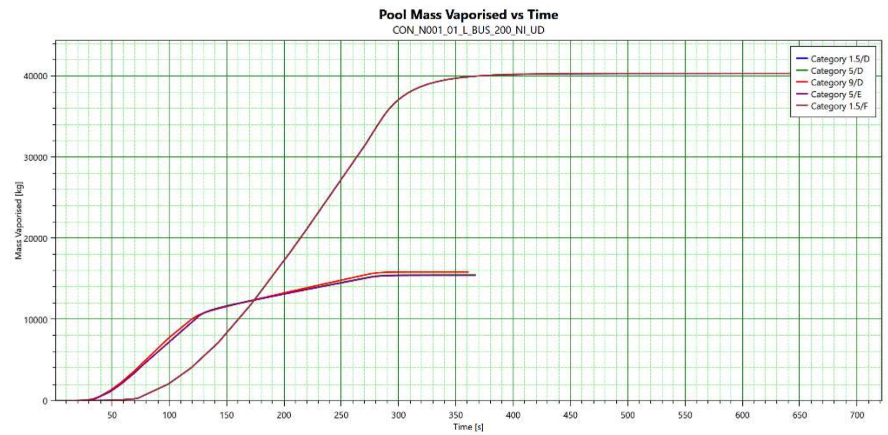
	DAY	NIGHT

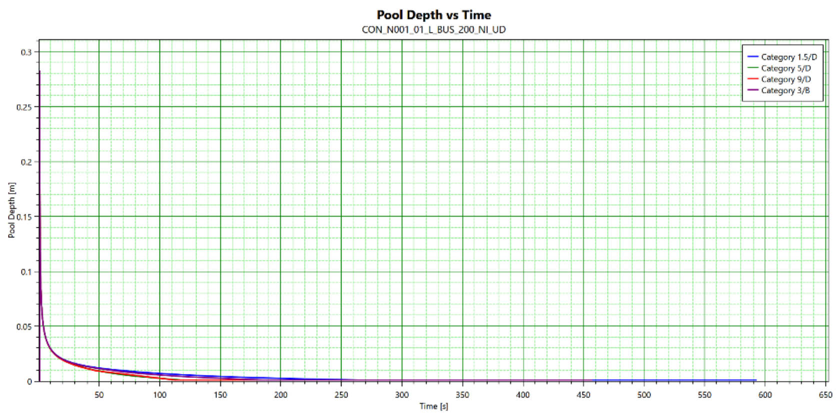
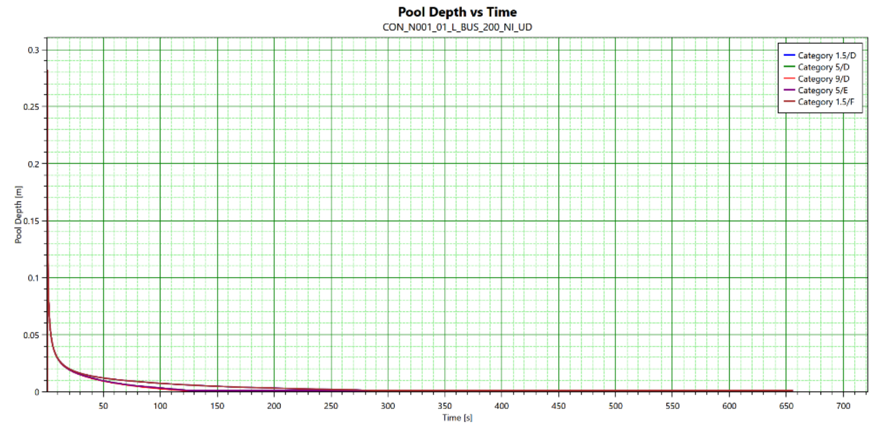
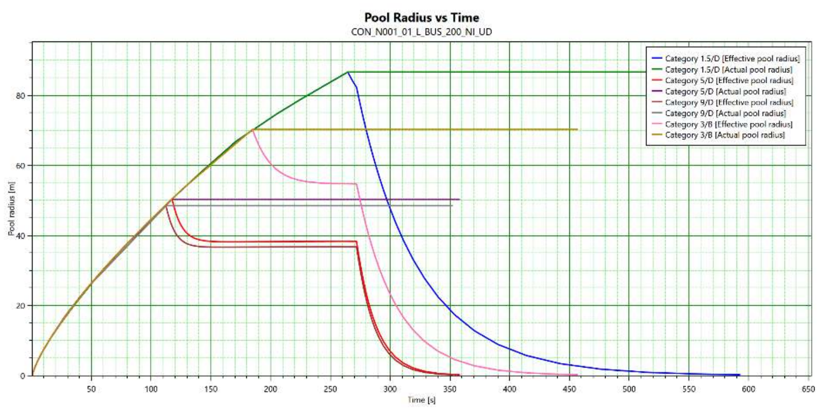
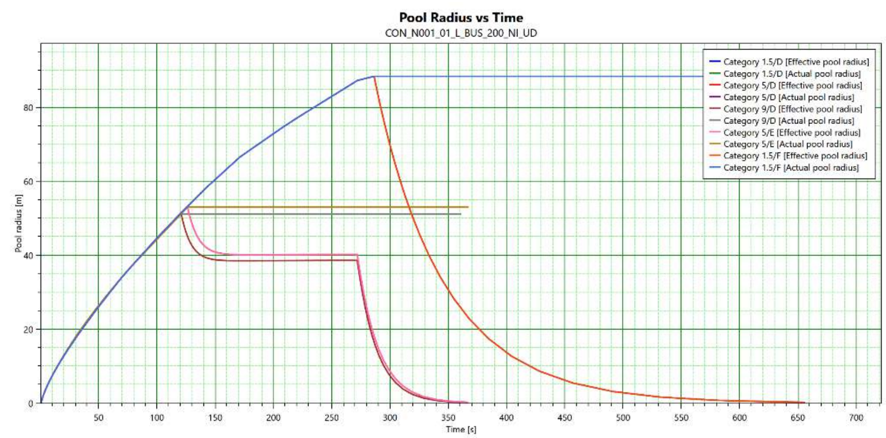
Mass Spilt

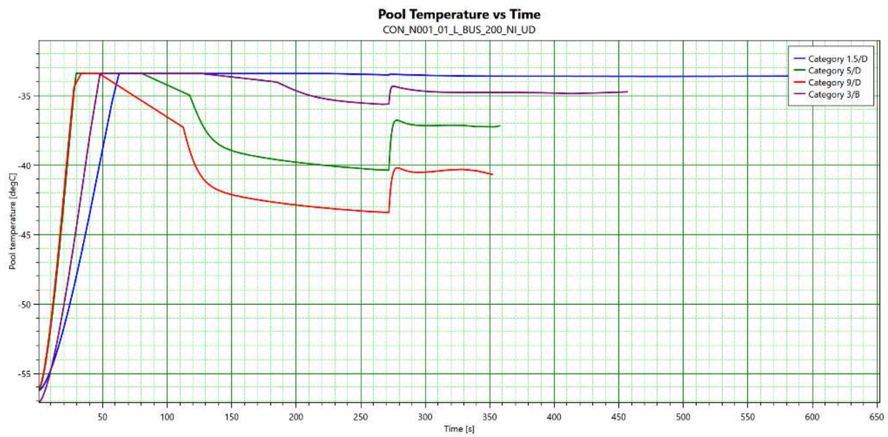
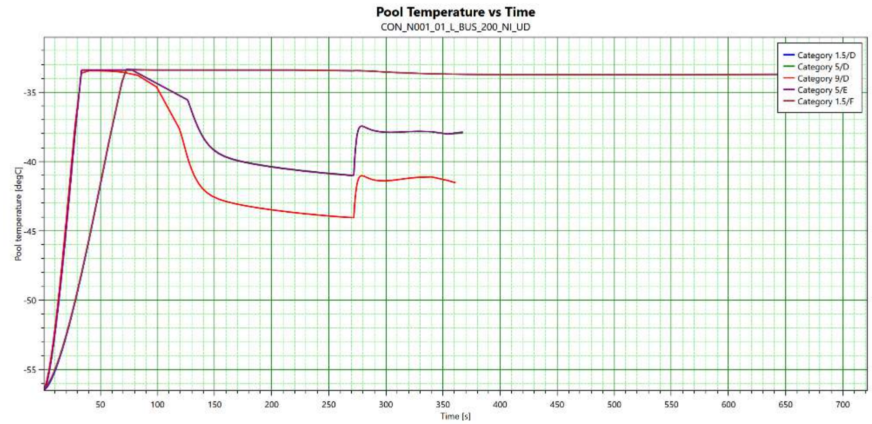
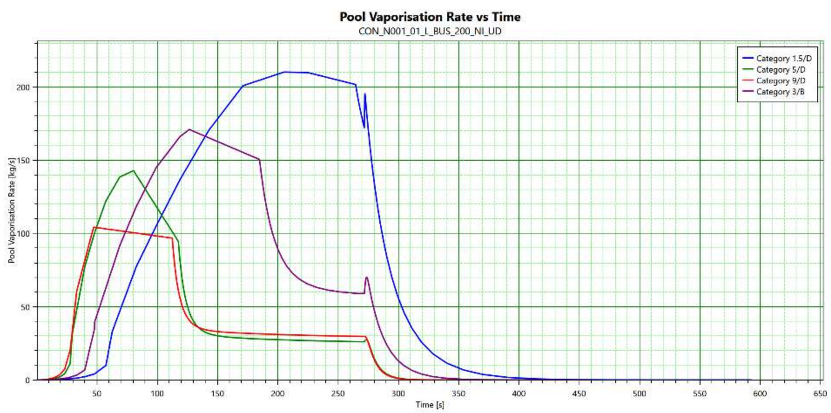
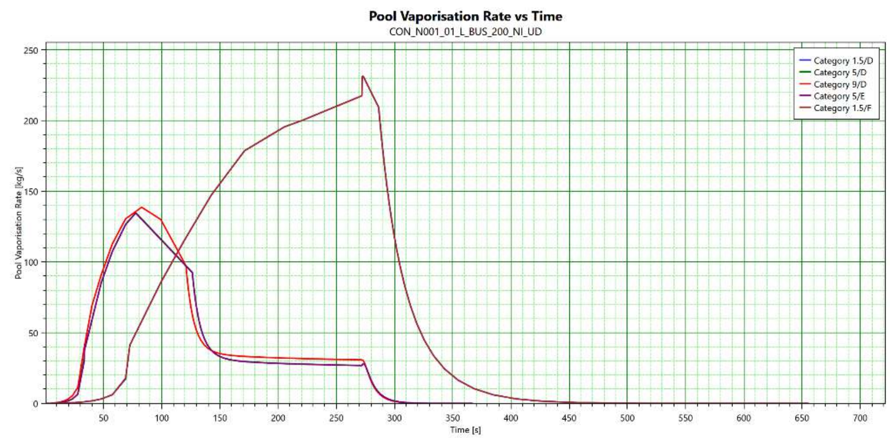


Mass Vaporised





	DAY	NIGHT
Pool Depth		
Pool Radius		

	DAY	NIGHT
Pool Temp		
Pool Vaporisation Rate		

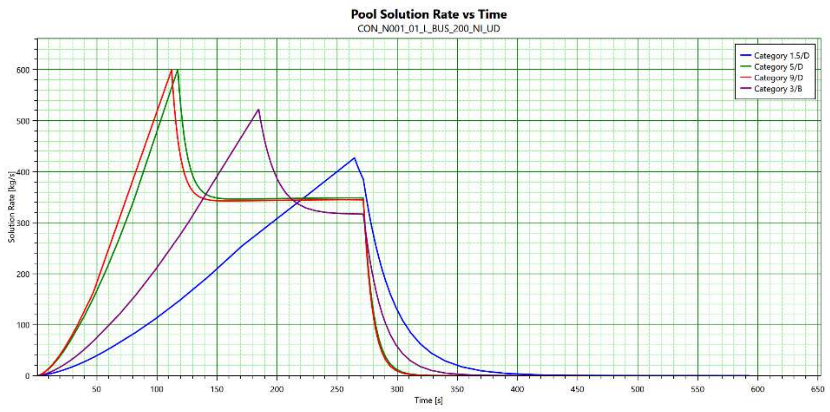
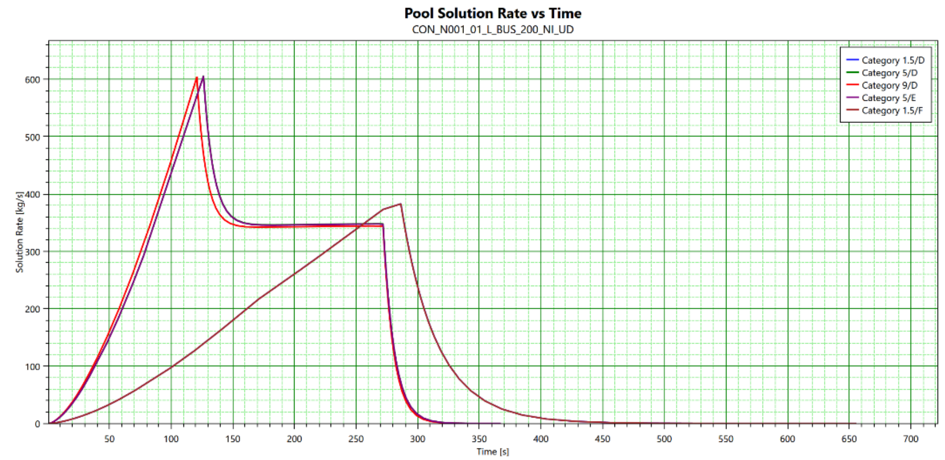
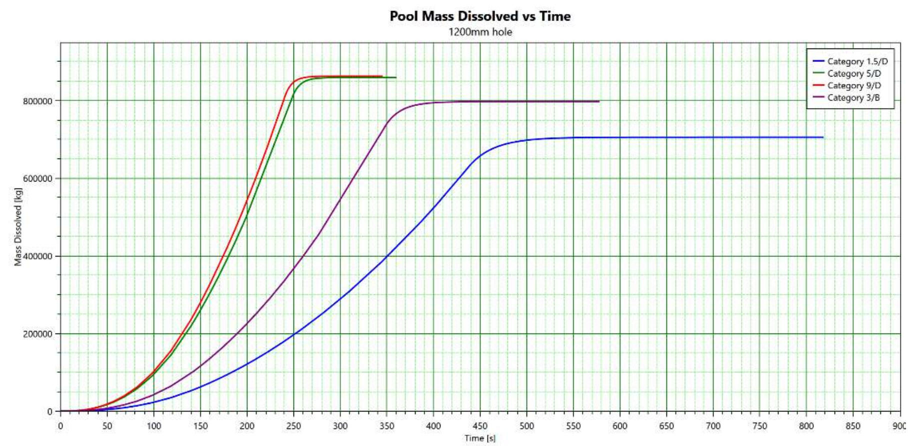
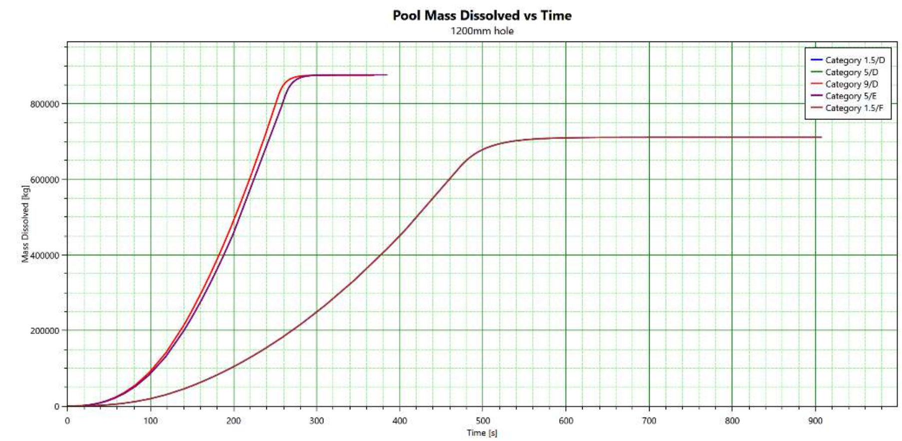
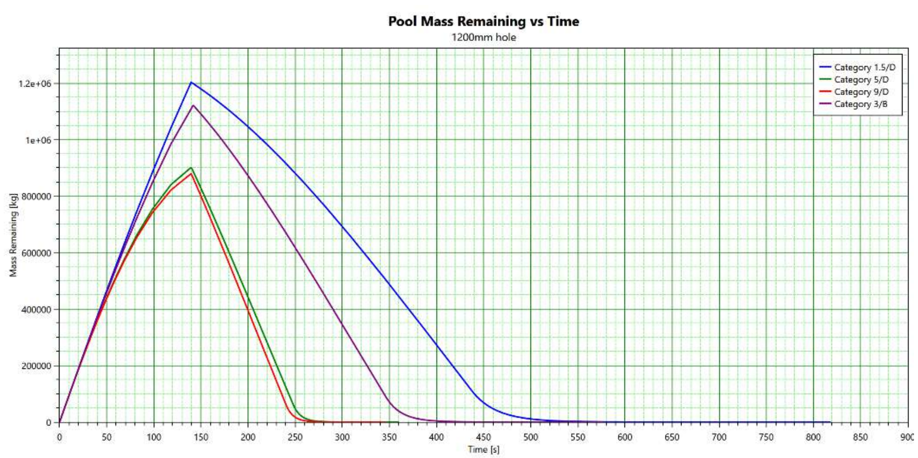
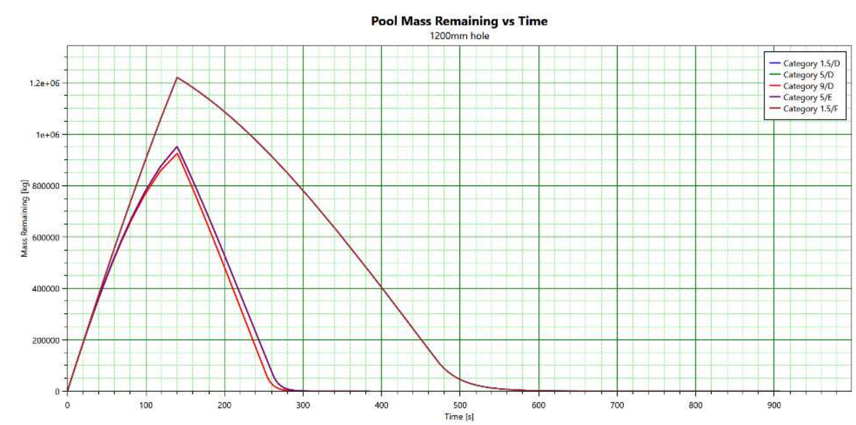
	DAY	NIGHT
Solution Rate		

Table A13 Results for Storage Tank Spill- Containership Collision, 1200mm hole, day/night

	DAY	NIGHT
Pool Mass Dissolved		
Pool Mass Remaining		

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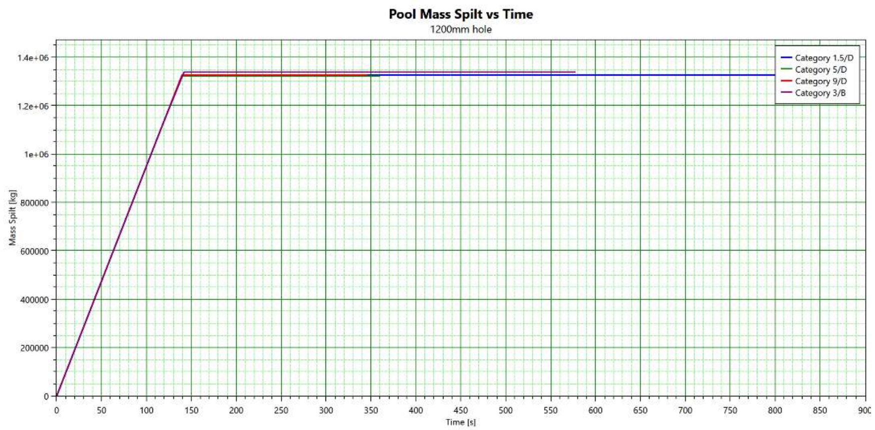
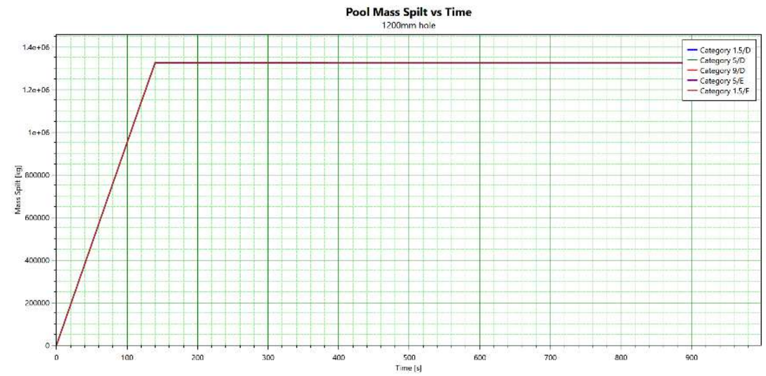
<tr><th></th><th>DAY</th><th>NIGHT</th></tr>
<tr><td>Mass Spilt</td><td>
</td><td>
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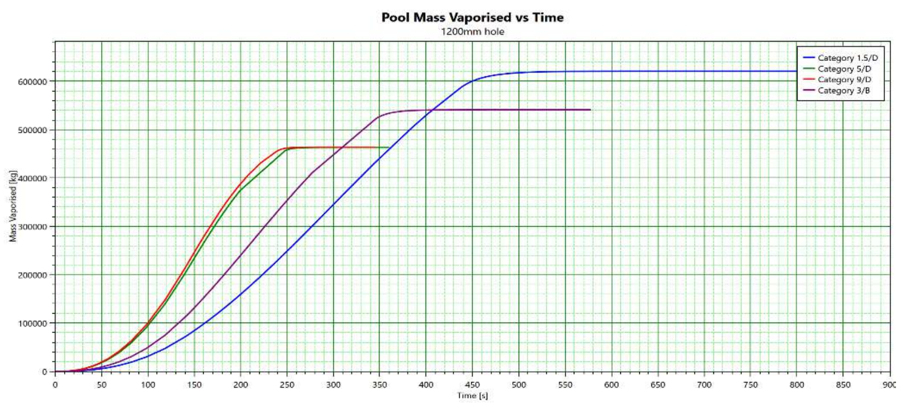
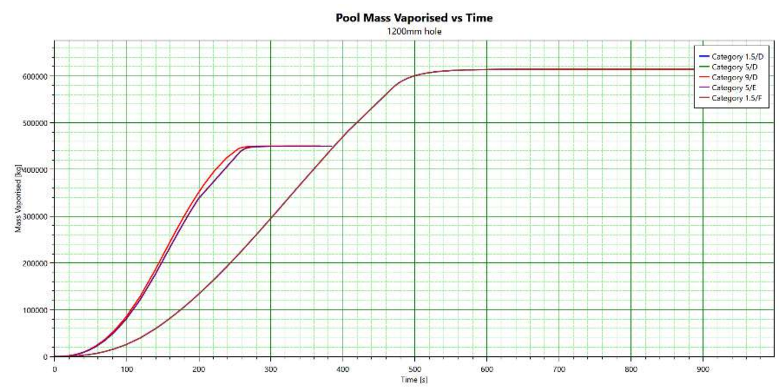
<tr><td>Mass Vaporised</td><td>
</td><td>
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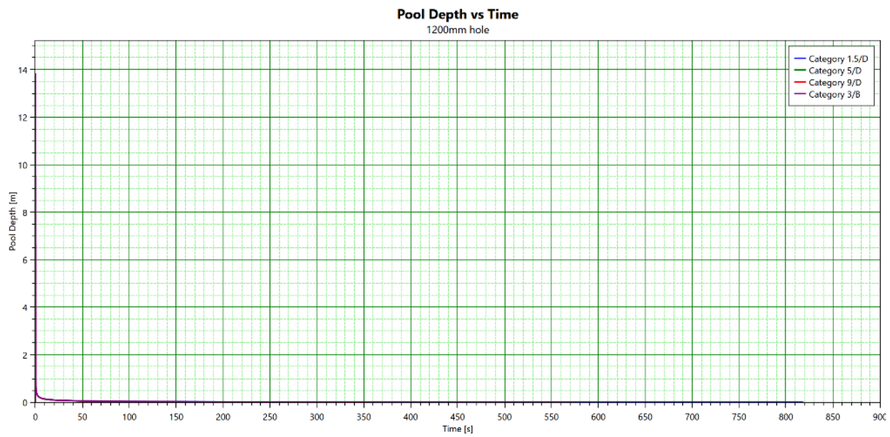
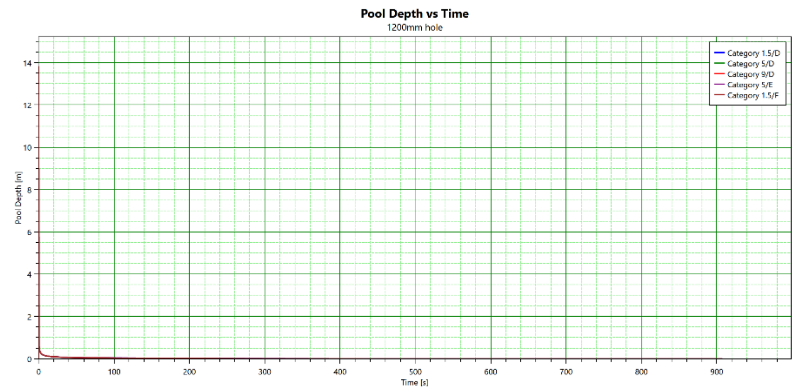
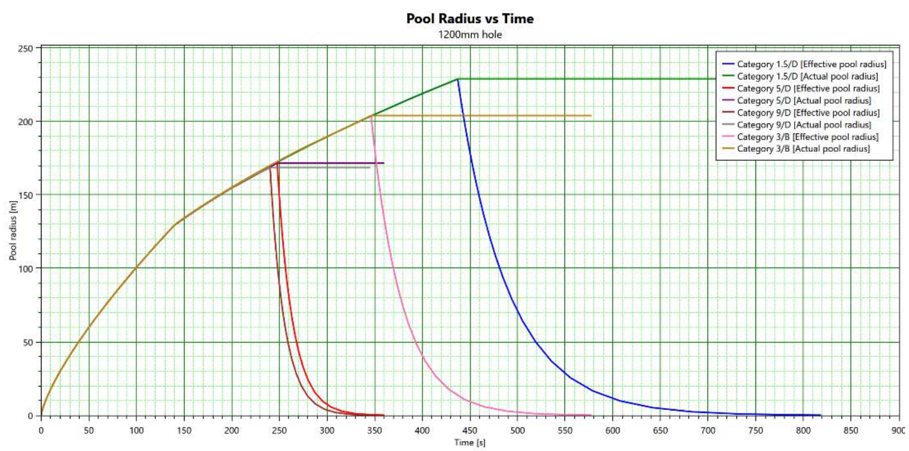
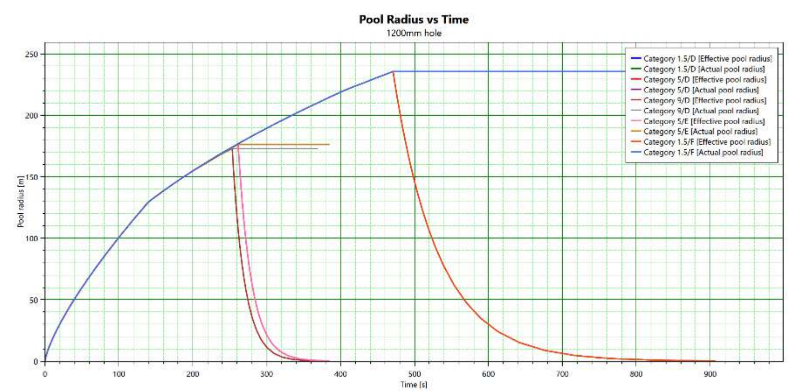
<tr><td>Pool Depth</td><td></td><td></td></tr>
<tr><td>Pool Radius</td><td></td><td></td></tr>
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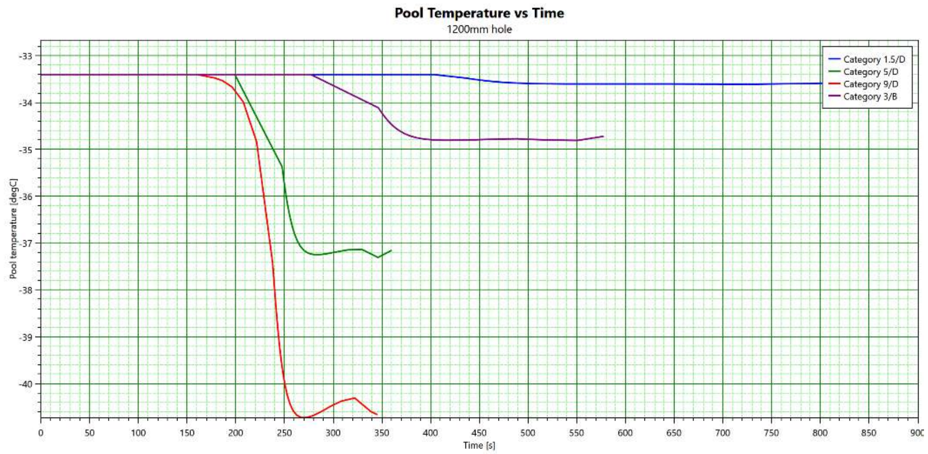
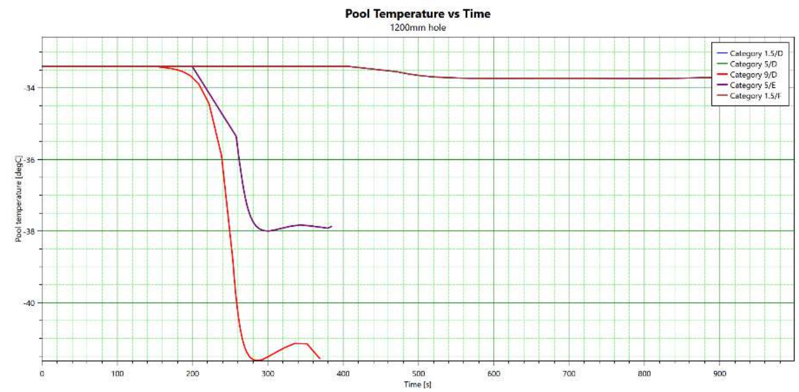
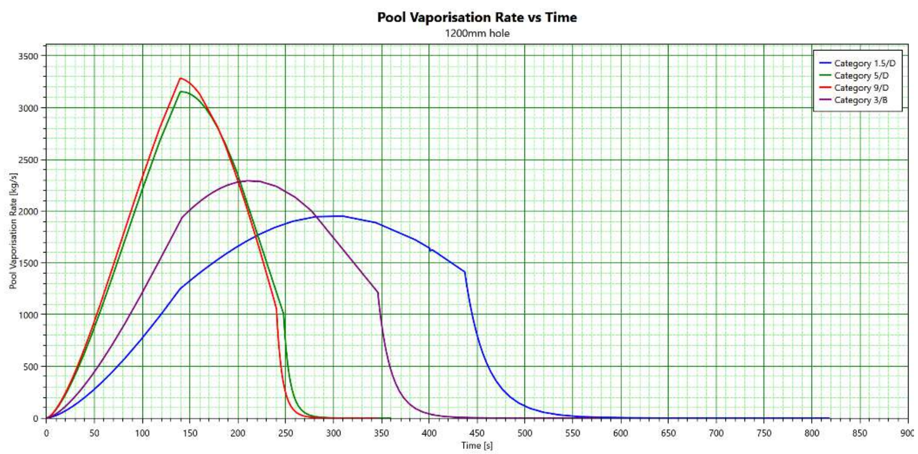
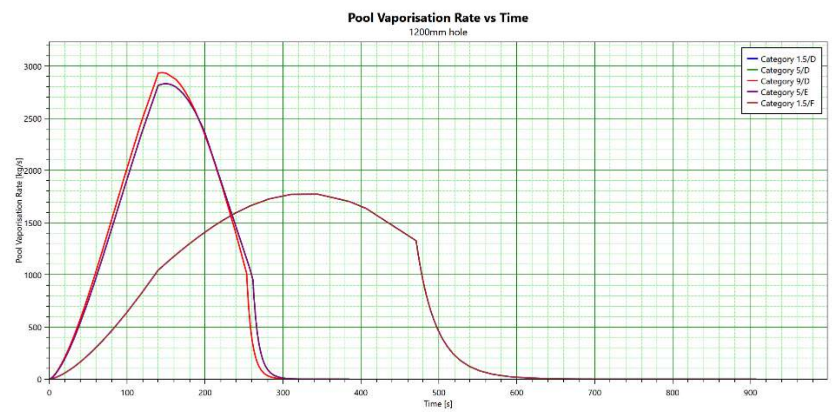
	DAY	NIGHT
Pool Temp		
Pool Vaporisation Rate		

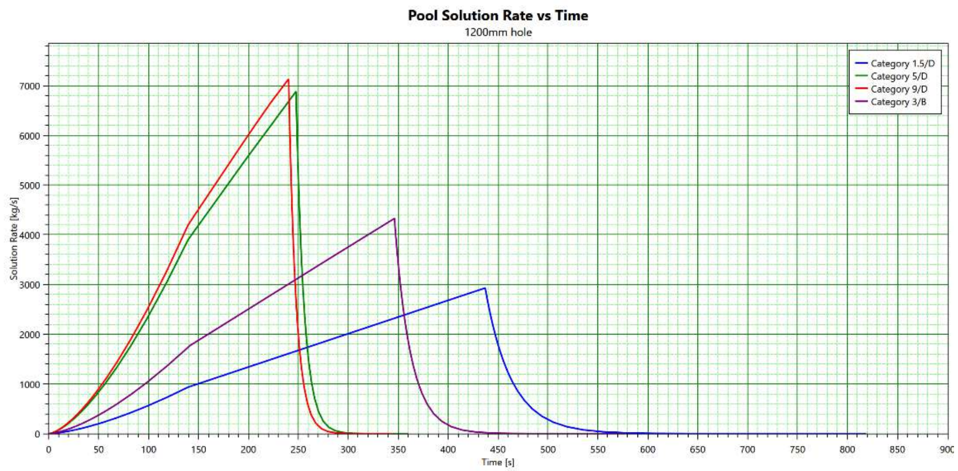
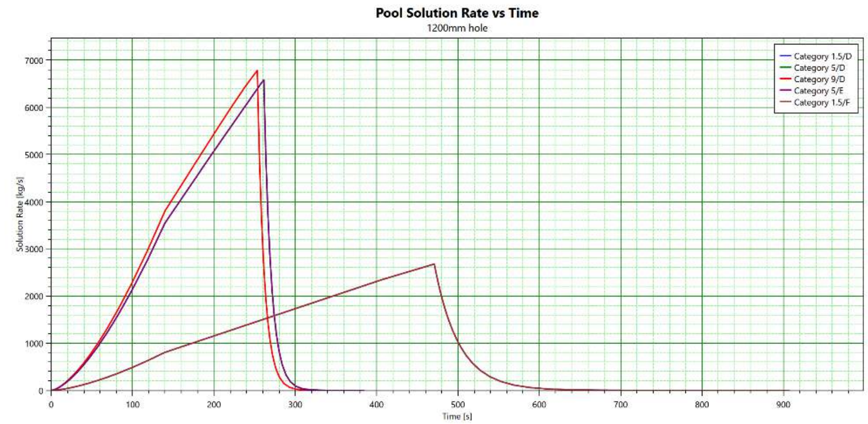
	DAY	NIGHT
Solution Rate		

Table A14 Results for Bunkering Spill, 2mm hole, day/night

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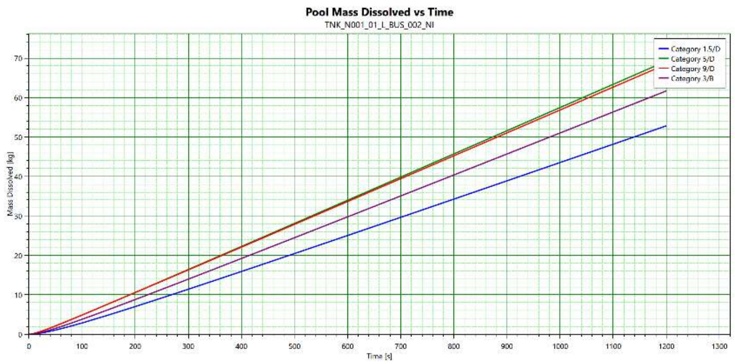
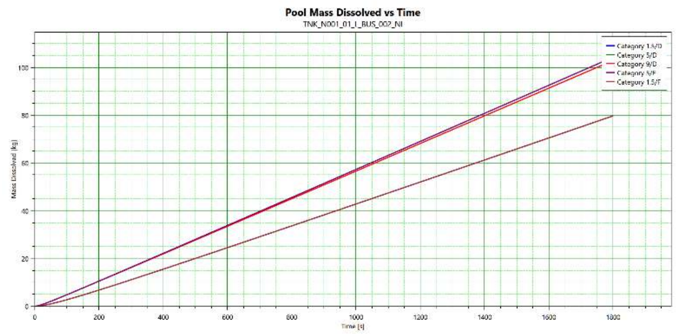
<tr><td>Pool Mass Dissolved</td><td>
</td><td>
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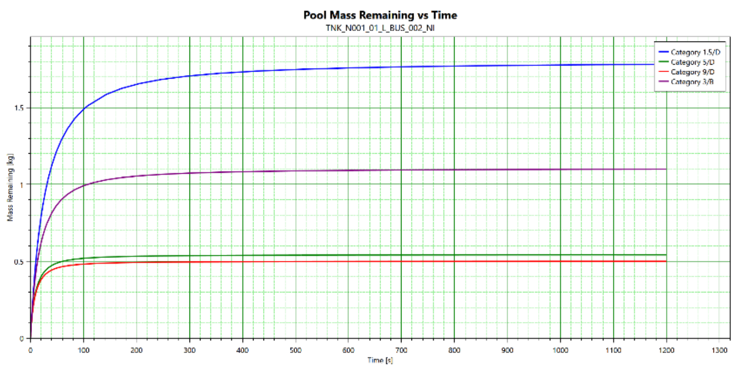
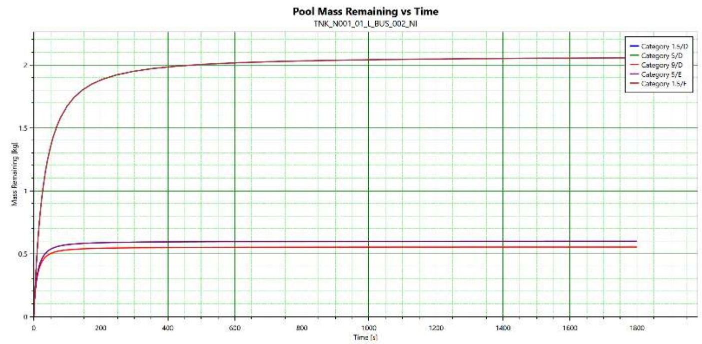
<tr><td>Pool Mass Remaining</td><td>
</td><td>
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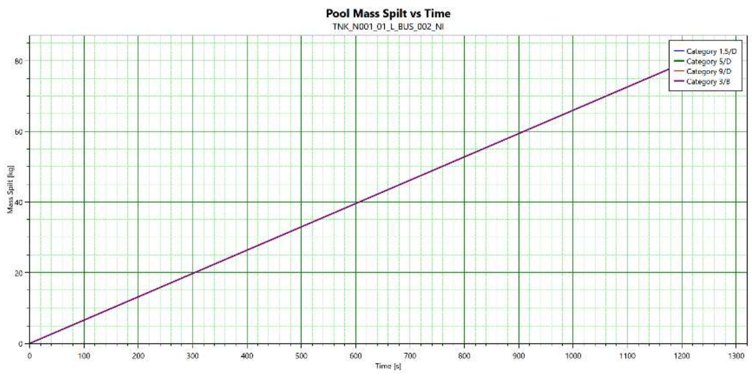
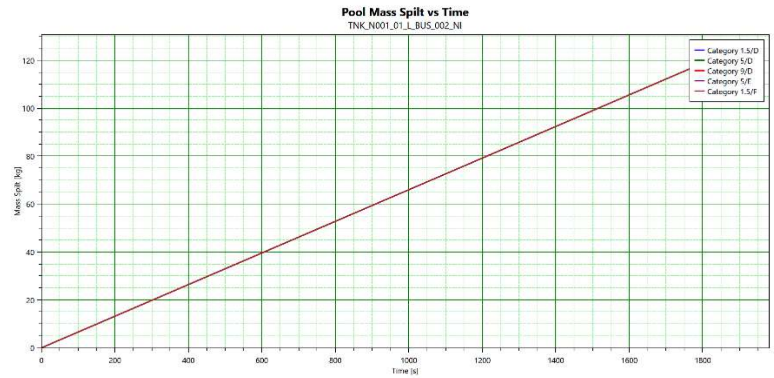
<tr><td>Mass Spilt</td><td>
</td><td>
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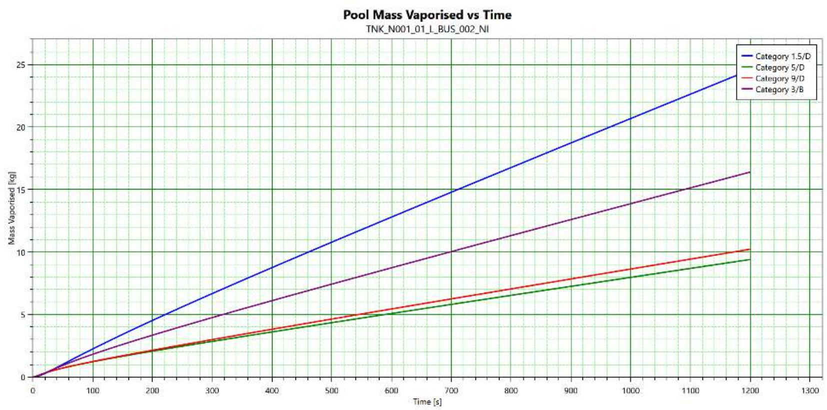
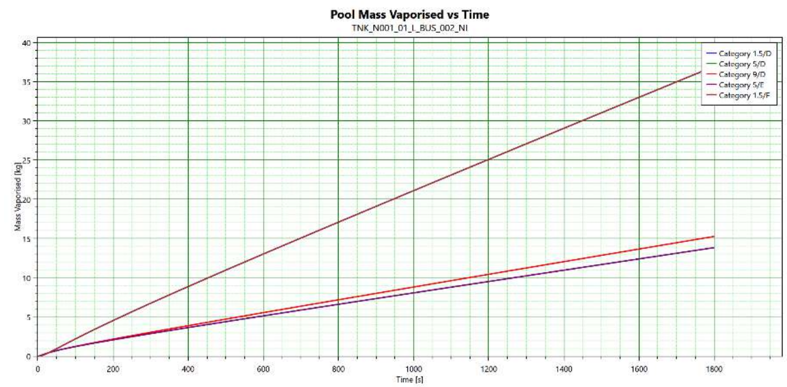
<tr><td>Mass Vaporised</td><td>
</td><td>
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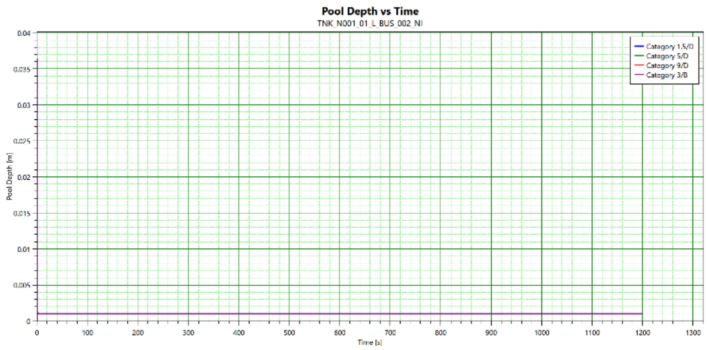
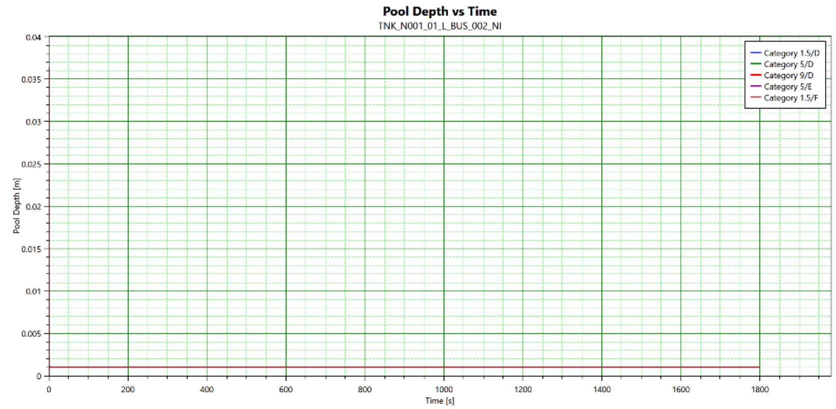
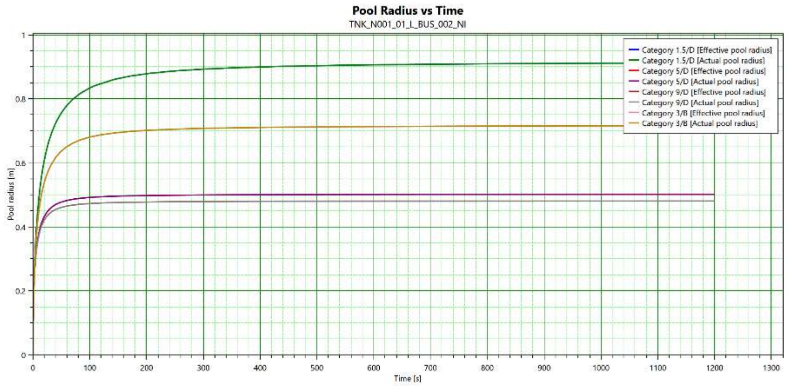
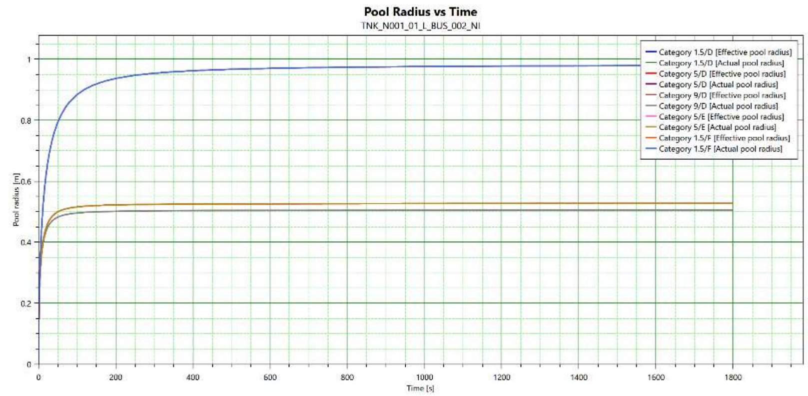
	DAY	NIGHT
Pool Depth		
Pool Radius		

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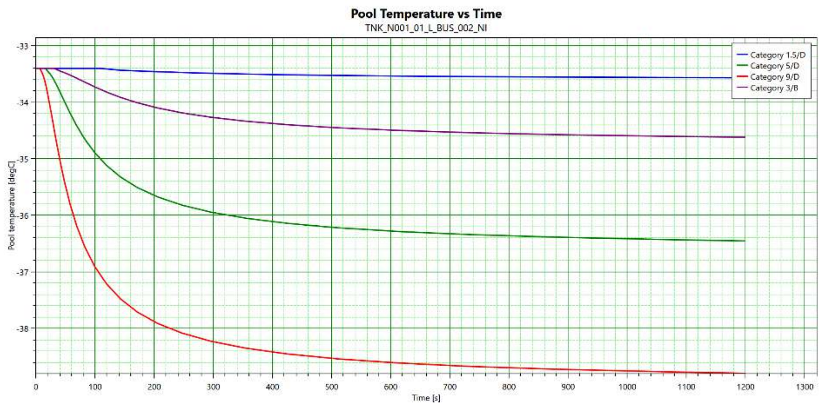
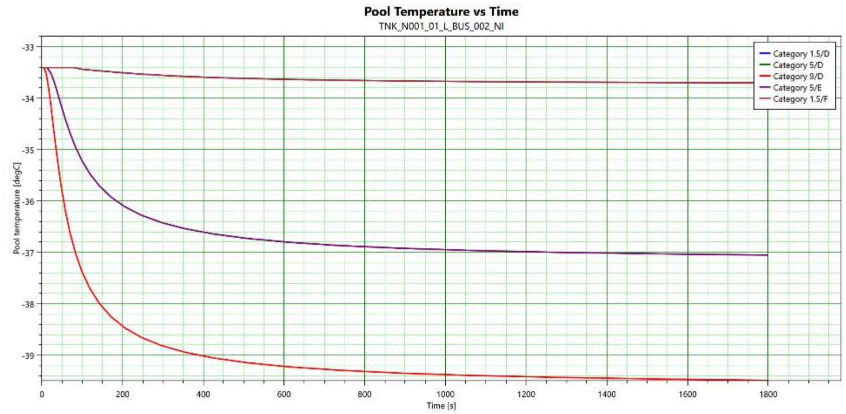
<tr><td>Pool Temp</td><td>
</td><td>
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<tr><td>Pool Vaporisation Rate</td><td>
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<table>
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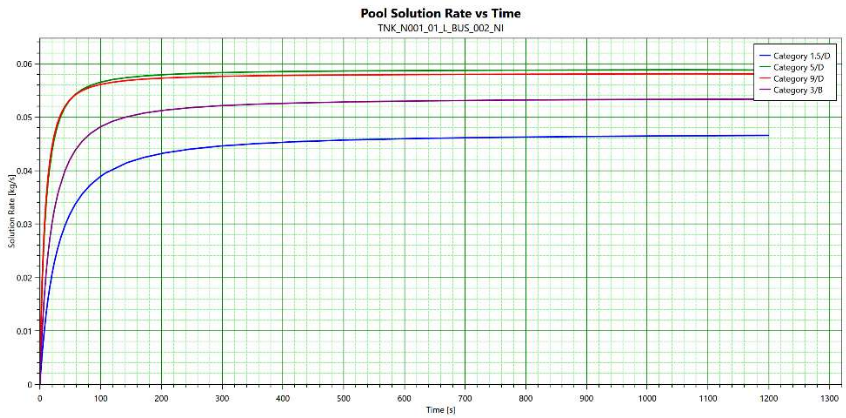
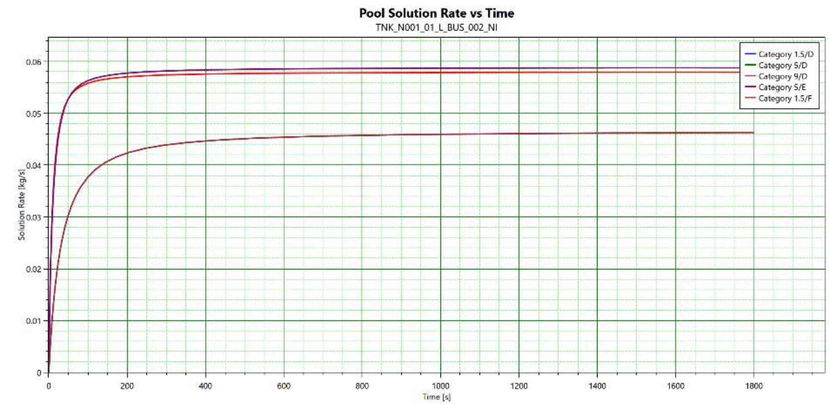
<tr><td>Solution Rate</td><td>
</td><td>
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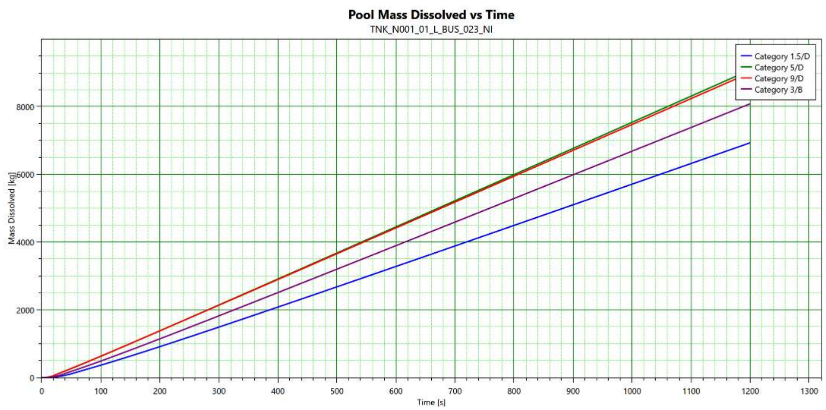
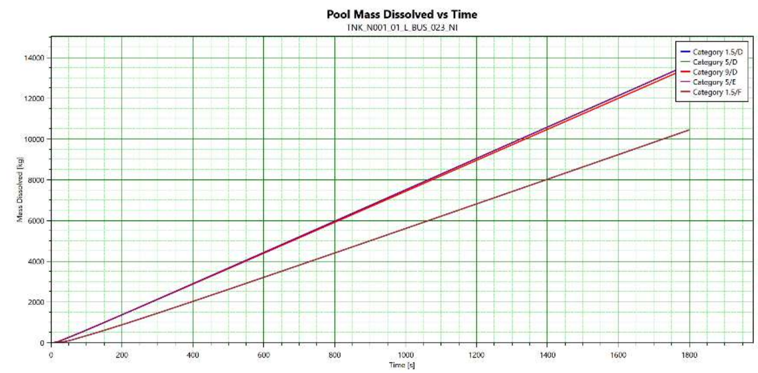
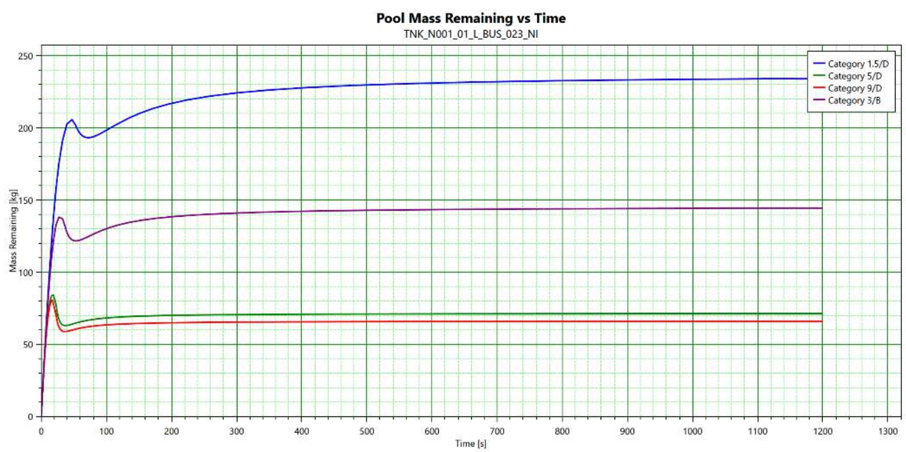
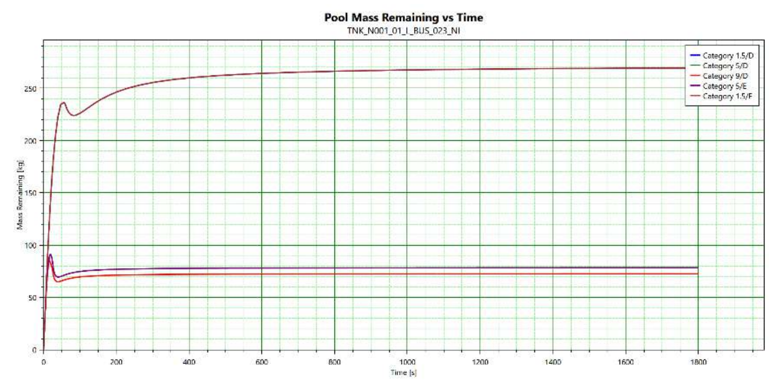
Table A15 Results for Bunkering Spill, 23mm hole, day/night

	DAY	NIGHT
Pool Mass Dissolved		
Pool Mass Remaining		

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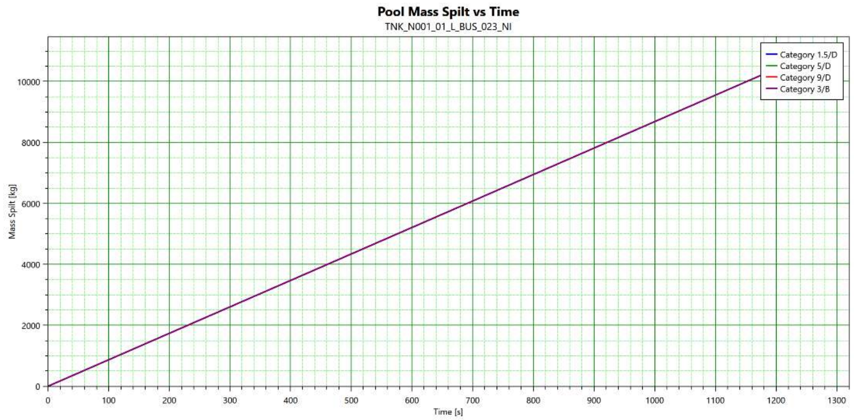
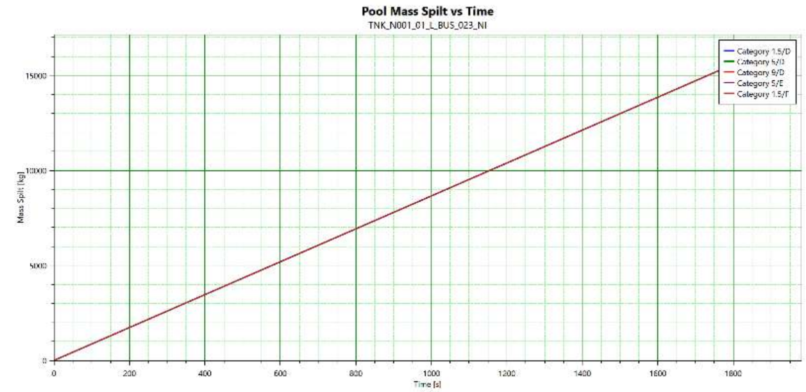
<tr><td>Mass Spilt</td><td>
</td><td>
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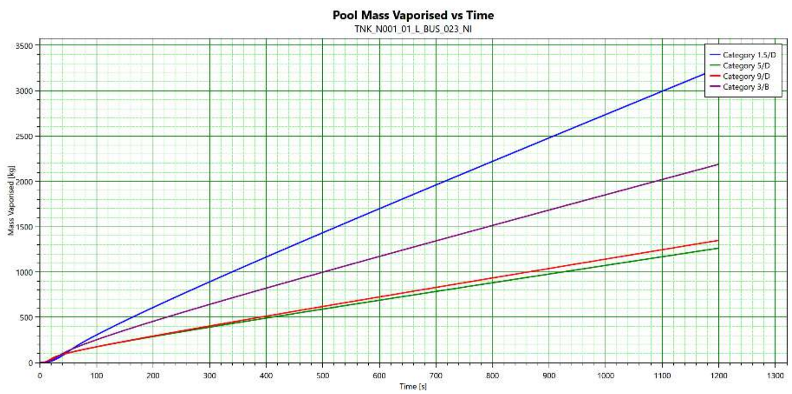
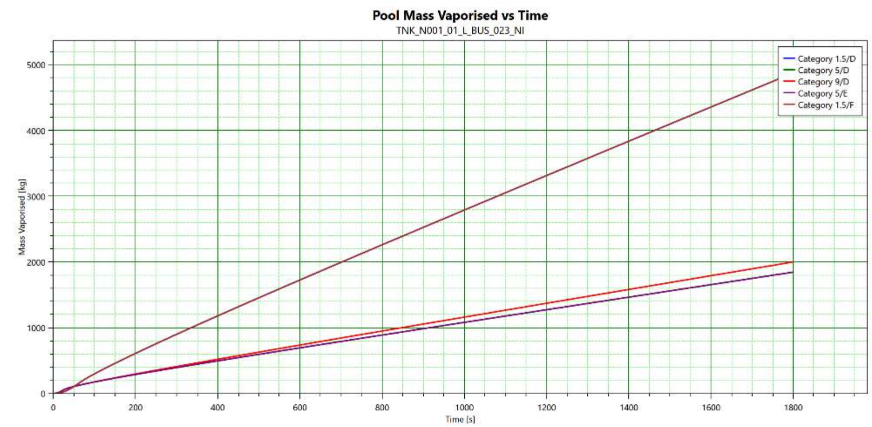
<tr><td>Mass Vaporised</td><td>
</td><td>
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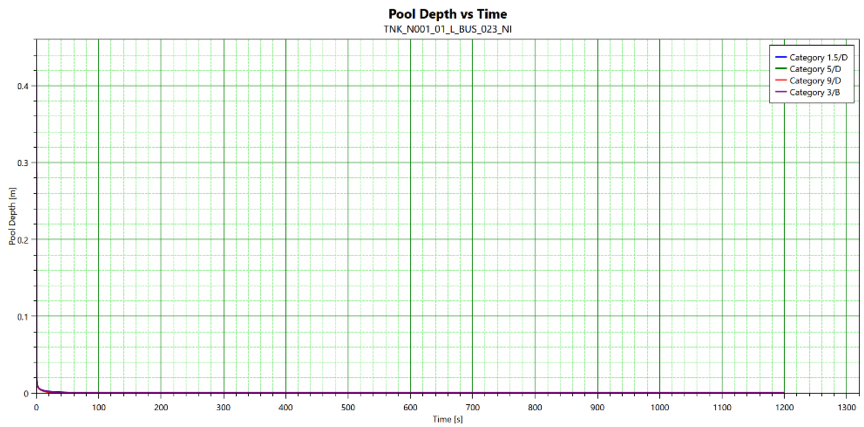
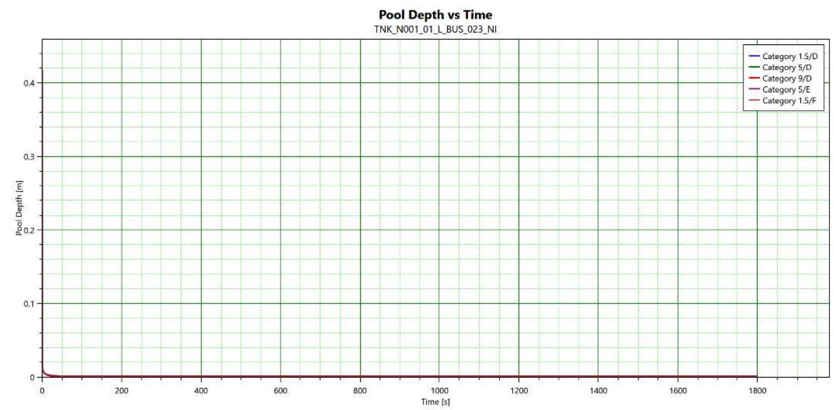
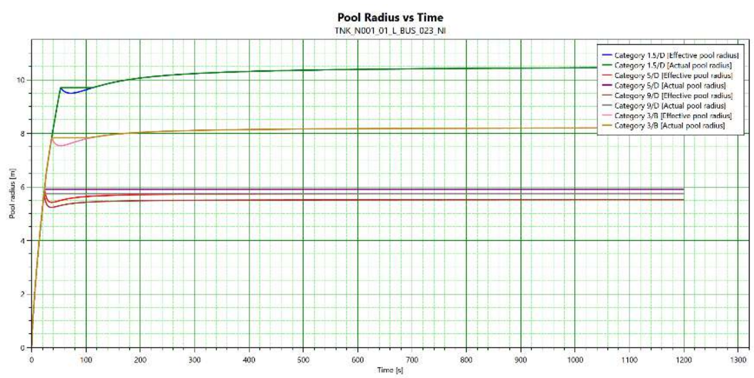
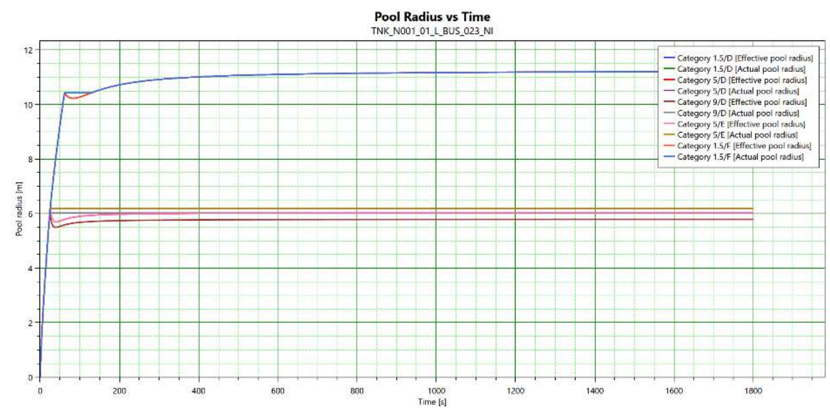
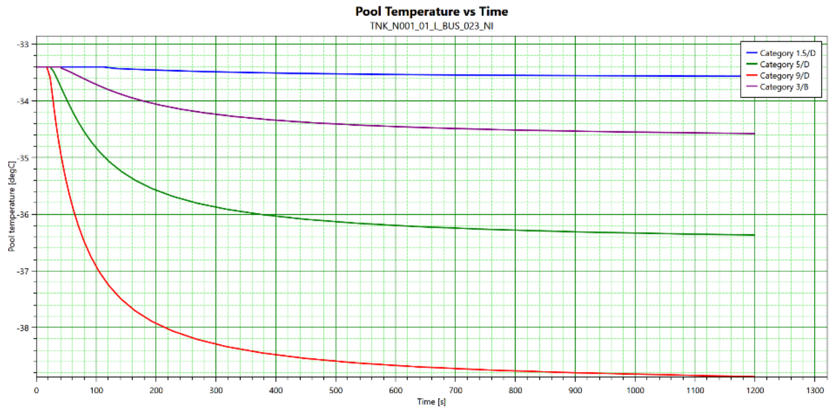
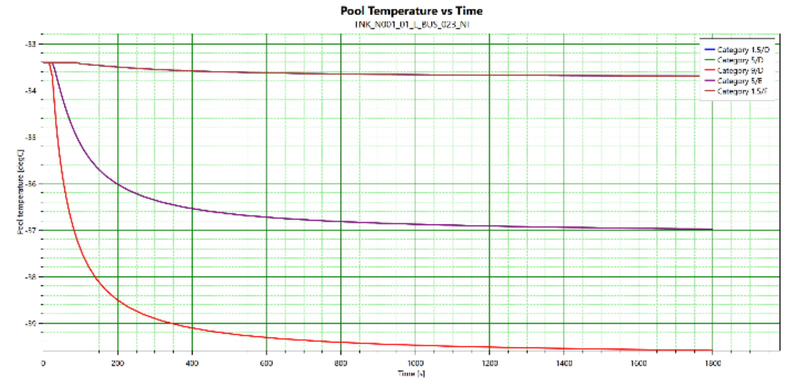
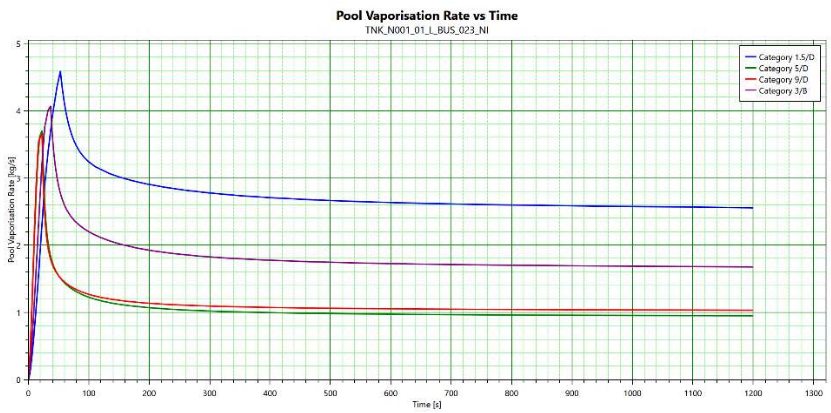
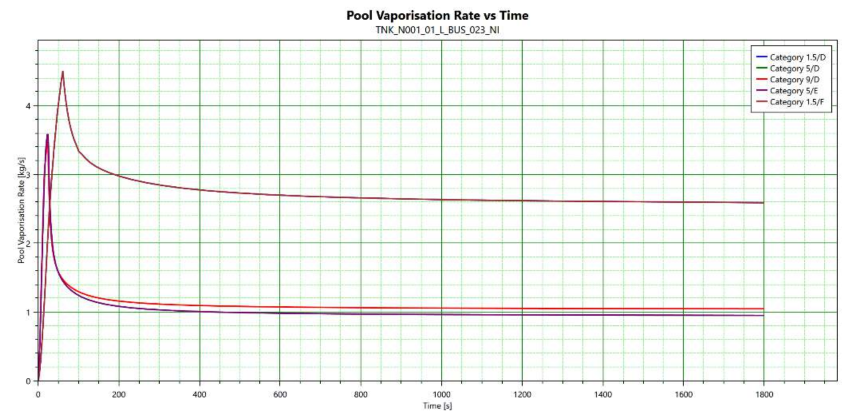
	DAY	NIGHT
Pool Depth		
Pool Radius		

	DAY	NIGHT
Pool Temp		
Pool Vaporisation Rate		

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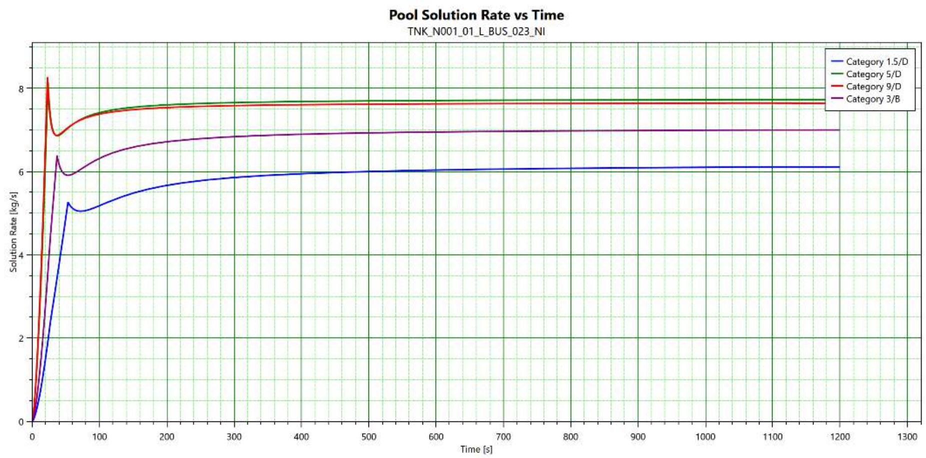
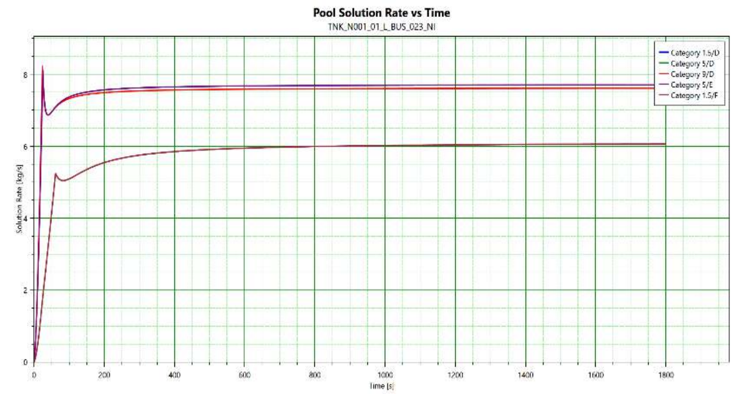
<tr><td>Solution Rate</td><td>
</td><td>
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Table A16 Results for Bunkering Spill, 200mm hole, day/night

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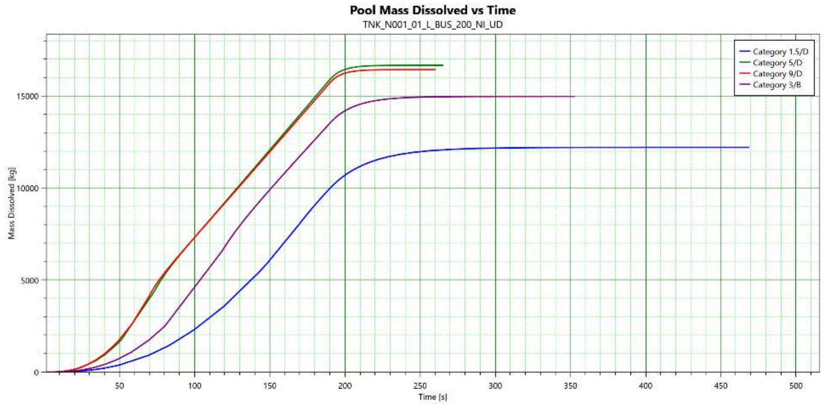
<tr><td>Pool Mass Dissolved</td><td>
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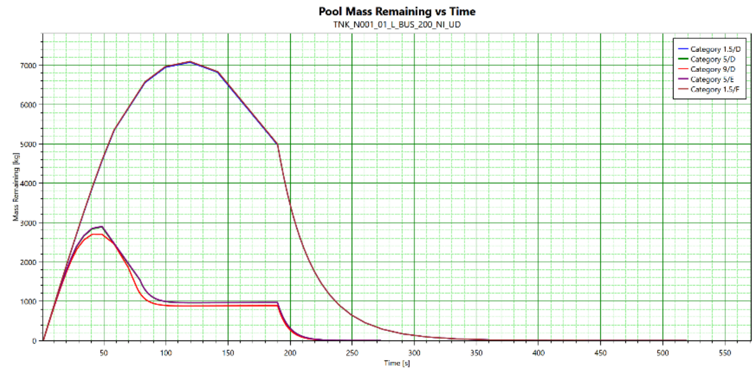
</td><td>
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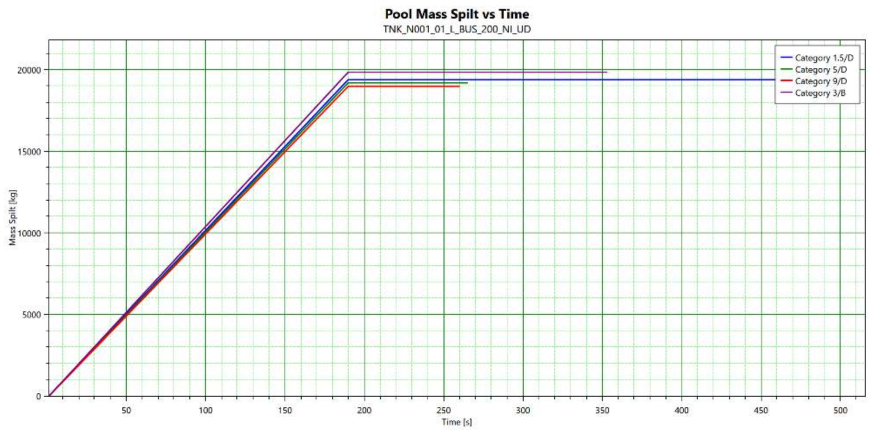
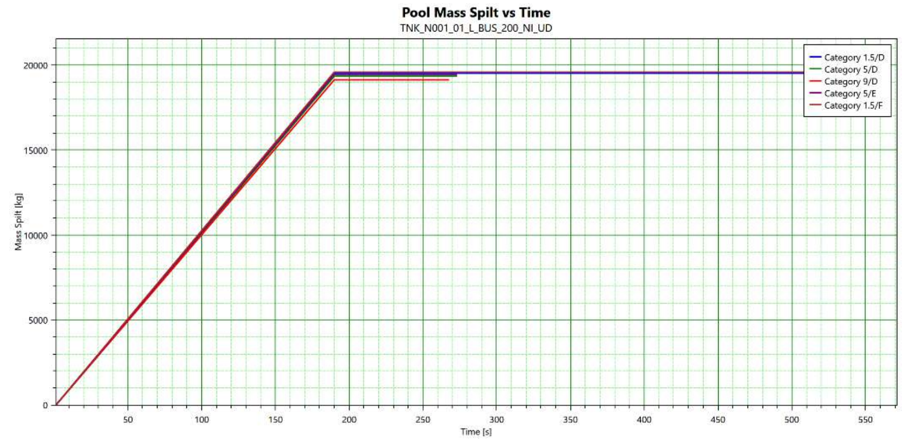
<tr><td>Mass Spilt</td><td>
</td><td>
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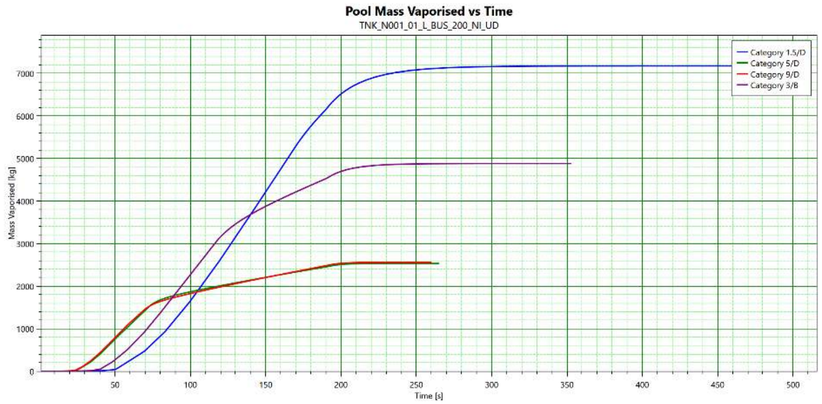
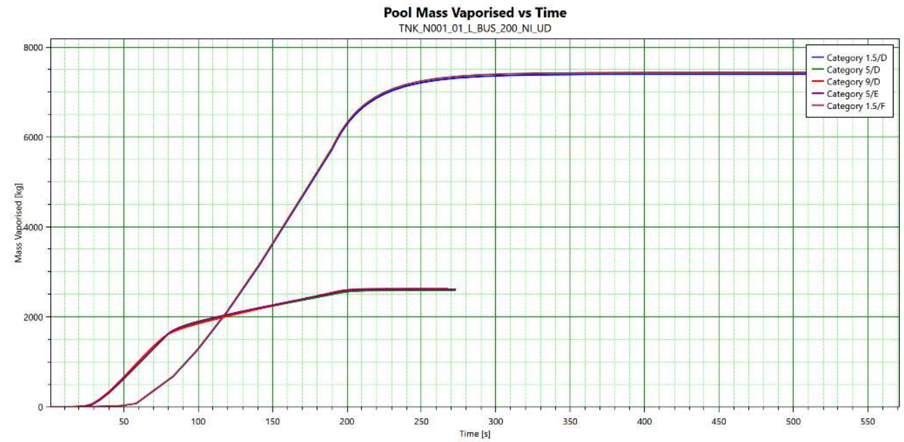
<tr><td>Mass Vaporised</td><td>
</td><td>
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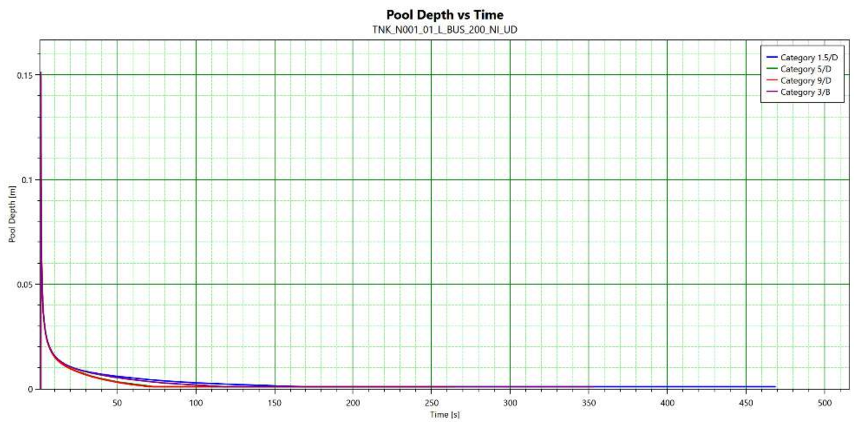
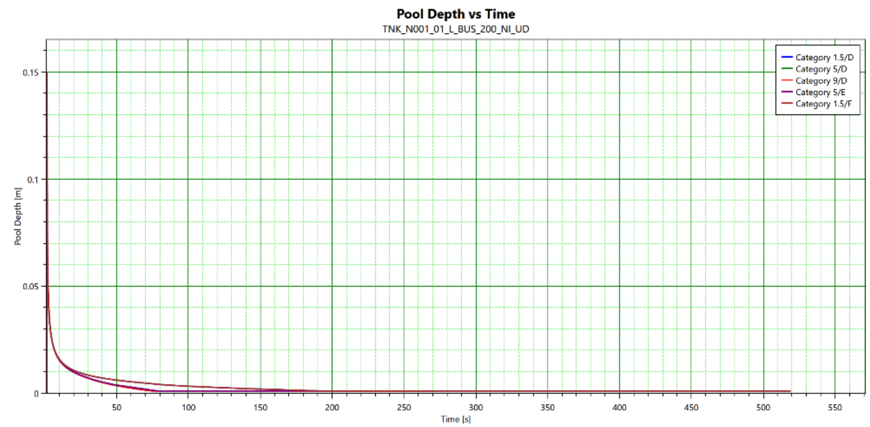
	DAY	NIGHT

Pool Depth

DAY

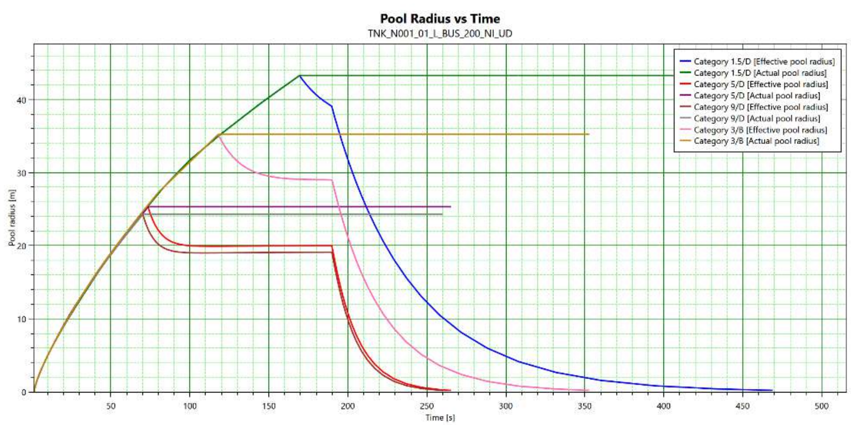


NIGHT

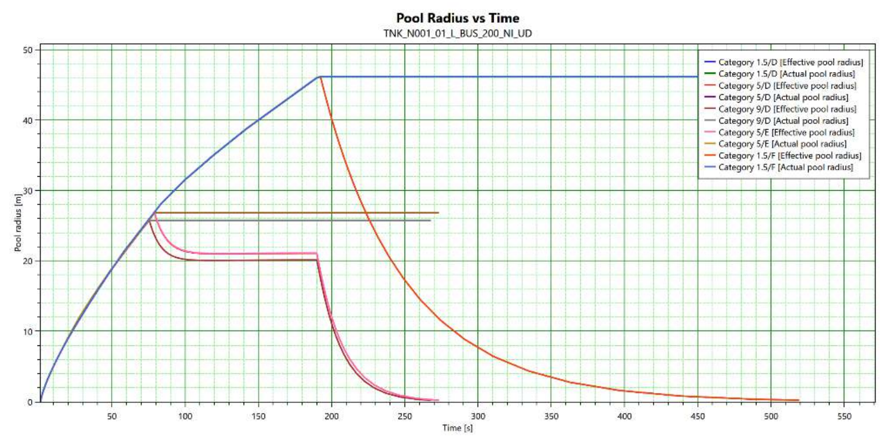


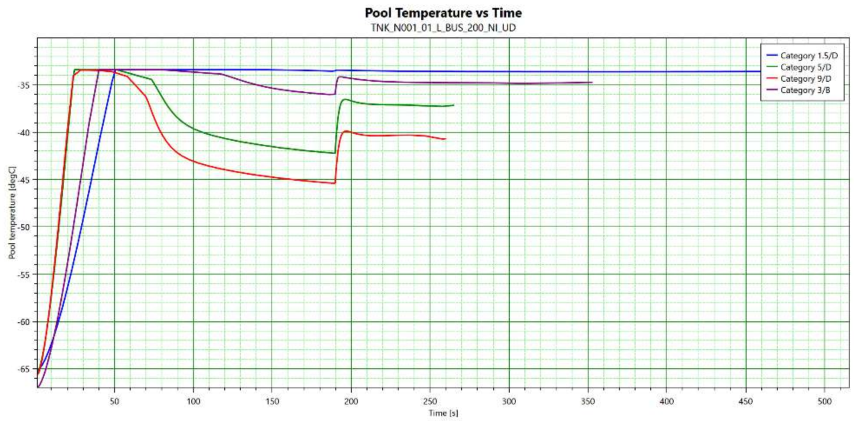
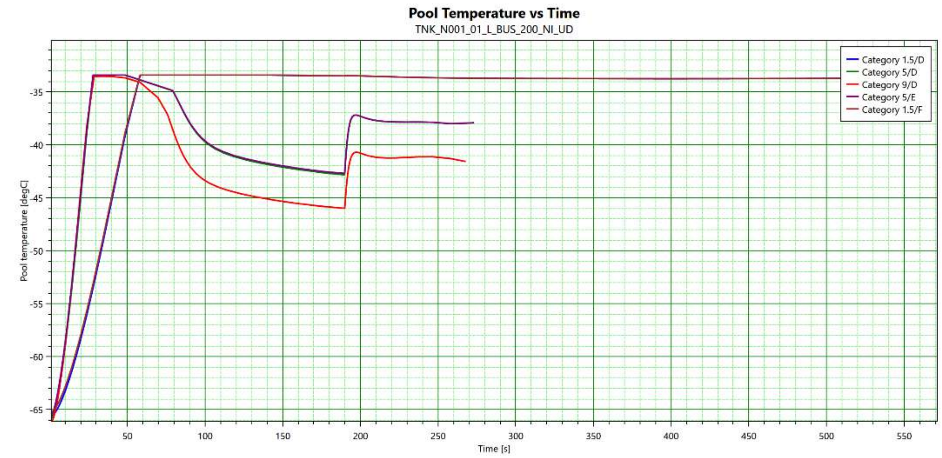
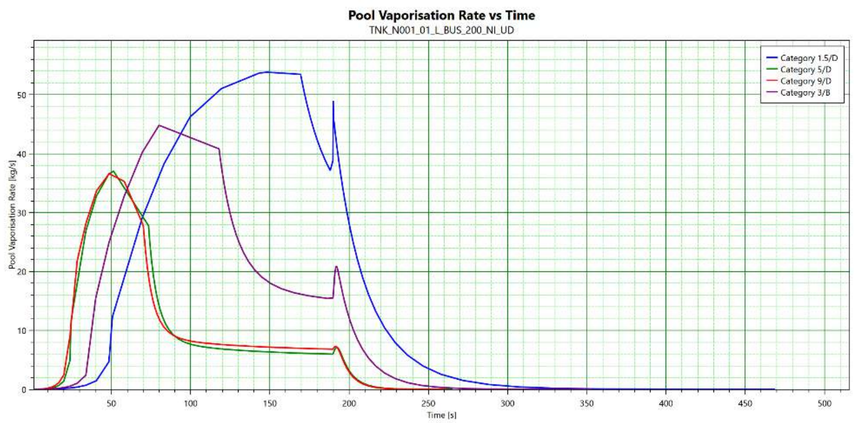
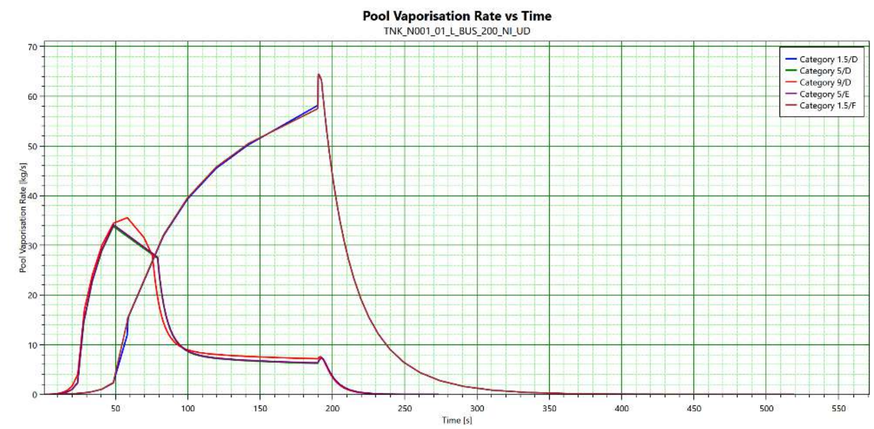
Pool Radius

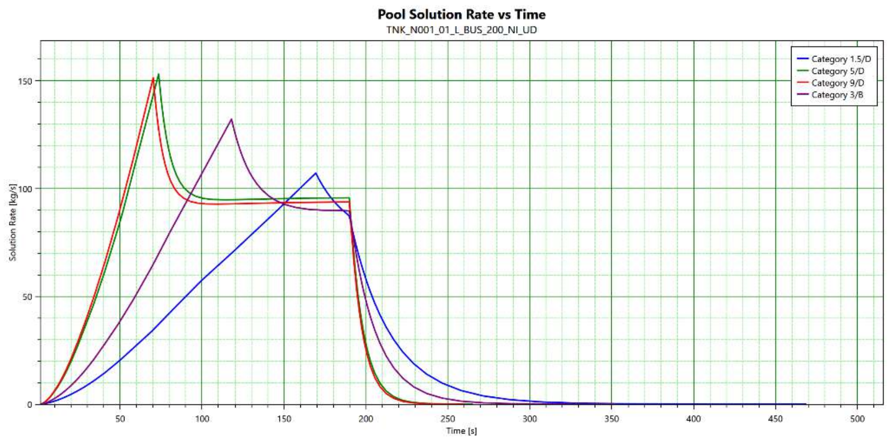
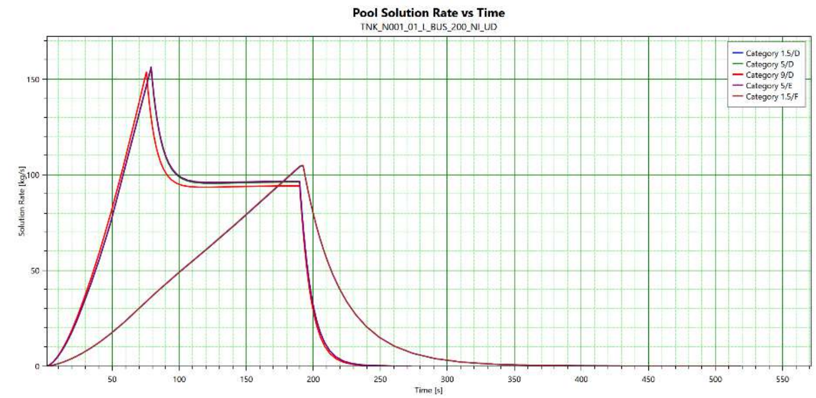
DAY



NIGHT



	DAY	NIGHT
Pool Temp		
Pool Vaporisation Rate		

	DAY	NIGHT
Solution Rate		

7.4. Appendix 4

PHAST Modelling for ammonia Summary

This section presents a high-level summary of the PHAST modelling results shown above in Appendix 3. The presentation shows the graphical outputs for each scenario ranked (according to the scale below) lowest to highest in terms of the greatest value displayed by the parameter. Note that the scaling does not take into account whether is 'highest' or 'lowest' values are a relative positive or a negative for that determinand and further that the greatest value refers to the greatest value achieved over the time modelled and is not necessarily a start or end value.

Scale

	(green)	Lowest
	(yellow)	
	(amber)	
	(orange)	Applicable to night scenarios
	(red)	Highest
	(blue)	All scenarios equal
	x	Weather condition not assessed under this scenario

Weather Conditions	Model output	Scenario																			
		Day										Night									
		Tanker			Bulker			Containership				Tanker			Bulker			Containership			
		2 mm	23 mm	200 mm	2 mm	23 mm	200 mm	2 mm	23 mm	200 mm	1200 mm	2 mm	23 mm	200 mm	2 mm	23 mm	200 mm	2 mm	23 mm	200 mm	1200 mm
1.5D	Mass spilt																				
5D	Mass spilt																				
9D	Mass spilt																				
3B	Mass spilt											x	x	x	x	x	x	x	x	x	x
5E	Mass spilt	x	x	x	x	x	x	x	x	x	x										
1.5F	Mass spilt	x	x	x	x	x	x	x	x	x	x										
1.5D	Pool depth																				
5D	Pool depth																				
9D	Pool depth																				
3B	Pool depth											x	x	x	x	x	x	x	x	x	x
5E	Pool depth	x	x	x	x	x	x	x	x	x	x										
1.5F	Pool depth	x	x	x	x	x	x	x	x	x	x										
1.5D	Pool radius																				
5D	Pool radius																				
9D	Pool radius																				
3B	Pool radius											x	x	x	x	x	x	x	x	x	x
5E	Pool radius	x	x	x	x	x	x	x	x	x	x										
1.5F	Pool radius	x	x	x	x	x	x	x	x	x	x										
1.5D	Pool temperature																				
5D	Pool temperature																				
9D	Pool temperature																				
3B	Pool temperature											x	x	x	x	x	x	x	x	x	x
5E	Pool temperature	x	x	x	x	x	x	x	x	x	x										
1.5F	Pool temperature	x	x	x	x	x	x	x	x	x	x										
1.5D	Solution rate																				
5D	Solution rate																				
9D	Solution rate																				

Weather Conditions	Model output	Scenario																			
		Day										Night									
		Tanker			Bulker			Containership				Tanker			Bulker			Containership			
		2 mm	23 mm	200 mm	2 mm	23 mm	200 mm	2 mm	23 mm	200 mm	1200 mm	2 mm	23 mm	200 mm	2 mm	23 mm	200 mm	2 mm	23 mm	200 mm	1200 mm
3B												x	x	x	x	x	x	x	x	x	x
5E		x	x	x	x	x	x	x	x	x	x										
1.5F		x	x	x	x	x	x	x	x	x	x										
1.5D	Mass dissolved																				
5D																					
9D																					
3B												x	x	x	x	x	x	x	x	x	x
5E		x	x	x	x	x	x	x	x	x	x										
1.5F		x	x	x	x	x	x	x	x	x	x										
1.5D	Pool vaporisation rate																				
5D																					
9D																					
3B												x	x	x	x	x	x	x	x	x	x
5E		x	x	x	x	x	x	x	x	x	x										
1.5F		x	x	x	x	x	x	x	x	x	x										
1.5D	Mass vaporised																				
5D																					
9D																					
3B												x	x	x	x	x	x	x	x	x	x
5E		x	x	x	x	x	x	x	x	x	x										
1.5F		x	x	x	x	x	x	x	x	x	x										
1.5D	Mass remaining																				
5D																					
9D																					
3B												x	x	x	x	x	x	x	x	x	x
5E		x	x	x	x	x	x	x	x	x	x										
1.5F		X	x	x	x	x	x	x	x	x	x										

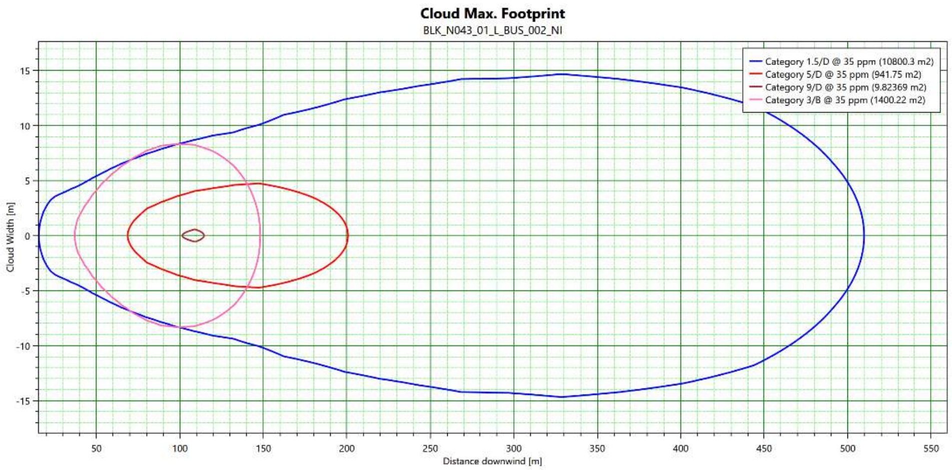
7.5. Appendix 5

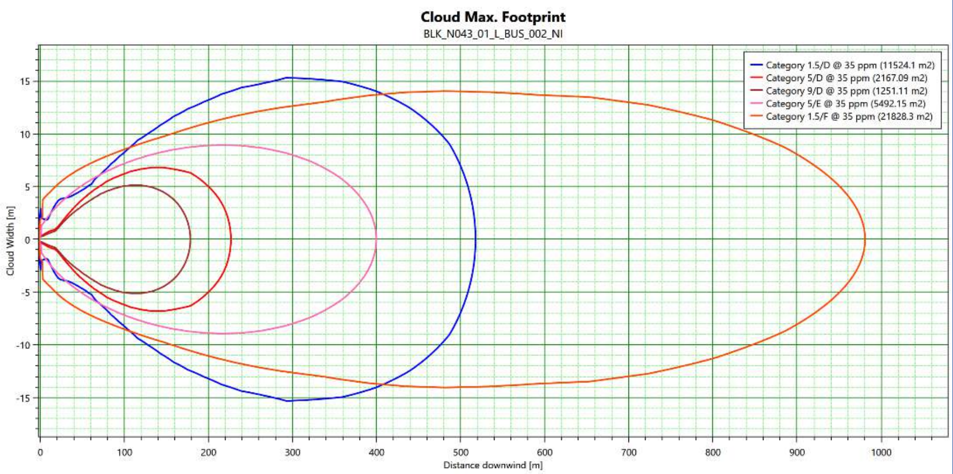
Air Dispersion Modelling

This section presents and describes the results of the gas cloud modelling. The results are presented by spillage scenario (ship type), hole size and by a receptor height. The contours show the area exceeding

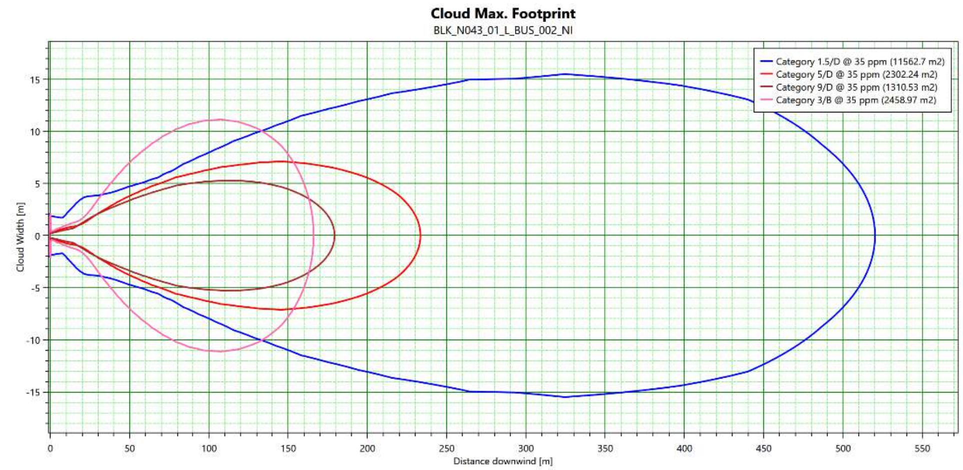
Table A17 Results for Bulker, 2mm hole – Comparison with the Short-Term Exposure Limit

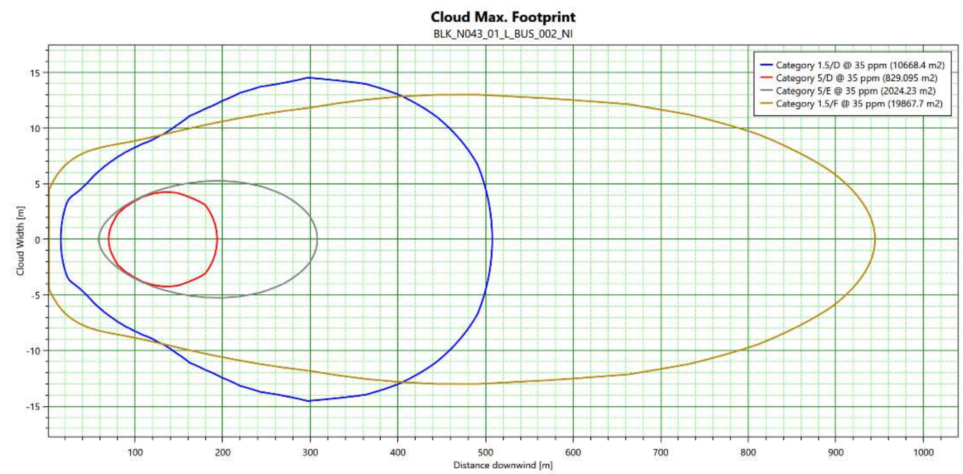
Height 0m



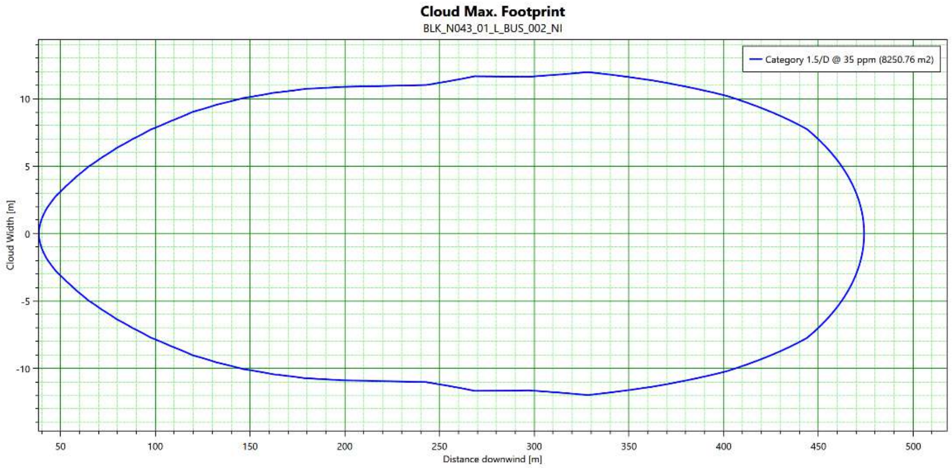


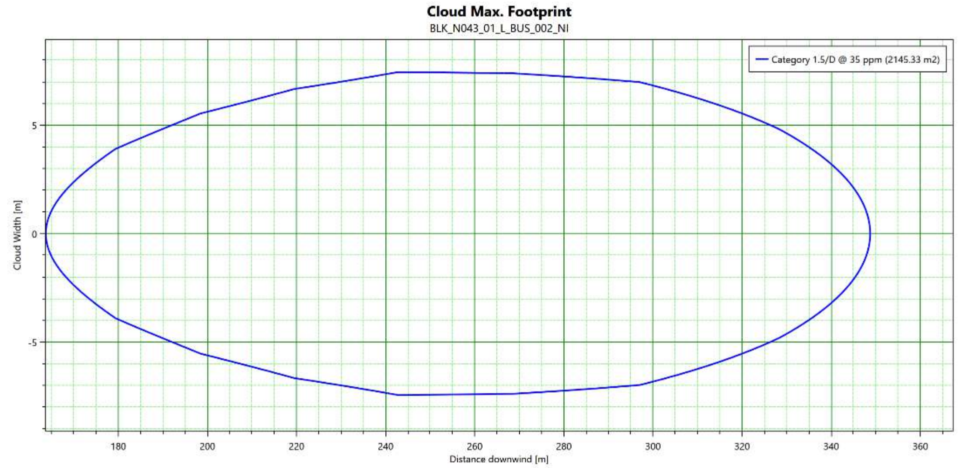
Height 5m

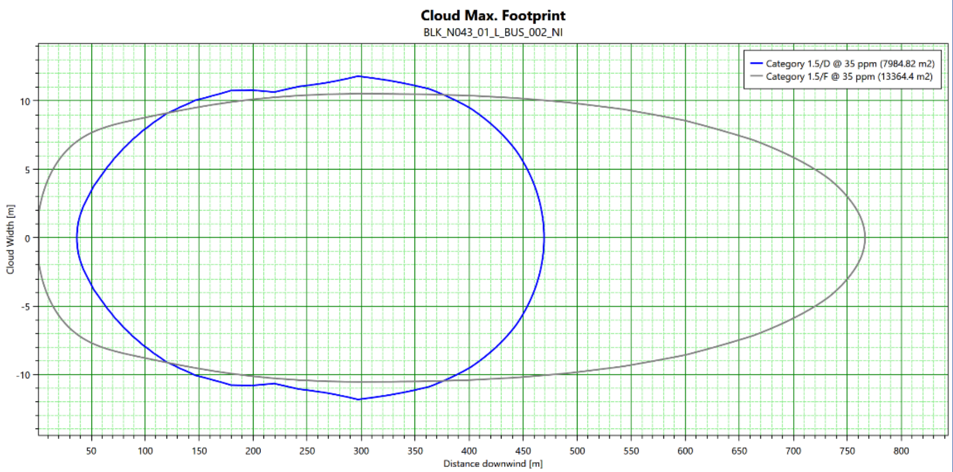


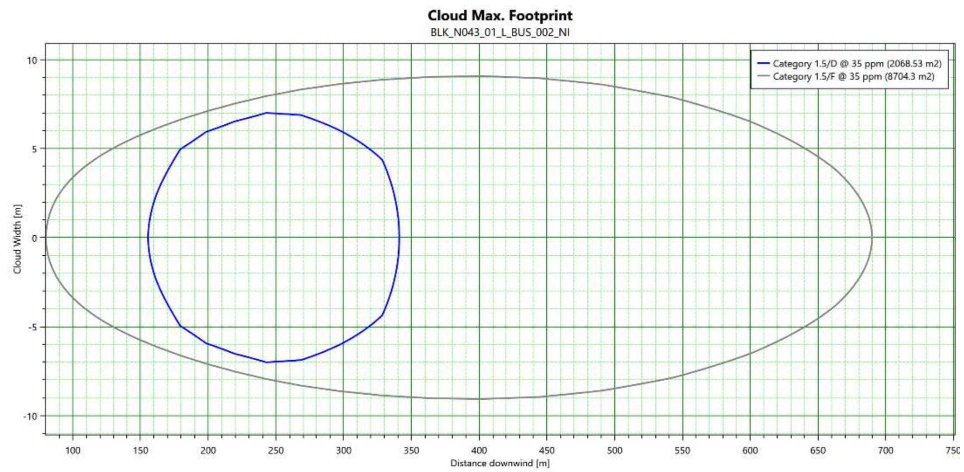


Height 0m	**Height 5m**
Height 10m	Height 20m







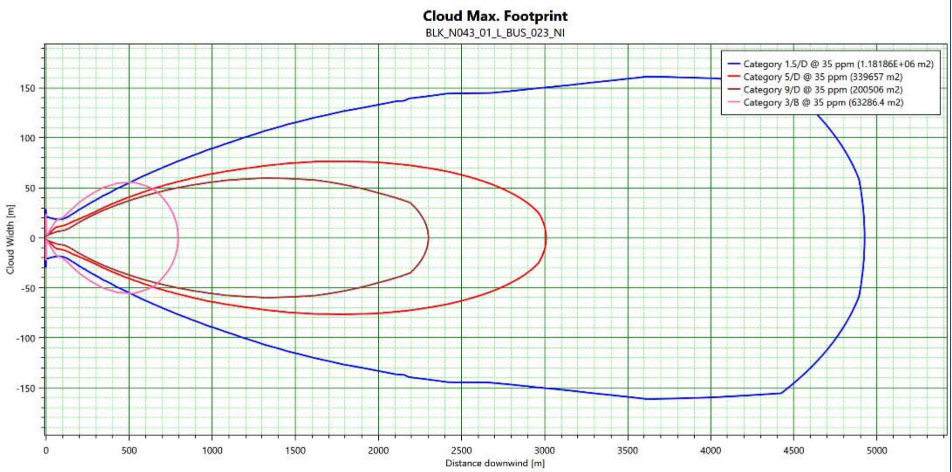


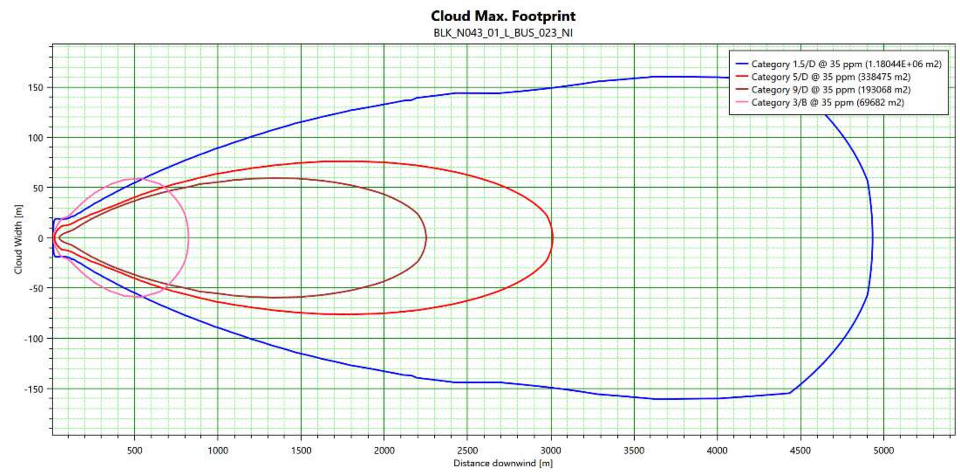
Height 25m	Height 180m
No daytime exceedances	No daytime exceedances

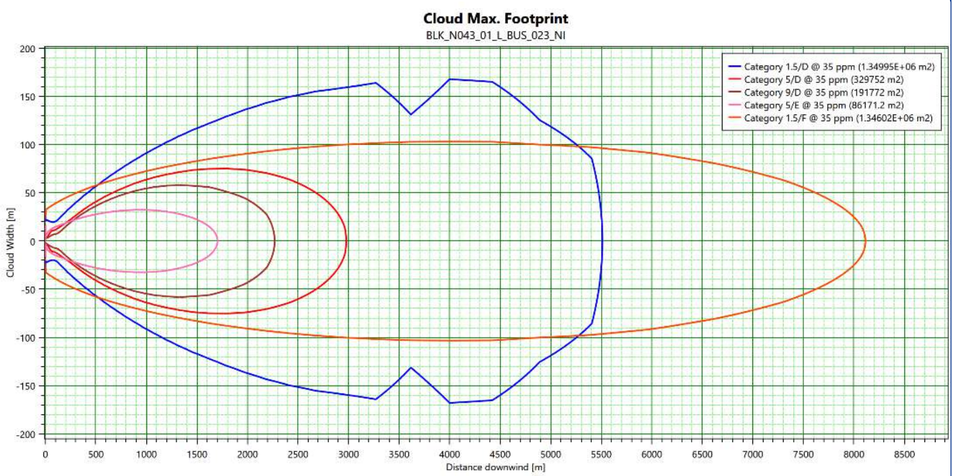
Height 0m	Height 5m
No night-time exceedances	No night-time exceedances

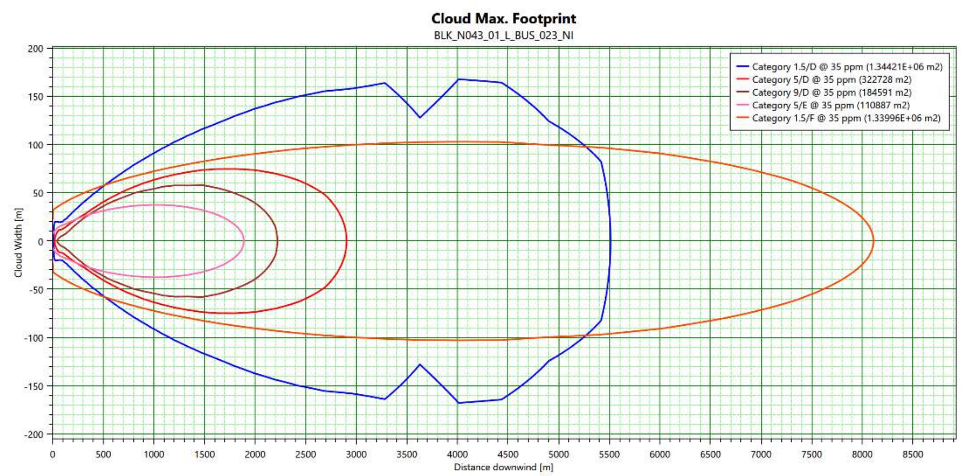
Table A18 Results for Bulker, 23mm hole – Comparison with the Short-Term Exposure Limit

Height 0m	Height 5m

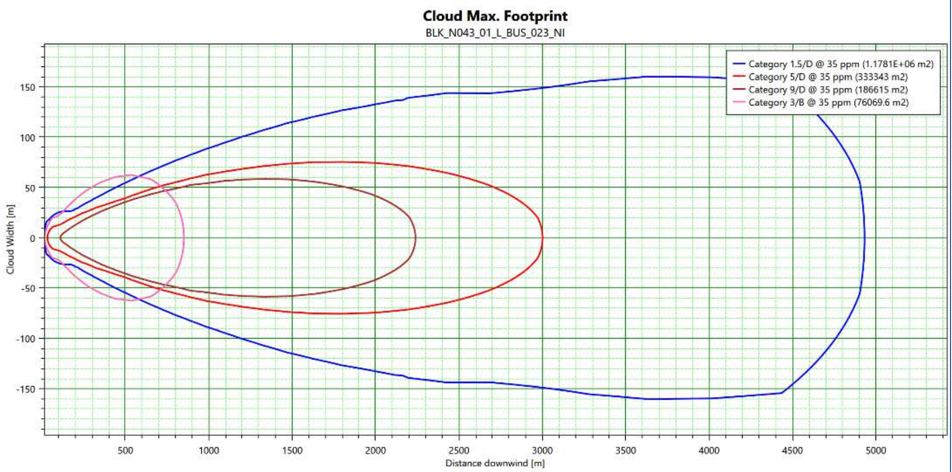


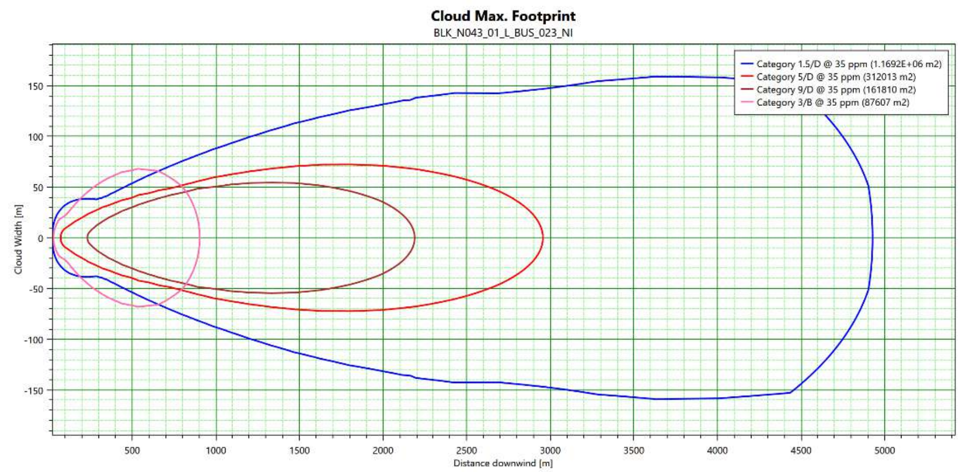


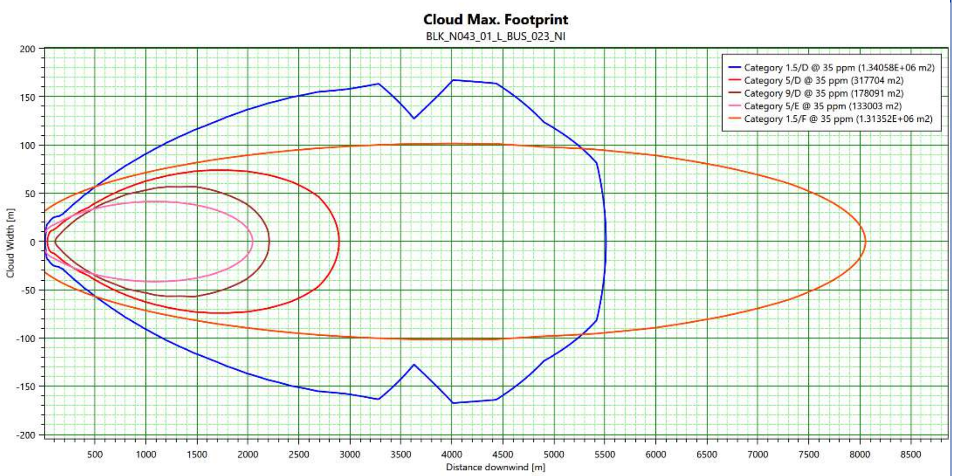


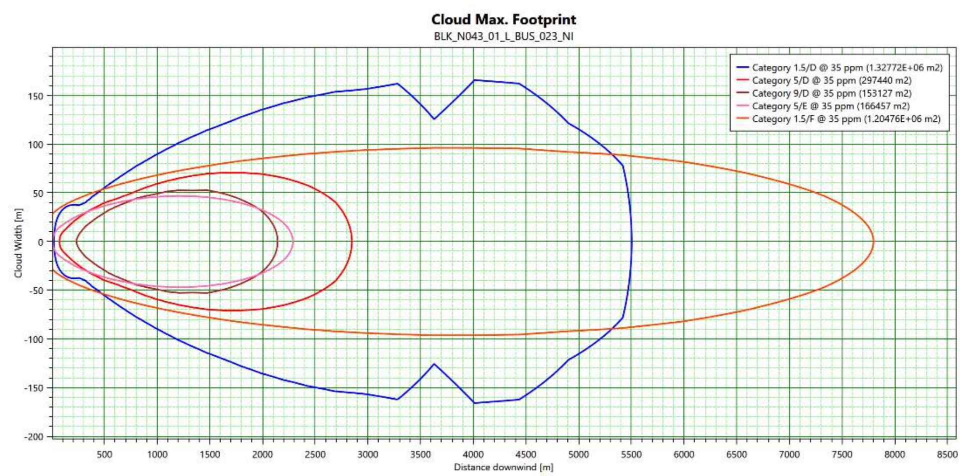


Height 0m	**Height 5m**
Height 10m	Height 20m

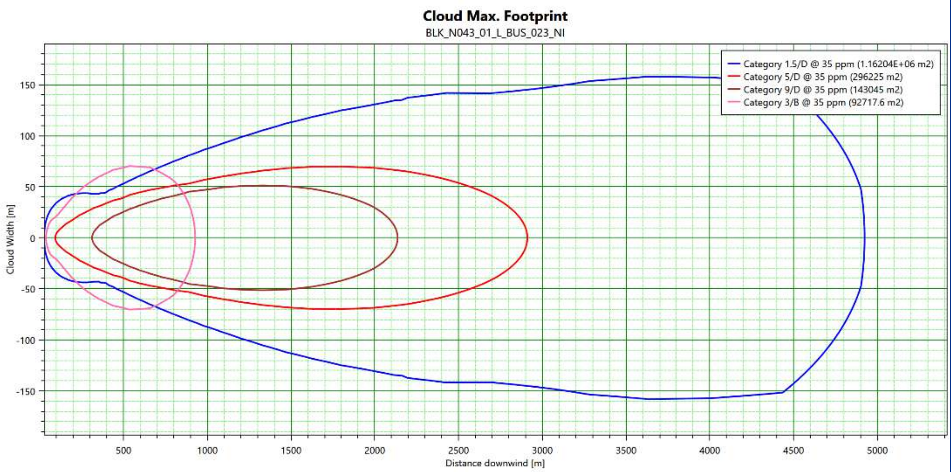




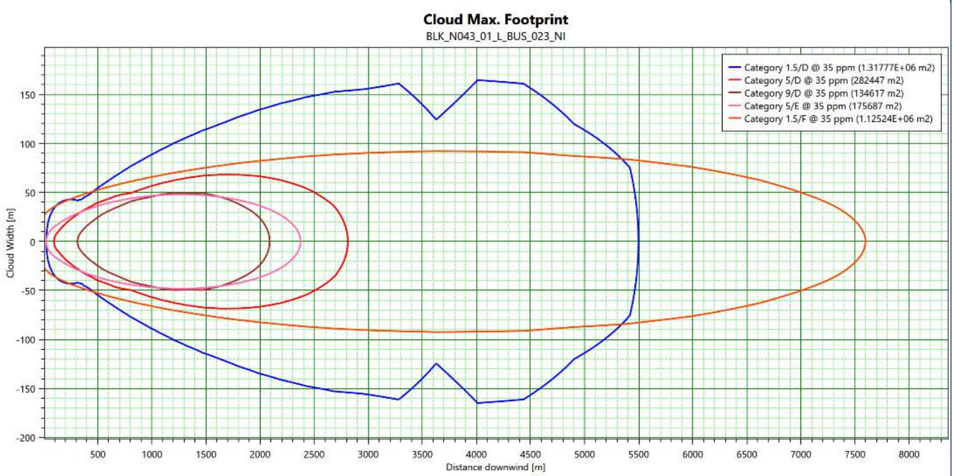




Height 0m	**Height 5m**
Height 25m	Height 180m



No daytime exceedances



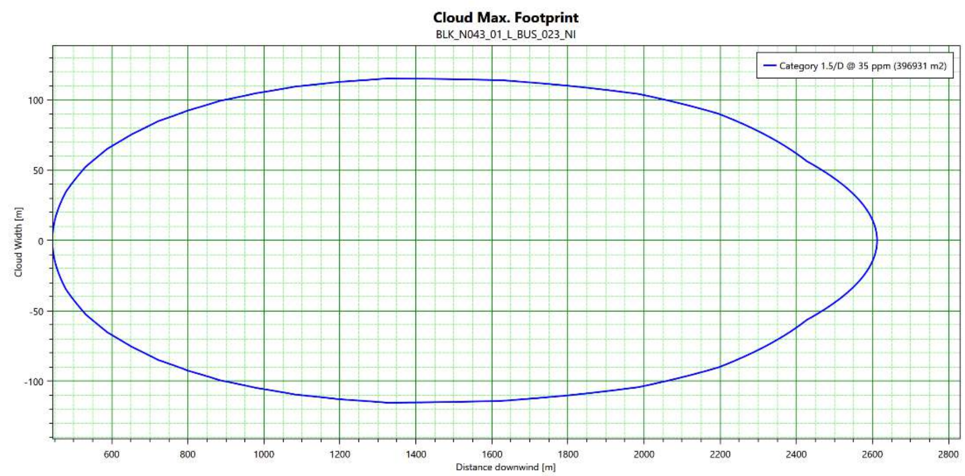


Table A19 Results for Bulker, 200mm hole – Comparison with the Short-Term Exposure Limit

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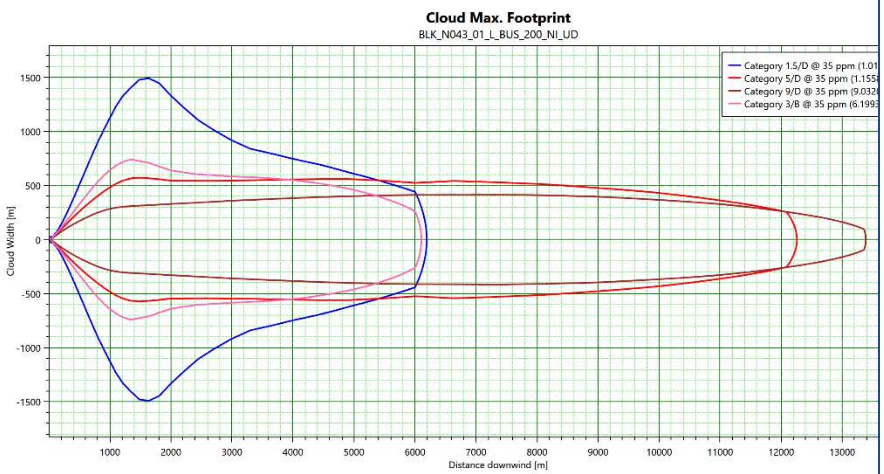

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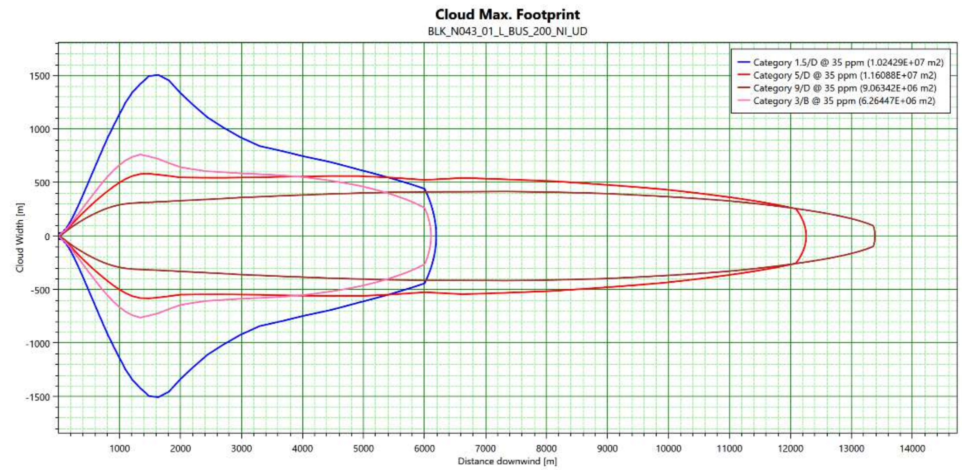

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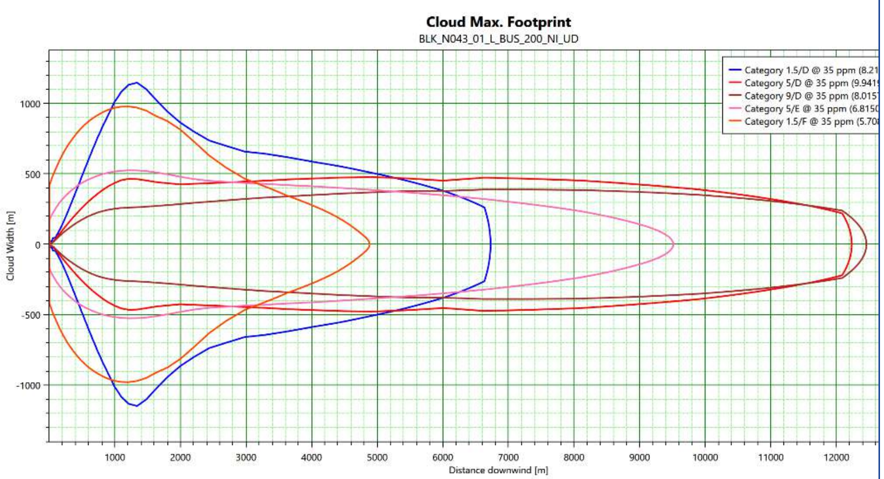

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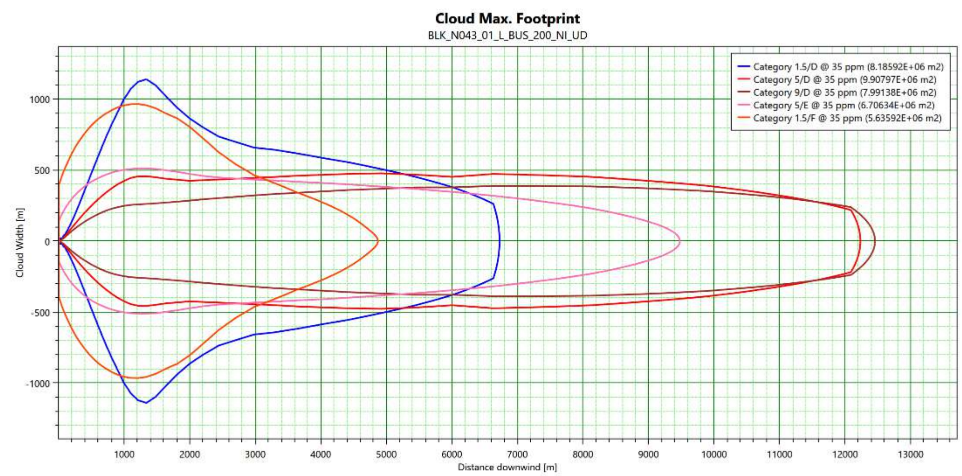

</td></tr>
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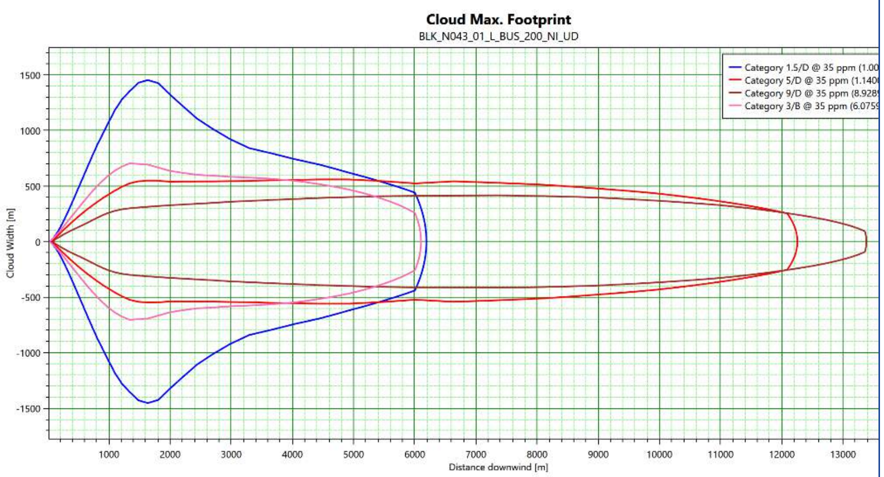
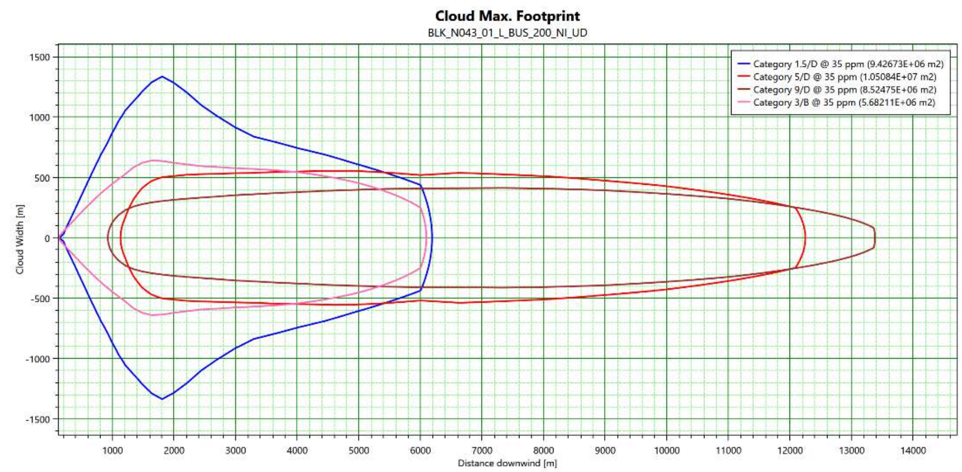
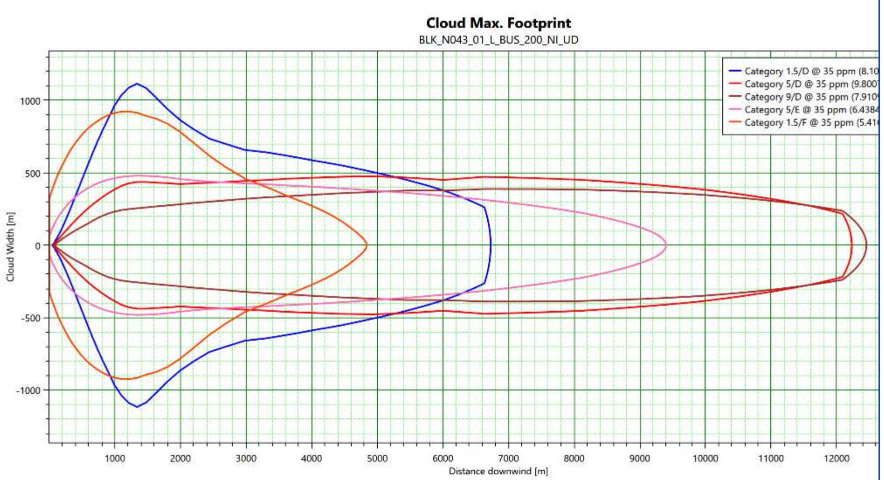
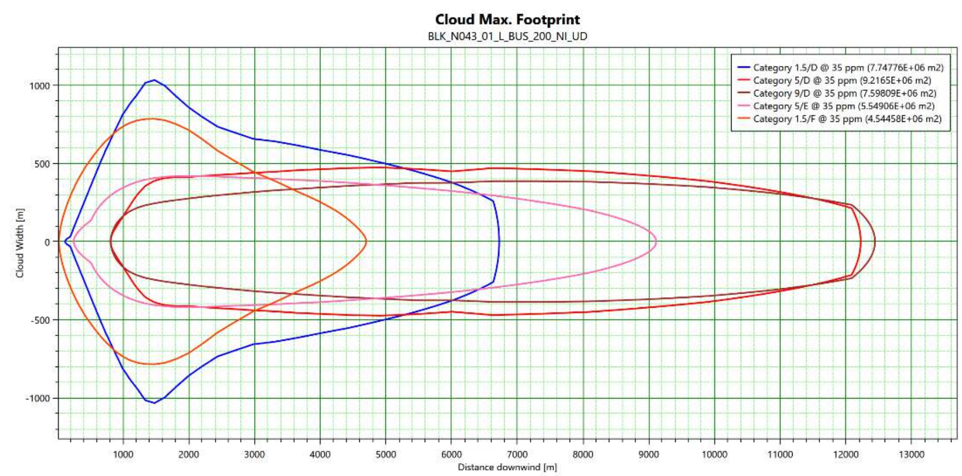
Height 0m	**Height 5m**
Height 10m	Height 20m

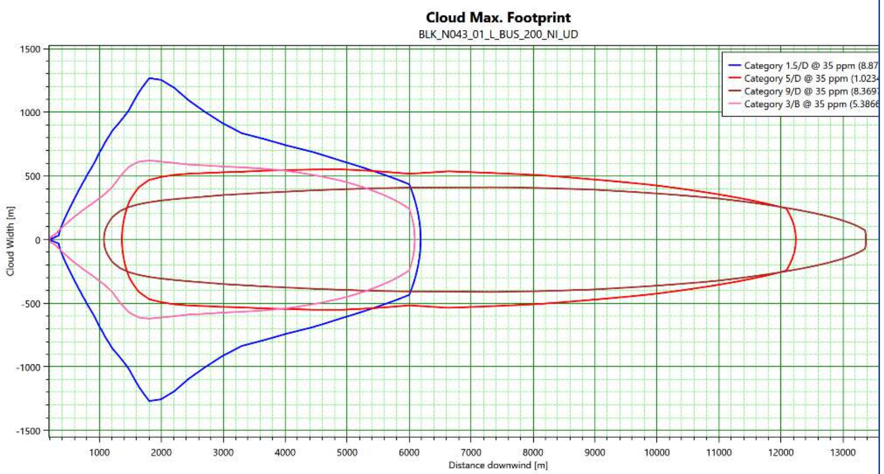


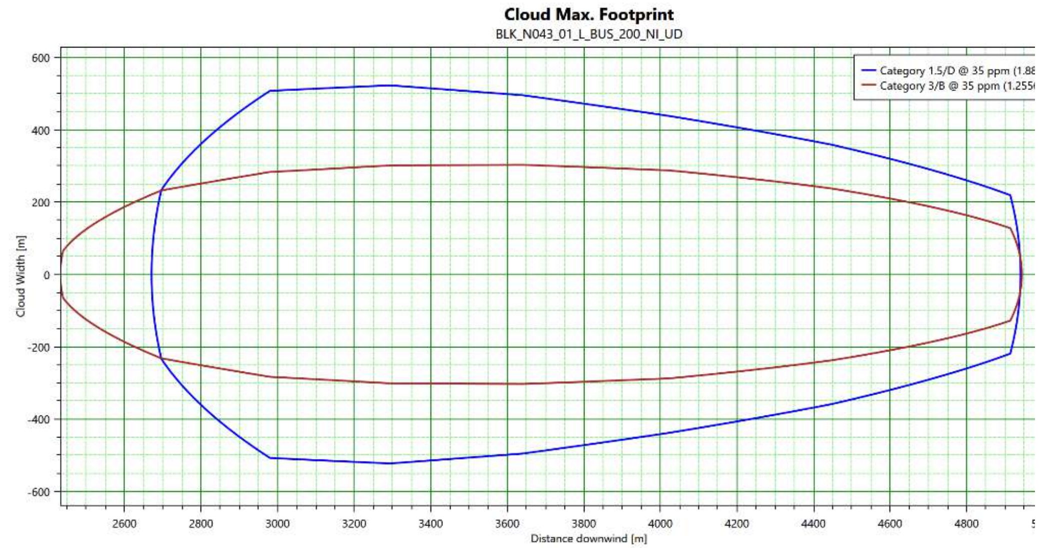


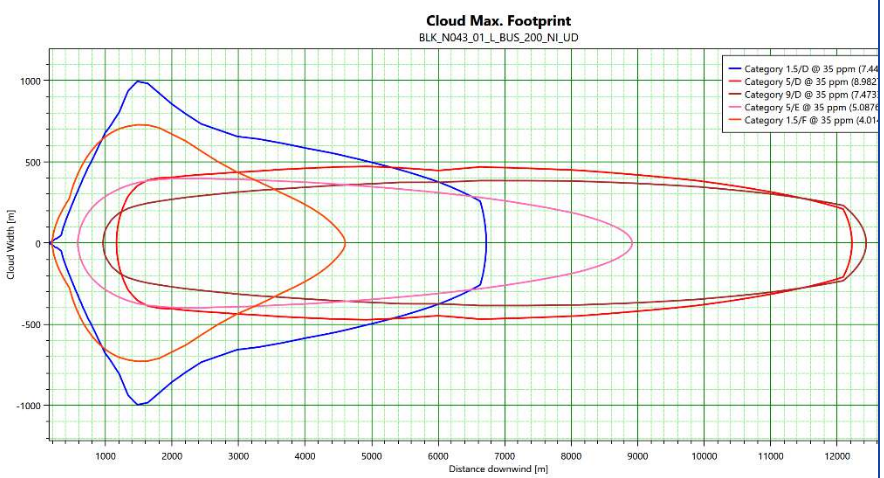




Height 0m	**Height 5m**
Height 25m	Height 180m







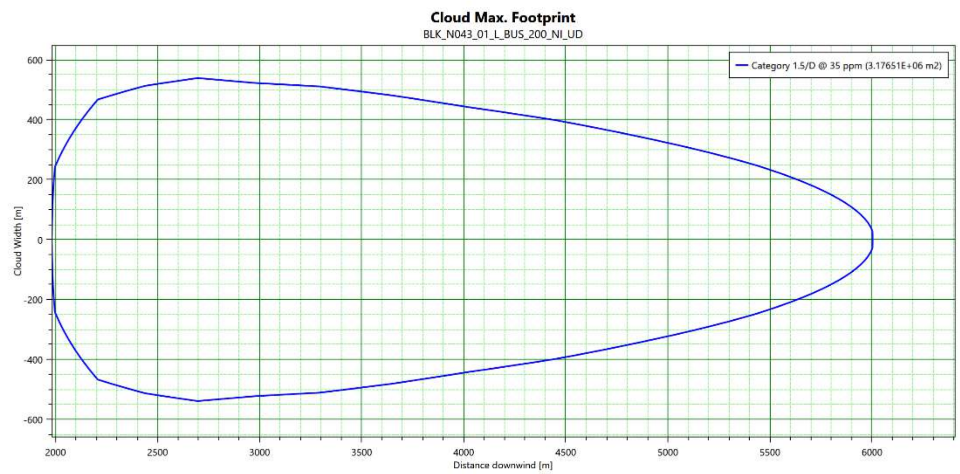
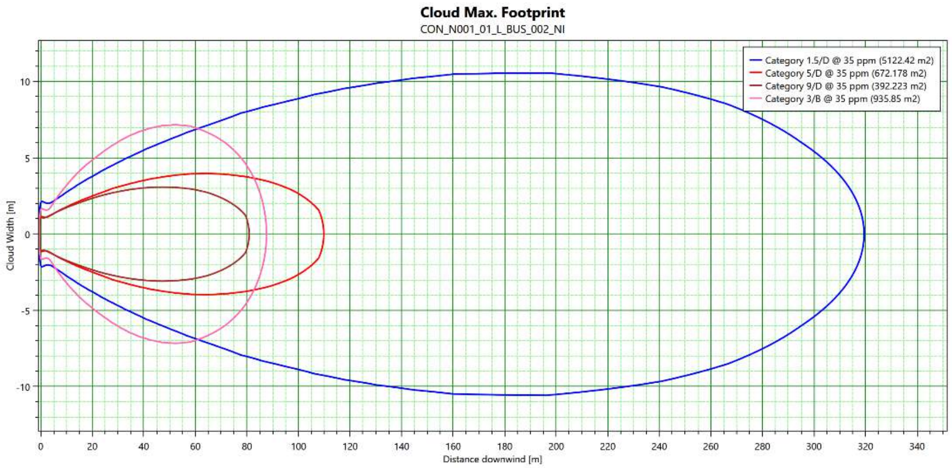
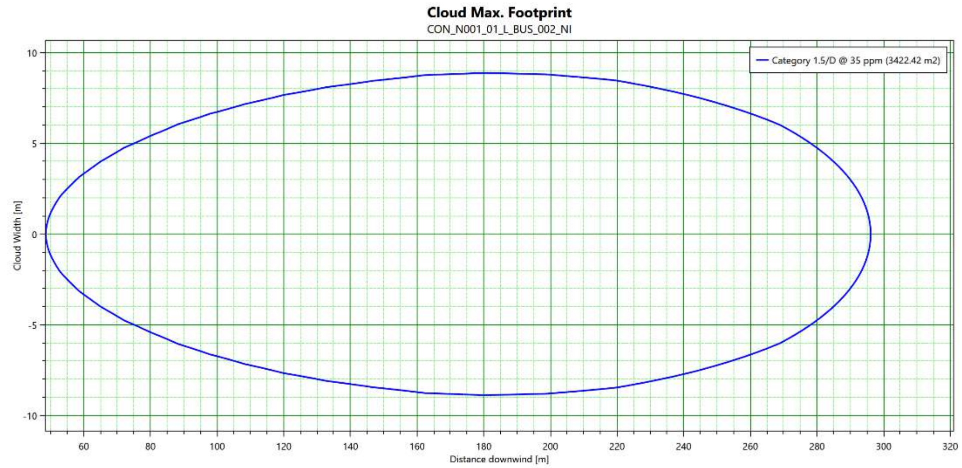
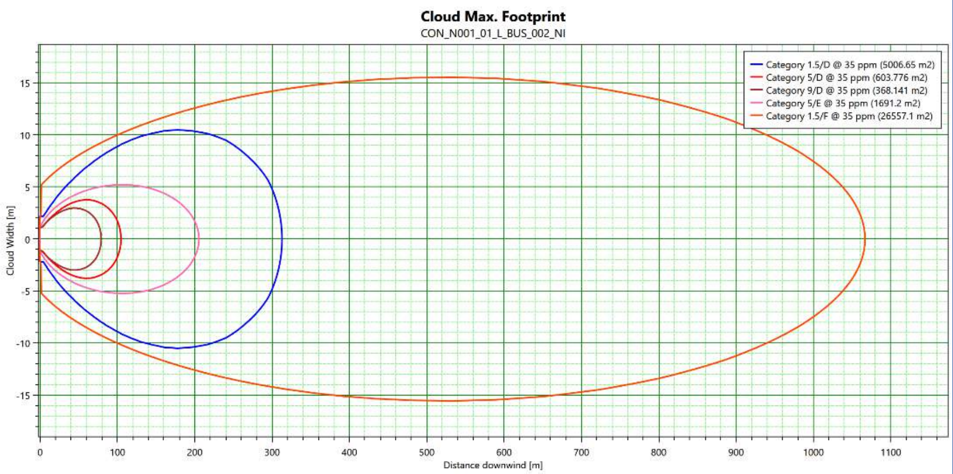
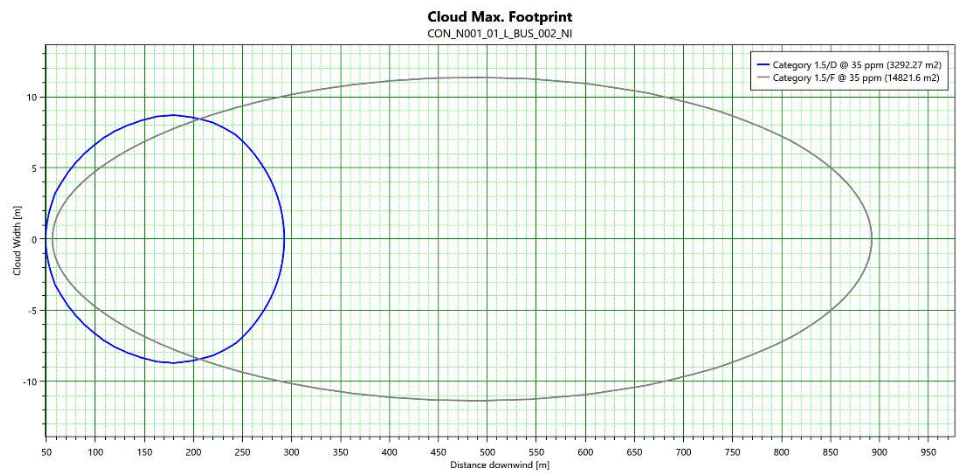


Table A 20 -15 Results for Containership, 2mm hole – Comparison with the Short-Term Exposure Limit

Height 0m	Height 5m
	
	

Height 0m	**Height 5m**
Height 10m	Height 20m
No daytime exceedances	No daytime exceedances
No night-time exceedances	No night-time exceedances
Height 25m	Height 180m
No daytime exceedances	No daytime exceedances
No night-time exceedances	No night-time exceedances

Table A20 Results for Containership, 23mm hole – Comparison with the Short-Term Exposure Limit

<table>
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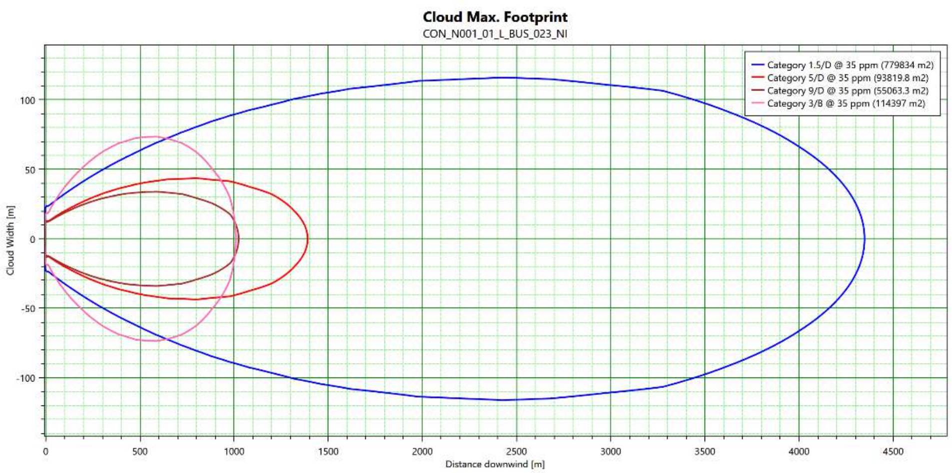

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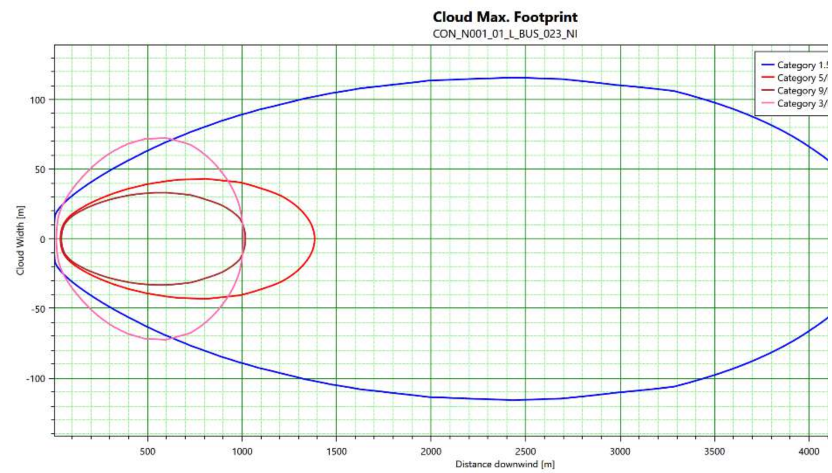
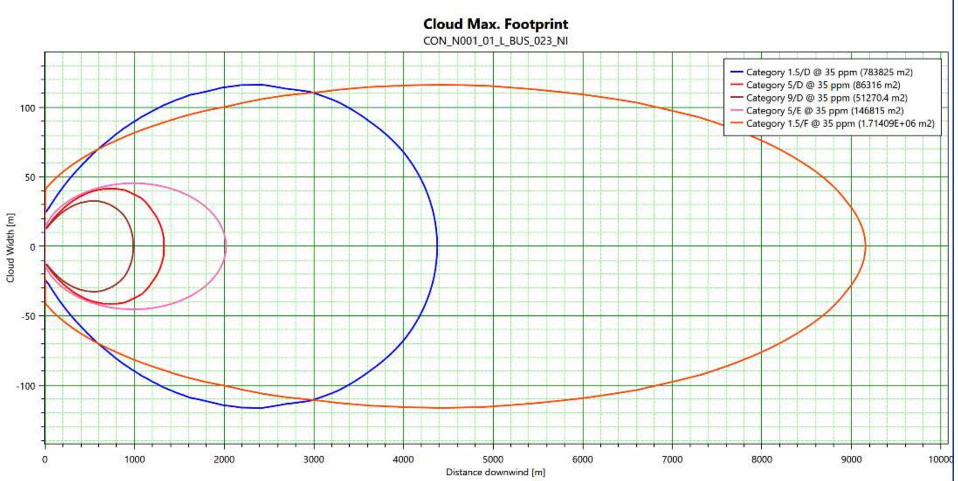


</td></tr>
<tr><td>


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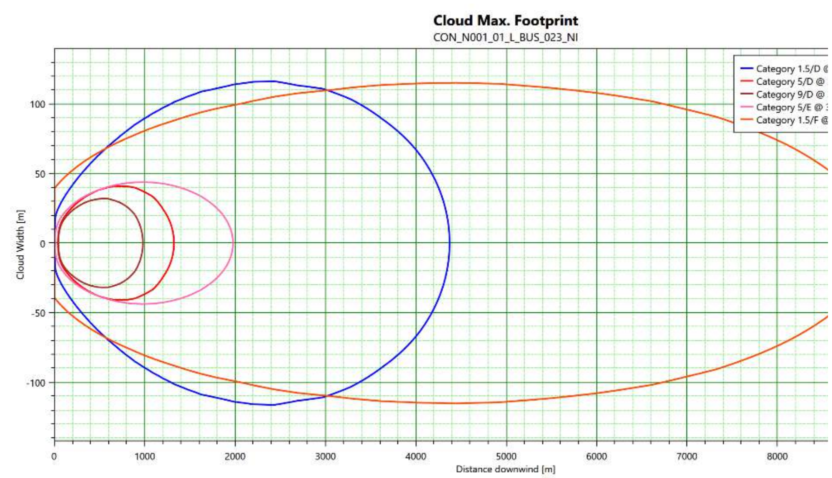

</td></tr>
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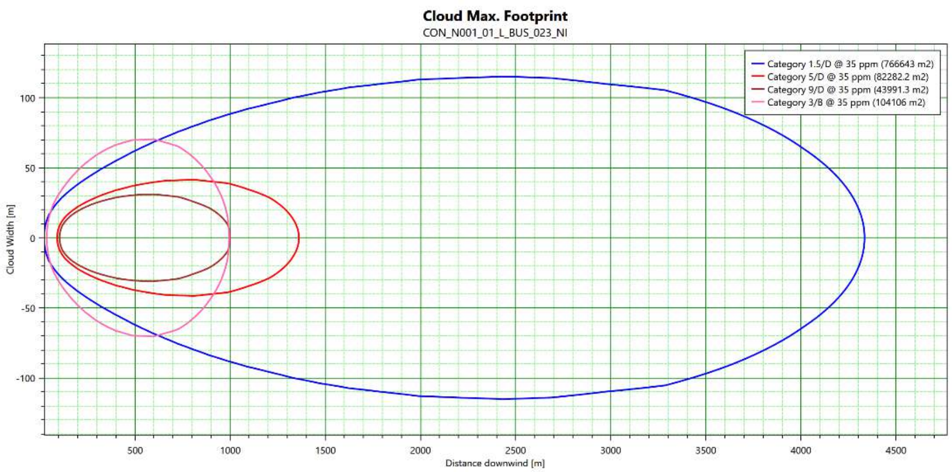
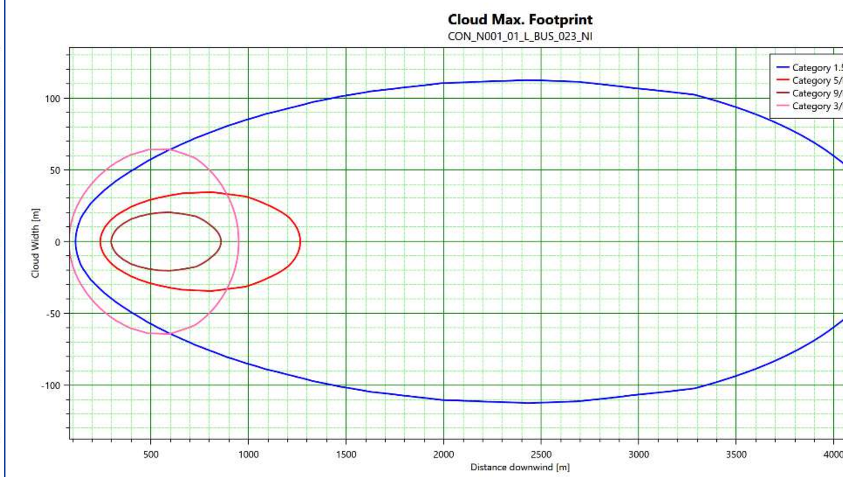
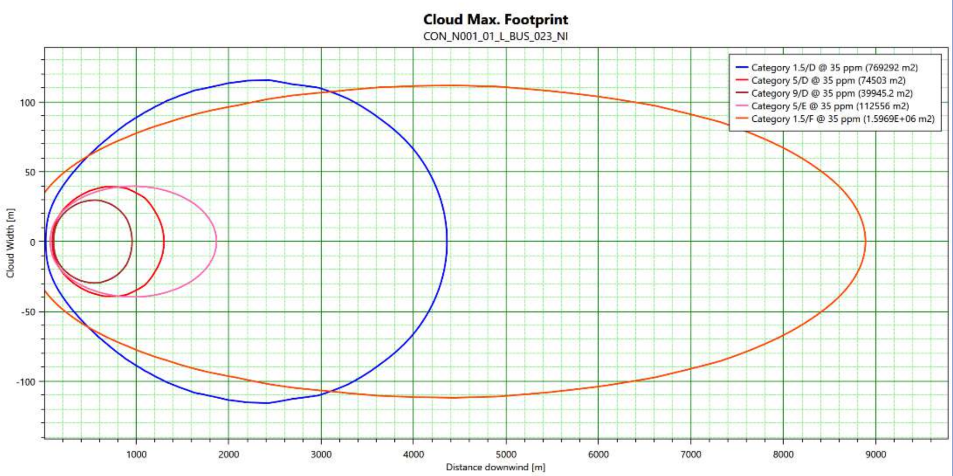
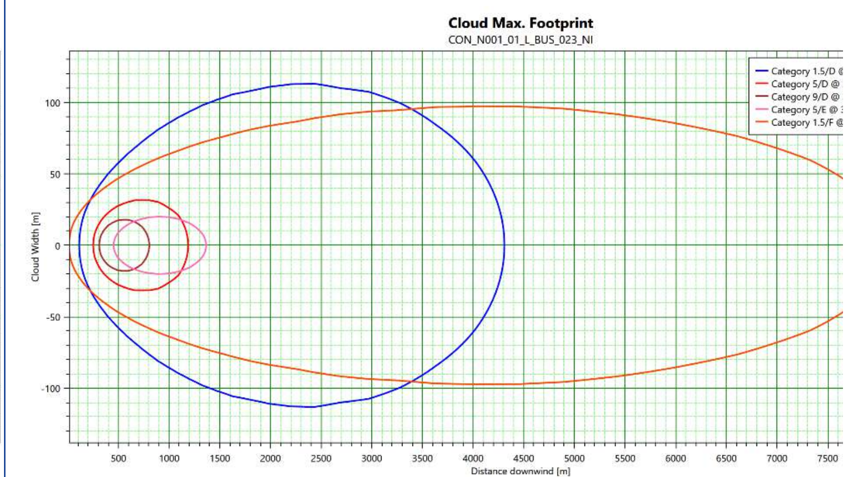
Height 0m	**Height 5m**
Height 10m	Height 20m









<table>
<tr><th>Height 0m
Height 25m</th><th>Height 5m
Height 180m</th></tr>
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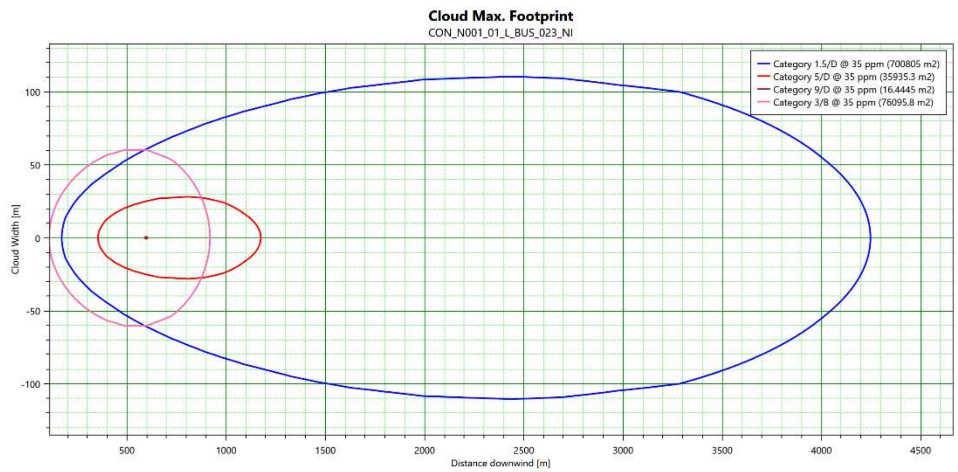

</td><td>No daytime exceedances</td></tr>
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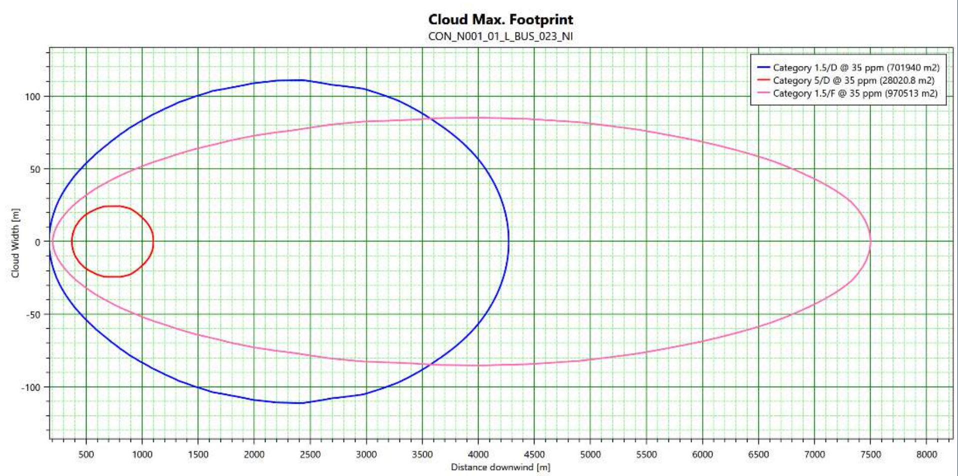

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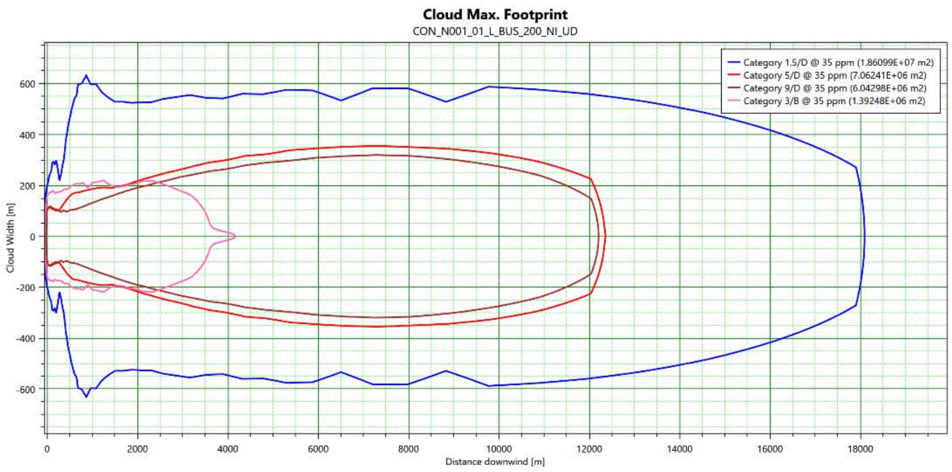
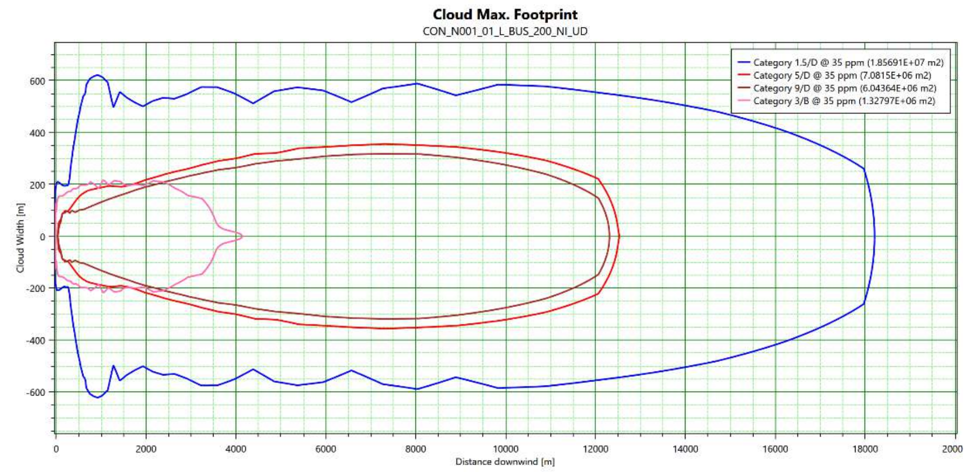
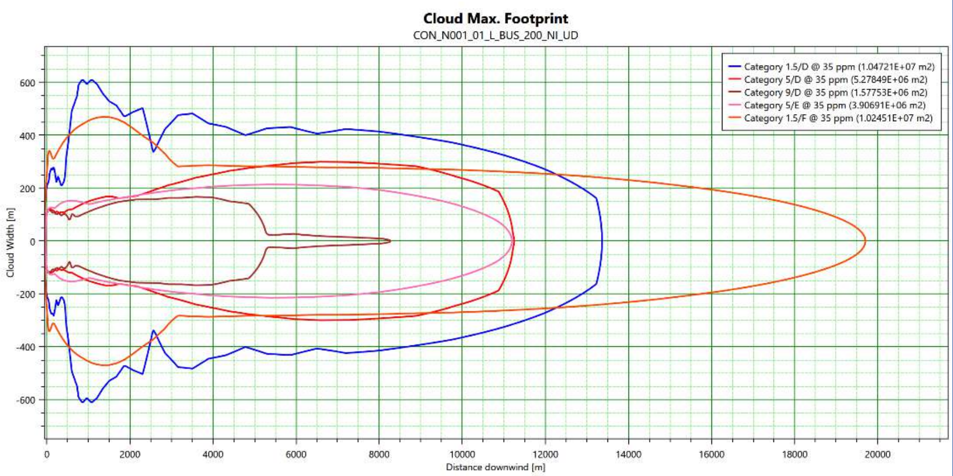
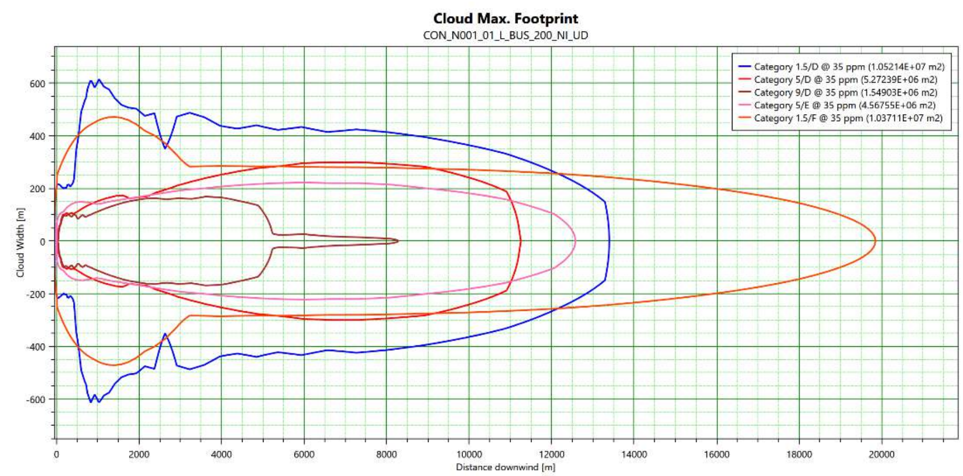
Table A21 Results for Containership, 200mm hole – Comparison with the Short-Term Exposure Limit

Height 0m	Height 5m

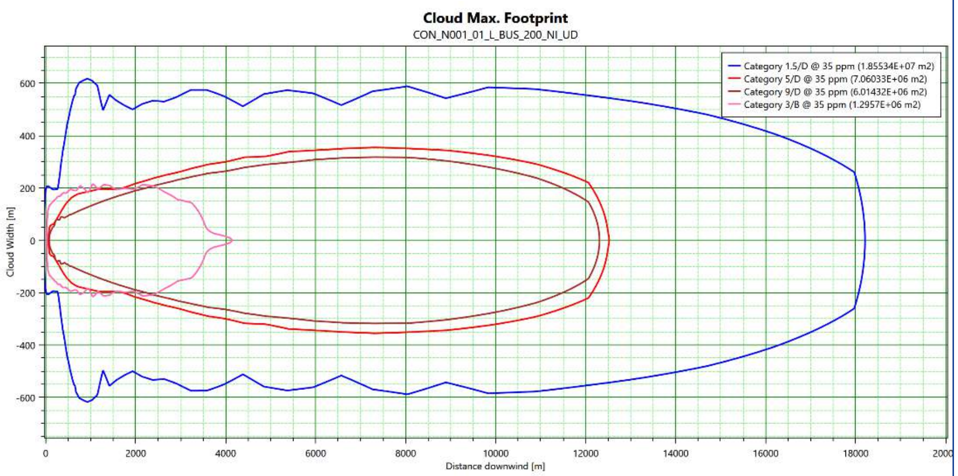


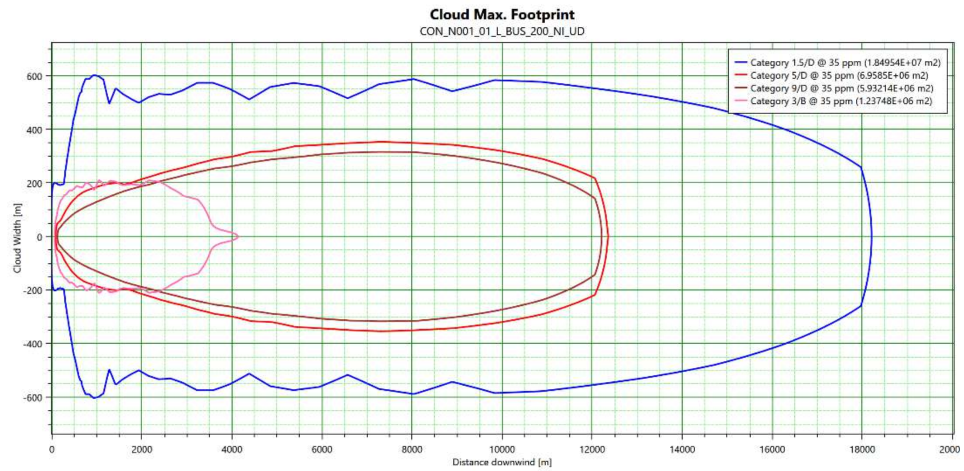


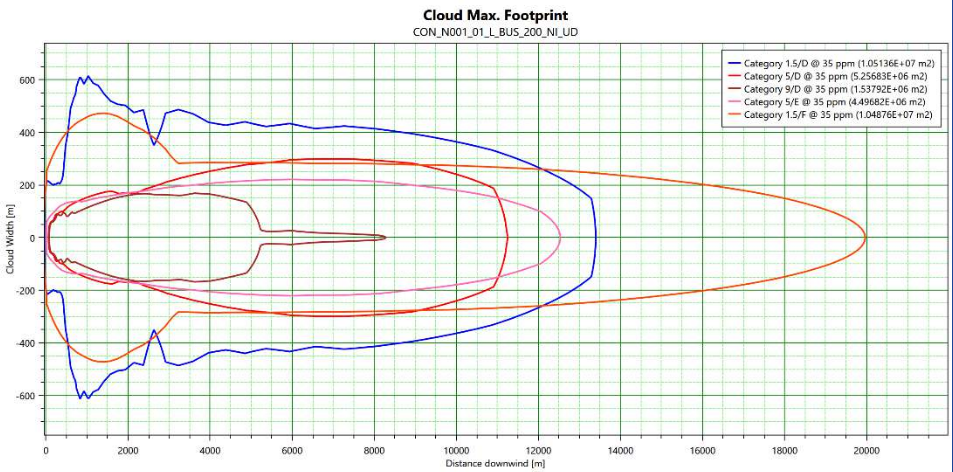


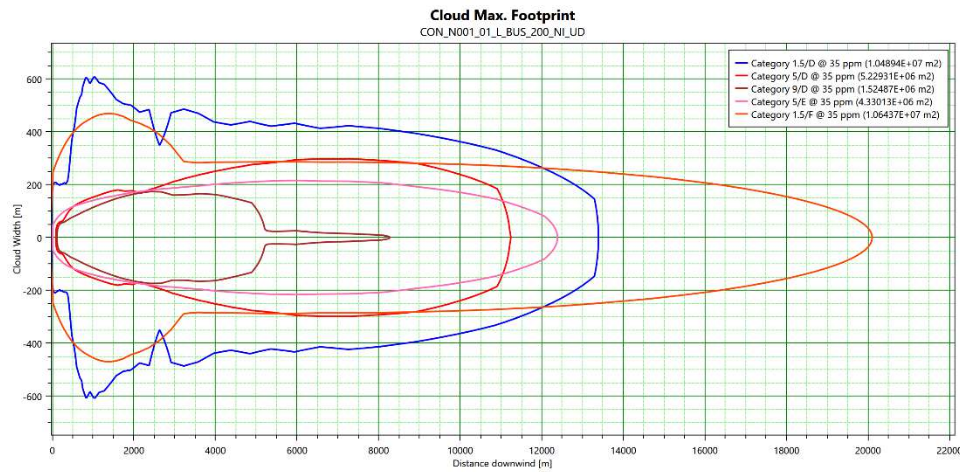


Height 0m	Height 5m
Height 10m	Height 20m

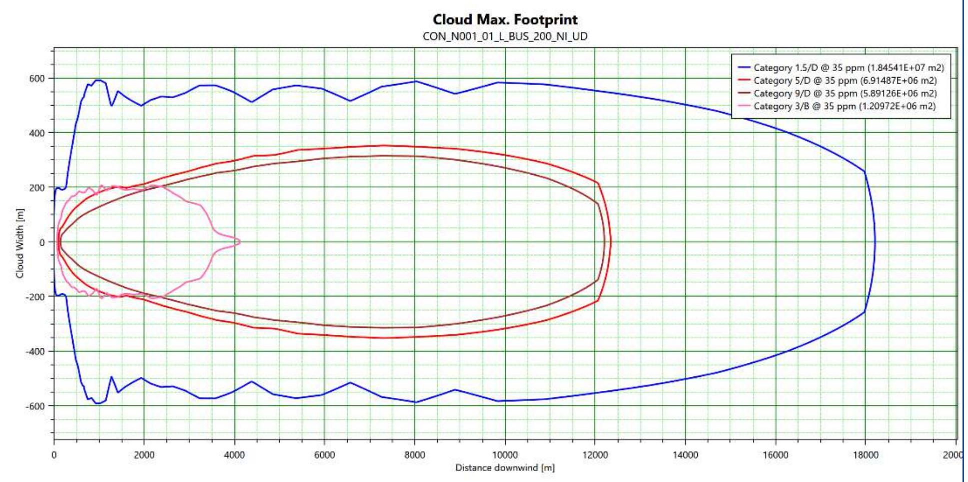


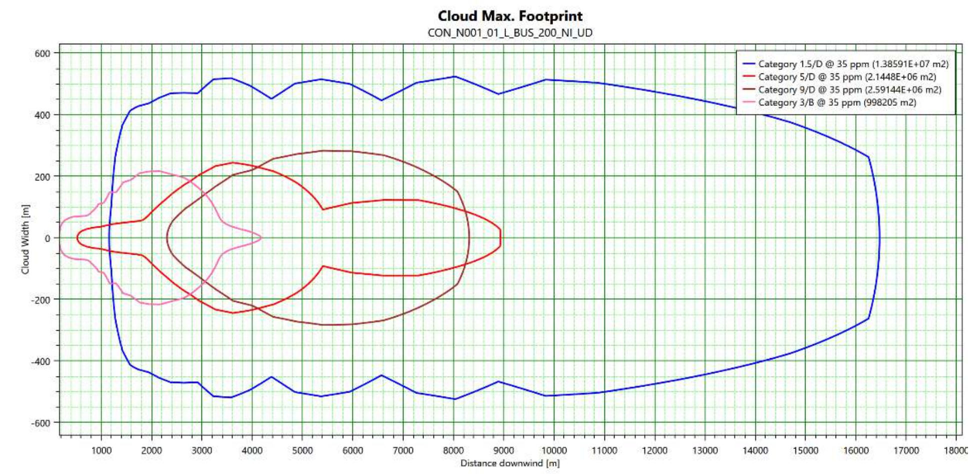


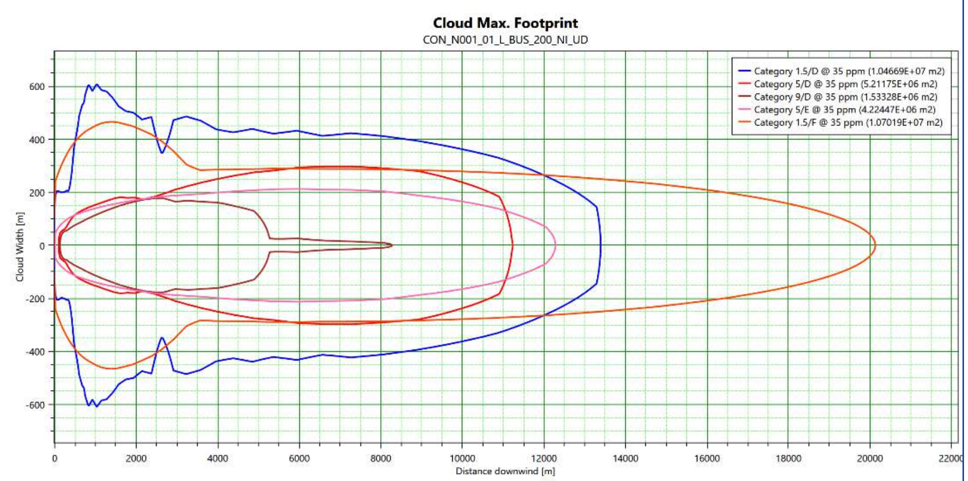




Height 0m	**Height 5m**
Height 25m	Height 180m







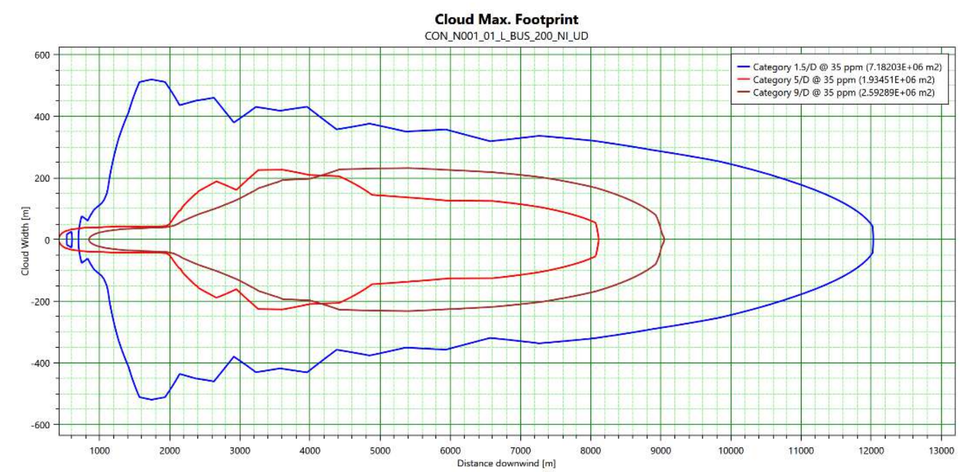
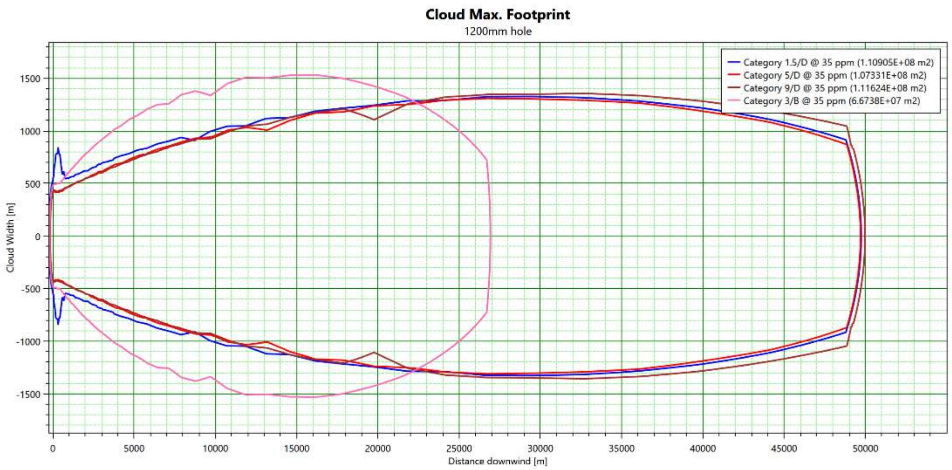
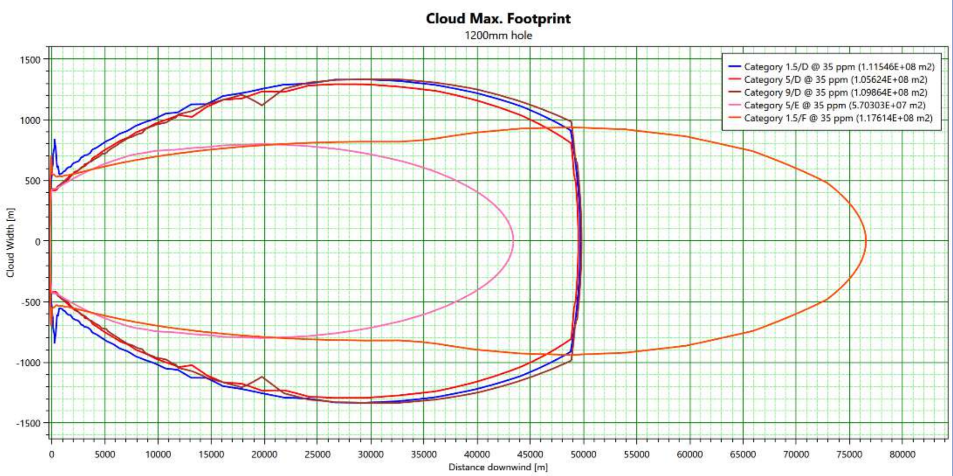


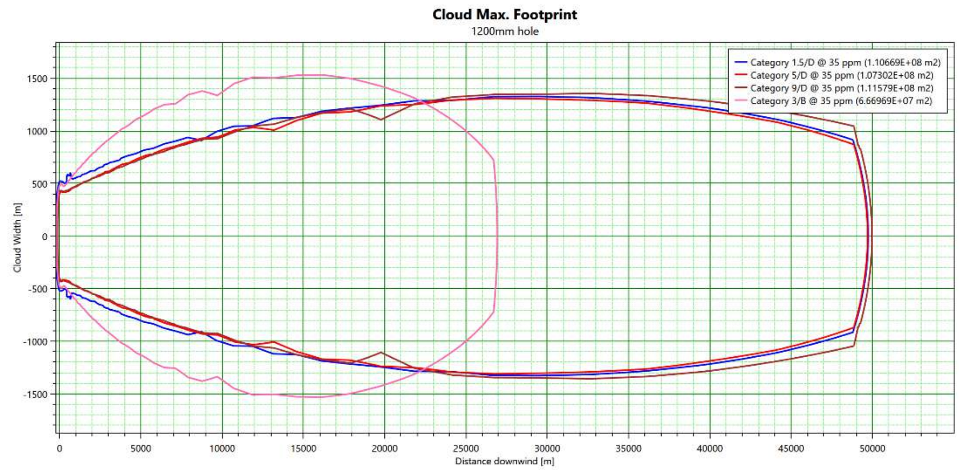
Table A22 Results for Storage tank spill, 1200mm hole – Comparison with the Short-Term Exposure Limit

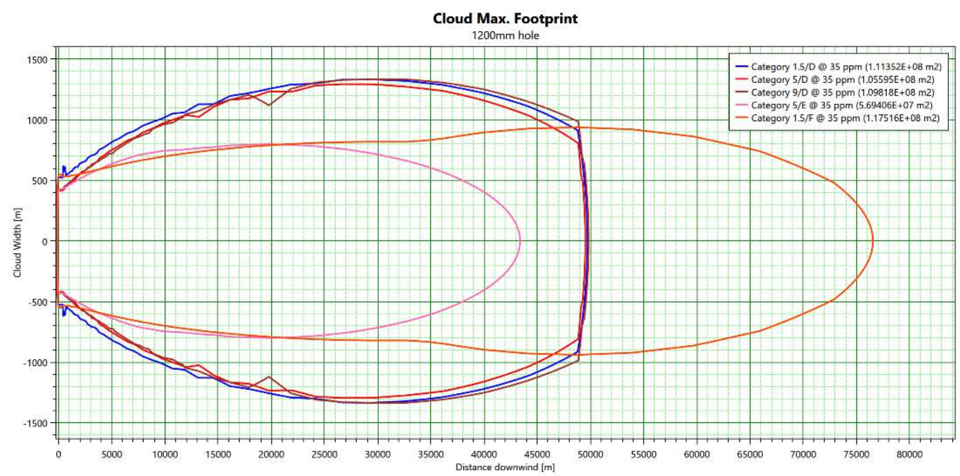
Height 0m



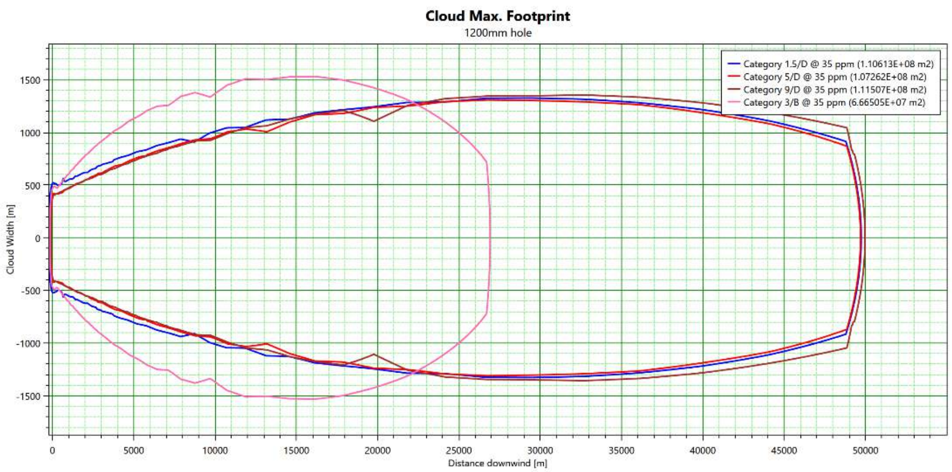


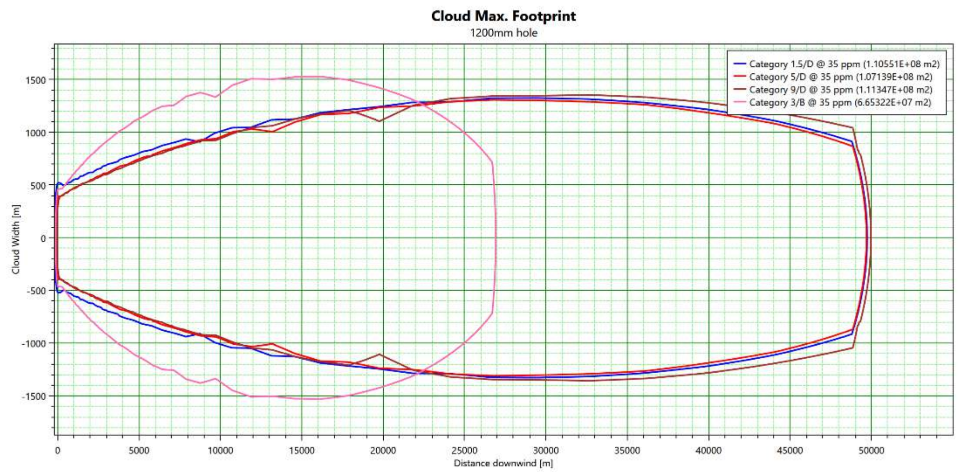
Height 5m

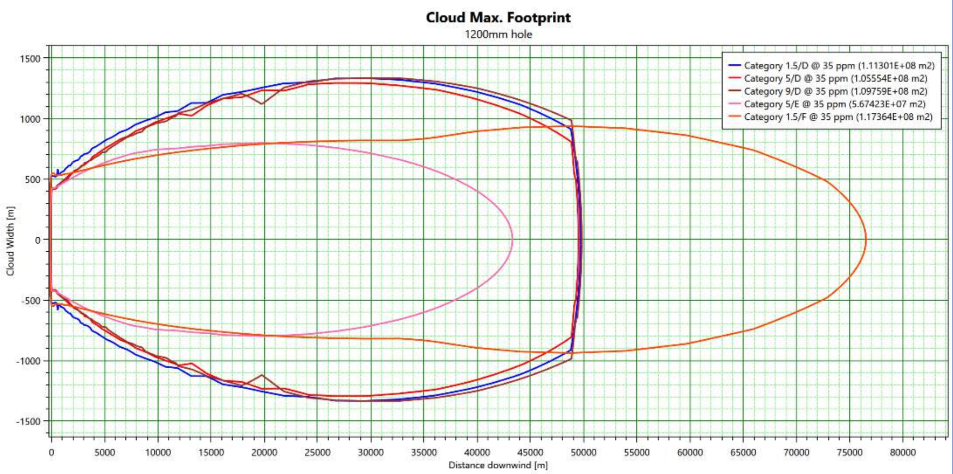


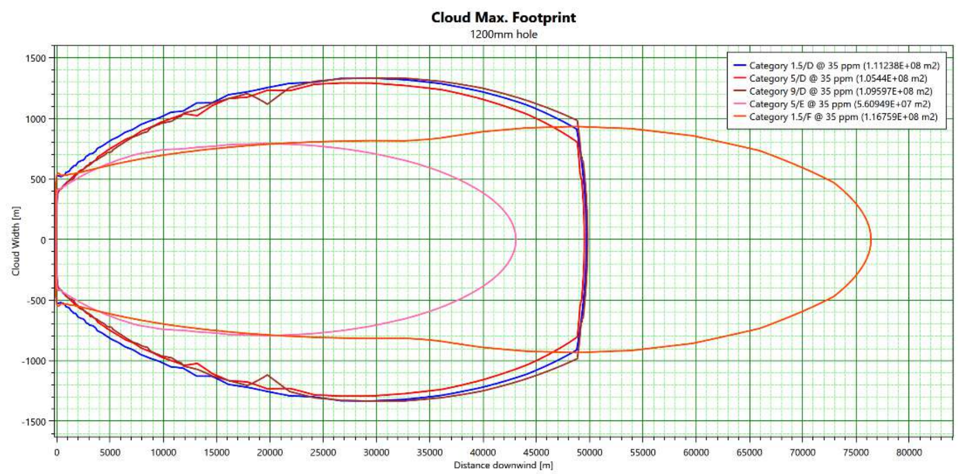


Height 0m	**Height 5m**
Height 10m	Height 20m

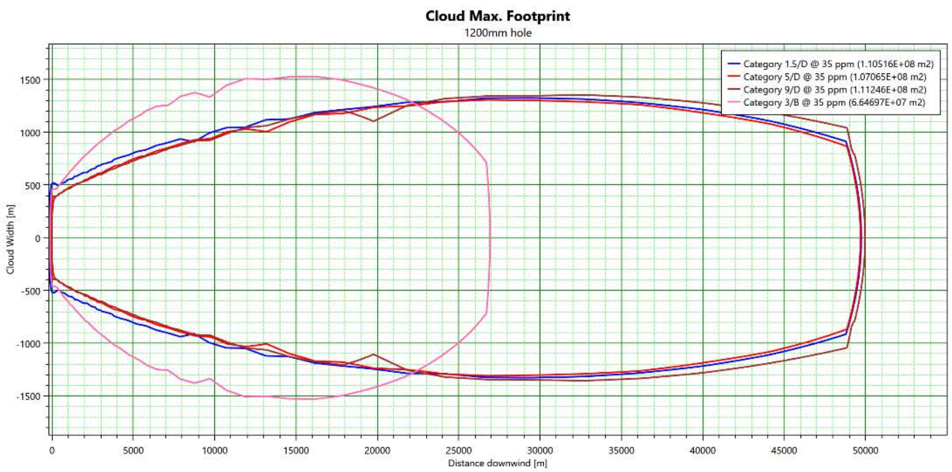


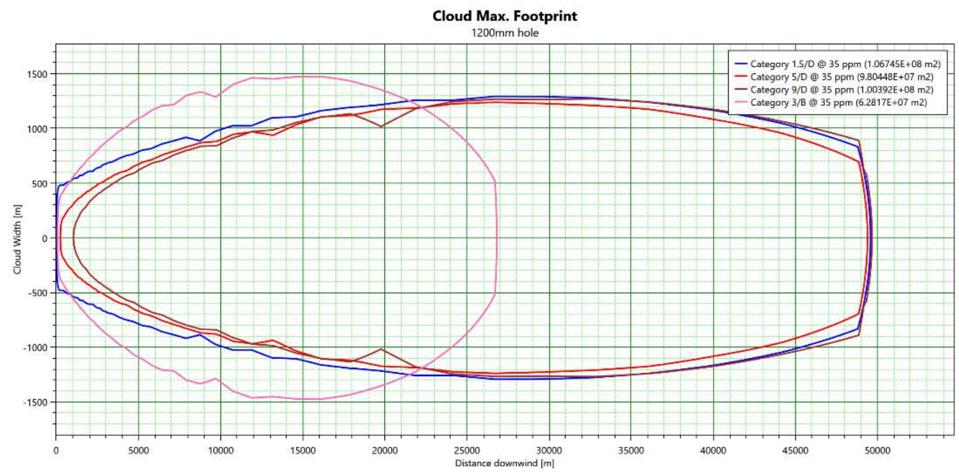


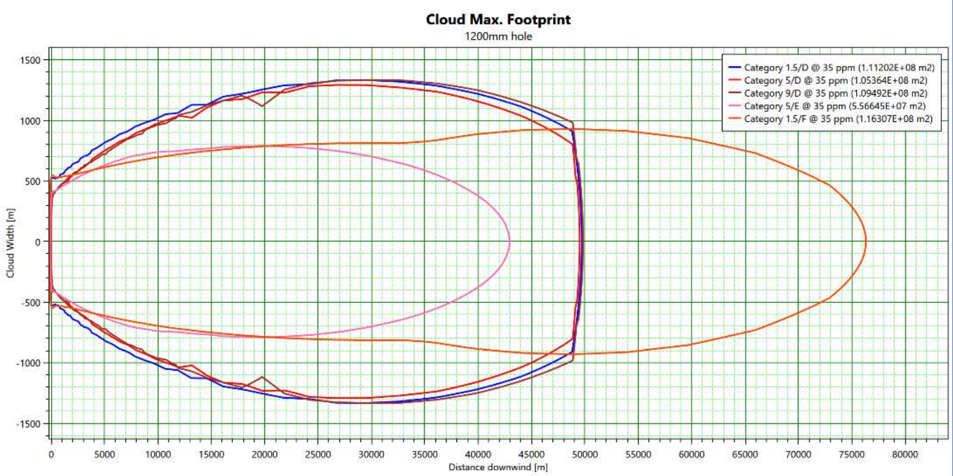




Height 0m	**Height 5m**
Height 25m	Height 180m







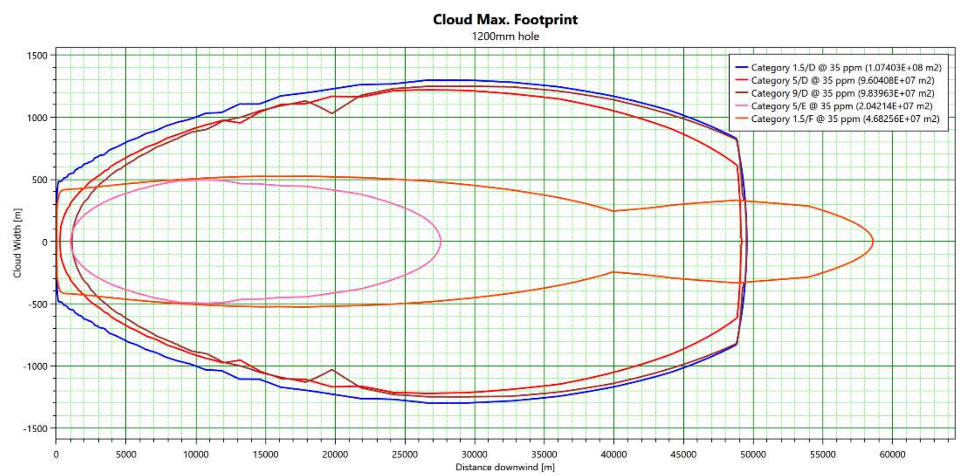
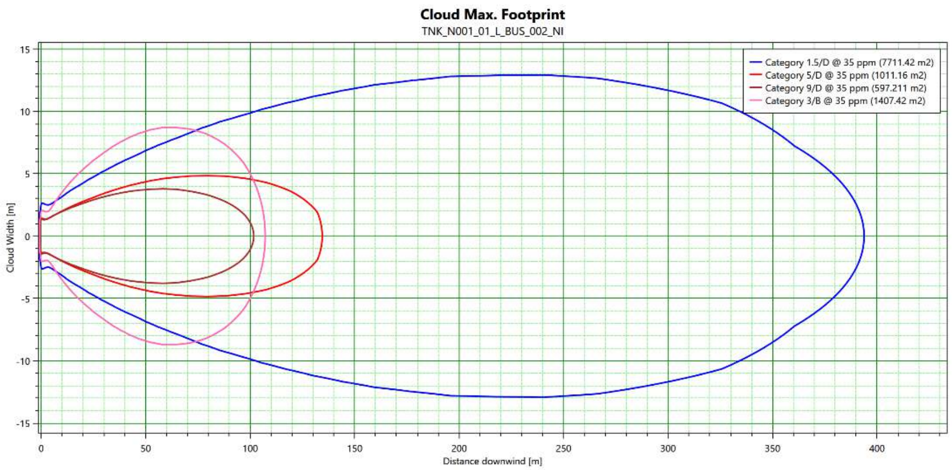
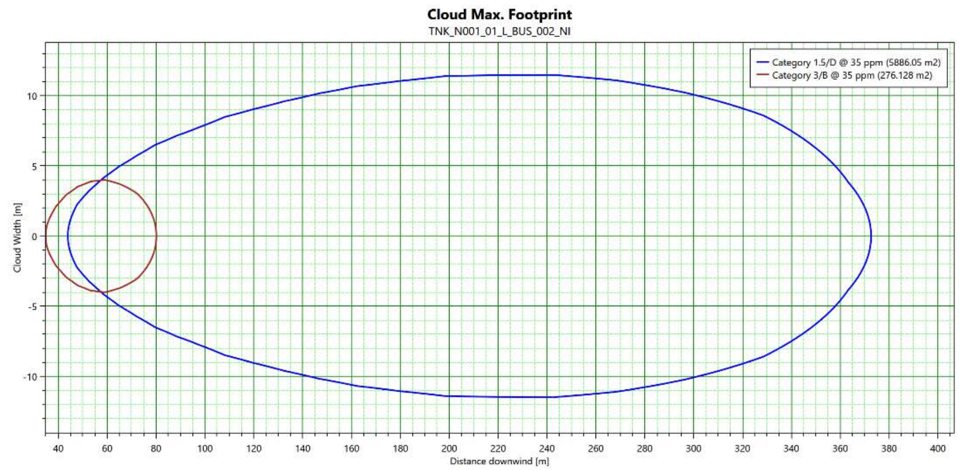
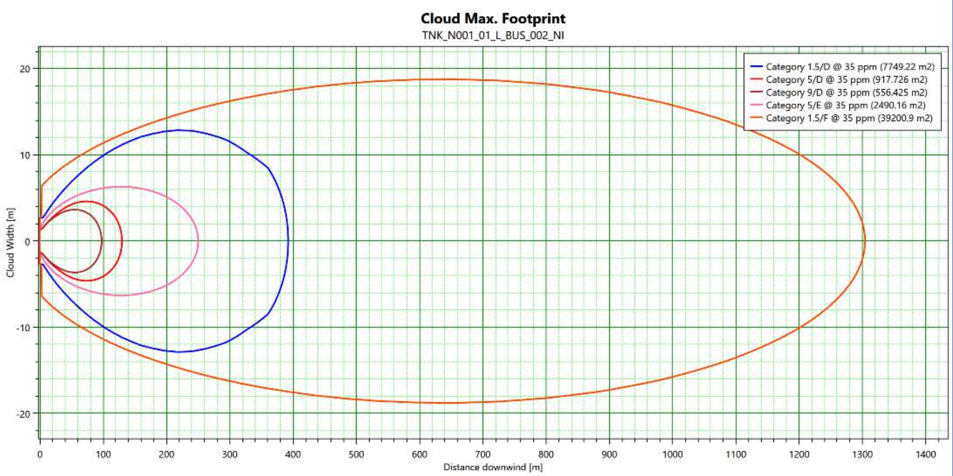
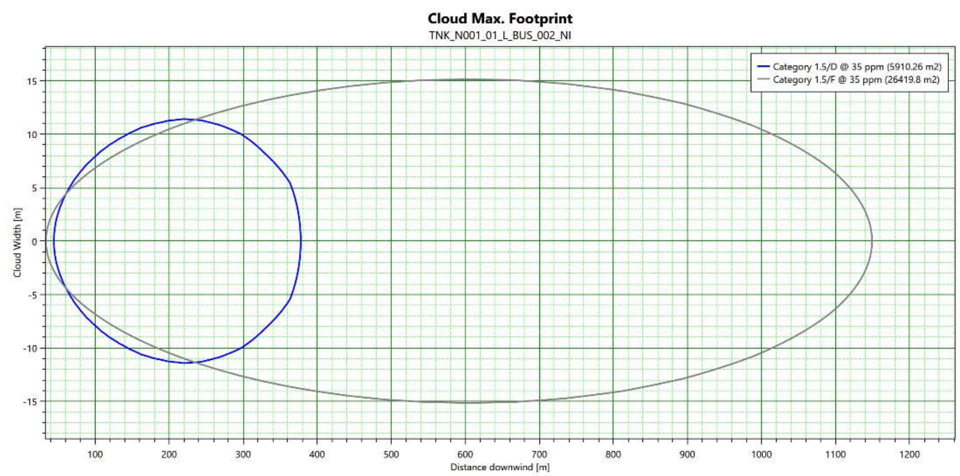
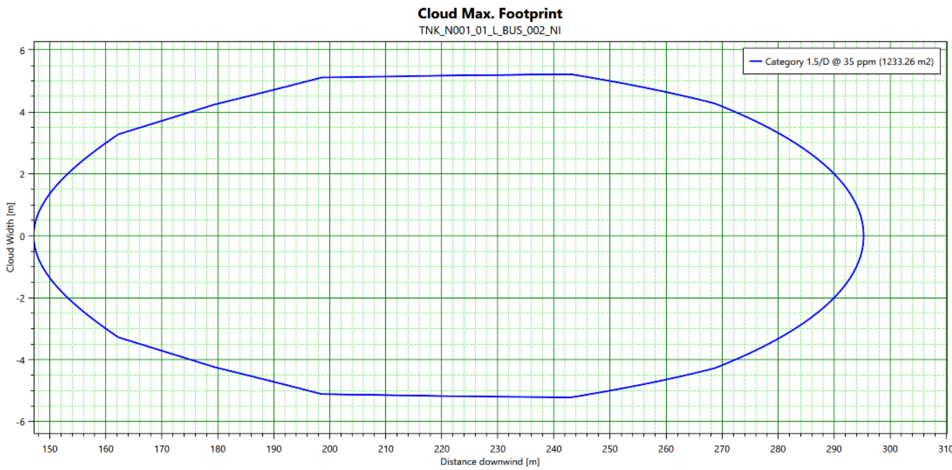
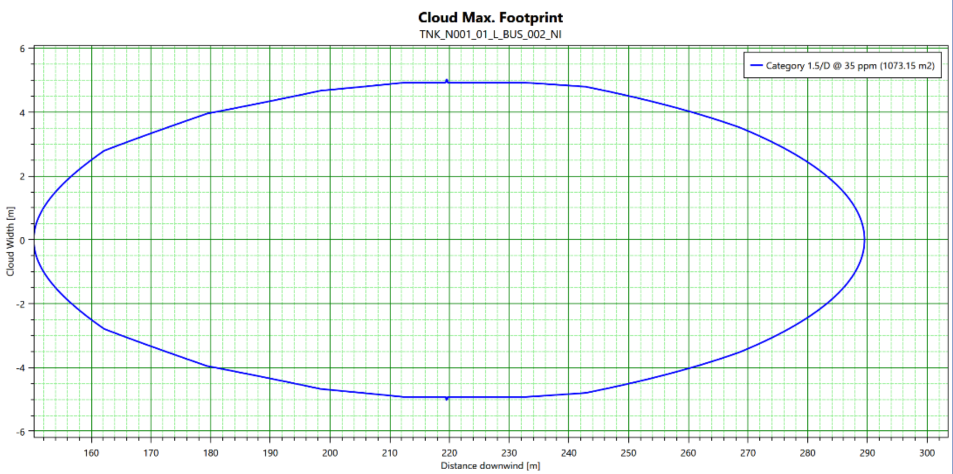


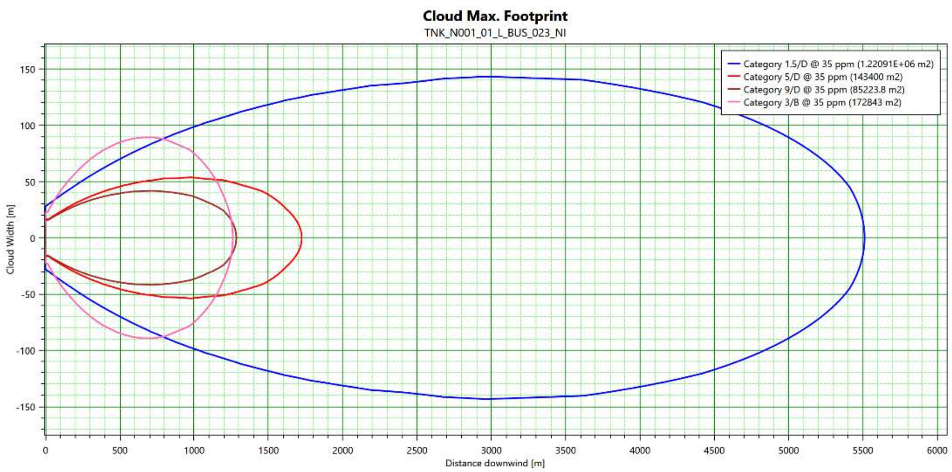
Table A23 Results for Tanker, 2mm hole – Comparison with the Short-Term Exposure Limit

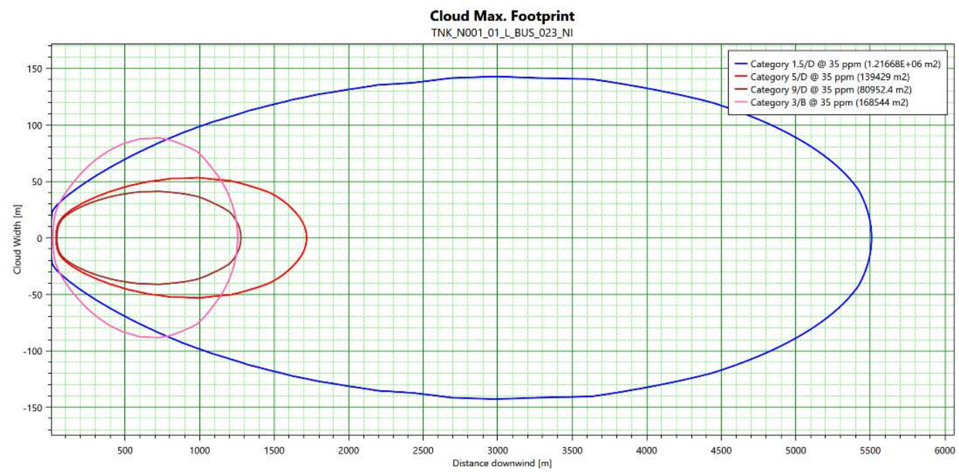
Height 0m	Height 5m
	
	

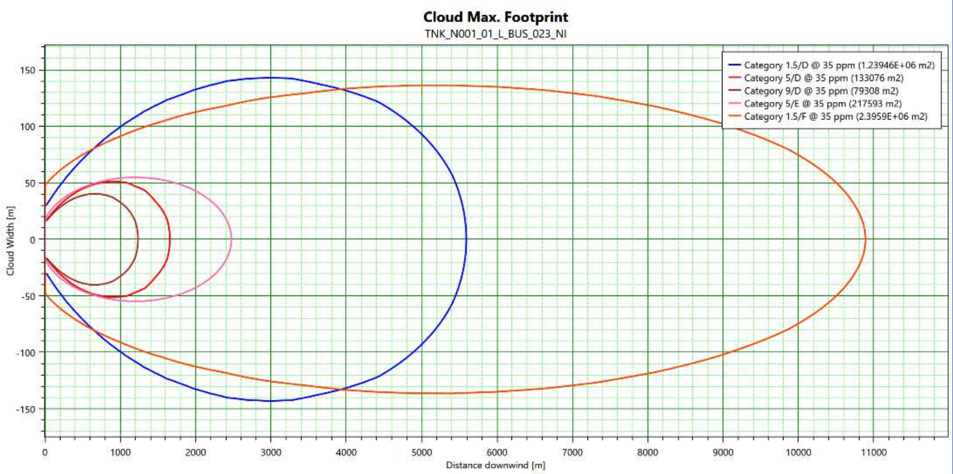
Height 0m	**Height 5m**
Height 10m	Height 20m
	No daytime exceedances
	No night-time exceedances
Height 25m	Height 180m
No daytime exceedances	No daytime exceedances

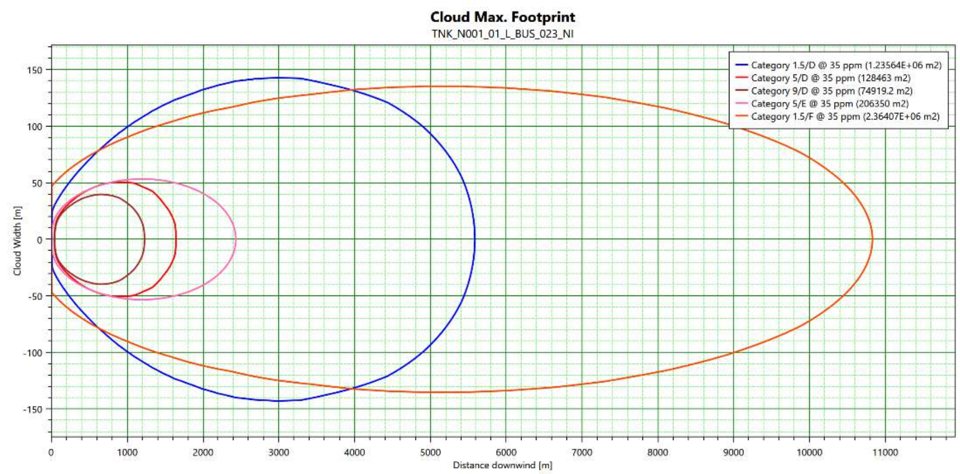
Height 0m	Height 5m
No night-time exceedances	No night-time exceedances

Table A24 Results for Tanker, 23mm hole – Comparison with the Short-Term Exposure Limit

<table>
<tr><th>Height 0m</th><th>Height 5m</th></tr>
<tr><td>


</td><td>


</td></tr>
<tr><td>


</td><td>


</td></tr>
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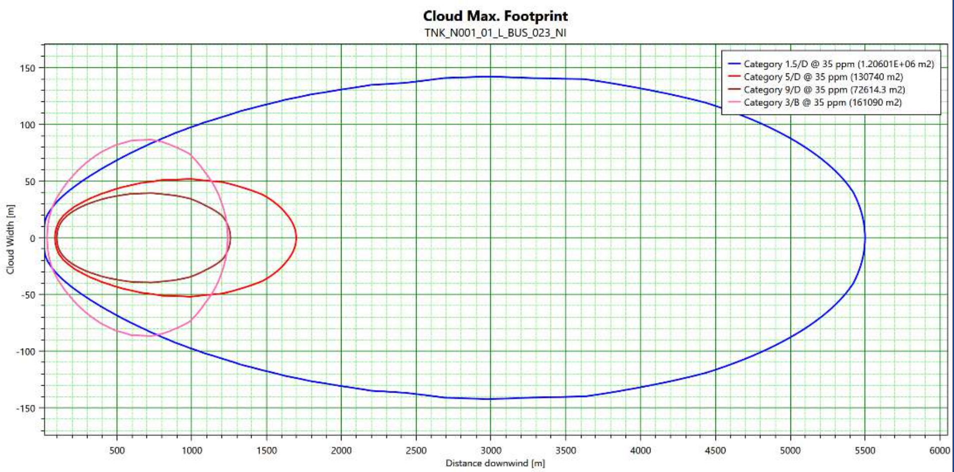
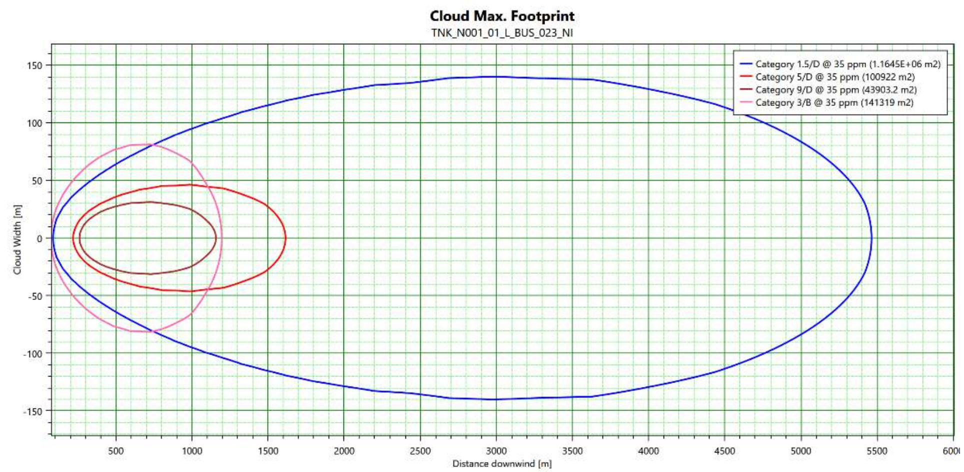
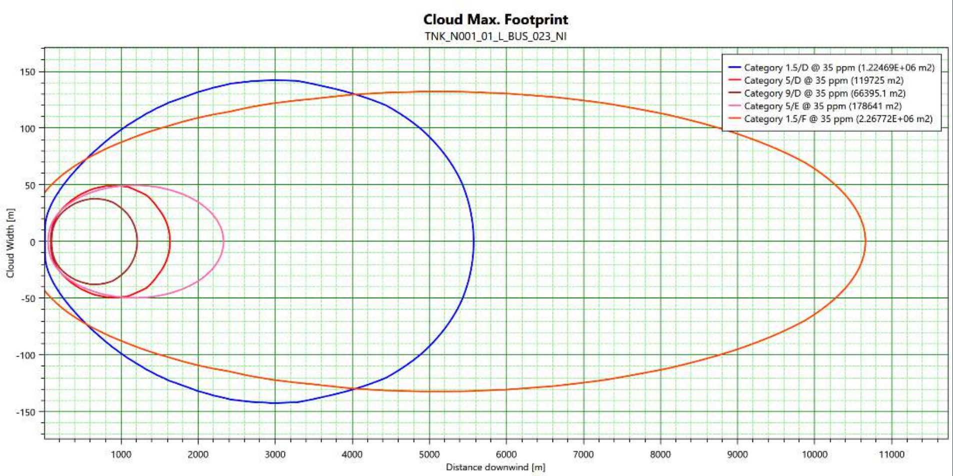
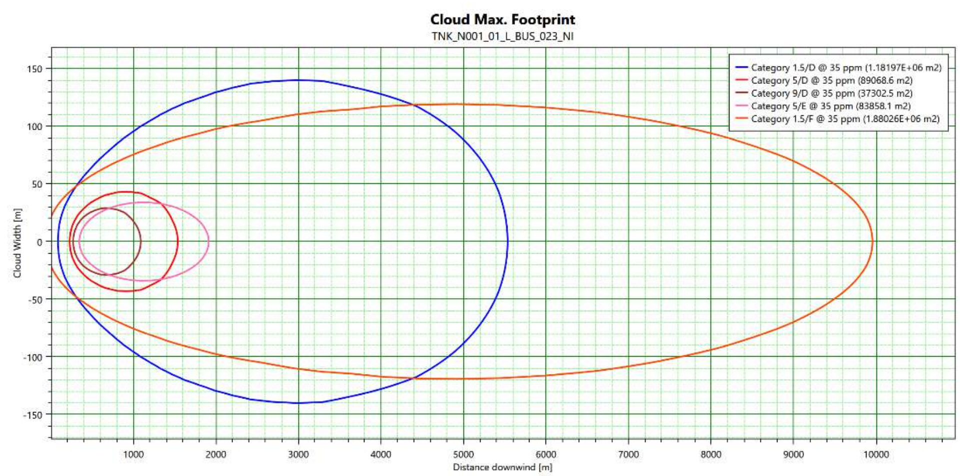
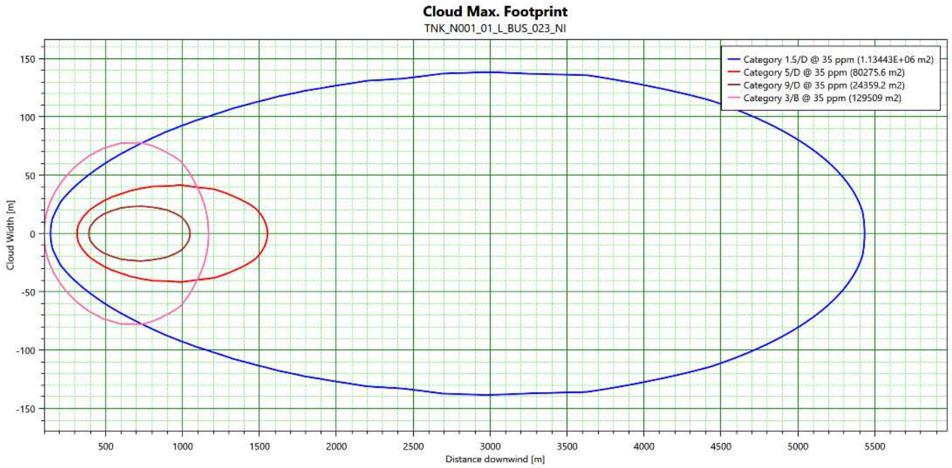
Height 0m	**Height 5m**
Height 10m	Height 20m

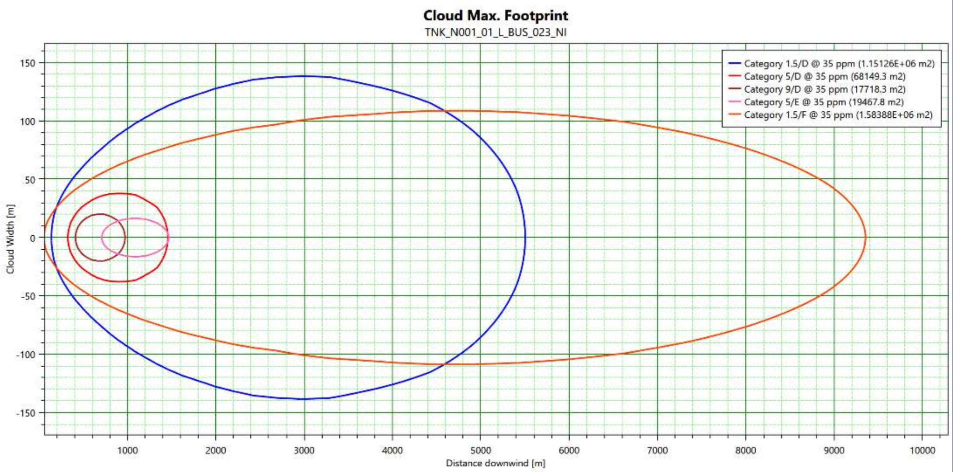






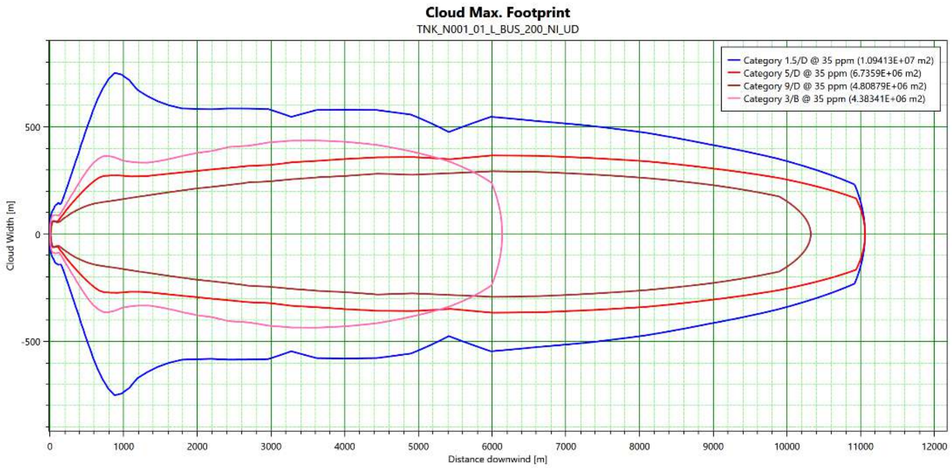


<table>
<tr><th>Height 0m</th><th>Height 5m</th></tr>
<tr><th>Height 25m</th><th>Height 180m</th></tr>
<tr><td>


</td><td>No daytime exceedances</td></tr>
<tr><td>


</td><td>No night-time exceedances</td></tr>
</table>

Table A25 Results for Tanker, 200mm hole – Comparison with the Short-Term Exposure Limit

<table>
<tr><th>Height 0m</th><th>Height 5m</th></tr>
<tr><td>


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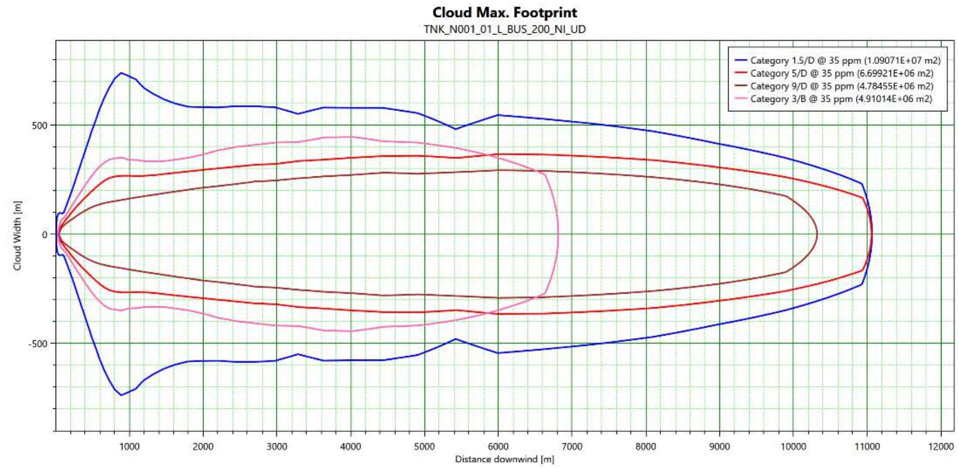

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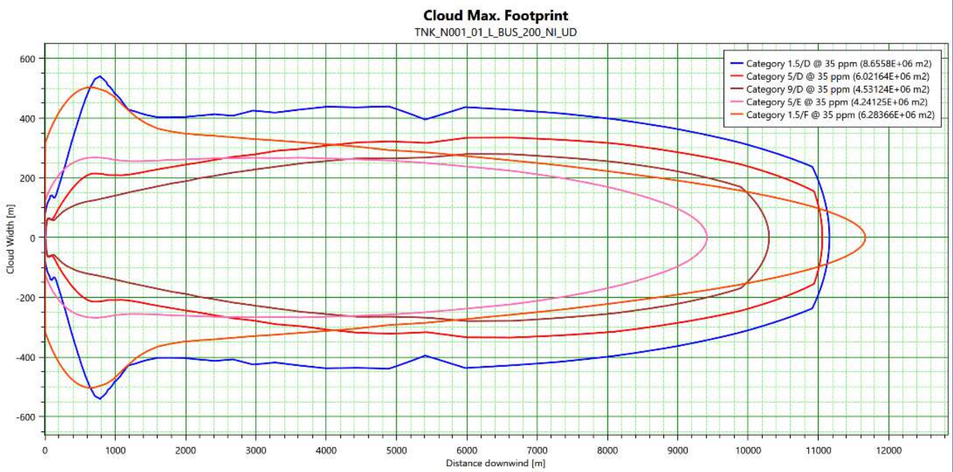
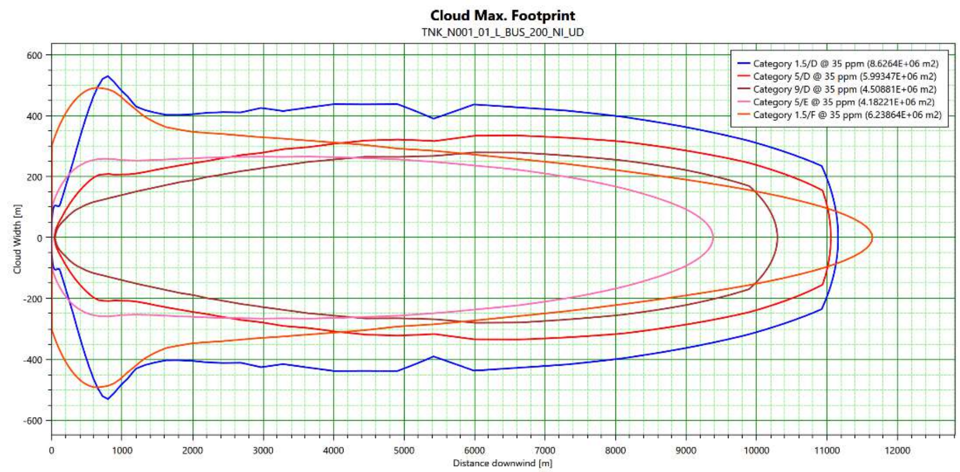


</td><td>


</td></tr>
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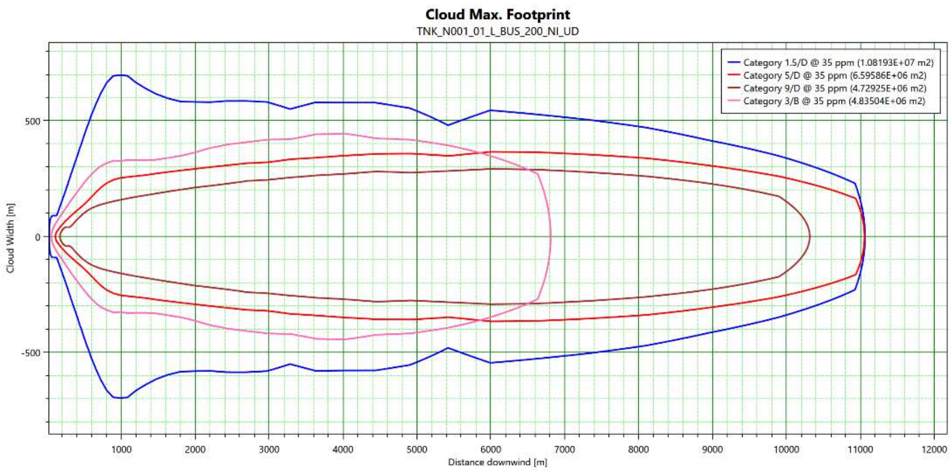
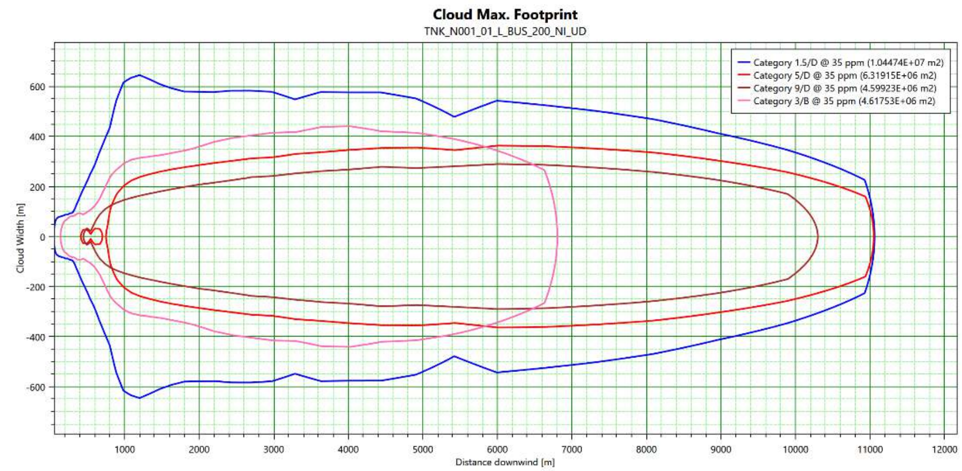
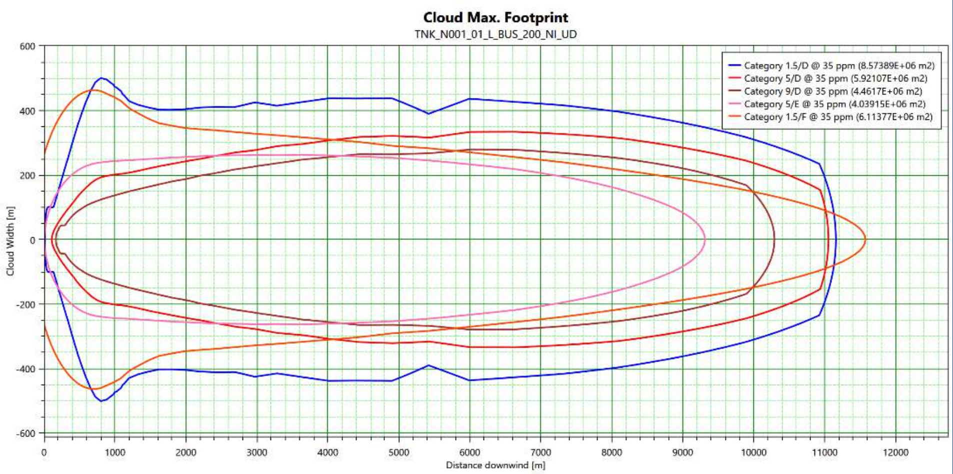
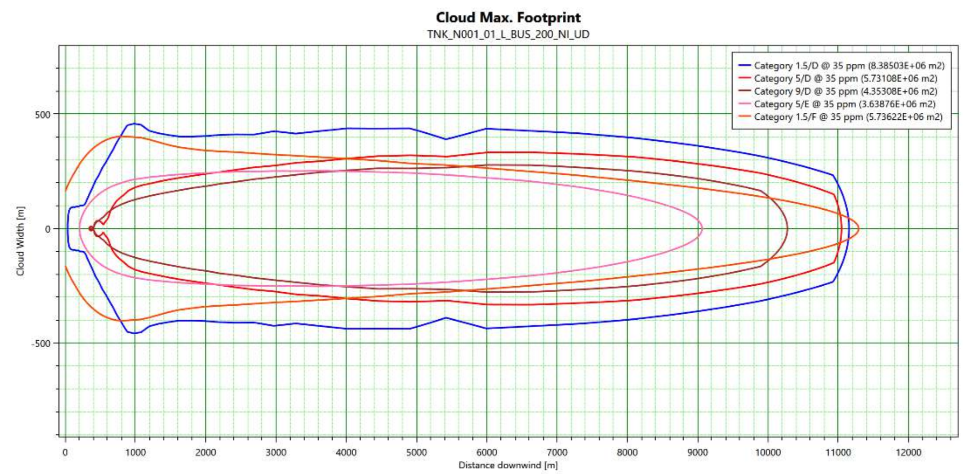
Height 0m	**Height 5m**
Height 10m	Height 20m



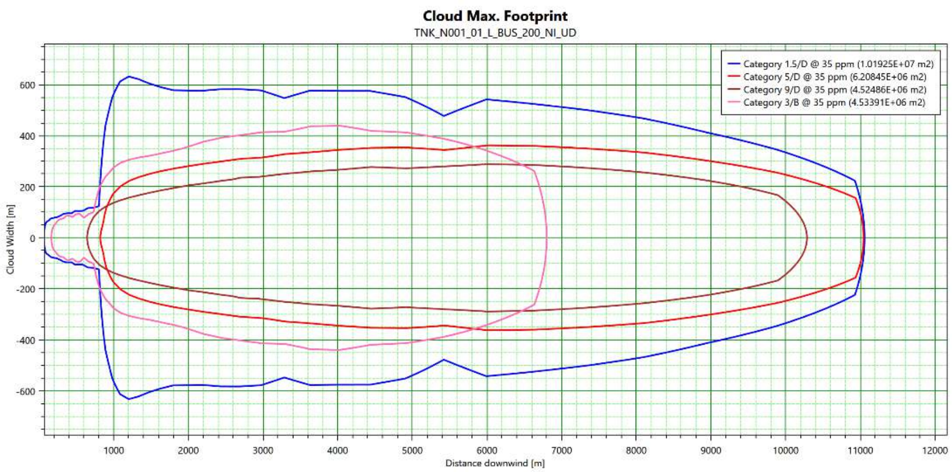




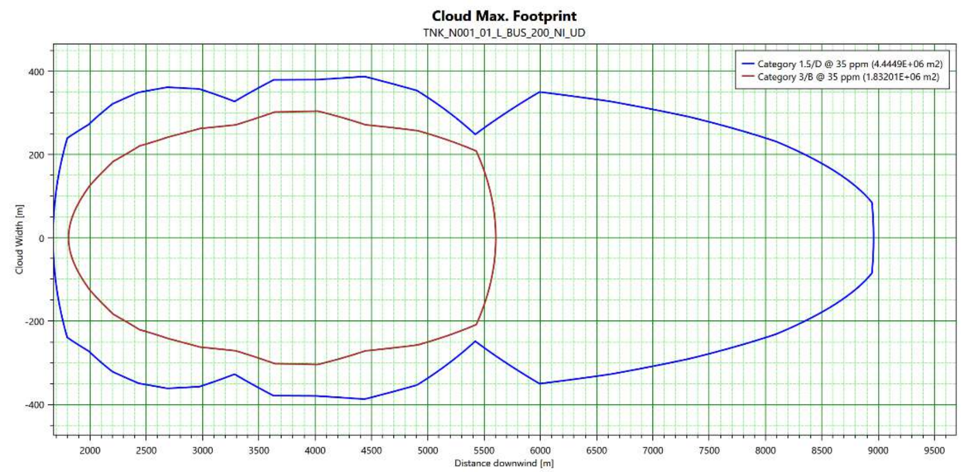


Height 0m	Height 5m
Height 25m	**Height 180m**

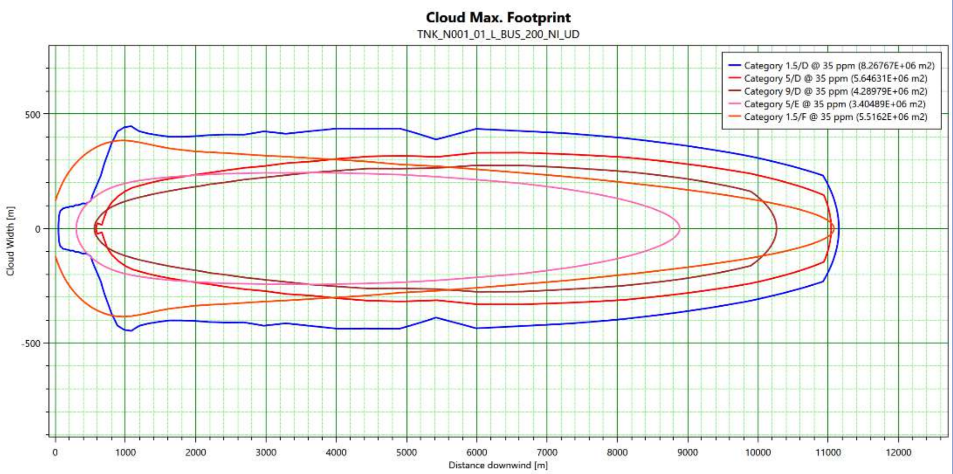
Height 0m



Height 5m



Height 25m



Height 180m

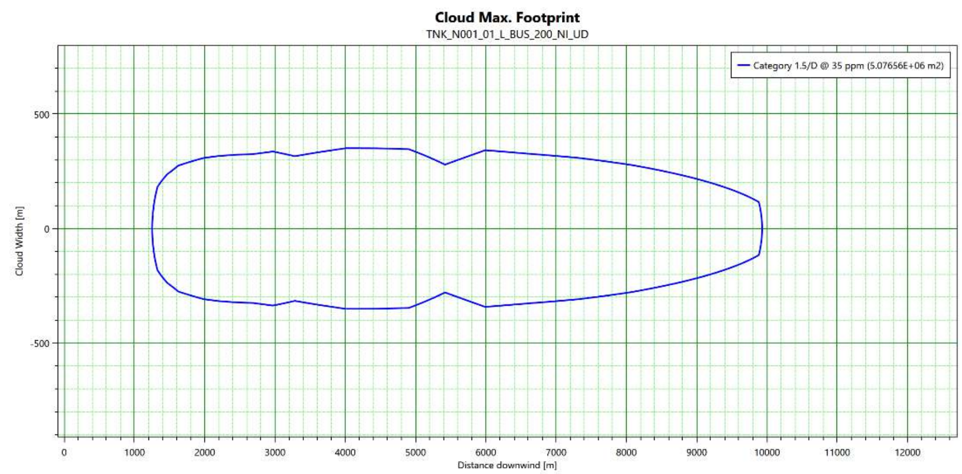


Table A26 Results for Bulker, 2mm hole – Comparison with the -Long Term Exposure Limit

<table>
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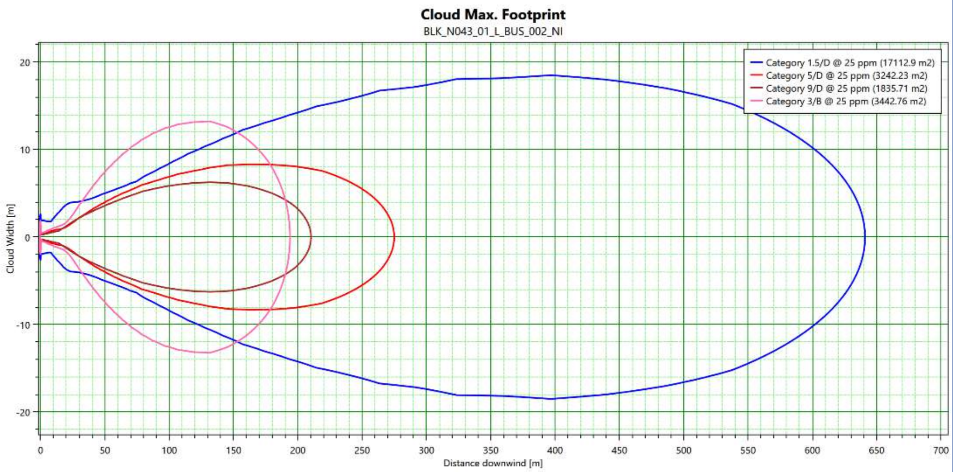
<tr><td>


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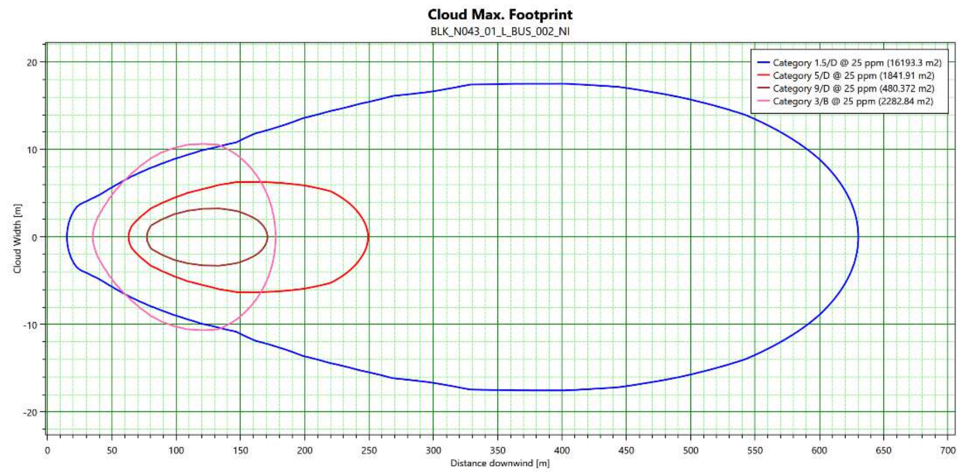

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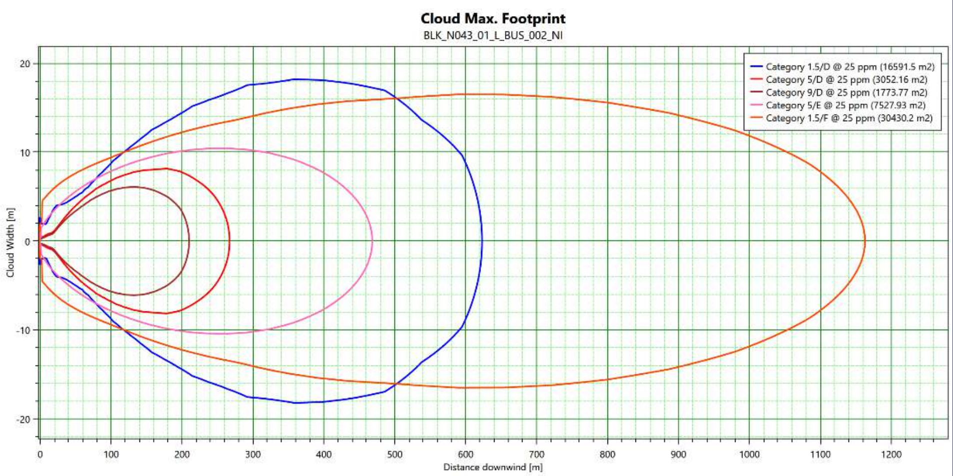

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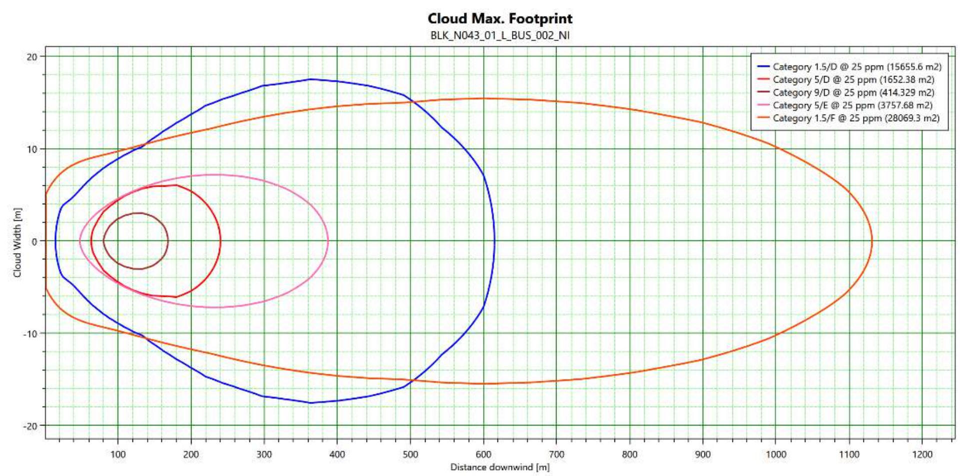

</td></tr>
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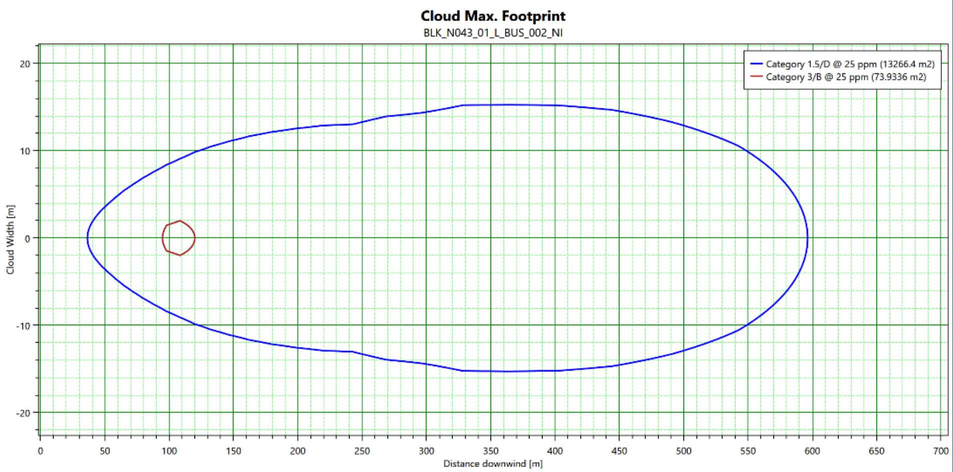
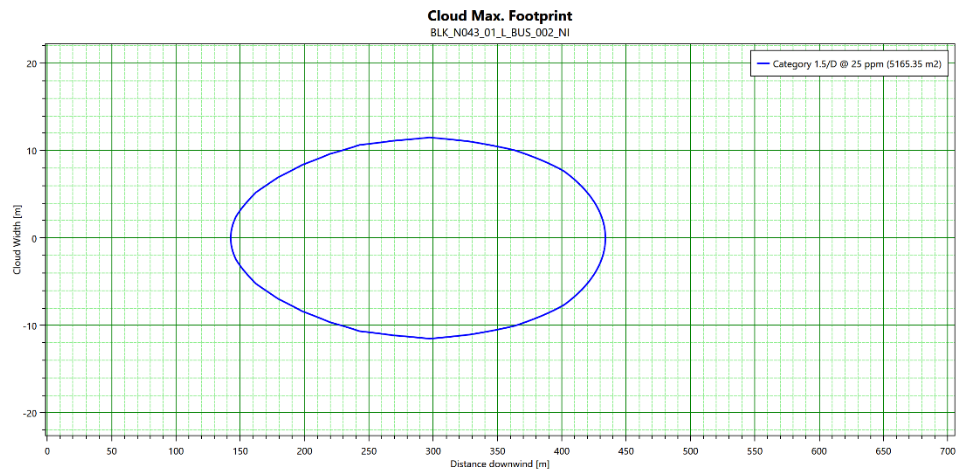
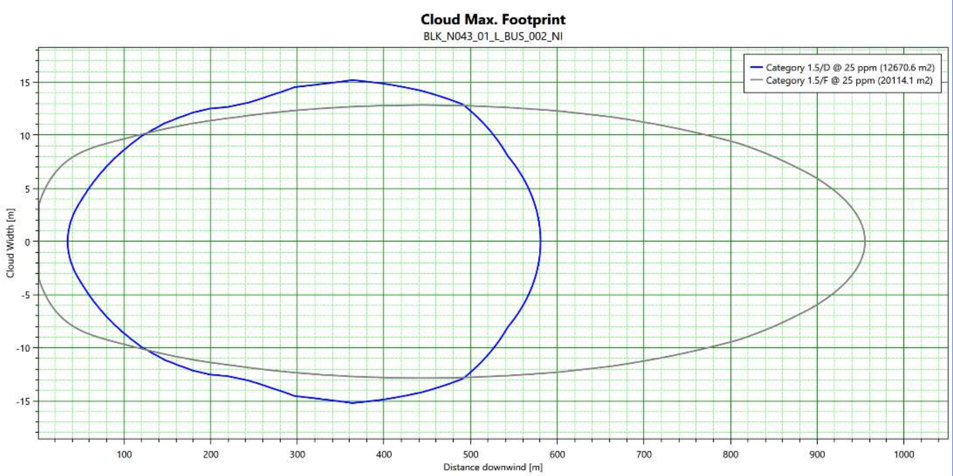
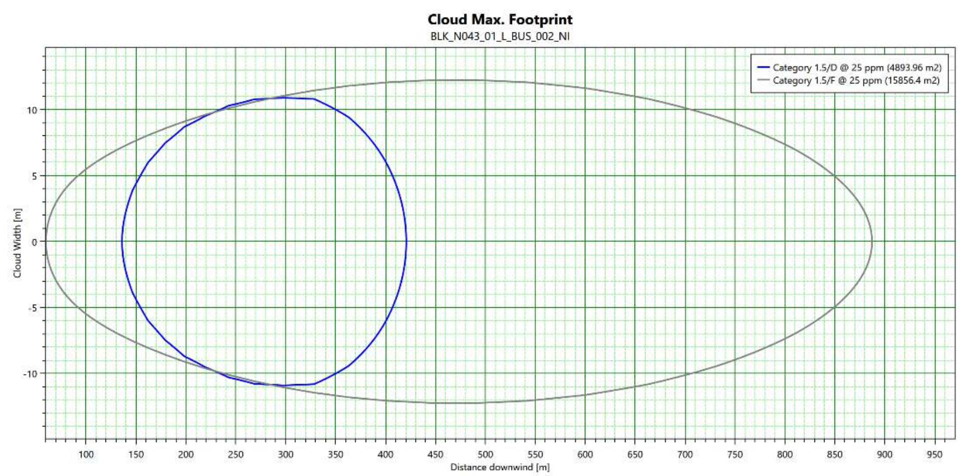
Height 0m Height 10m	**Height 5m** Height 20m
 	
 	

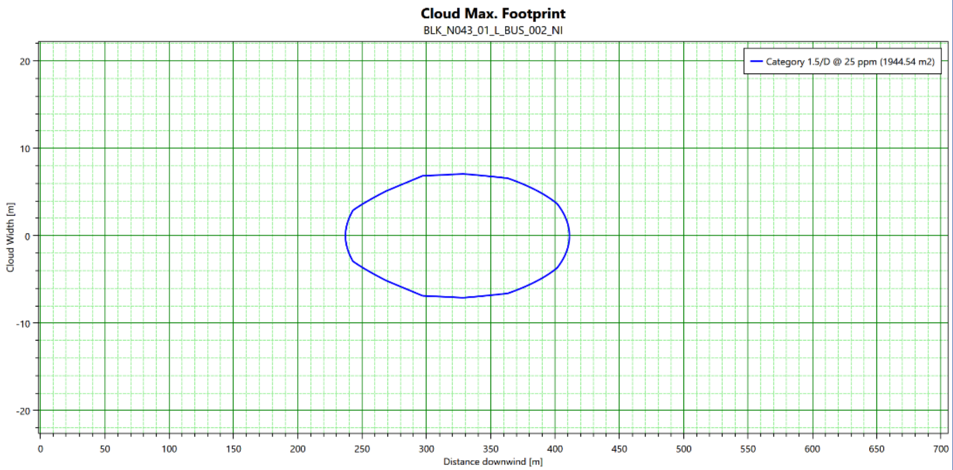
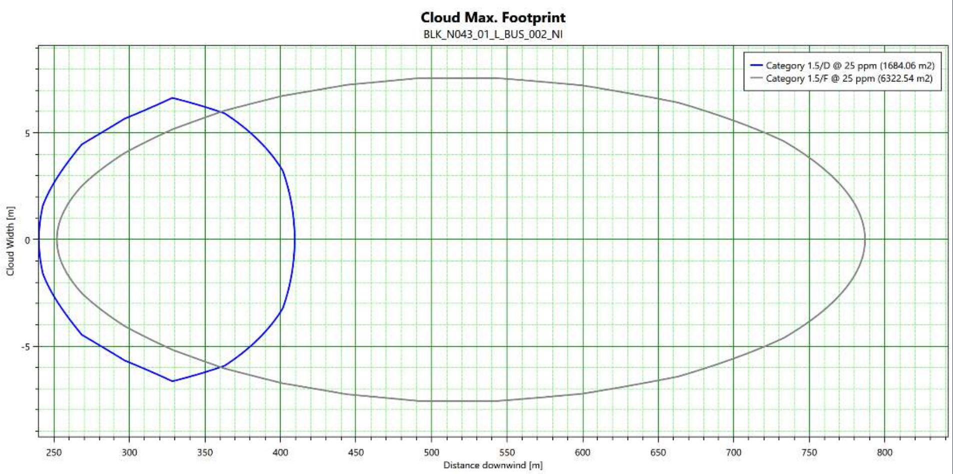
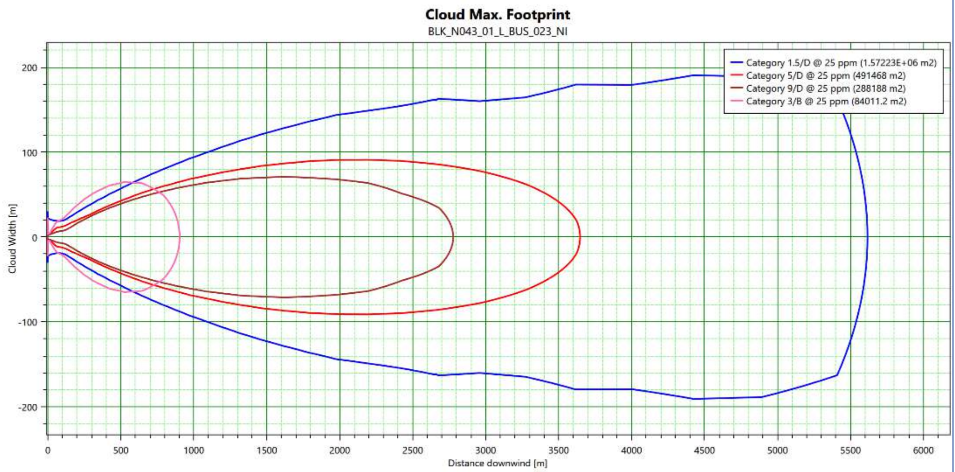
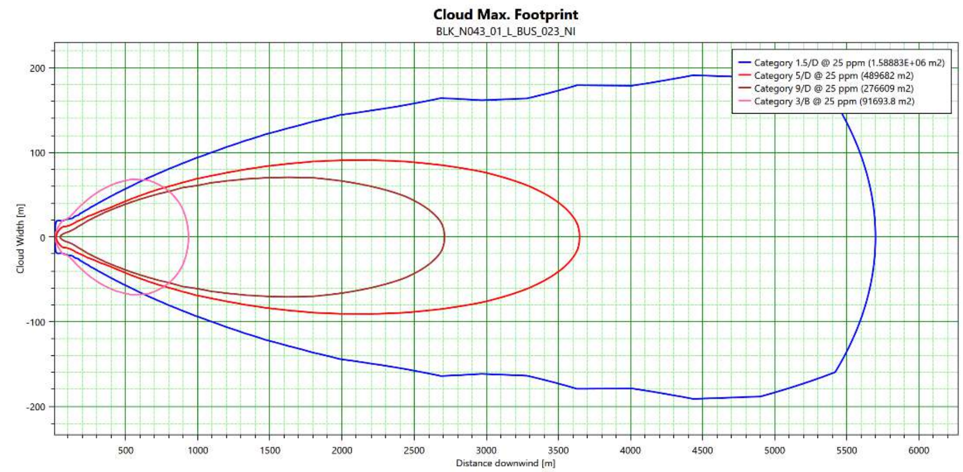
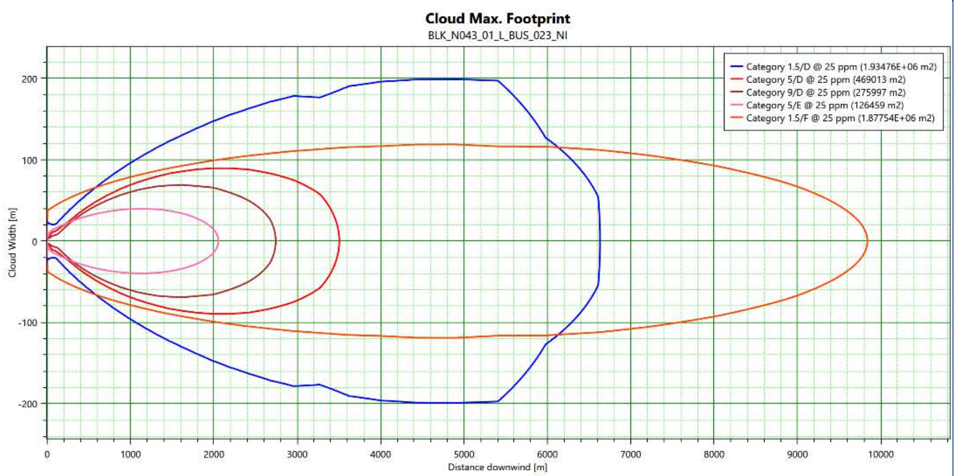
Height 0m	**Height 5m**
Height 25m	Height 180m
	No daytime exceedances
	No night-time exceedances

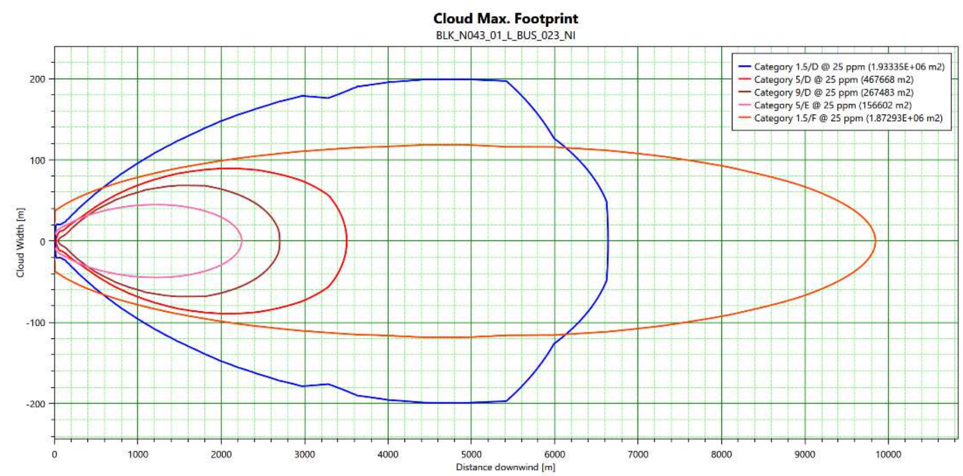
Table A27 Results for Bulker, 23mm hole – Comparison with the Long-Term Exposure Limit

Height 0m	Height 5m

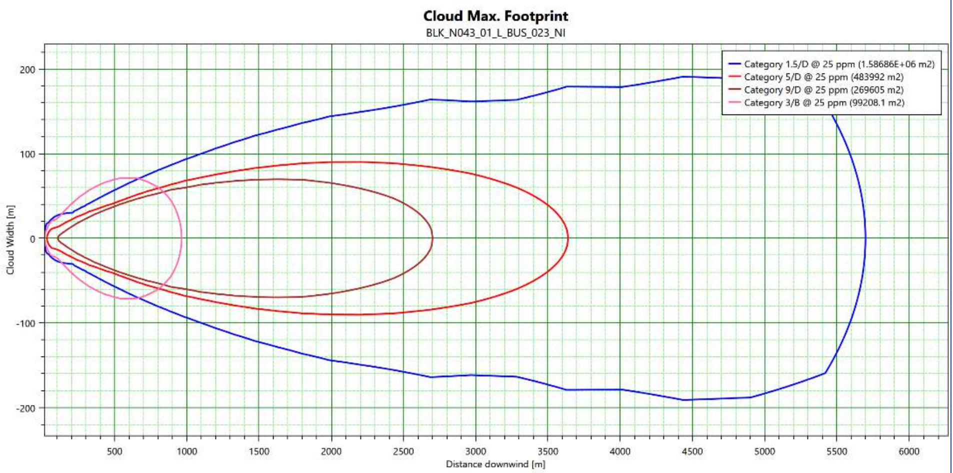


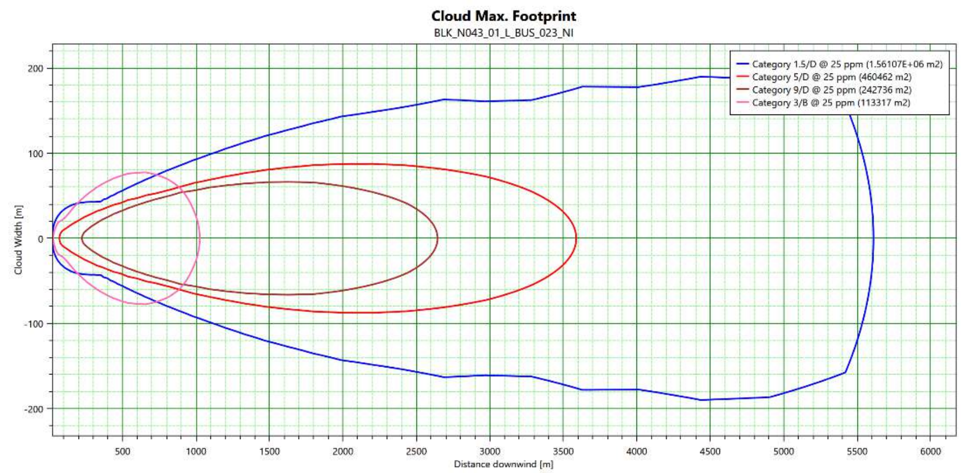


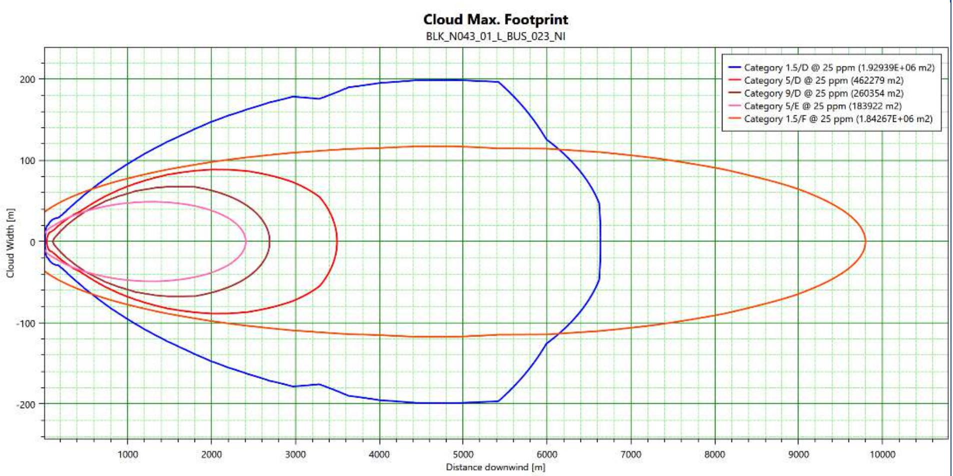


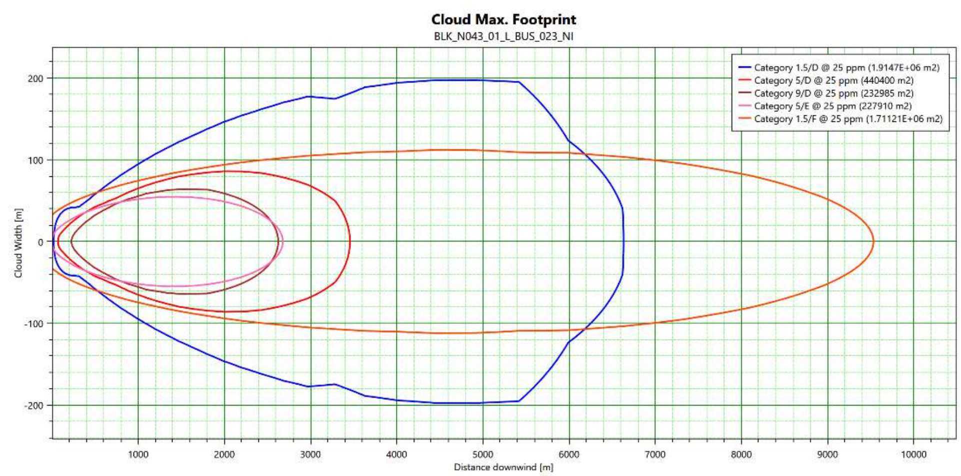


Height 0m Height 10m	**Height 5m** Height 20m

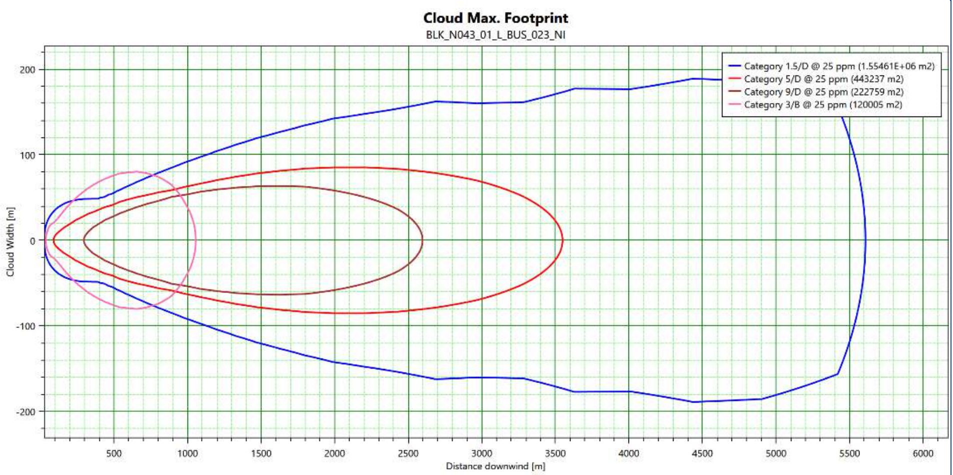


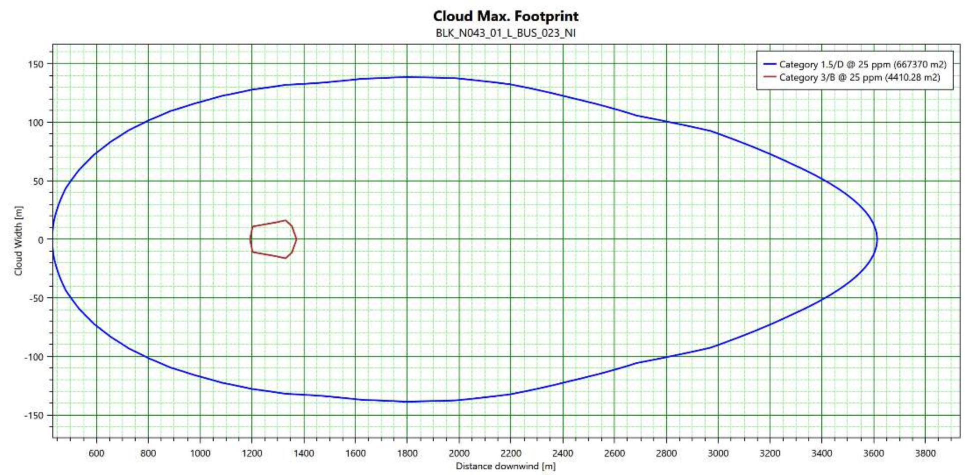


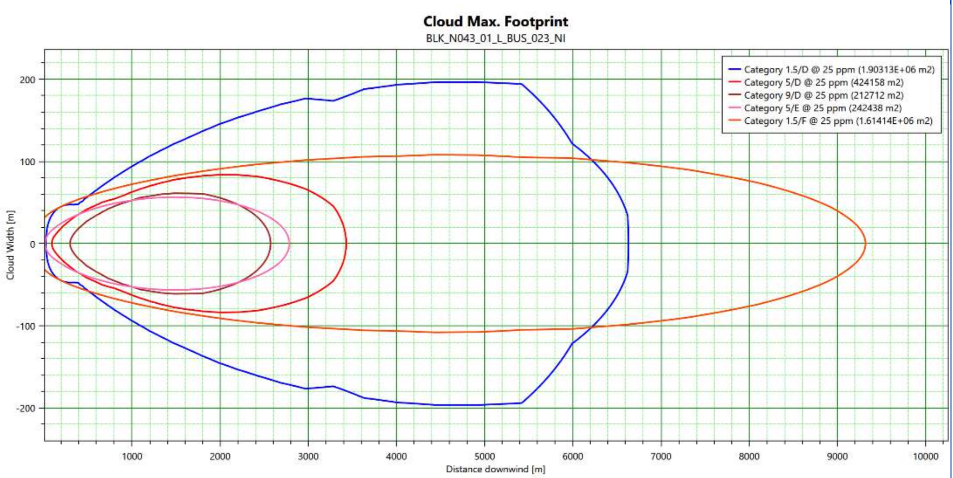




Height 0m	**Height 5m**
Height 25m	Height 180m







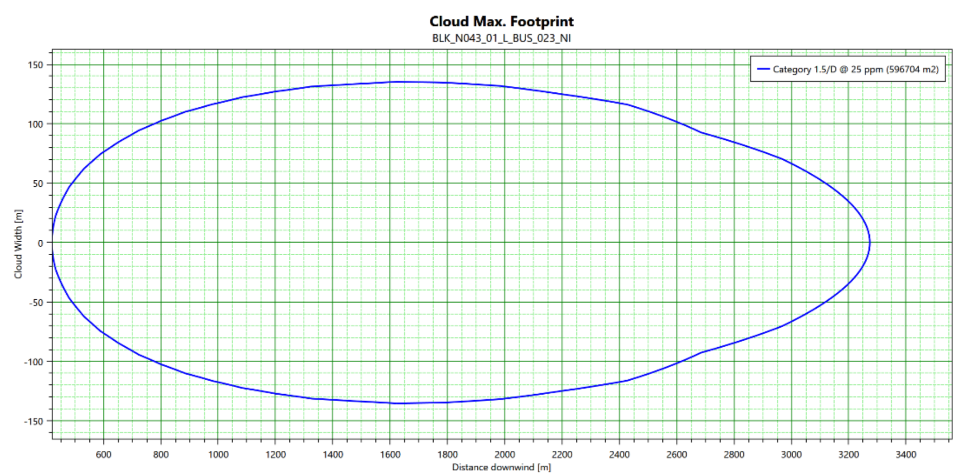


Table A28 Results for Bulker, 200mm hole – Comparison with the Long-Term Exposure Limit

<table>
<tr><th>Height 0m</th><th>Height 5m</th></tr>
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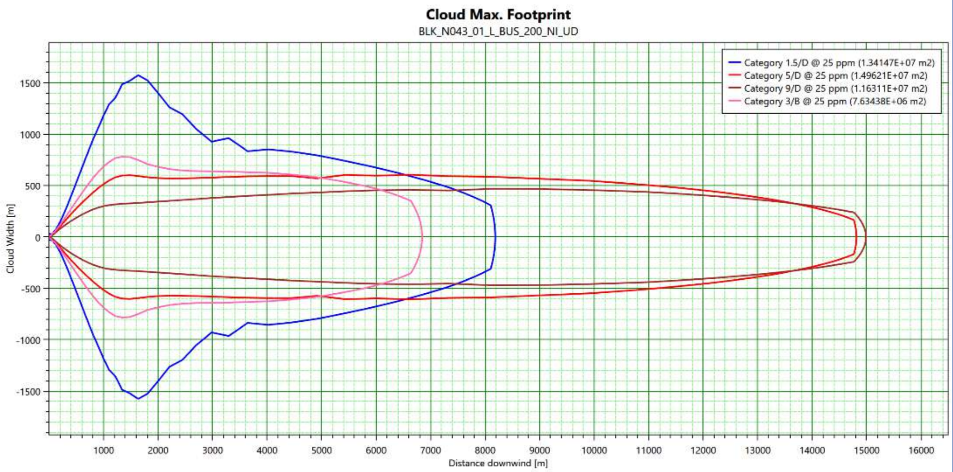

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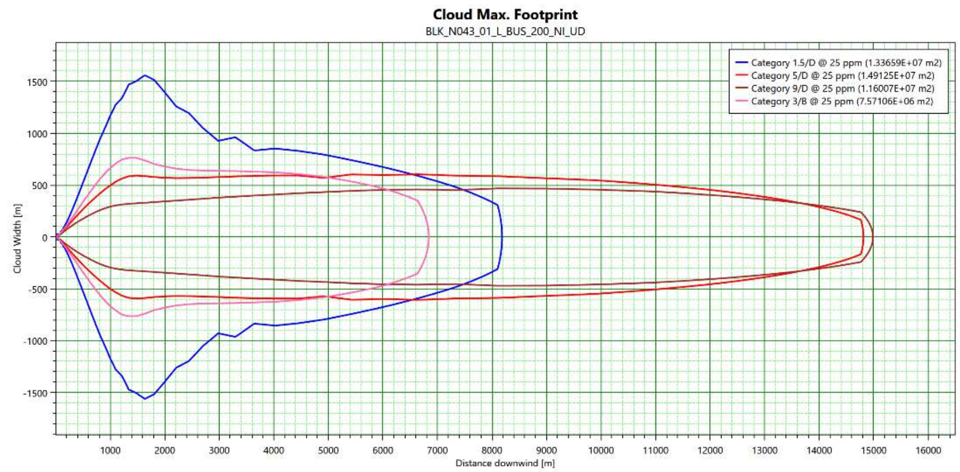

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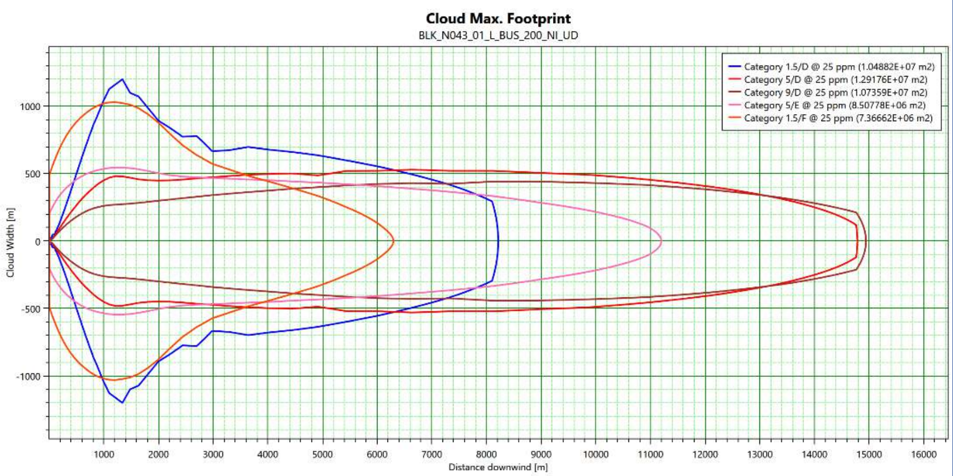

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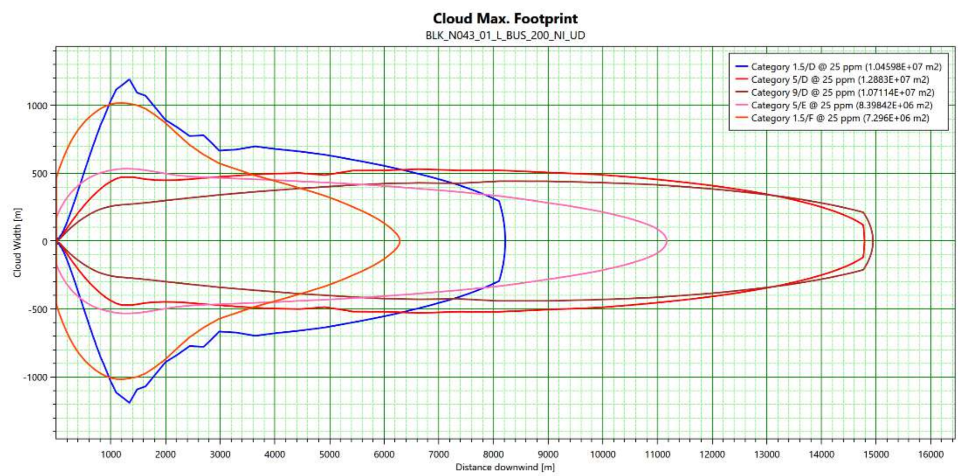

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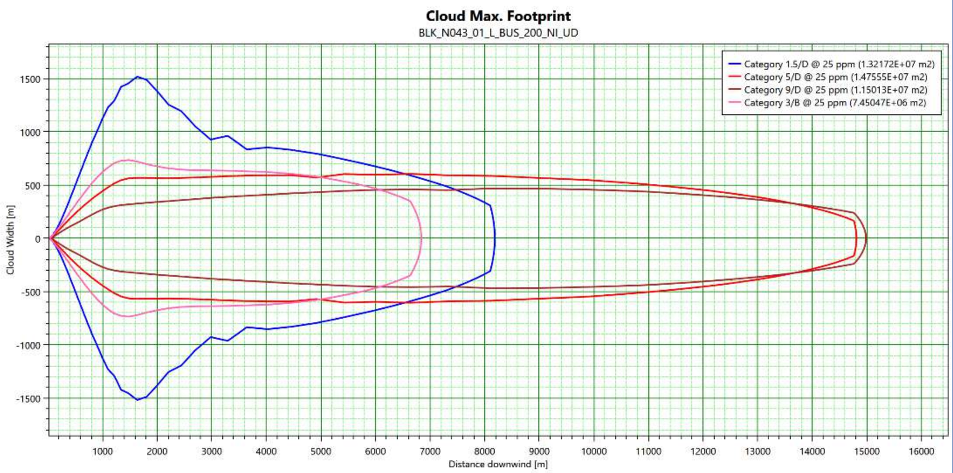
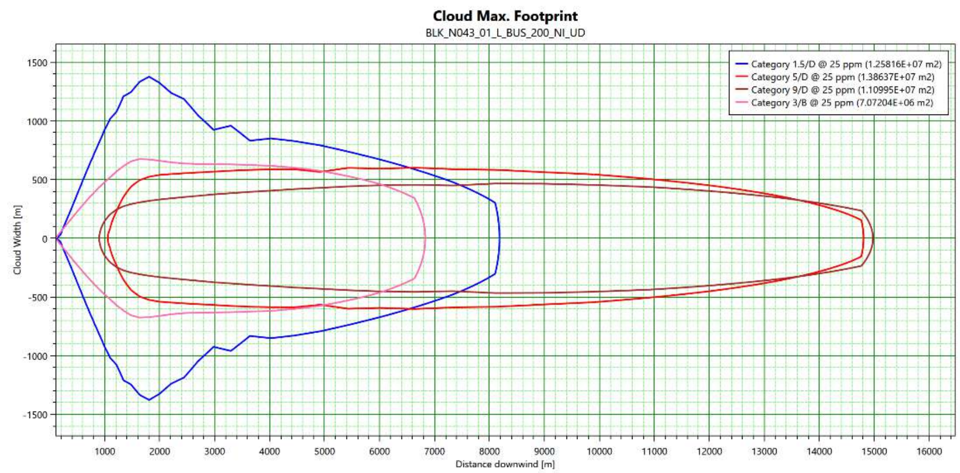
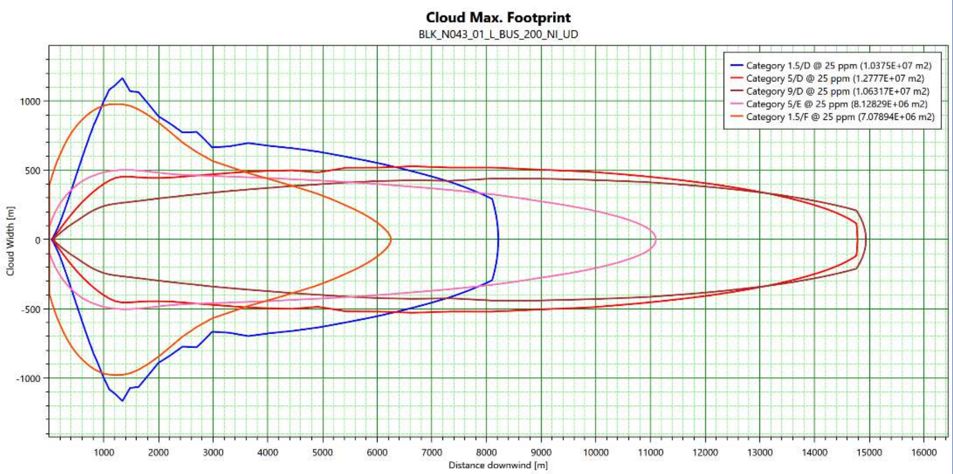
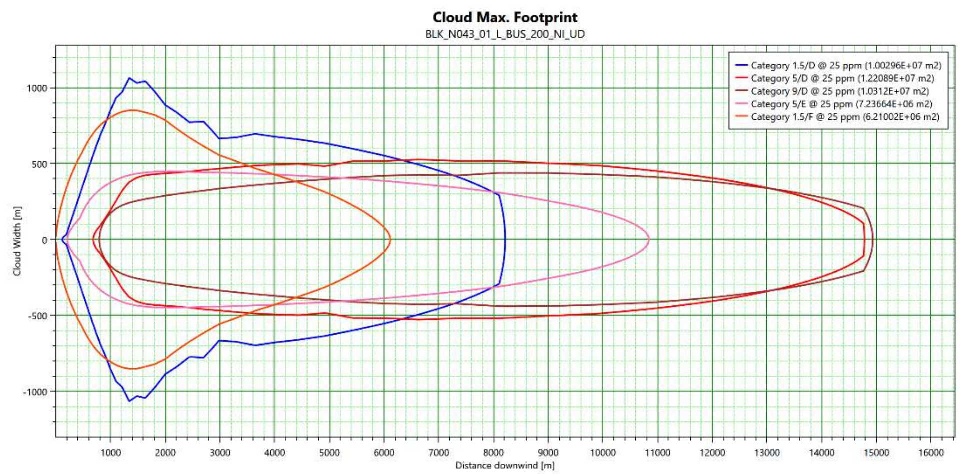
Height 0m	**Height 5m**
Height 10m	Height 20m

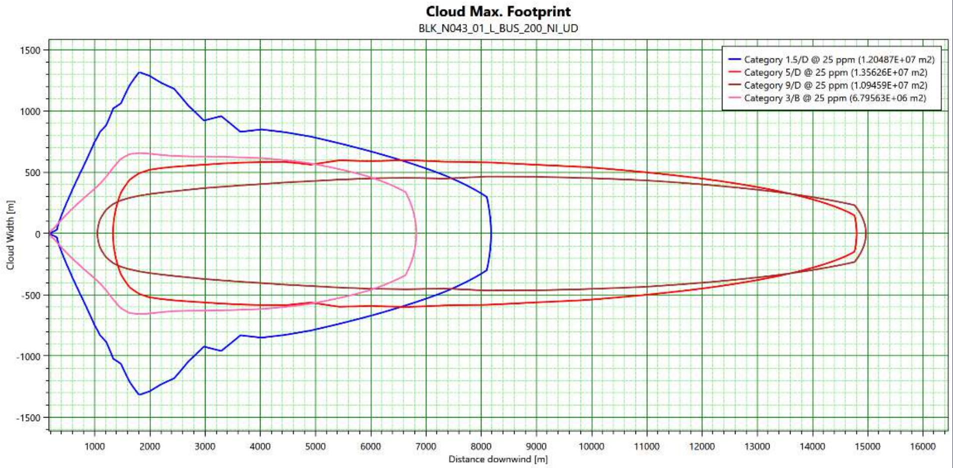


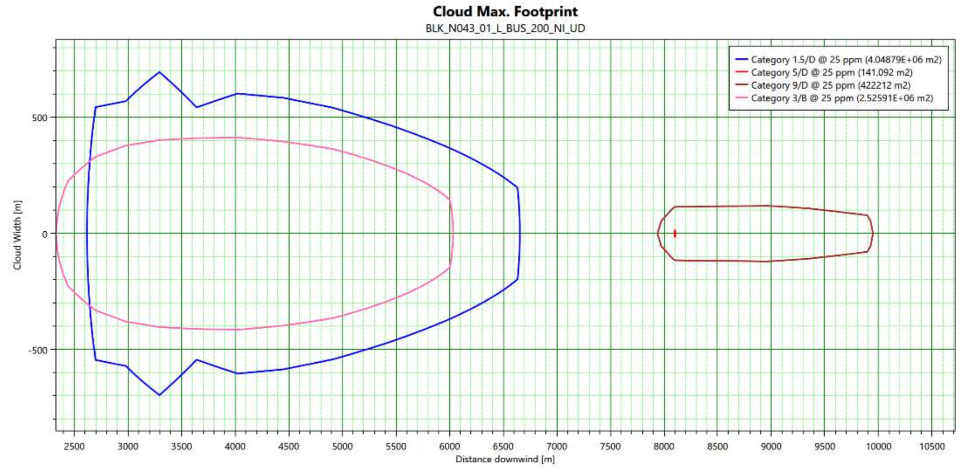


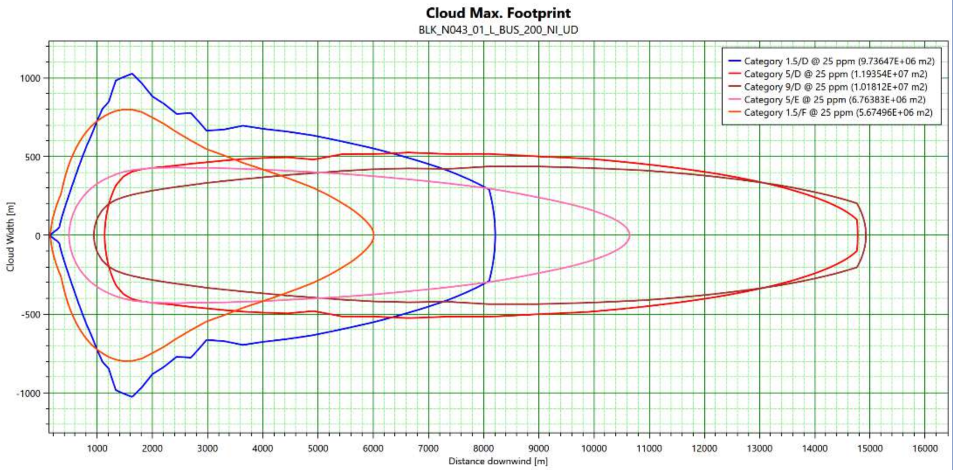




Height 0m	**Height 5m**
Height 25m	Height 180m







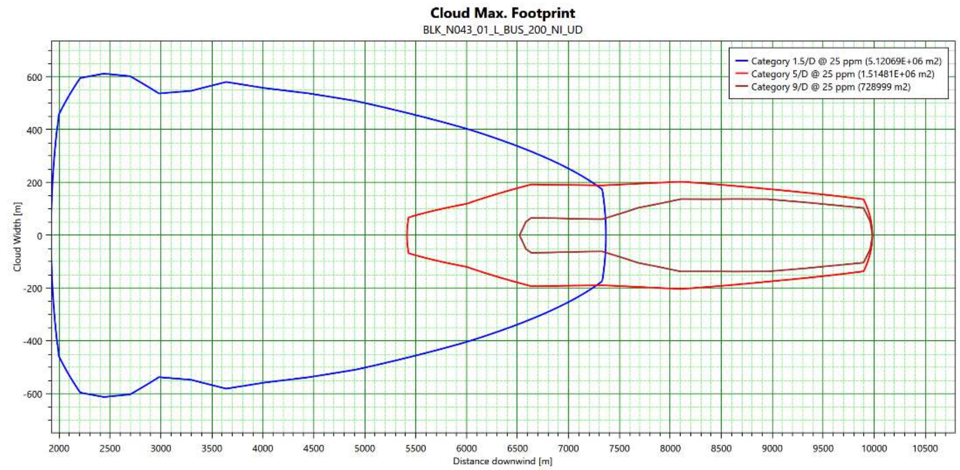
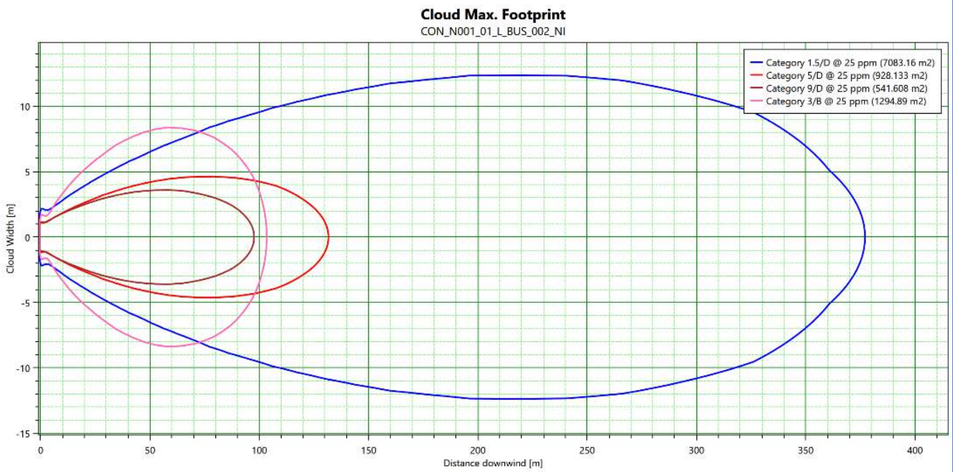
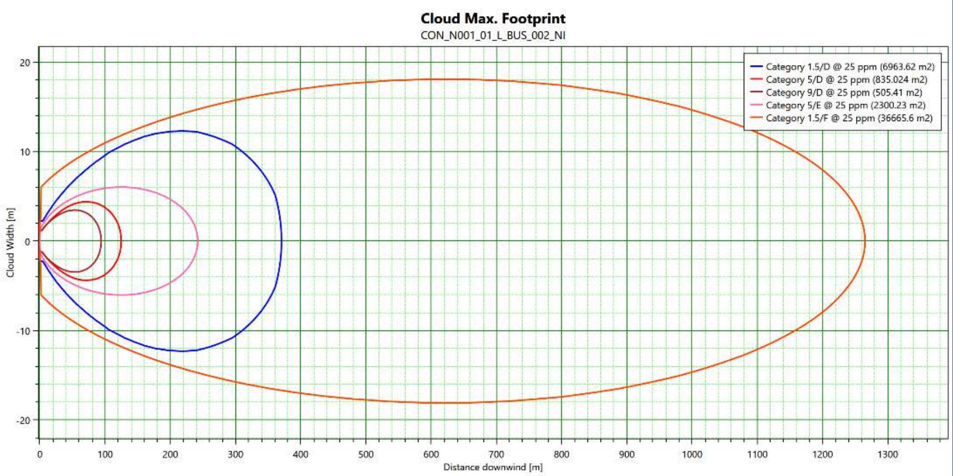


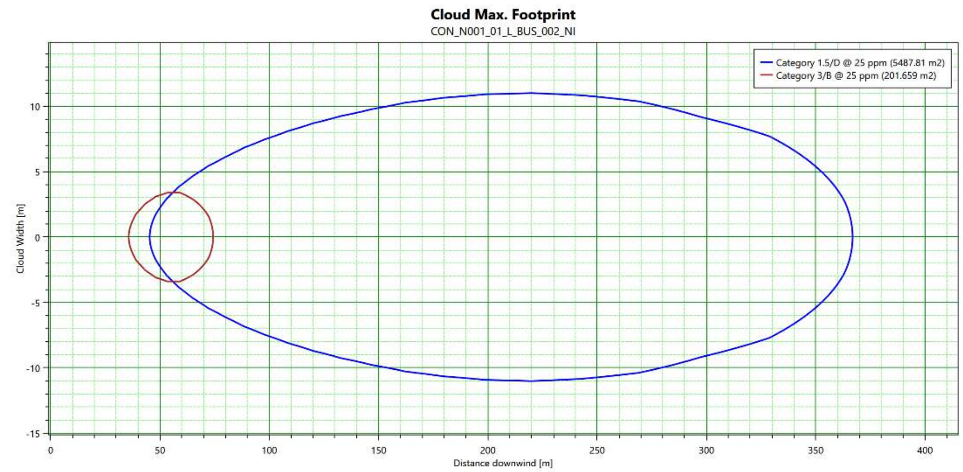
Table A29 Results for Containership, 2mm hole – Comparison with the Long-Term Exposure Limit

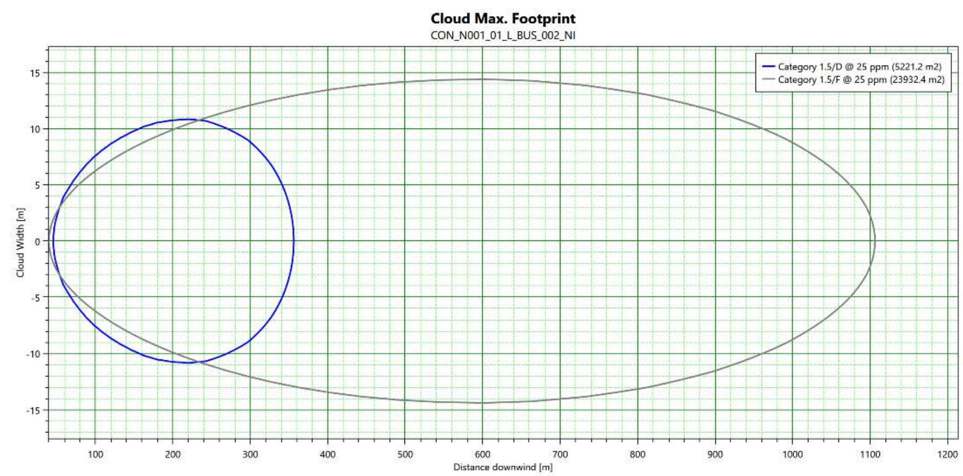
Height 0m

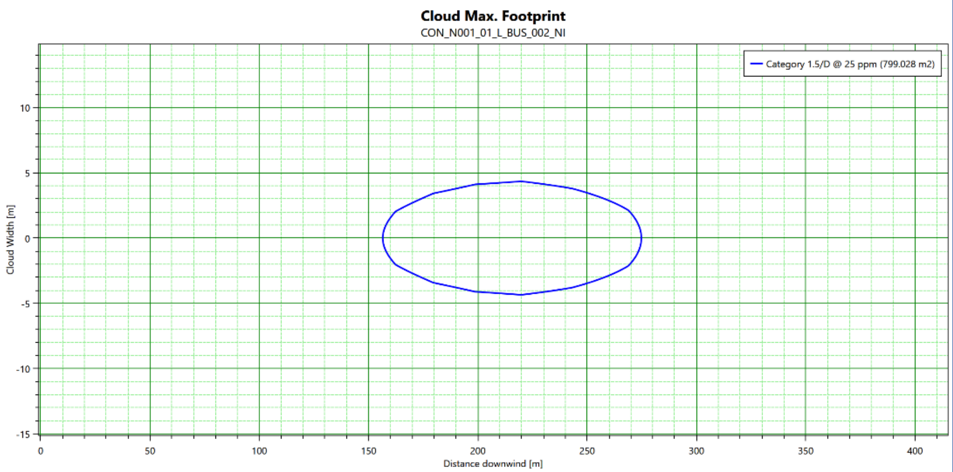
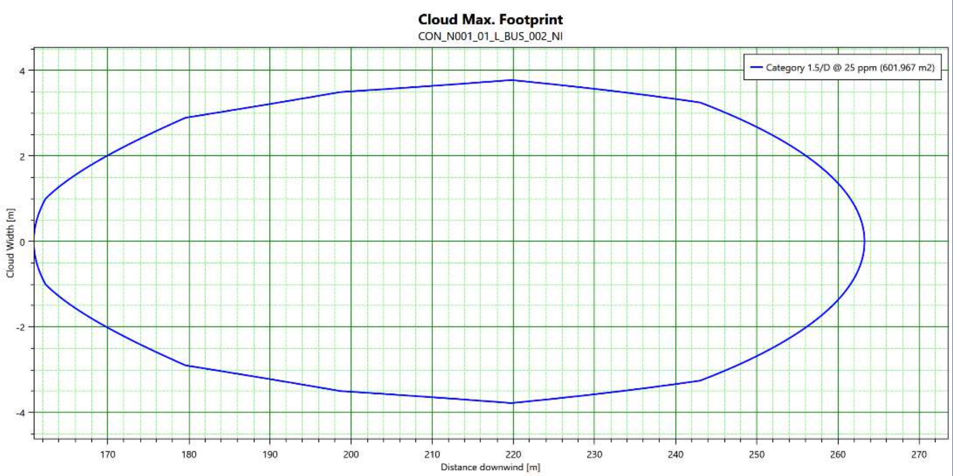




Height 5m





Height 0m Height 10m	**Height 5m** Height 20m
	No daytime exceedances
	No night-time exceedances
Height 25m	Height 180m
No daytime exceedances	No daytime exceedances

Height 0m	Height 5m
No night-time exceedances	No night-time exceedances

Table A30 Results for Containership, 23mm hole – Comparison with the Long-Term Exposure Limit

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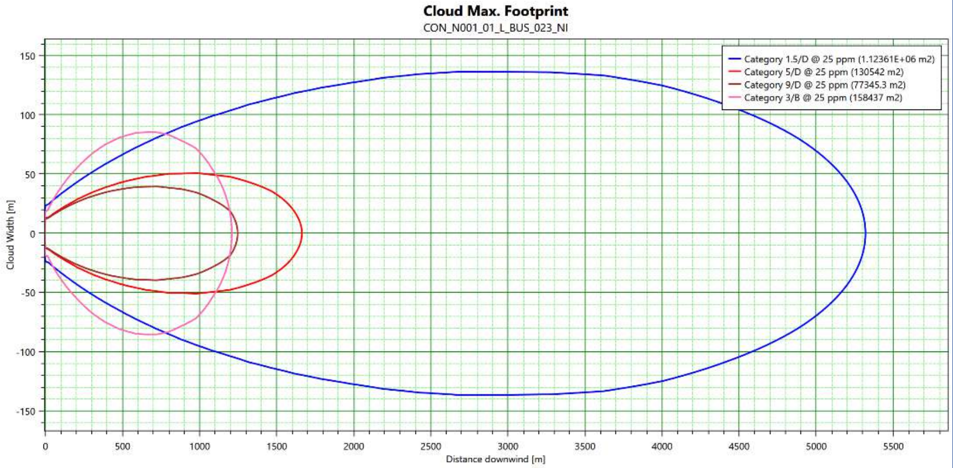

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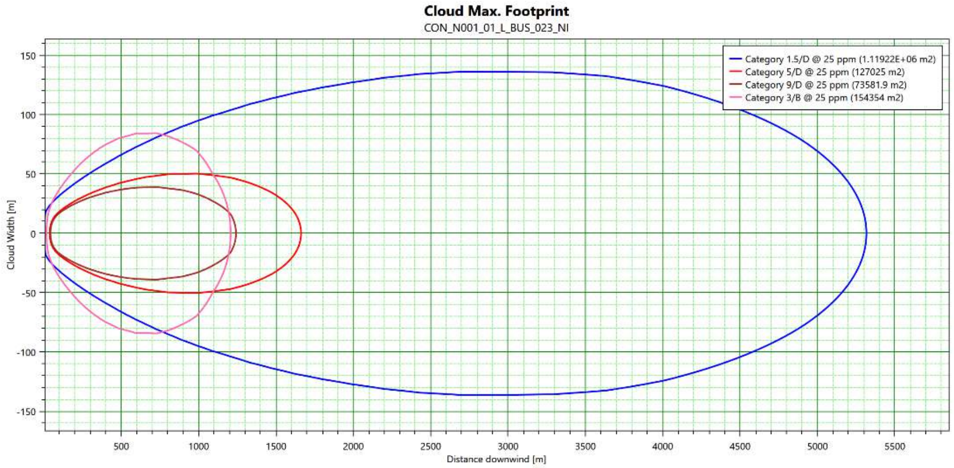

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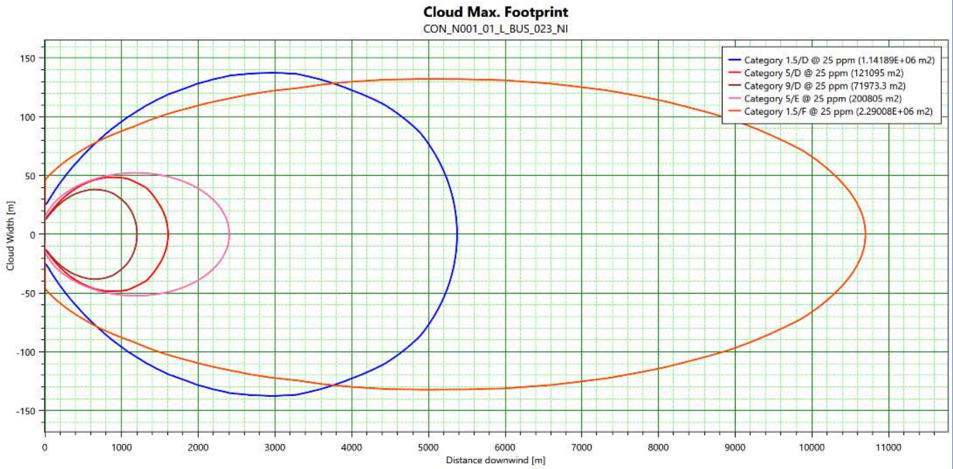

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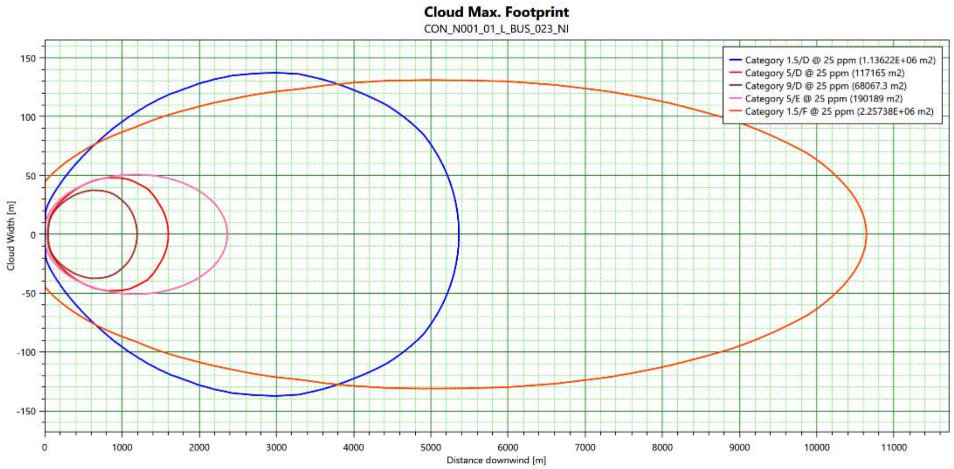

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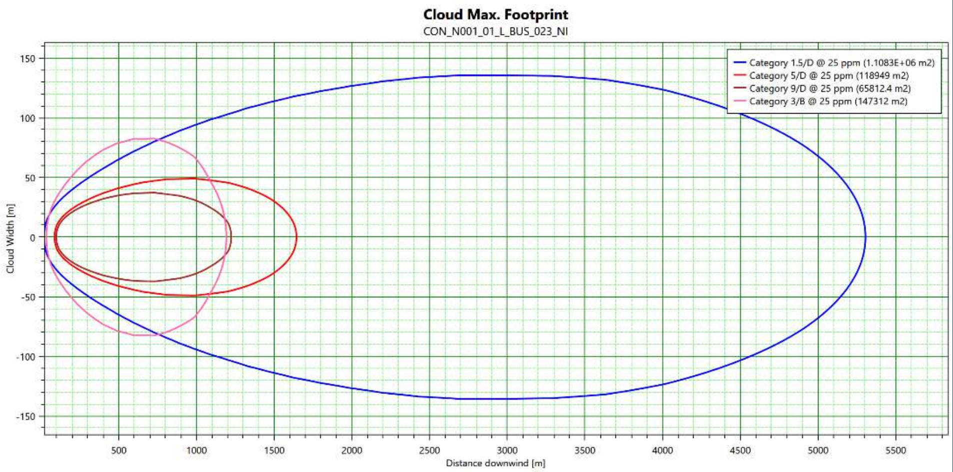
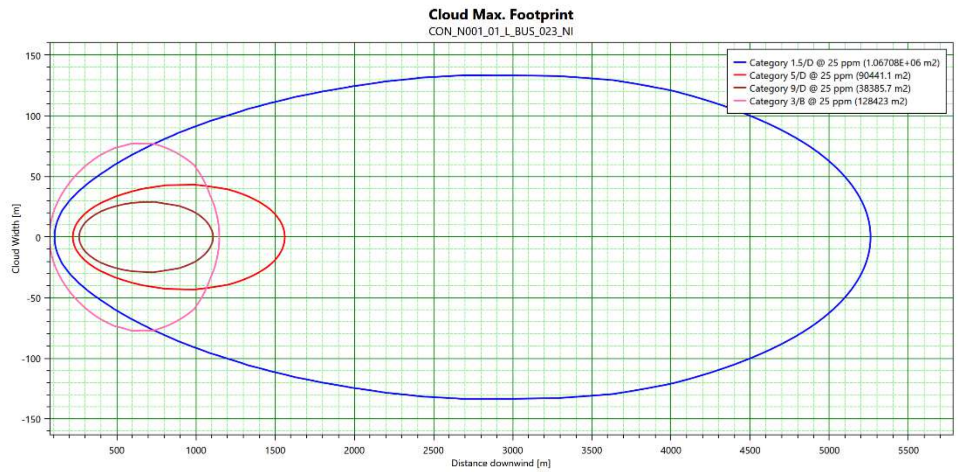
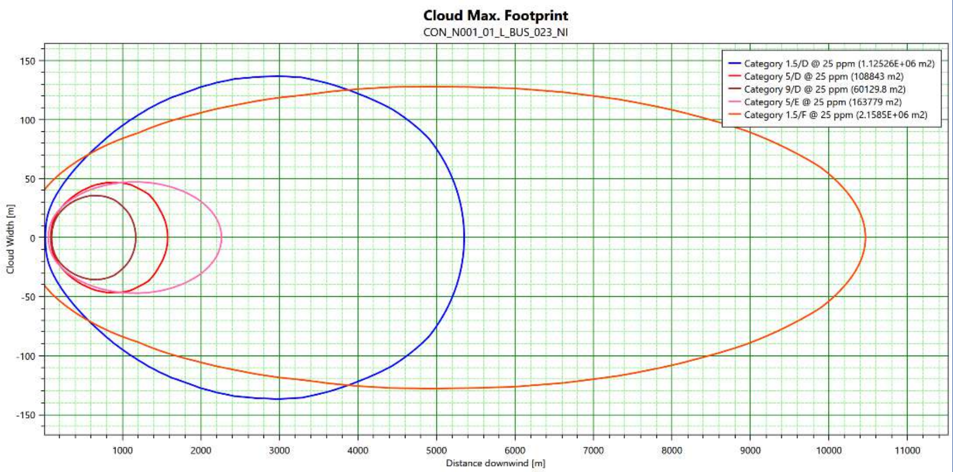
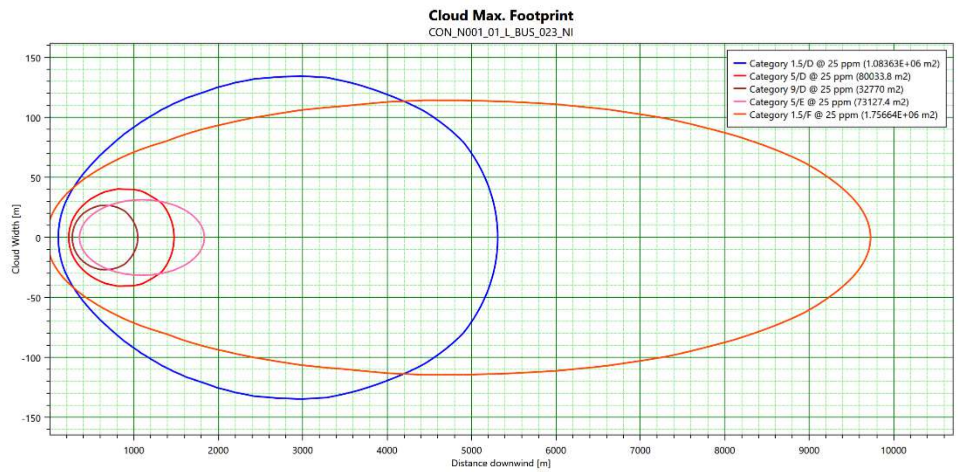
Height 0m	**Height 5m**
Height 10m	Height 20m









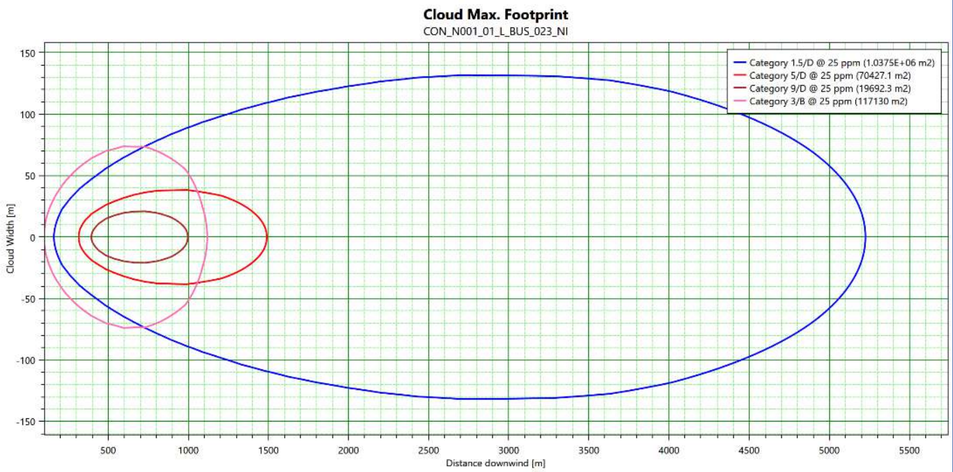
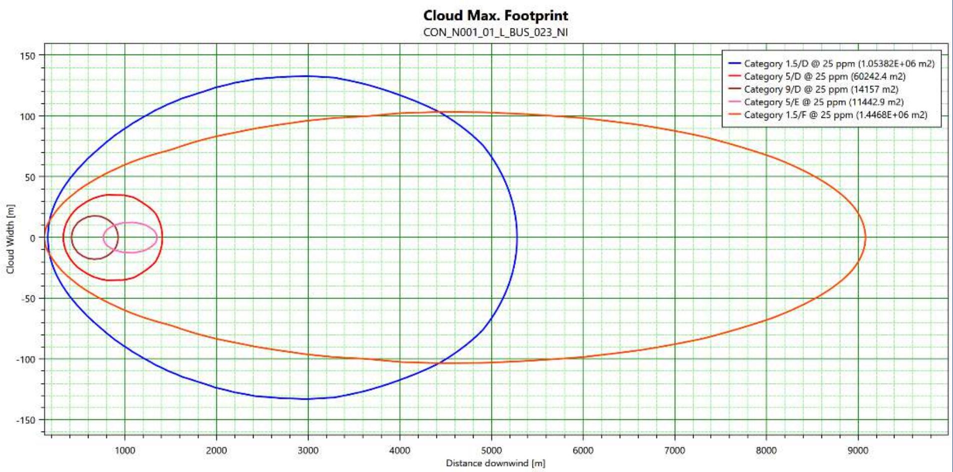
<table>
<tr><th>Height 0m</th><th>Height 5m</th></tr>
<tr><td>Height 25m</td><td>Height 180m</td></tr>
<tr><td>
</td><td>No daytime exceedances</td></tr>
<tr><td>
</td><td>No night-time exceedances</td></tr>
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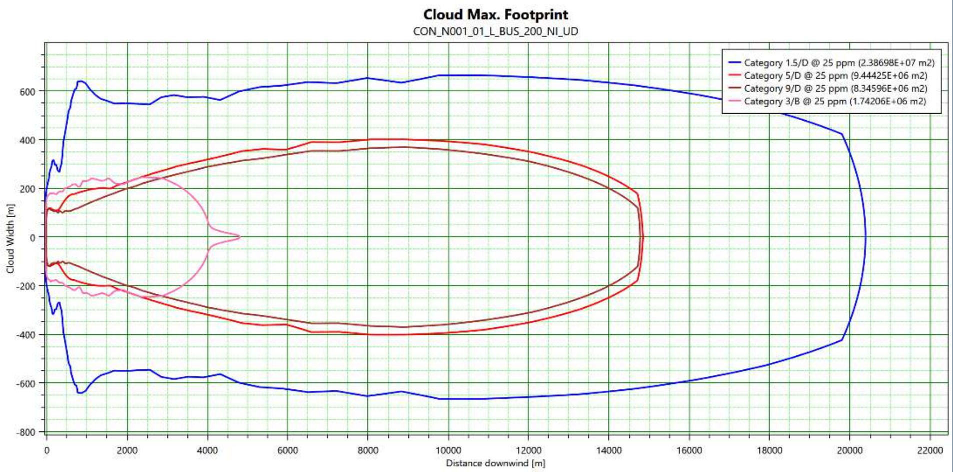
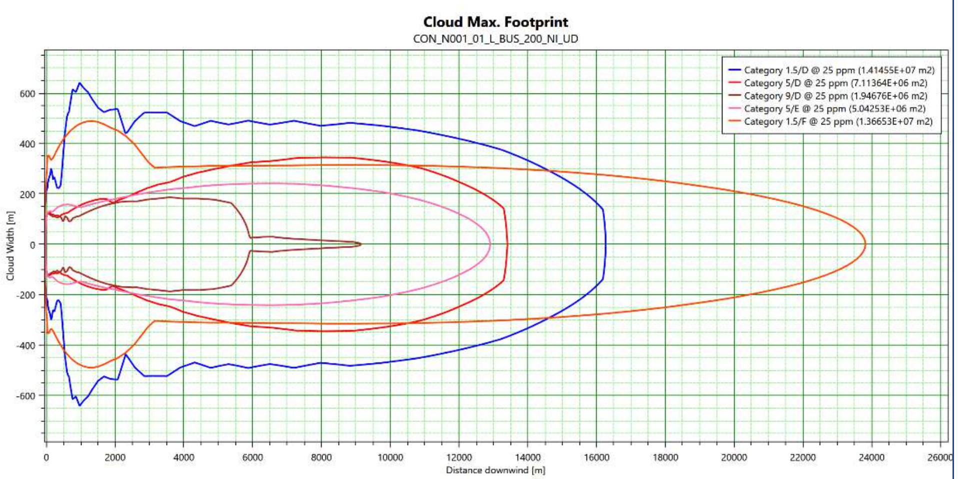
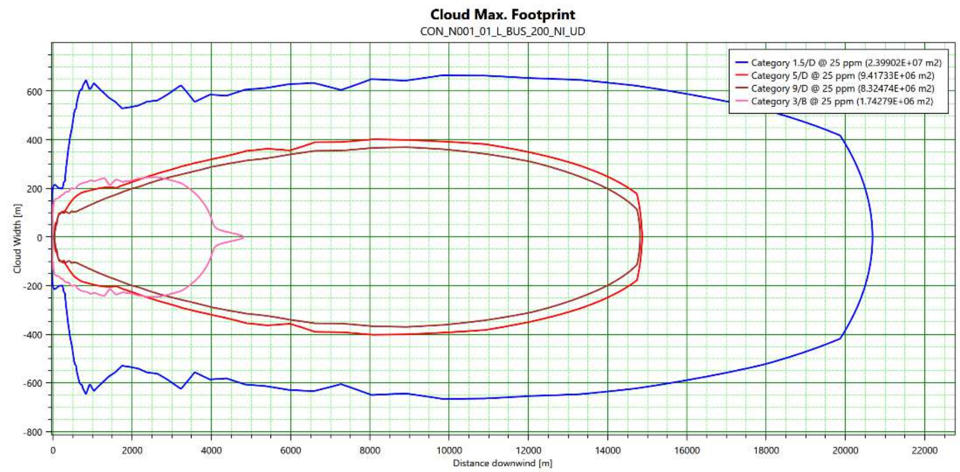
Table A31 Results for Containership, 200mm hole – Comparison with the Long-Term Exposure Limit

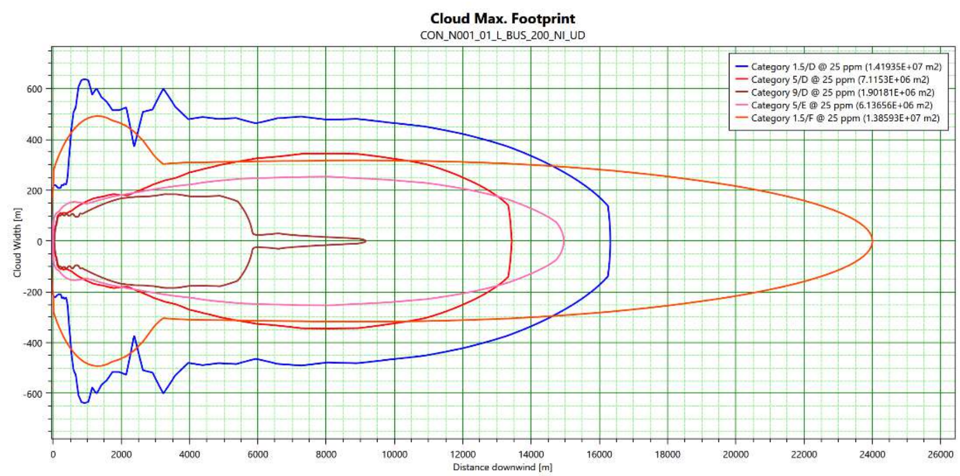
Height 0m



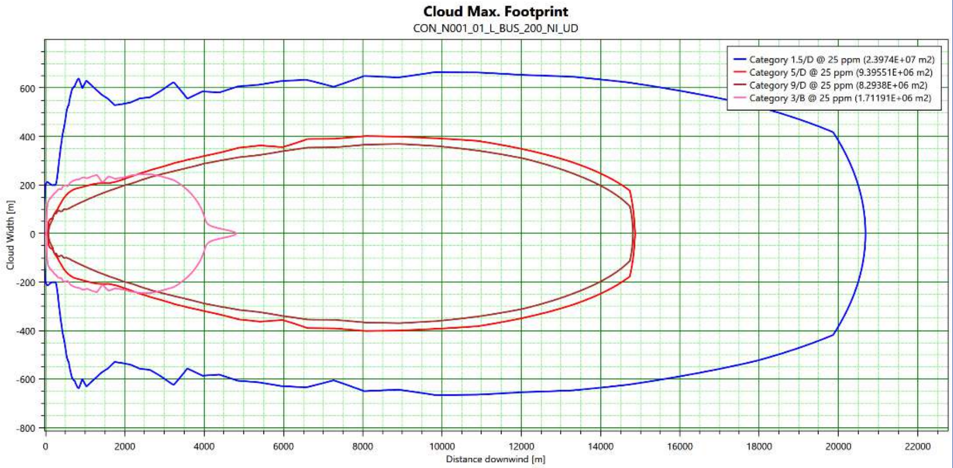


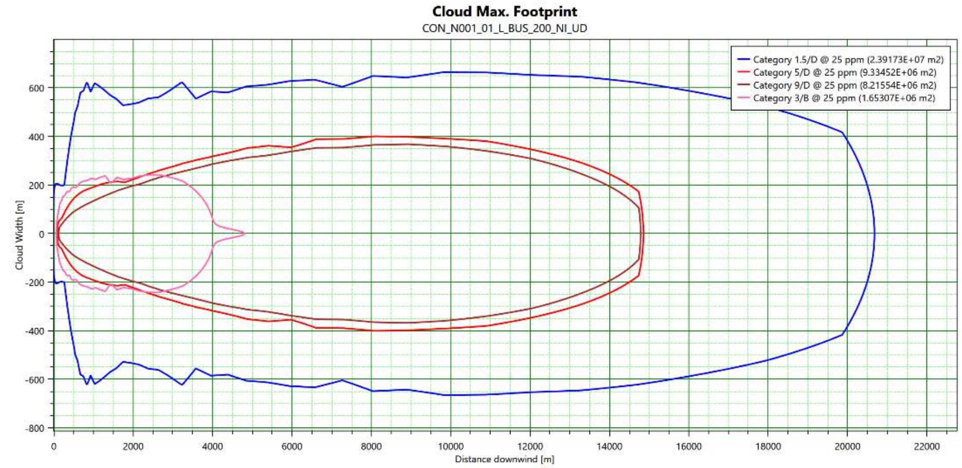
Height 5m

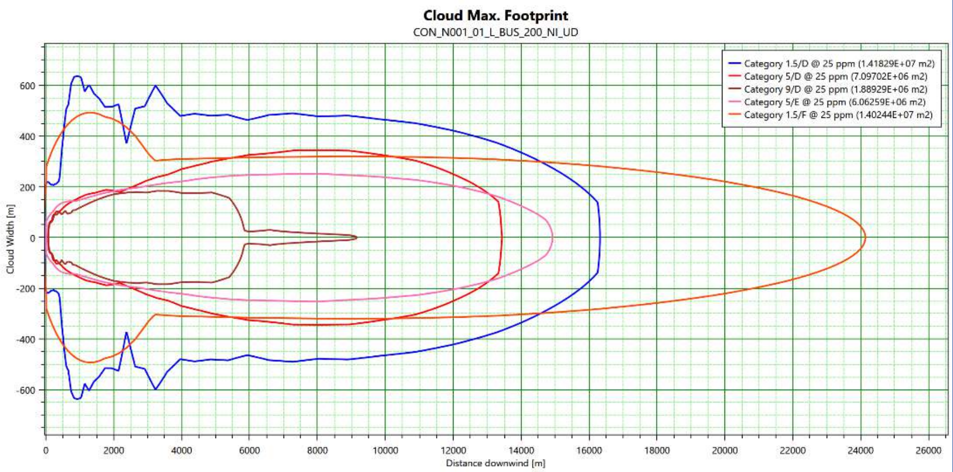


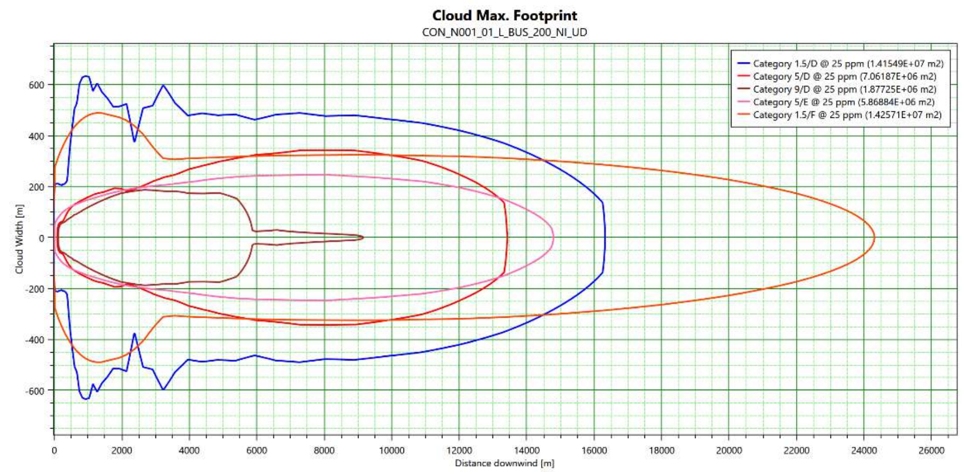


Height 0m	Height 5m
Height 10m	Height 20m

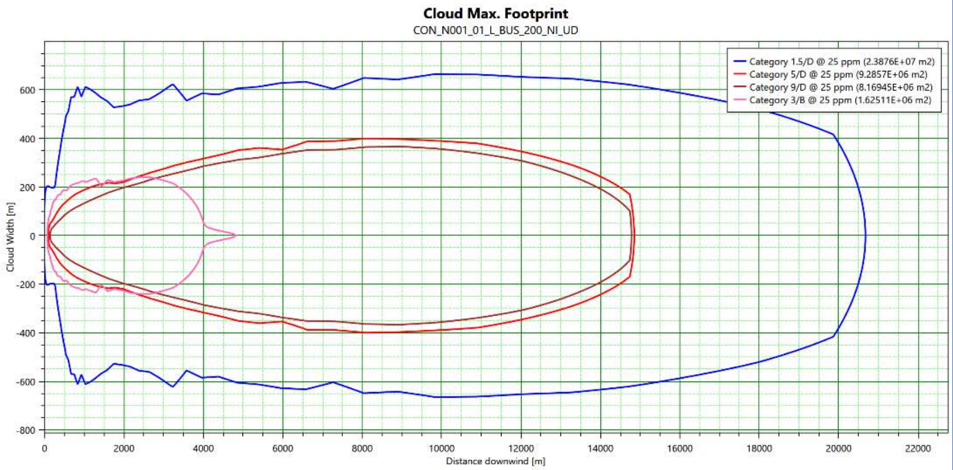


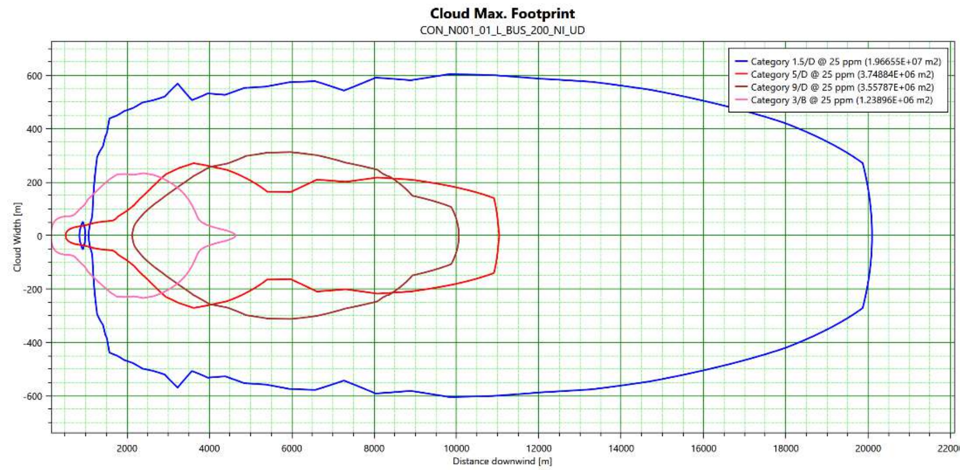


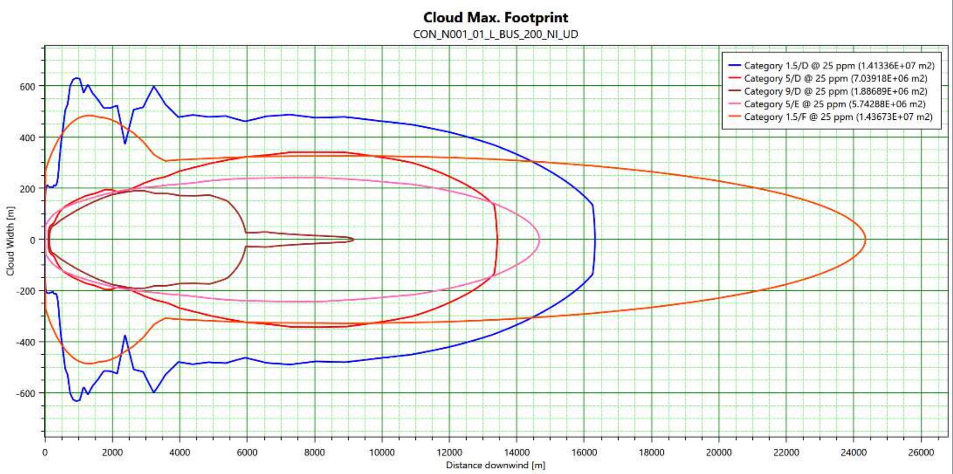




Height 0m	**Height 5m**
Height 25m	Height 180m







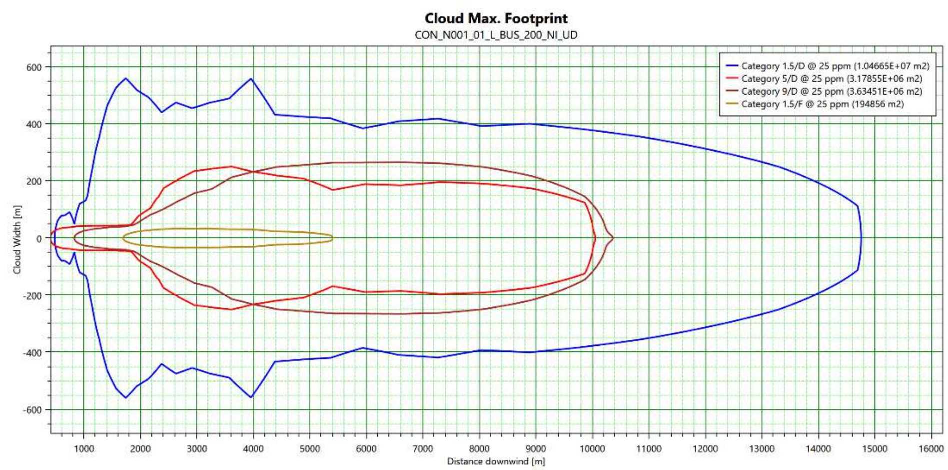
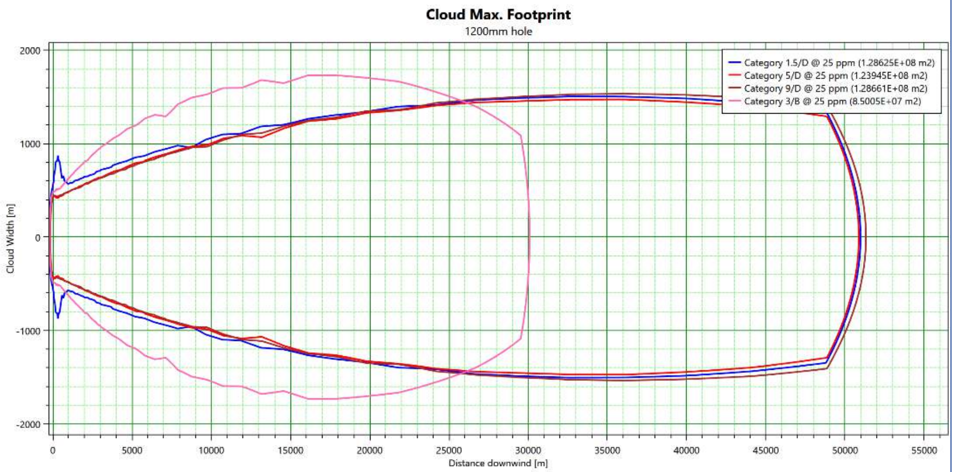
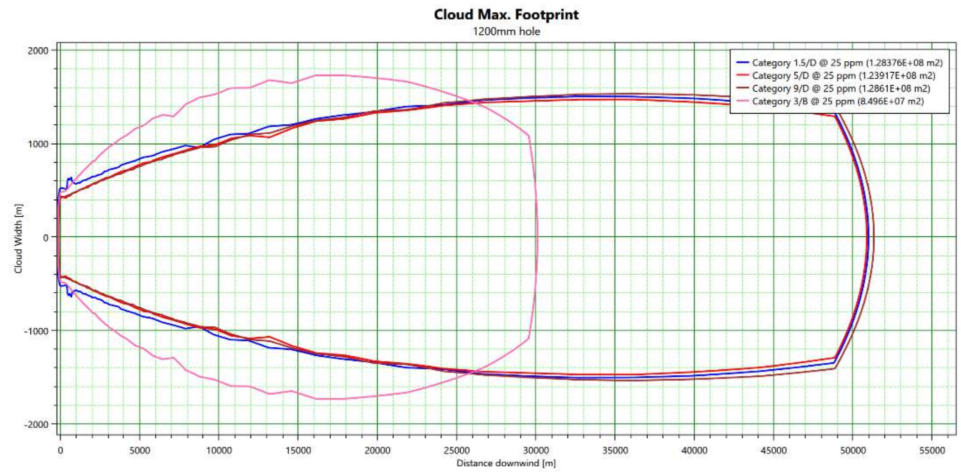
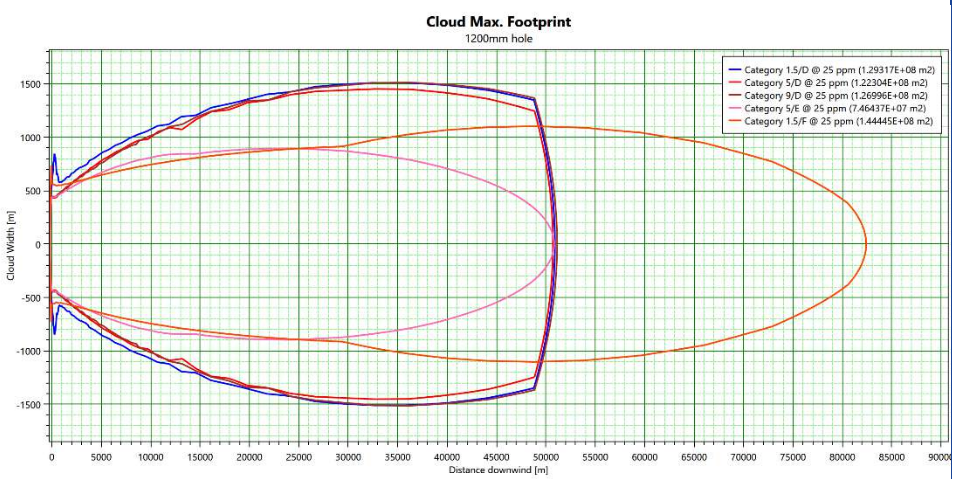
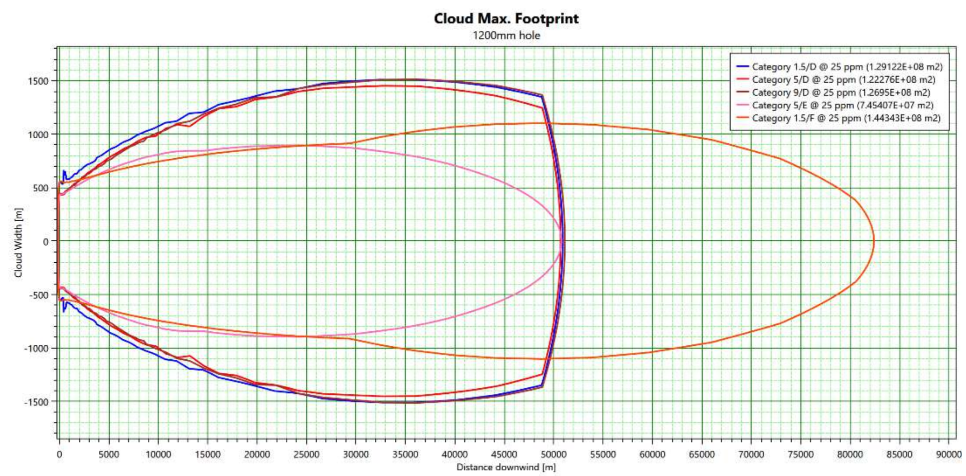
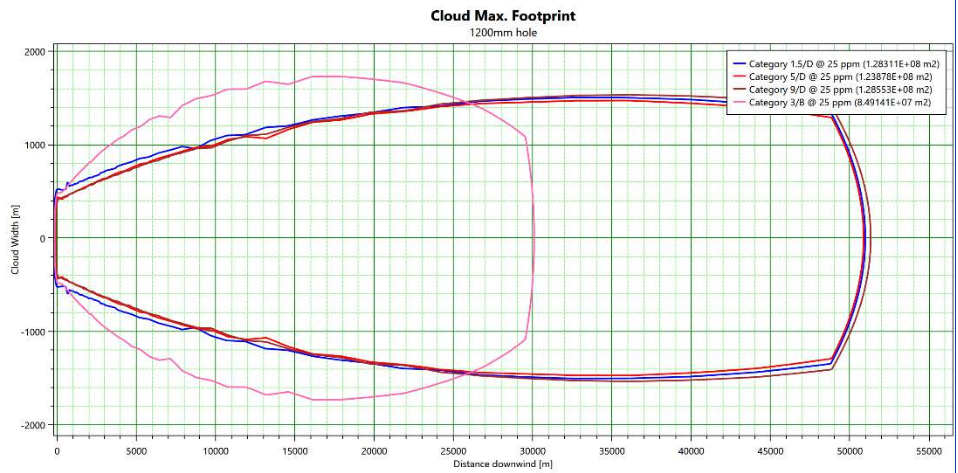
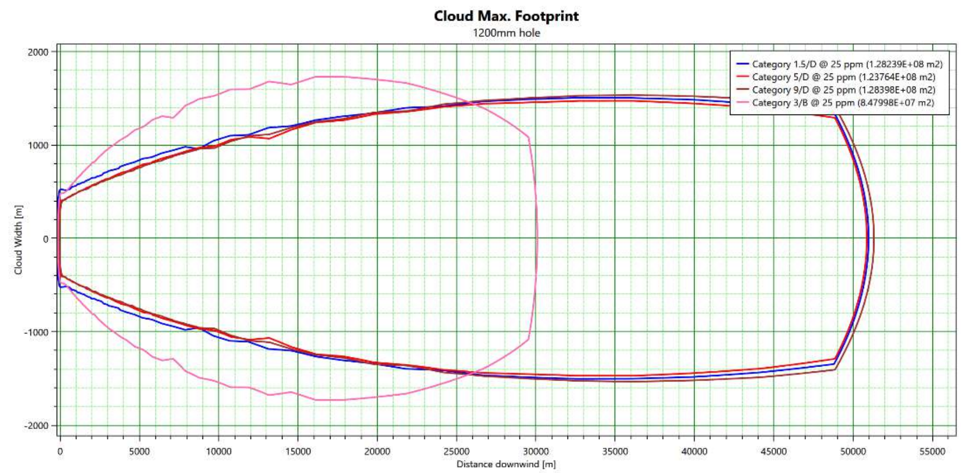


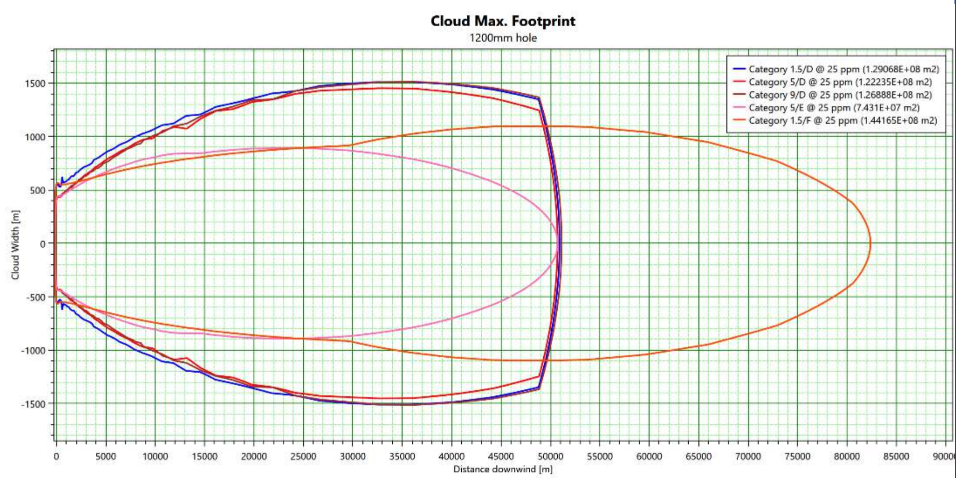
Table A32 Results for Storage tank spill, 1200mm hole – Comparison with the Long-Term Exposure Limit

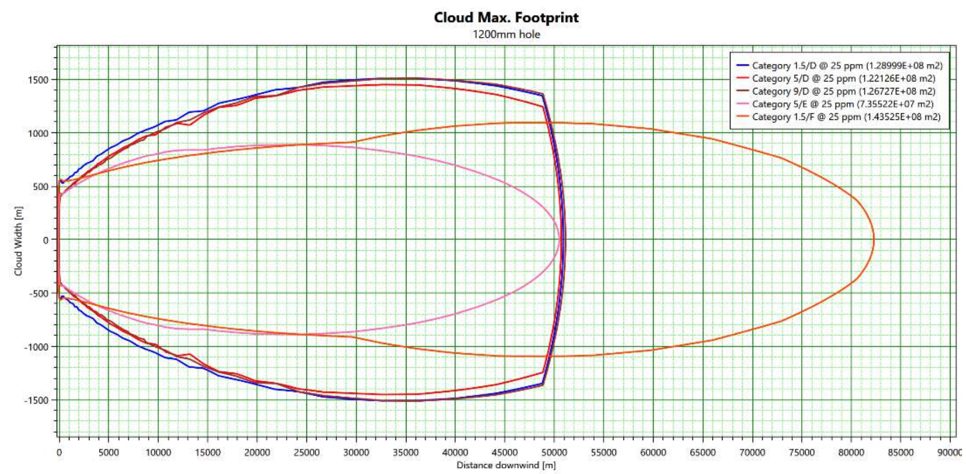
Height 0m	Height 5m
	
	

Height 0m	**Height 5m**
Height 10m	Height 20m

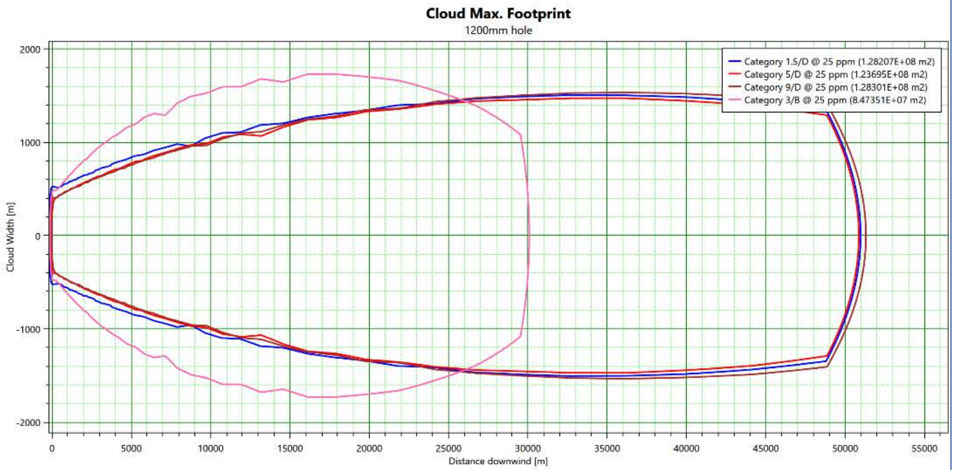


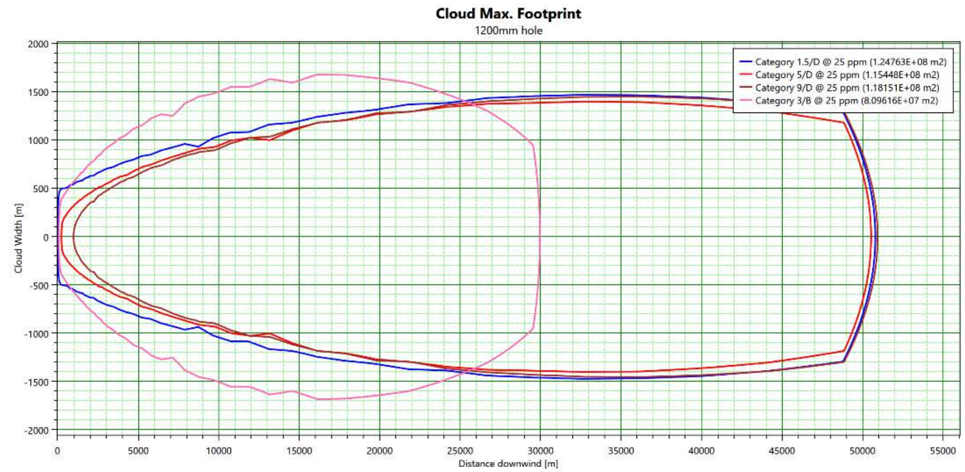


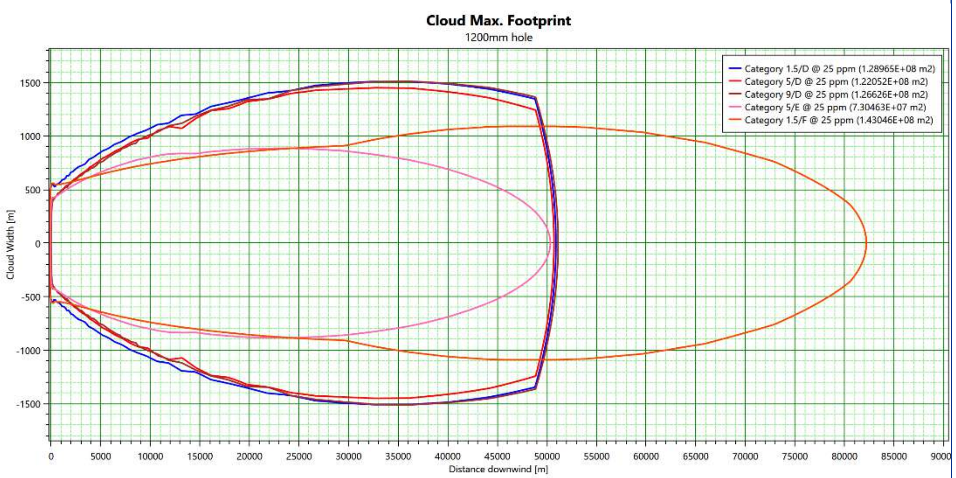




Height 0m	**Height 5m**
Height 25m	Height 180m







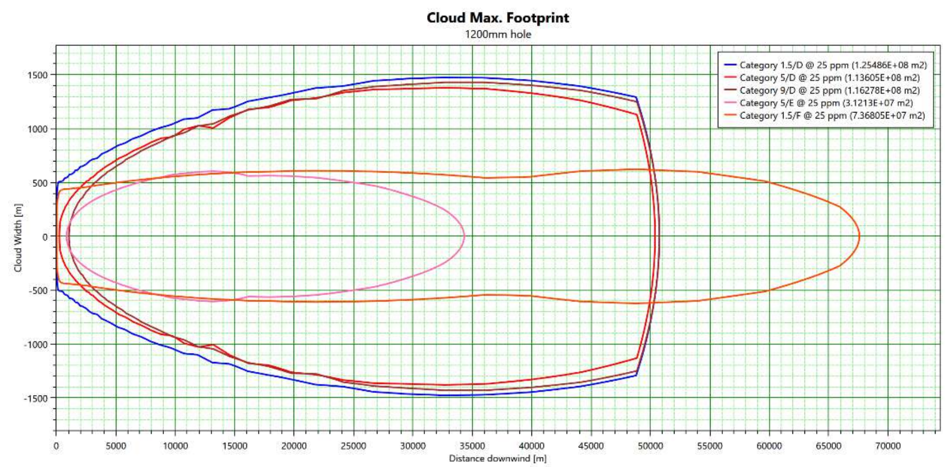


Table A33 Results for Tanker, 2mm hole – Comparison with the Long-Term Exposure Limit

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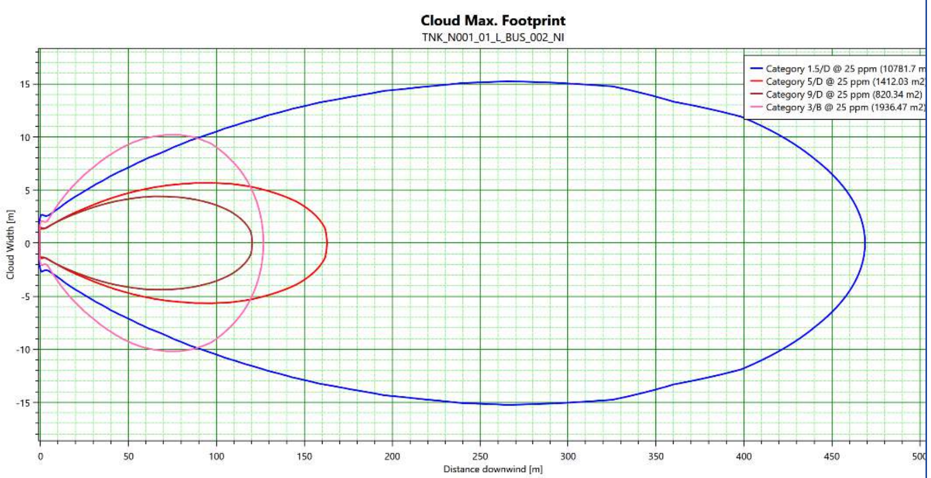

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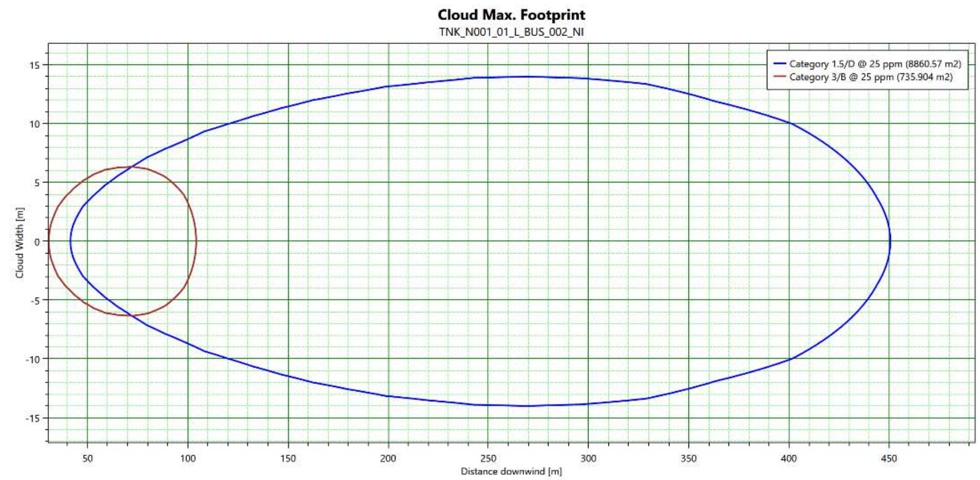

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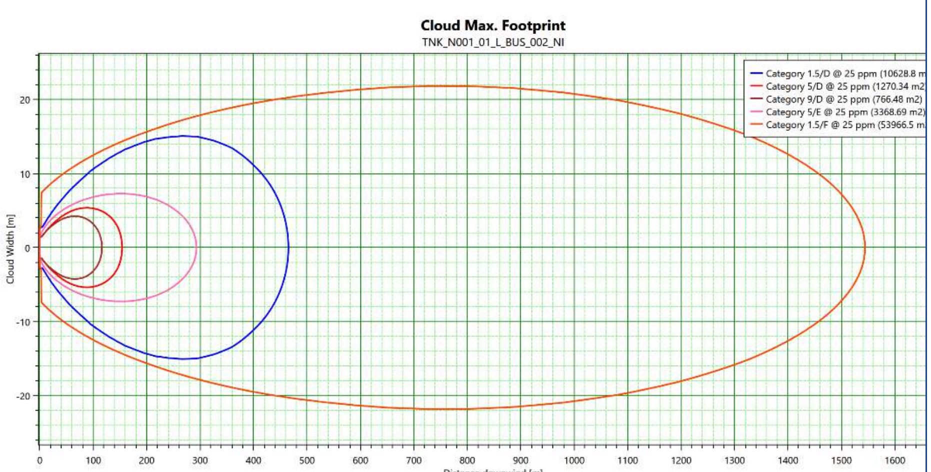

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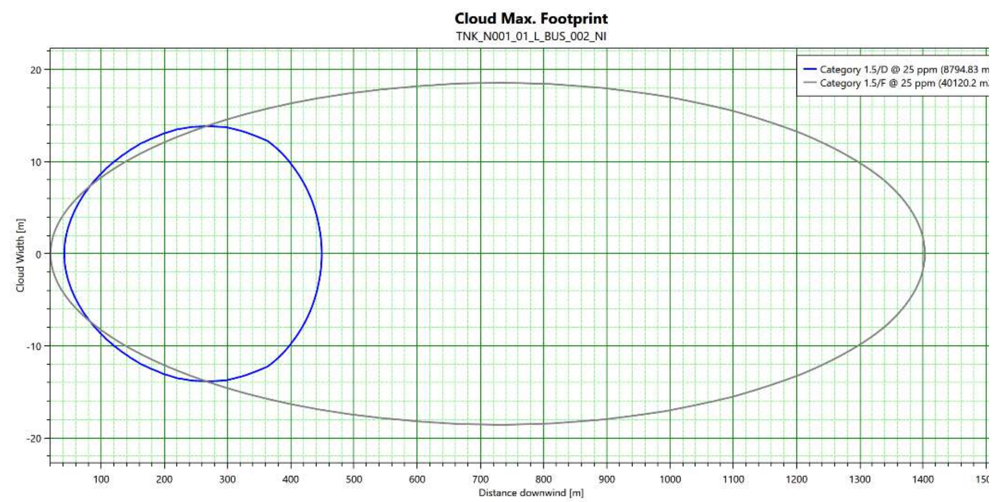

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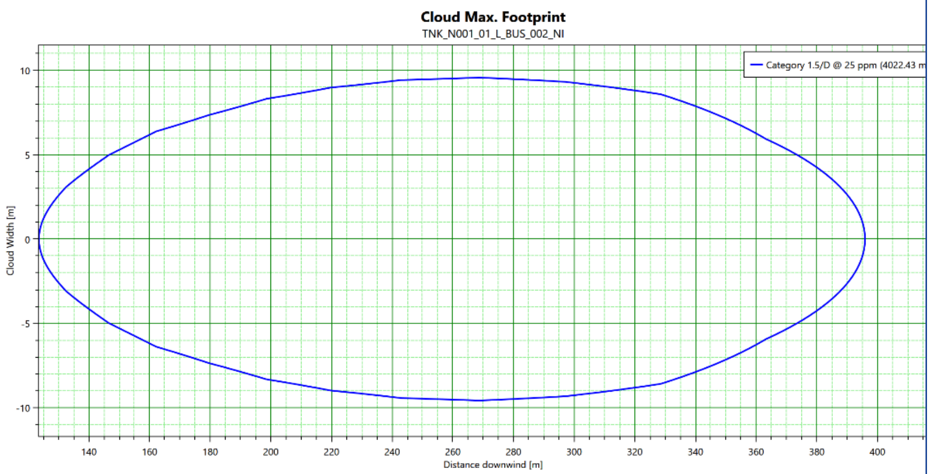
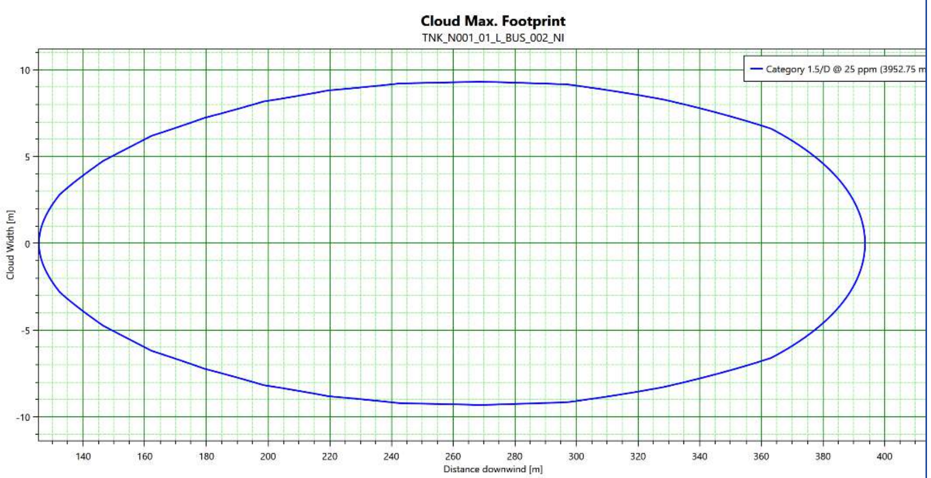
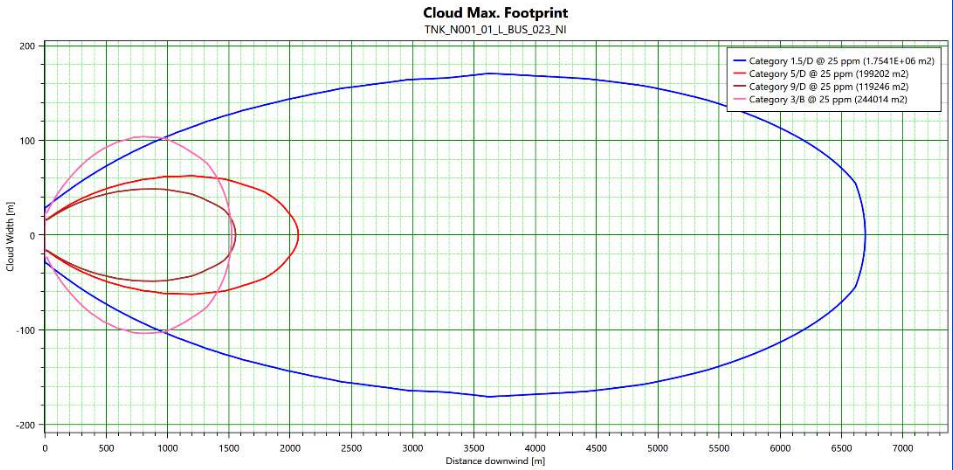
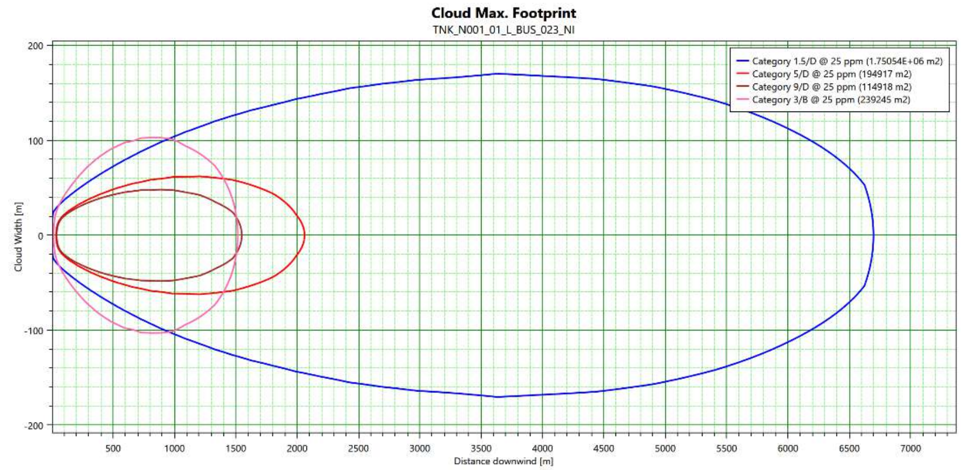
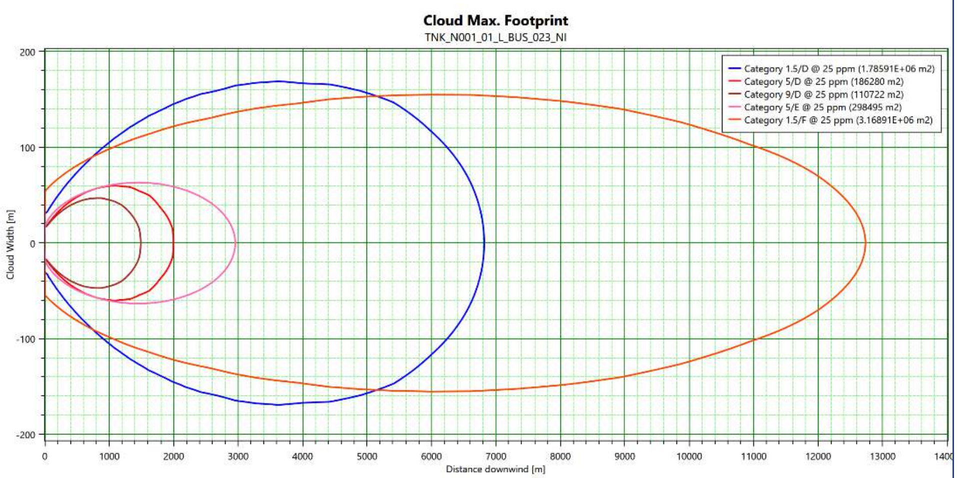
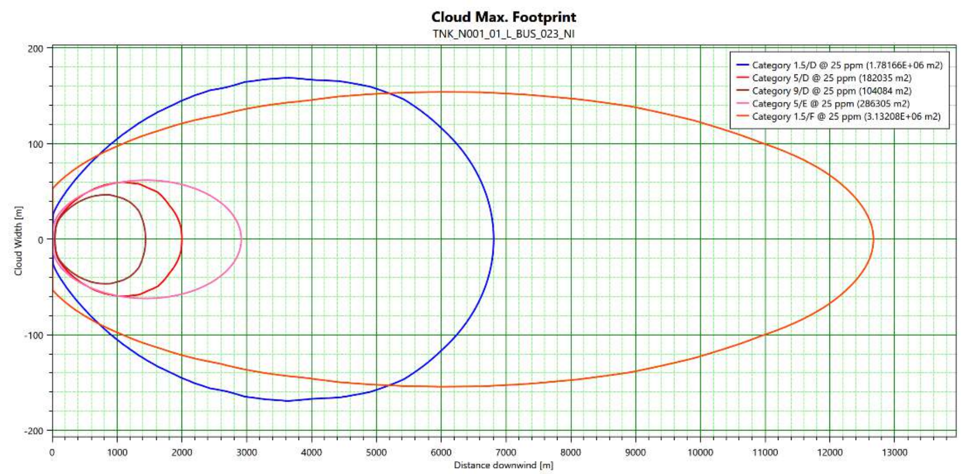
Height 0m	Height 5m
Height 10m	Height 20m
	No daytime exceedances
	No night-time exceedances
Height 25m	Height 180m
No daytime exceedances	No daytime exceedances

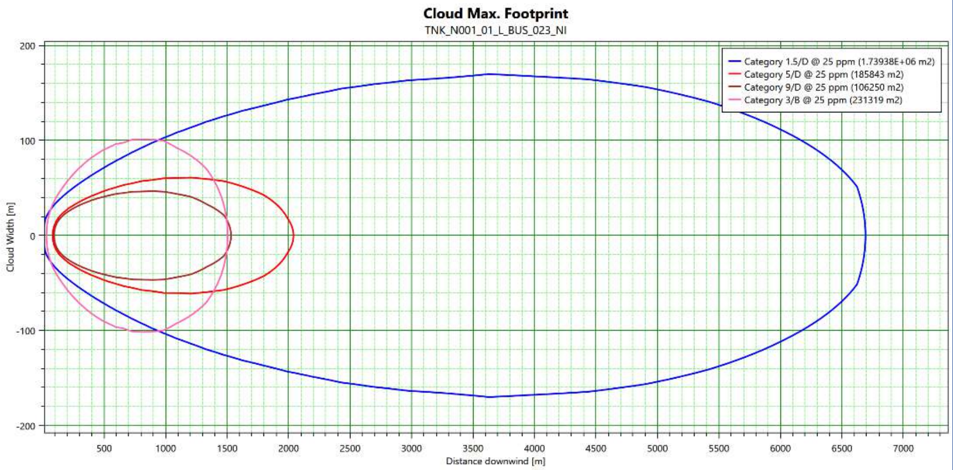
Height 0m	Height 5m
No night-time exceedances	No night-time exceedances

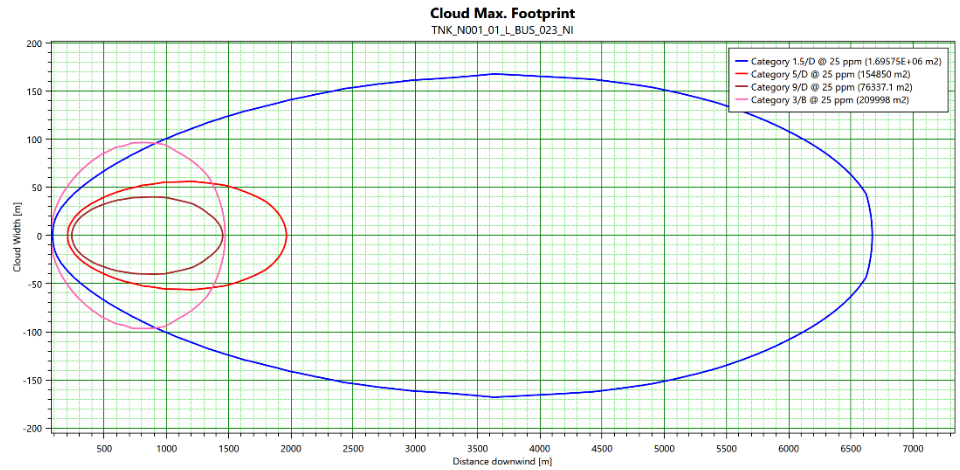
Table A34 Results for Tanker, 23mm hole – Comparison with the Long-Term Exposure Limit

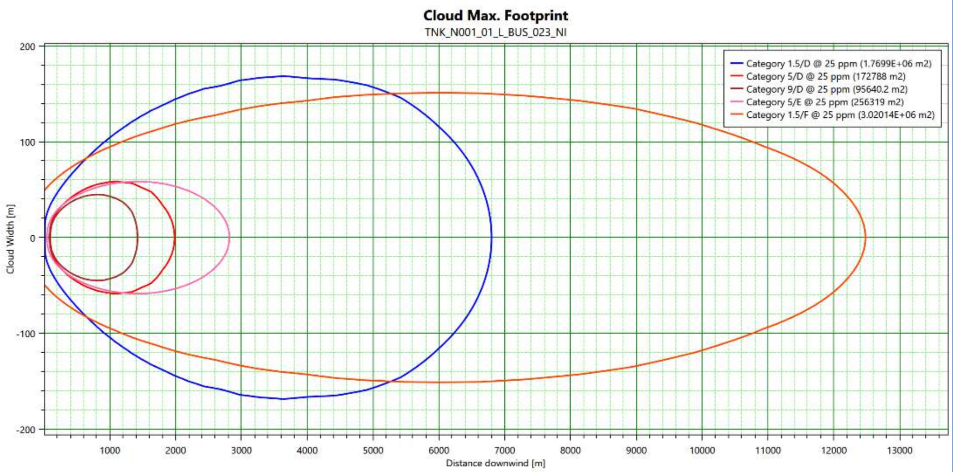
Height 0m	Height 5m
	
	

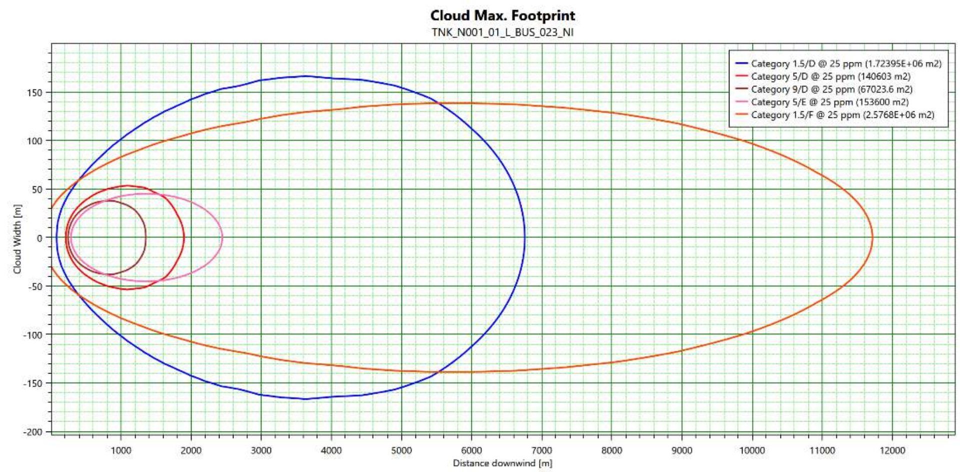
Height 0m | **Height 5m**

Height 10m | Height 20m









<table>
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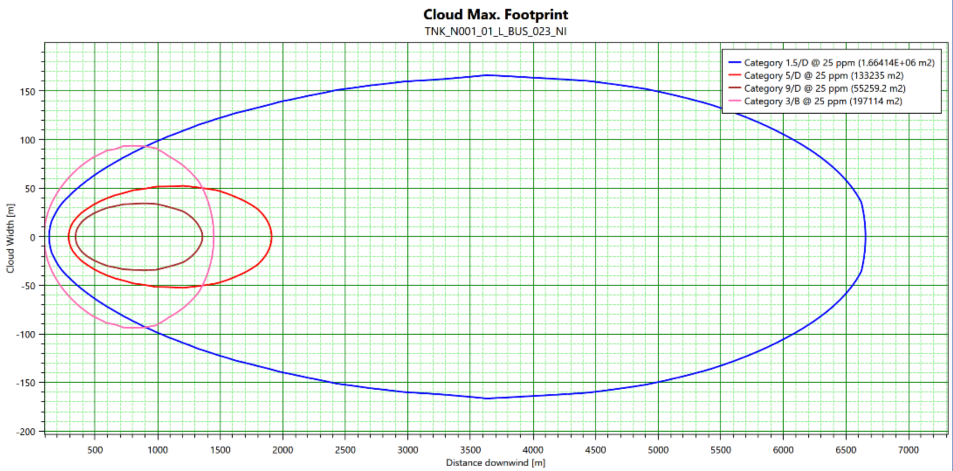
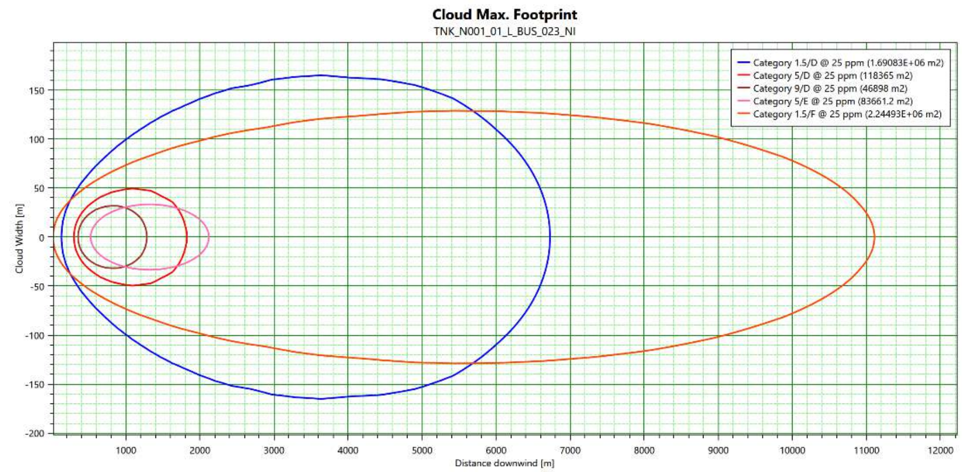
Height 25m</th><th>Height 5m
Height 180m</th></tr>
<tr><td>
</td><td>
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<tr><td>No night-time exceedances</td><td>No night-time exceedances</td></tr>
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Table A35 Results for Tanker, 200mm hole – Comparison with the Long-Term Exposure Limit

<table>
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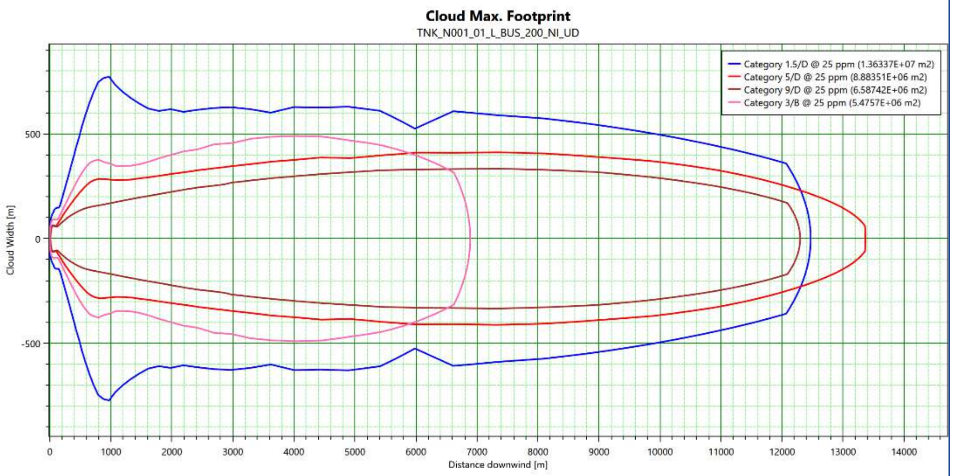

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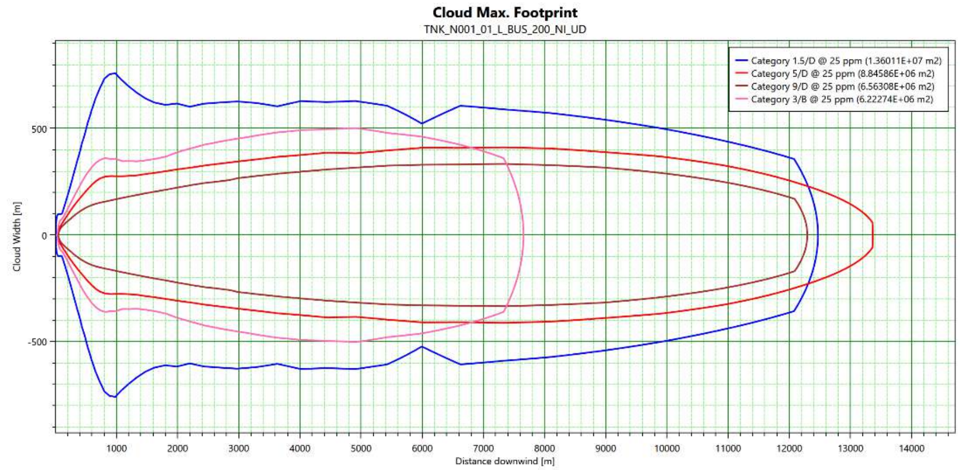

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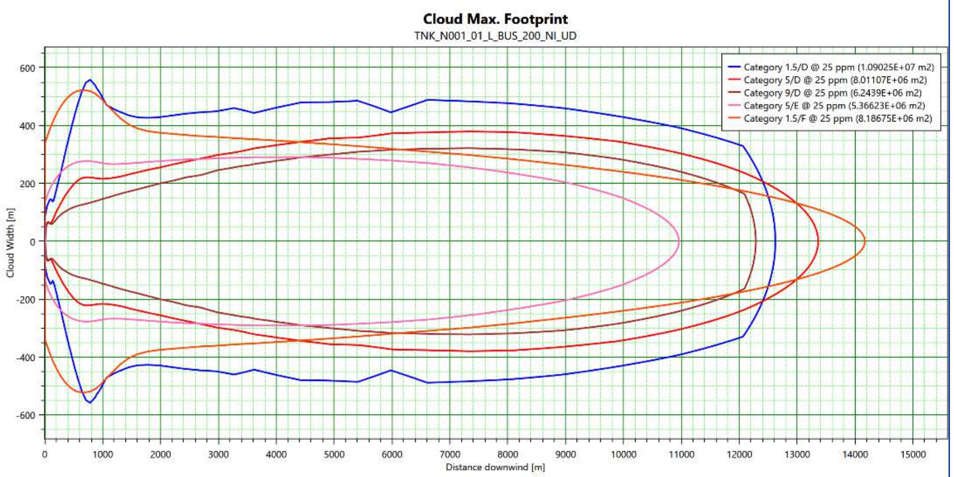

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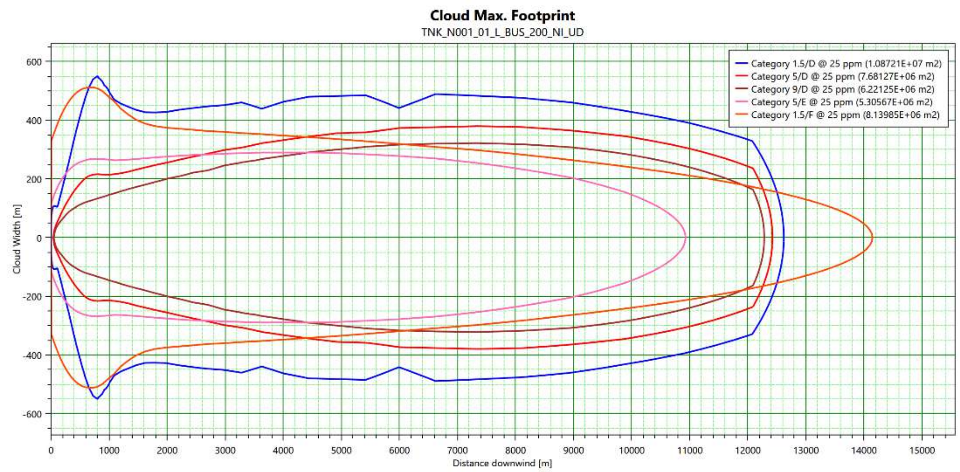

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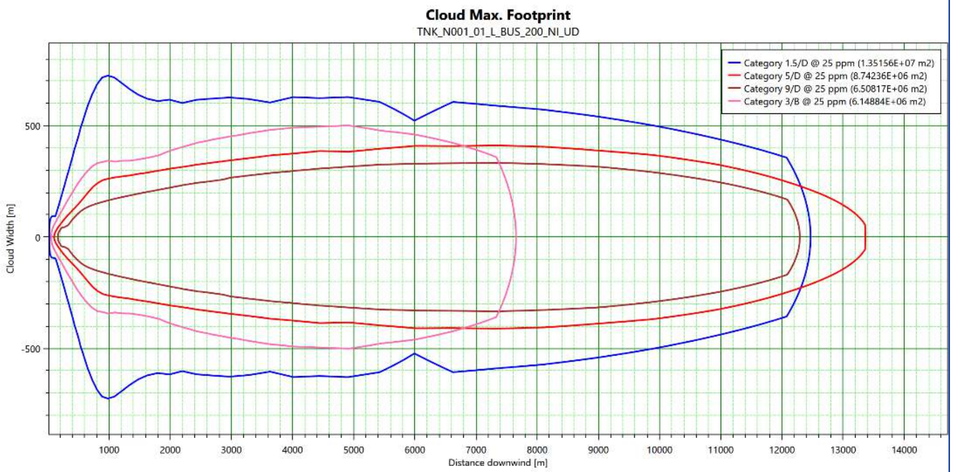
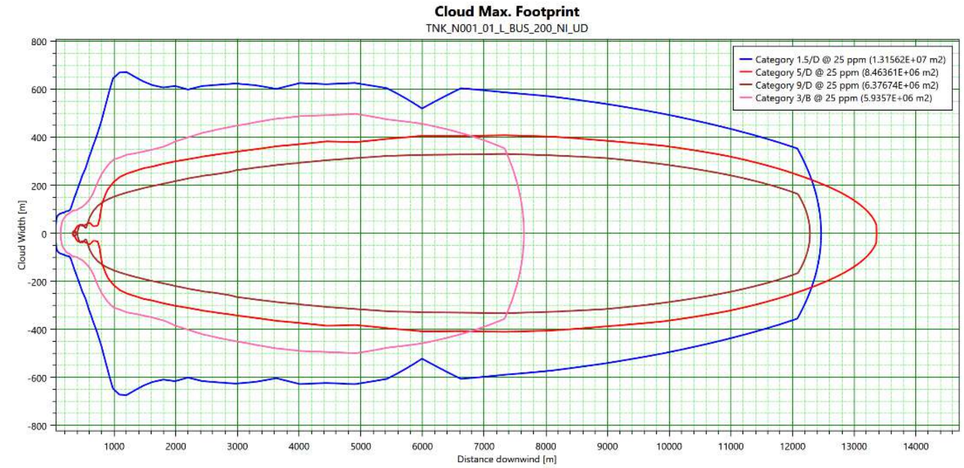
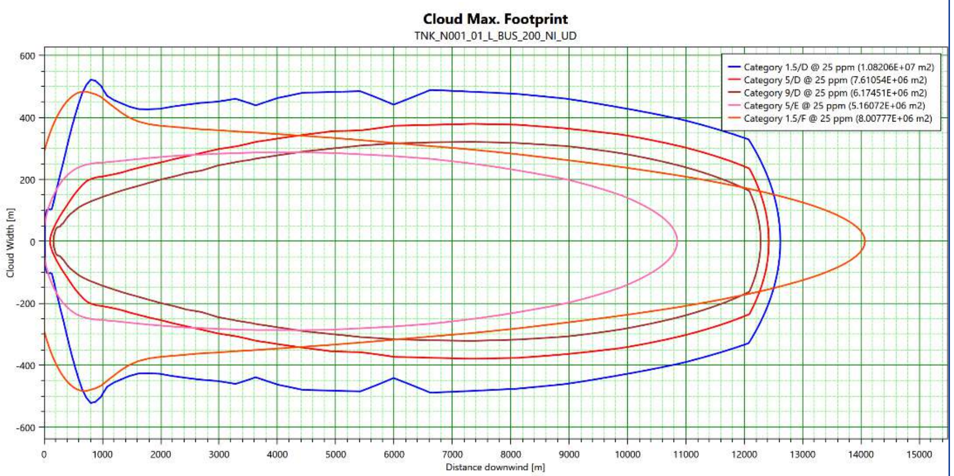
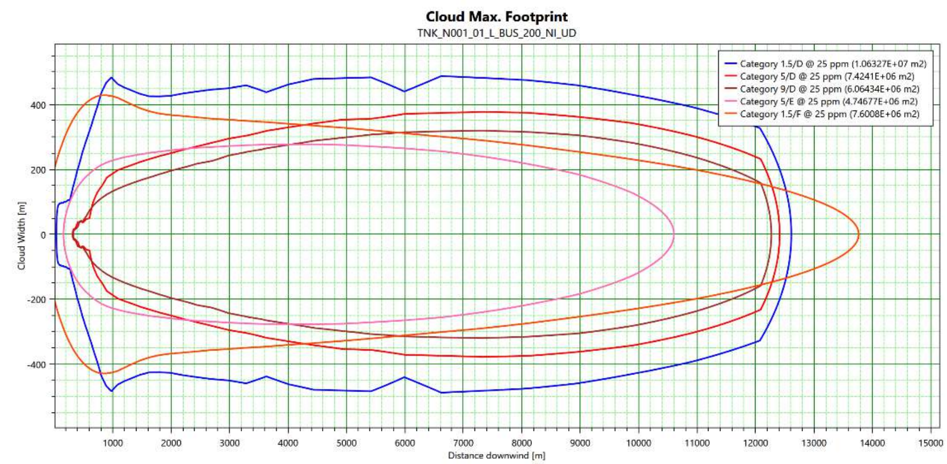
Height 0m | **Height 5m**

Height 10m | Height 20m

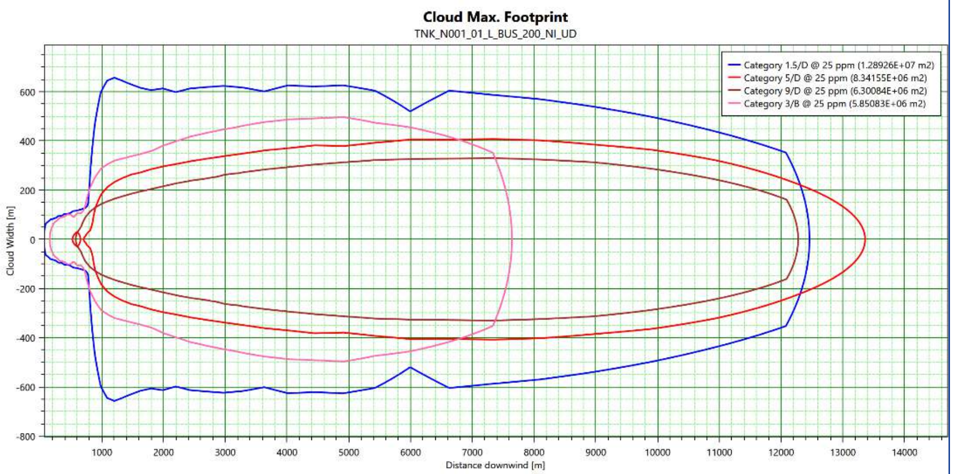


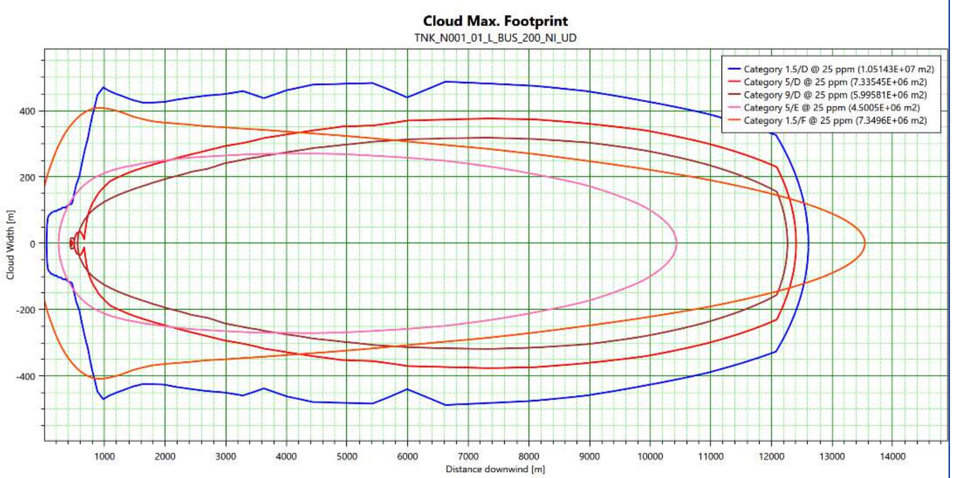






Height 0m	**Height 5m**
Height 25m	Height 180m





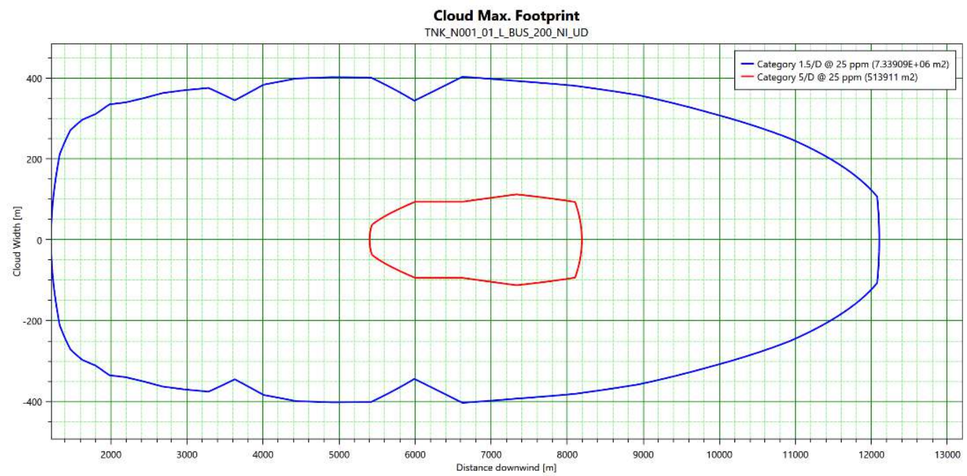


Table A36 and Table A37 show the size of the areas at ground level that exceed the short-term exposure limit of 35 ppm (25 mg m^{-3}) and long-term exposure limit of 25 ppm (18 mg m^{-3}), respectively. Similar results are seen at heights up to 25 m. At a height of 130 m the areas exceeding the exposure limits are noticeable smaller. Clearly, the larger the hole the greater the area that exceeds the exposure limits. The Storage tank spill has the largest impact with an area of up to 118 square kilometres exceeding the short-term exposure limit and area of up to 144 square kilometres exceeding the long-term exposure limit. However, for the smaller holes only the areas in the immediate vicinity of the spills are affected.

Table A36 Area (km^2) with ground level concentrations exceeding the short-term exposure limit of 35 ppm (25 mg m^{-3})

Spillage scenario	Hole size	Daytime meteorological conditions				Night-time meteorological conditions				
		1.5 D	5 D	9 D	3 B	1.5 D	5 D	9 D	5 E	1.5 F
Bulker	2 mm	0.001	<0.001	<0.001	0.001	0.001	0.002	0.001	0.005	0.02
	23 mm	1.2	0.34	0.2	0.063	1.3	0.33	0.19	0.086	1.3
	200 mm	10	12	9.0	6.2	8.2	9.9	8.0	6.8	5.7
Containership	2 mm	0.005	<0.001	<0.001	0.001	0.005	0.001	<0.001	0.02	0.027
	23 mm	0.78	0.94	0.55	0.11	0.78	0.86	0.051	0.14	1.7
	200 mm	19	7.1	6.0	1.4	10	5.3	1.5	3.9	10
Storage tank spill	1200 mm	111	107	112	67	111	105	110	57	118
Tanker	2 mm	0.008	0.001	0.001	0.001	0.008	0.001	0.001	0.002	0.039
	23 mm	1.2	0.14	0.85	0.17	1.2	0.13	0.79	0.22	2.4
	200 mm	11	6.7	4.8	4.3	8.7	6.0	4.5	4.2	6.3

Table A37 Area (km^2) with ground level concentrations exceeding the long-term exposure limit of 25 ppm (18 mg m^{-3})

Spillage scenario	Hole size	Daytime meteorological conditions				Night-time meteorological conditions				
		1.5 D	5 D	9 D	3 B	1.5 D	5 D	9 D	5 E	1.5 F
Bulker	2 mm	0.17	0.003	0.002	0.003	0.17	0.003	0.002	0.007	0.03
	23 mm	1.6	0.49	0.28	0.84	1.6	0.47	0.28	0.13	0.19
	200 mm	13	15	12	7.6	10	13	11	8.5	7.4
Containership	2 mm	0.007	0.001	0.001	0.001	0.007	0.001	0.001	0.002	0.37
	23 mm	1.1	0.13	0.77	0.16	1.1	0.12	0.72	0.2	2.3
	200 mm	23	9.4	8.3	1.7	14	7.1	1.9	5.0	13
Storage tank spill	1200 mm	129	124	129	85	129	122	127	75	144
Tanker	2 mm	0.011	0.001	0.001	0.002	0.011	0.001	0.001	0.003	0.54
	23 mm	1.8	0.20	0.12	0.24	1.8	0.18	0.11	0.3	3.1
	200 mm	14	8.9	6.6	5.5	11	8.0	6.2	5.4	8.2

7.5.1. H0

The H0 flight height band has been analysed using the air dispersion modelling results at 0 m and analysed per fuel storage type below.

7.5.1.1.Bulker

Generally, between hole sizes, the greater the size of the hole the greater the footprint in cloud across all weather conditions.

Under the 2 mm hole size scenario, the greatest cloud footprint is experienced in the night-time, under category 1.5/F weather conditions where distance downwind was ~980 m and the cloud width was ~28 m. In the daytime the largest dispersal is under the Category 1.5/D weather condition where the distance downwind was ~520 m and the cloud width was ~30 m. The other weather conditions displayed much smaller cloud footprints in this scenario.

Under the 23 mm hole size scenario, the greatest cloud footprint is experienced in the night-time under the Category 1.5/F weather condition where the distance downwind was ~8,100 m and the cloud width was ~200 m. Category 1.5/D night-time weather conditions provides a similar sized dispersal although the downwind dispersal is shorter at ~5,500 m with a broader cloud width of ~340 m. The other weather conditions, including all daytime conditions, displayed much smaller cloud footprints, particularly under in the Category 3/B condition, in this scenario.

Under the 200 mm hole size scenario, the cloud footprint was largest in the daytime under the Category 1.5/D weather condition and the Category 5/D and Category 9/D conditions are similar though the former is generally shorter and wider compared to the latter conditions. The maximum downwind distance was under Category 9/D conditions, extending ~13,000 m, and the greatest cloud width was used Category 1.5/D, extending ~3,000 m. The Category 3/B condition footprint is smaller, both laterally and longitudinally, than the other conditions.

7.5.1.2. Tanker

Generally, between hole sizes, the greater the size of the hole the greater the footprint in cloud across all weather conditions.

Under the 2 mm hole size scenario, the greatest cloud footprint is experienced in the night-time under the Category 1.5/F weather condition where the distance downwind was ~1,300 m and the cloud width was ~36 m. The other weather conditions displayed much smaller cloud footprints in this scenario.

Under the 23 mm hole size scenario, the greatest cloud footprint is also experienced in the night, under the Category 1.5/F weather condition where the distance downwind was ~10,800 m and the cloud width was ~280 m. The daytime category 1.5/D weather condition scenario displays the second greatest cloud footprint with a downwind distance of ~5500 m and a cloud width of ~280 m. The other weather conditions displayed much smaller cloud footprints.

Under the 200 mm hole size scenario, the cloud footprint was largest in the night-time scenario under the Category 1.5/F weather condition with a distance downwind of ~9400 m and a maximum cloud width of ~220 m. Though having a smaller footprint than the category 1.5/F night-time scenario, the cloud width under the night-time Category 1.5/D weather scenario is larger, extending ~280 m. The other scenarios displayed smaller footprints with the category 1.5/D weather scenario being the largest in the daytime, the other conditions displayed much smaller cloud footprints.

7.5.1.3. Containership

Generally, between hole sizes, the greater the size of the hole the greater the footprint in cloud across all weather conditions.

Under the 2 mm hole size scenario, the greatest cloud footprint is experienced in the night-time under the Category 1.5/F weather condition where the distance downwind was ~1060m and the cloud width was ~31 m. The other weather conditions displayed much smaller cloud footprints in this scenario with the most significant daytime cloud footprint occurring under category 1.5/D with a distance downwind of ~320 m and a cloud width of ~22 m.

Under the 23 mm hole size scenario, the greatest cloud footprint is experienced in the night, under the Category 1.5/F weather condition where the distance downwind was ~9200 m and the cloud width was ~220 m. The day and night category 1.5/D weather condition scenarios display the second greatest cloud footprints with downwind distances of ~4400 m and a cloud width of ~220 m. The other weather conditions displayed much smaller cloud footprints.

Under the 200 mm hole size scenario, the cloud footprint was largest in the night-time scenario under the Category 1.5/F weather condition with a distance downwind of ~19,500 m and a maximum cloud width of ~500,m. Though having a smaller footprint than the category 1.5/F night-time scenario, the cloud width under the night-time Category 1.5/D weather scenario is larger, extending ~1200 m. The other scenarios displayed smaller footprints with the category 1.5/D weather scenario being the largest in the daytime.

Under the 1200 mm storage tank hole size scenario, the cloud footprint was largest in the night-time under the category 1.5/F weather conditions with a downwind distance of ~76,000 m and a maximum cloud width of ~1,800 m. The cloud footprints for both day and night under the weather conditions Category 1.5/D, Category 5/D and Category 9/D are similar with the distance downstream of ~50,000 m and a cloud width of ~2,600 m. The Category 3/B condition footprint is smaller though the cloud width was wider at ~2,800 m.

Figure A918 Summary of Worst Case Dispersal for 0 m

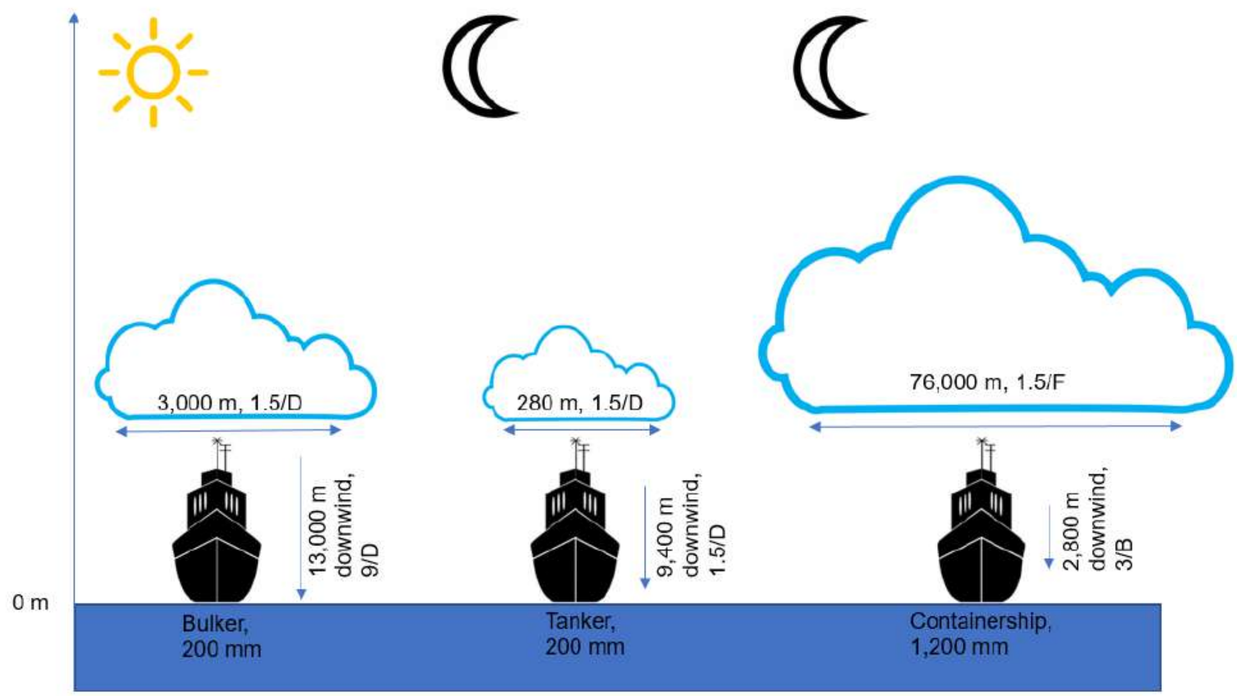


Figure A9 Summary of 'worst case' air dispersal for 0m or each container type.

7.5.2. H1

The H1 flight height band has been analysed using the air dispersion modelling results at 5 m and analysed per fuel storage type below.

7.5.2.1. Bulker

Generally, between hole sizes, the greater the size of the hole the greater the footprint in cloud across all weather conditions.

Under the 2 mm hole size scenario, the greatest cloud footprint is experienced in the night-time, under category 1.5/F weather conditions where distance downwind was ~1880m and the cloud width of ~26 m. In the daytime the largest dispersal is under the Category 1.5/D weather condition where the distance downwind was ~520m and the cloud width was ~32 m. The other weather conditions displayed much smaller cloud footprints in this scenario. Compared to the H0 modelling, at H1 the cloud starts a short distance from the 2 mm hole.

Under the 23 mm hole size scenario, the greatest cloud footprint is experienced in the night-time under the Category 1.5/F weather condition where the distance downwind was ~8,100 m and the cloud width was ~200 m. Category 1.5/D night-time weather conditions provides a similar sized dispersal although the downwind dispersal is shorter at ~5,500 m with a broader cloud width of ~340 m. Category 1.5/D weather conditions provided the largest dispersal in the daytime with a downwind distance of ~4,800 m, and a cloud width of ~320 m. The other weather conditions, displayed much smaller cloud footprints, particularly under in the Category 3/B condition, in this scenario. Unlike the 2 mm hole, at H1 for the 23 mm hole, the cloud starts immediately at the hole.

Under the 200 mm hole size scenario, the cloud footprint in both day and night under the Category 1.5/D weather condition and the Category 5/D and Category 9/D conditions are similar though the former is generally shorter and wider compared to the latter conditions. The maximum downwind distance was under Category 9/D daytime conditions, extending ~13,500 m, and the greatest cloud width used Category 1.5/D, daytime conditions, extending ~3,000 m. The Category 3/B condition footprint is smaller, both laterally and longitudinally, than the other conditions.

As can be seen from these results, for a given hole size, there is very little difference between the cloud footprint at H0 and H1 for the bulker vessel.

7.5.2.2. Tanker

Generally, between hole sizes, the greater the size of the hole the greater the footprint in cloud across all weather conditions.

Under the 2 mm hole size scenario, the greatest cloud footprint is experienced in the night-time under the Category 1.5/F weather condition where the distance downwind was ~1,150 m and the cloud width was ~30 m. The other weather conditions displayed much smaller cloud footprints in this scenario with the greatest day-time cloud footprint under category 1.5/D weather conditions where distance downwind was ~370 m and the cloud width was ~24 m. Both Category 9/D and Category 5/D conditions displayed no footprint whilst Category 3B only displayed a small footprint.

Under the 23 mm hole size scenario, the greatest cloud footprint is also experienced in the night, under the Category 1.5/F weather condition where the distance downwind was ~10,800 m and the cloud width was ~260 m. The day and night category 1.5/D weather condition scenarios are near identical and represent the second greatest cloud footprints with a downwind distance of ~5,500 m and a cloud width of ~280 m. The other weather conditions displayed much smaller cloud footprints, particularly under in the Category 9/D condition, in this scenario.

Under the 200 mm hole size scenario, the largest cloud footprint under the Category 1.5/D weather condition is largest with a distance downwind of ~11,050 m and a maximum cloud width of ~1,500 m for both day and night. The other weather conditions displayed similar, although smaller cloud footprints, with the daytime category 3/B being the smallest.

For a given hole size scenario, in comparison to at H0, the cloud footprints at H1 are generally slightly smaller at H0 for the containership vessel.

7.5.2.3. Containership

Generally, between hole sizes, the greater the size of the hole the greater the footprint in cloud across all weather conditions.

Under the 2 mm hole size scenario, the greatest cloud footprint is experienced in the night-time, under category 1.5/F weather conditions where distance downwind was ~1,100 m and a cloud width of ~28 m. In the daytime, the largest dispersal is under the Category 1.5/D weather condition where the distance downwind was ~360 m and the cloud width was ~22 m. Only weather category scenarios 1.5/D & 3/B in the daytime and 1.5/D & 1.5/F in the night-time displayed cloud footprints in this scenario; The other weather conditions had no cloud footprints for this scenario.

Under the 23 mm hole size scenario, the greatest cloud footprint is experienced in the night, under the Category 1.5/F weather condition where the distance downwind was ~10,600 m and the cloud width was ~260 m. The day and night category 1.5/D weather condition scenarios display the second greatest cloud footprints with downwind distances of ~5,300 m and a cloud width of ~280 m. The other weather conditions displayed much smaller cloud footprints.

Under the 200 mm hole size scenario, the greatest cloud footprint is experienced in the daytime under the Category 1.5/D weather condition where the distance downwind was ~20,500 m and the cloud width was ~1,250 m. In the night-time, the greatest distance downwind occurs under category 1.5/F at ~24,000 m and the largest cloud width of ~1200 m occurs under category 1.5/D weather conditions. The other scenarios displayed smaller cloud footprints.

Under the 1200 mm storage tank hole size scenario, the cloud footprint was largest in the night-time under the category 1.5/F weather conditions with a downwind distance of ~8,250 m and a maximum cloud width of ~2,200 m. Category 1.5/D, Category 5/D and Category 9/D, for both day and night-time, are similar with the distance downstream of ~50,000 m and a cloud width of ~3,000 m. The Category 3/B day-time condition footprint is smaller though the cloud width was wider at ~3,600 m.

For a given hole size scenario, in comparison to at H0, the cloud footprints at H1 are generally slightly smaller at H0 for the containership vessel.

Figure A1019 Summary of 'worst case' air dispersal for 5 m

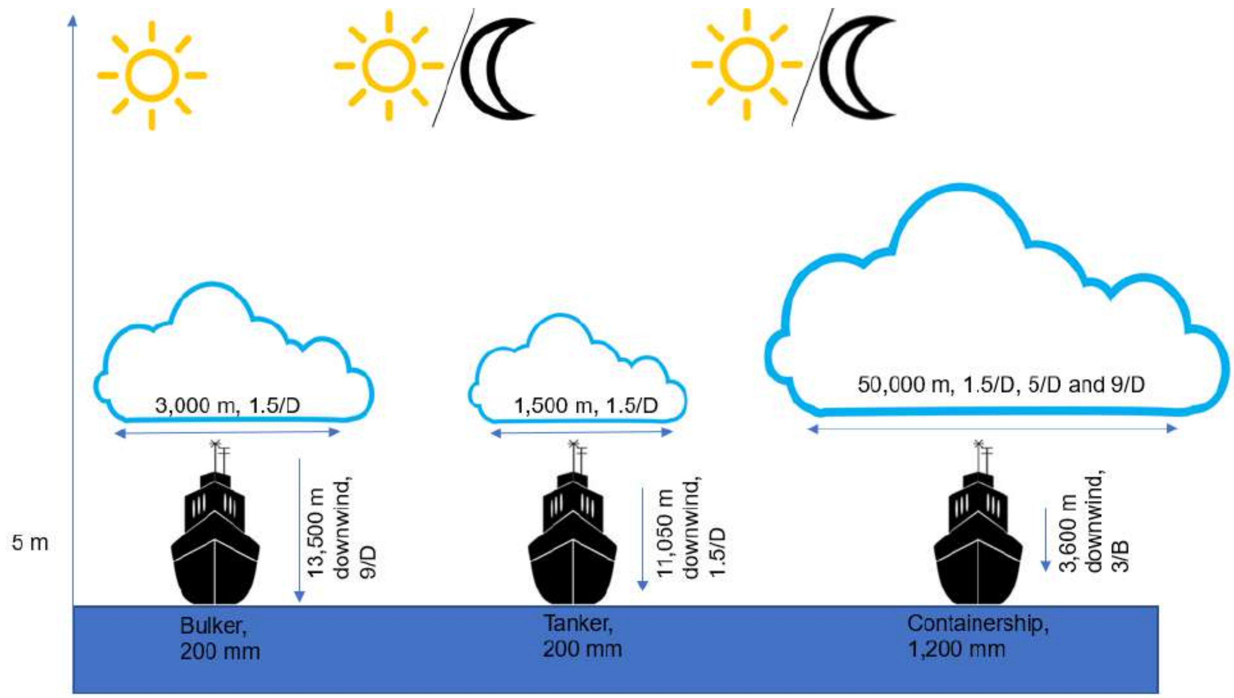


Figure A10 Summary of 'worst case' air dispersal for 5 m for each container type

7.5.3. H2

The H2 flight height band has been analysed using the air dispersion modelling results at 10m and analysed per fuel storage type below.

7.5.3.1. Bulker

Generally, between hole sizes, the greater the size of the hole the greater the footprint in cloud across all weather conditions.

Under the 2 mm hole size scenario, only weather category 1.5/D produced a cloud plume in both day and night scenarios, the night-time scenario also produced a category 1.5/F plume. The greatest cloud footprint is experienced in the night-time, under category 1.5/F weather conditions where distance downwind is ~770 m and the cloud width of ~22 m. The other weather conditions displayed smaller, yet still significant, cloud footprints in this scenario.

Under the 23 mm hole size scenario, the greatest cloud footprint is experienced in the night-time under the Category 1.5/F weather condition where the distance downwind was ~8,000 m and the cloud width was ~200 m. Category 1.5/D night-time weather conditions provides a similar sized dispersal although the downwind dispersal is shorter at ~5,500 m with a broader cloud width of ~340 m. The other weather conditions displayed smaller cloud footprints, particularly under in the Category 3/B condition, in this scenario.

Under the 200 mm hole size scenario, the cloud footprint was largest in the daytime under the Category 9/D weather condition with a downwind distance of ~13,400 m and a cloud width of ~1200 m. Similar sized cloud footprints are experienced for both day and night scenarios for categories 5/D, 9/D and 1.5/D however the later produces a shorter and wider footprint with a cloud width of ~2,800 m and a distance downwind of ~6,200 m. The other weather conditions displayed smaller cloud footprints, particularly under in the Category 3/B daytime and 1.5/F night-time conditions, in this scenario.

7.5.3.2. Tanker

Under the 2 mm hole size scenario, only category 1.5/D displayed a cloud footprint which is slightly larger in the day with a downwind distance of ~590 m and a cloud width of ~10 m.

Under the 23 mm hole size scenario, the greatest cloud footprint is experienced in the night-time under category 1.5/F weather conditions where the cloud width was ~260 m and the downwind distance was ~10,600 m. Category 1.5/D weather condition for both day and night-time produced a significant footprint however the other weather conditions displayed much smaller cloud footprints.

Under the 200 mm hole size scenario, all weather categories displayed significant cloud footprints with the greatest under category 1.5/D weather conditions in the daytime with a cloud width of ~1,400 m and a downwind distance of ~11,000 m. The category 3/B weather condition produces the smallest footprint for both day and night scenarios.

7.5.3.3. Containership

Under the 2 mm hole size scenario, only category 1.5/D displayed a cloud footprint. The largest cloud footprint is during the night-time with a downwind distance of ~260 m and a cloud width of ~7 m. In the day, the cloud footprint begins far away from the hole.

Under the 23 mm hole size scenario, the greatest cloud footprint is experienced in the night-time under category 1.5/F weather conditions where the cloud width was ~260 m and the downwind distance was ~10,500 m. Category 1.5/D weather condition for both day and night-time produced a significant footprint however the other weather conditions displayed much smaller cloud footprints.

Under the 200 mm hole size scenario, the greatest cloud footprint is displayed in the day under category 1.5/D where a downwind distance of ~20,500 m and a cloud width of ~1,300 m. In the night, category 1.5/F and 1.5/D weather conditions display footprints of similar sizes with the former producing a narrower and longer footprint reaching a downwind distance of ~24,000 m at its peak. The other weather conditions produced smaller cloud footprints particularly category 3/B in the day and 9/D in the night.

Under 1200 mm hole size scenario, category 1.5/D, 5/D, 9/D in both day and night produce near identical footprints with downwind distances of ~5,200 m and cloud width of ~3,000 m. Category 1.5/F weather conditions during the night-time produce a cloud footprint which reaches a similar scale although narrower and with a larger downwind distance with ~8,200m reached. Category 3/B in the day and 5/E in the night produced the smallest cloud footprints in this scenario.

Figure A1120 Summary of 'worst case' air dispersal for 10 m

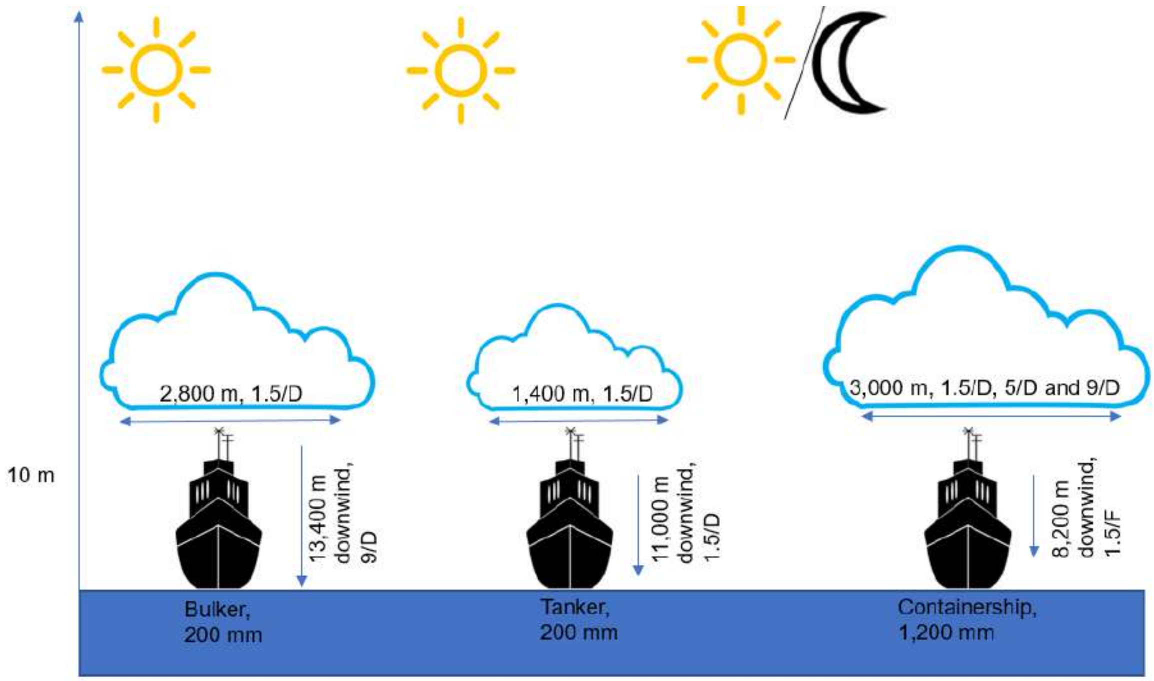


Figure A11 Summary of 'worse case' air dispersal for 10 m

7.5.4. H3

The H3 flight height band has been analysed using the air dispersion modelling results at 20 m and analysed per fuel storage type below.

7.5.4.1. Bulker

Under the 2 mm hole size scenario, only weather categories 1.5/D for both day and night and 1.5/F in the night-time display cloud footprints. The night-time category 1.5/F weather conditions produce the largest footprint with a downwind distance of ~890 m and a cloud width of ~24 m. The category 1.5/D weather conditions occur away from the hole and produce smaller cloud footprints.

Under the 23 mm hole size scenario, weather category 1.5/D in the night-time produced the greatest cloud footprint with a distance downwind of ~6,600 m and a cloud width of ~400 m. The daytime category 1.5/D and night-time category 1.5/F weather conditions produced cloud footprints of similar sizes however the latter produces a much narrower and longer footprint reaching a downwind distance of ~9,500 m. The other weather conditions produced much smaller cloud footprints.

Under the 200 mm hole size scenario, category 5/D weather conditions in the daytime produced the greatest cloud footprint with a downwind distance of ~14,800 m and a cloud width of ~1200 m. Category 9/D and 5/D weather conditions for both day and night produce similar cloud footprints. Category 1.5/D in the daytime produces the greatest cloud width at ~2,800 m, the other weather conditions produce smaller footprints.

7.5.4.2. Tanker

Under the 2 mm hole size scenario, there were no daytime or night-time exceedances for the short-term limit or the long-term limit.

Under the 23 mm hole size scenario, the greatest cloud footprint occurred under weather category 1.5/F where the cloud width was ~280 m and the downwind distance was ~11,700 m. Category 1.5/D was similar for both day and night reaching a cloud width of ~320 m and a downwind distance of ~6,600 m. The other weather conditions produced much smaller cloud footprints.

Under the 200 mm hole size scenario, the largest cloud footprint occurred in the daytime under category 1.5/D weather conditions with a downwind distance of ~12,500 m and a cloud width of ~1,300 m. The other weather conditions produced footprints of similar scale with the smallest occurring in the in the night under category 5/E night-time weather conditions.

7.5.4.3. Containership

Under the 2 mm hole size scenario, there were no daytime or night-time exceedances for the short-term limit or the long-term limit.

Under the 23 mm hole size scenario, the greatest cloud footprint occurred in the night-time under weather category 1.5/F where the distance downwind was ~9,700 m and the cloud width was ~220 m. For both day and night, category 1.5/D weather conditions produced a cloud footprint of similar scale yet broader and shorter, with a downwind distance of ~5,200 m and a larger cloud width of ~260 m. The other weather conditions produced much smaller cloud footprints.

Under the 200 mm hole size scenario, the largest cloud footprint occurred in the daytime under category 1.5/D where the distance downwind reached ~20,500 m and the cloud width was ~1,300 m. The cloud footprint travelled further downwind in the night-time under category 1.5/F weather conditions reaching a distance of ~24,500 m. The other weather conditions produced smaller cloud footprints, particularly category 3/B in the day and category 9/D in the night.

Under the 1200 mm hole size scenario, the largest cloud footprint occurred in the night-time under category 1.5/F weather conditions where a downwind distance of ~82,000 m and a cloud width of ~2,200 m was reached. Weather categories 3/B in the day and 5/E in the night produced the smallest plumes with downward wind distances of ~30,000 m and ~50,000 m and cloud widths of ~3,600 m and ~3,000 m respectively. All other weather categories produced near identical and significant footprints of ~5,000 m downwind distance and cloud widths of ~3,000 m.

Figure A1221 Summary for 'worst case' air dispersal for 20 m

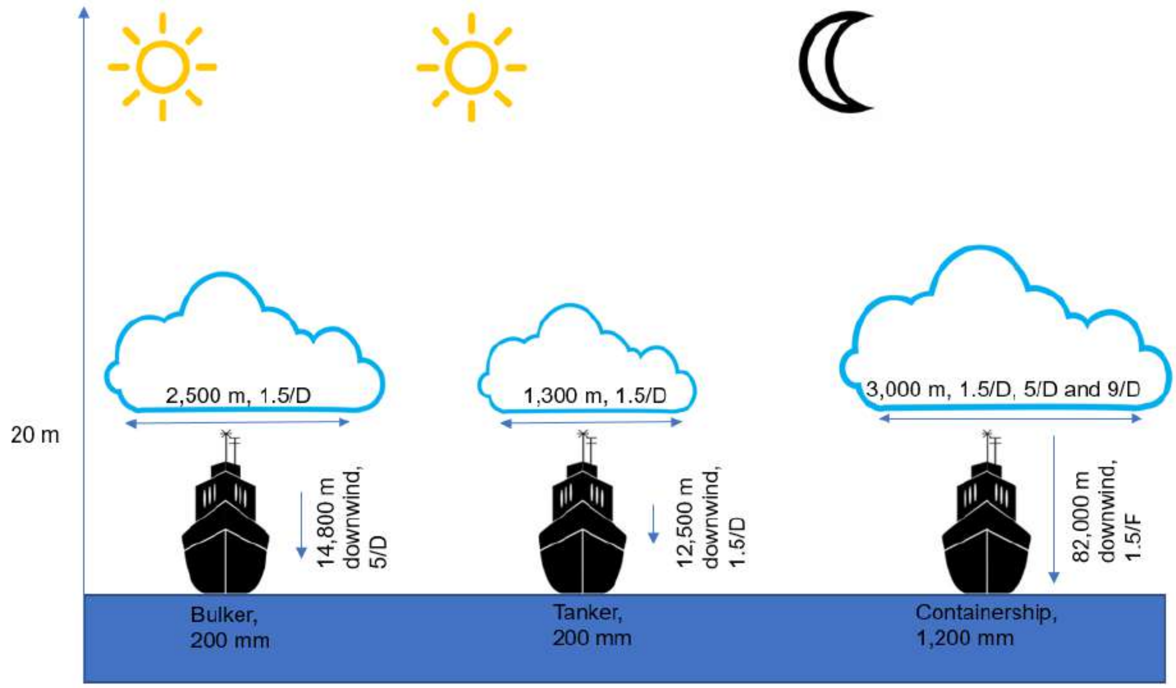


Figure A12 Summary of 'worst case' air dispersal for 20 m for each container type

7.5.5. H4

The H4 flight height band has been analysed using the air dispersion modelling results at 25 m and analysed per fuel storage type below.

7.5.5.1. Bulker

Under the 2 mm hole size scenario, only weather categories 1.5/D for both day and night and 1.5/F in the night-time display cloud footprints. The night-time category 1.5/F weather conditions produce the largest footprint with a downwind distance of ~780 m and a cloud width of ~15 m. The category 1.5/D weather conditions in the daytime occurs away from the hole and produce smaller cloud footprint.

Under the 23 mm hole size scenario, the greatest cloud footprint is experienced in the night-time under category 1.5/D where the distance downwind was ~6,500 m and the cloud width was ~400 m; a similar dispersal is observed under the same weather condition in the daytime. Category 1.5/F night-time weather condition produces a similar scaled cloud footprint however the downward distance was longer reaching ~9,400 m and the cloud width was ~200 m. The other weather categories produce much smaller cloud footprints.

Under the 200 mm hole size scenario, category 5/D weather conditions in the daytime produced the greatest cloud footprint with a downwind distance of ~14,800 m and a cloud width of ~1200 m. Category 9/D and 5/D weather conditions for both day and night produce near identical cloud footprints. Category 1.5/D in the daytime produces the greatest cloud width at ~2,600 m, the other weather conditions produce smaller footprints.

7.5.5.2. Tanker

Under the 2 mm hole size scenario, there were no daytime or night-time exceedances for the short-term limit or the long-term limit.

Under the 23 mm hole size scenario, there were no night-time exceedances for the short-term limit or long-term limit. In the daytime, all weather conditions display a cloud footprint with the greatest occurring under weather condition 1.5/D with a downwind distance of ~6,600 m and a cloud width of ~320 m. The other weather categories produce significantly smaller cloud footprints.

Under the 200 mm hole size scenario, the greatest cloud footprint is experienced in the daytime under category 1.5/D where the downwind distance was ~12,500 m and the cloud width was of ~1,300 m. The other weather conditions produced footprints of similar scale with the smallest occurring in the in the night under category 5/E weather conditions.

7.5.5.3. Containership

Under the 2 mm hole size scenario, there were no daytime or night-time exceedances for the short-term limit or the long-term limit.

Under the 23 mm hole size scenario, the greatest cloud footprint occurred in the night-time under weather category 1.5/F where the distance downwind was ~9,000 m and the cloud width was ~200 m. For both day and night, category 1.5/D weather conditions produced a cloud footprint of similar scale yet broader and shorter, with a downwind distance of ~5,200 m and a larger cloud width of ~260 m. The other weather conditions produced much smaller cloud footprints.

Under the 200,mm hole size scenario, the largest cloud footprint occurred in the daytime under category 1.5/D where the distance downwind reached ~20,500 m and the cloud width was ~1,300 m. The cloud footprint travelled further downwind in the night-time under category 1.5/F weather conditions reaching ~24,500 m. The other weather conditions produced smaller cloud footprints, particularly category 3/B in the day and category 9/D in the night.

Under the 1200 mm hole size scenario, the largest cloud footprint occurred in the night-time under category 1.5/F weather conditions where a downwind distance of ~82,000 m and a cloud width of ~2,200 m was reached. Weather categories 3/B in the day and 5/E in the night produced the smallest plumes with downward wind distances of ~30,000 m and ~50,000 m and cloud widths of ~3,600 m and ~1,500 m respectively. All other weather categories produced near identical and significant footprints of ~5,000 m downwind distance and cloud widths of ~3,000 m.

Figure A1322 Summary for 'worst case' air dispersal for 25 m

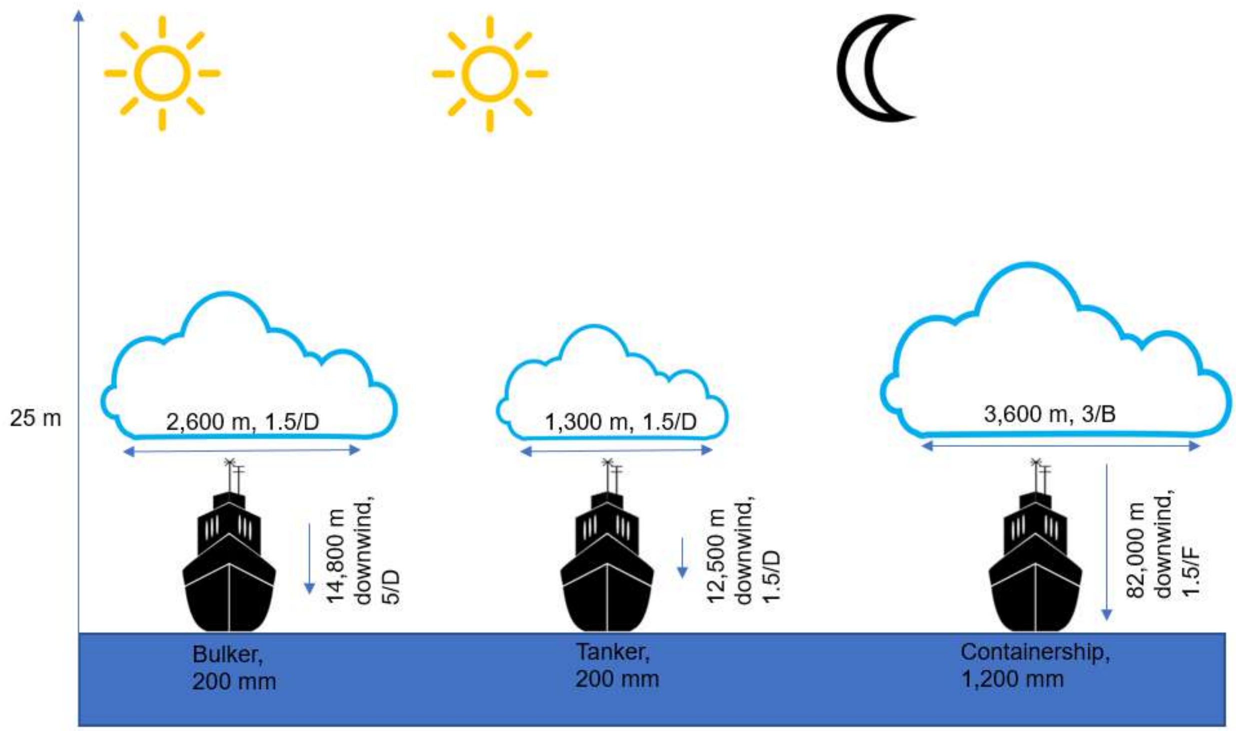


Figure A13 Summary of 'worst case' air dispersal for 25m for each container type

7.5.6. H5

The H5 flight height band has been analysed using the air dispersion modelling results at 180 m and analysed per fuel storage type below.

7.5.6.1. Bulker

Under the 2 mm hole size scenario, there were no daytime or night-time exceedances for the short-term limit or the long-term limit.

Under the 23 mm hole size scenario, the greatest cloud footprint is experienced in the night-time under the Category 1.5/D weather condition where the distance downwind was ~3,200 m and the cloud width was ~280 m. Category 1.5/D day-time weather conditions provides a similar sized dispersal although the downwind dispersal is longer at ~3,600 m with a slimmer cloud width of ~140 m. Category 3/B weather conditions provided the only other dispersal in the day time with a downwind distance of ~200 m, and a cloud width of ~20 m and did not exceed under the short-term limit.

Under the 200 mm hole size scenario, the greatest cloud footprint is experienced in both the daytime and night-time under the Category 1.5/D weather condition where the distance downwind was ~2,000 m and the cloud width was ~900 m. Category 3/B weather conditions provided the only other dispersal in the daytime with a downwind distance of ~2,200 m, and a cloud width of ~500 m.

7.5.6.2. Tanker

Under the 2 mm hole size scenario, there were no daytime or night-time exceedances for the short-term limit or the long-term limit.

Under the 23 mm hole size scenario, the greatest cloud footprint is experienced in the night-time under the Category 1.5/F weather condition where the distance downwind was ~1,300 m and the cloud width was ~38 m. Category 3/B and 1.5D weather conditions provided the only other dispersals in the daytime and night-time respectively and there were no exceedances under the short-term limit.

Under the 200 mm hole size scenario, the greatest cloud footprint is experienced in the night-time under the Category 1.5/D weather condition where the distance downwind was ~11,000 m and the cloud width was ~800 m. There was also a much smaller exceedance during the 5/D weather scenario (nigh-time) and smaller exceedances from both 3/B and 1.5D (daytime).

7.5.6.3. Containership

Under the 2 mm hole size scenario, there were no daytime or night-time exceedances for the short-term limit or the long-term limit.

Under the 23 mm hole size scenario, there were no daytime or night-time exceedances for the short-term limit or the long-term limit.

Under the 200 mm hole size scenario, all modelled weather scenarios exceed the limits with the greatest cloud footprint being experienced in the night-time under the Category 1.5/D weather condition where the distance downwind was ~15,000 m and the cloud width was ~1,100 m.

Under the 1200 mm hole size scenario, during the day all weather scenarios had a similar dispersal pattern of ~50,000 m downwind distance and 3,000 m cloud width, except 3/B which was wider but considerably shorter. During the night all weather scenarios had a similar dispersal pattern of, again, ~50,000 m downwind distance and 3,000 m cloud width, except 5/E which was much smaller and 1.5F which was much slimmer but ~11,000 m longer. The same pattern was observed for both exposure limits.

Figure A1423 Summary of 'worst case' air dispersal or 180 m

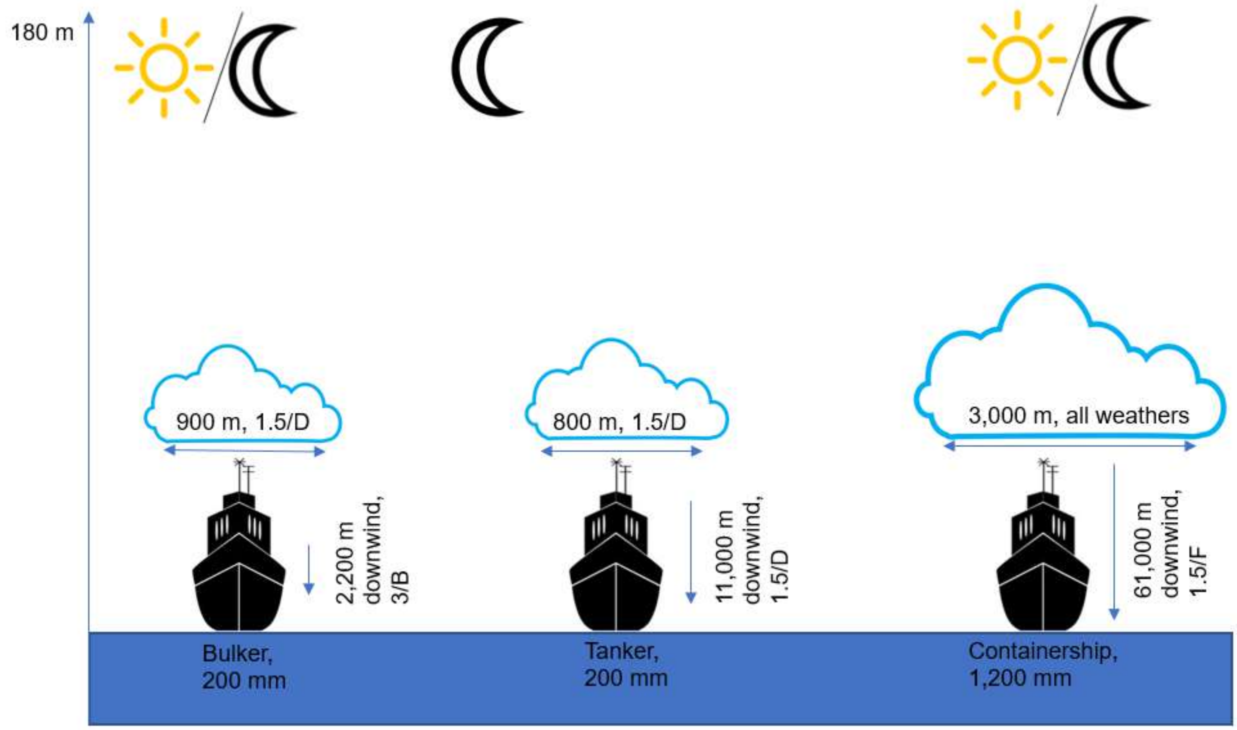


Figure A14 Summary of ‘worst case’ air dispersal for 180m for each container type

7.6. Appendix 6

Graphical Results of PHAST Modelling for MGO

This section presents and describes the graphical results of the PHAST modelling for MGO spill scenarios. The results are presented by ship type, hole size and by a day/night comparison.

Table A38 Results for Bunkering spill of MGO, 2mm hole, day/night

<table>
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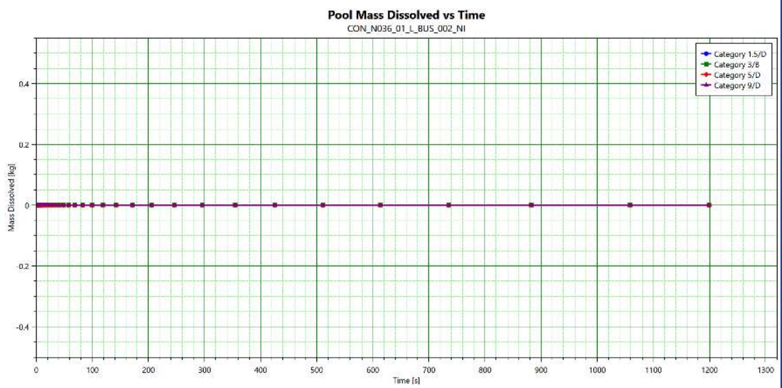
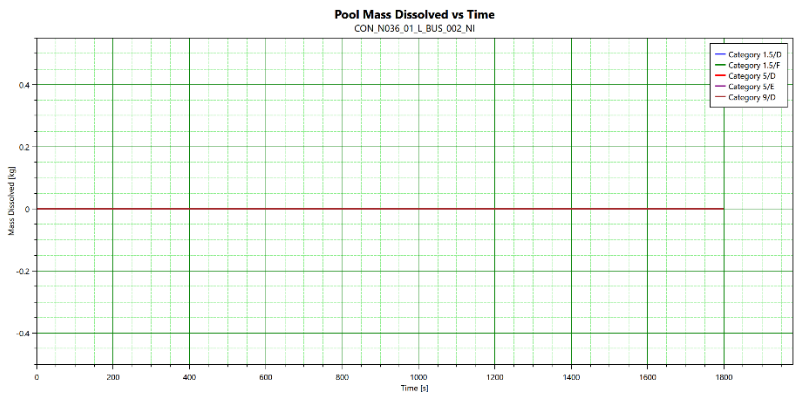
<tr><td>Pool Mass Dissolved</td><td>
</td><td>
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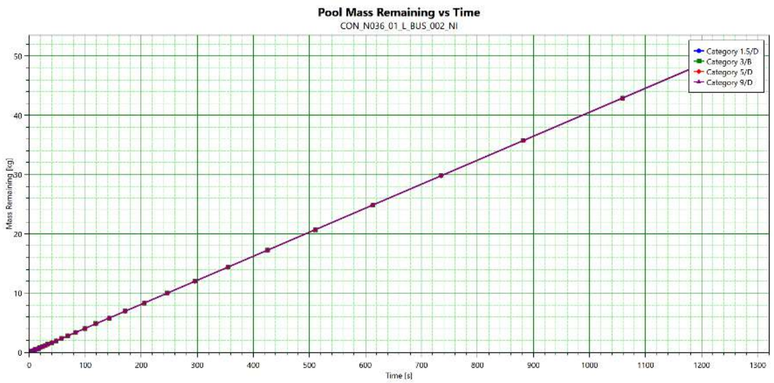
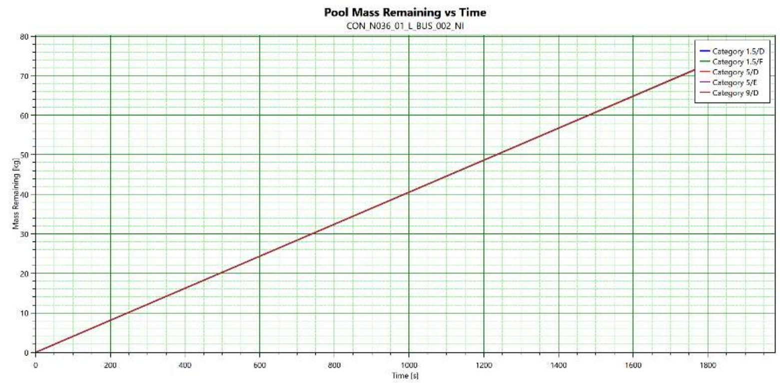
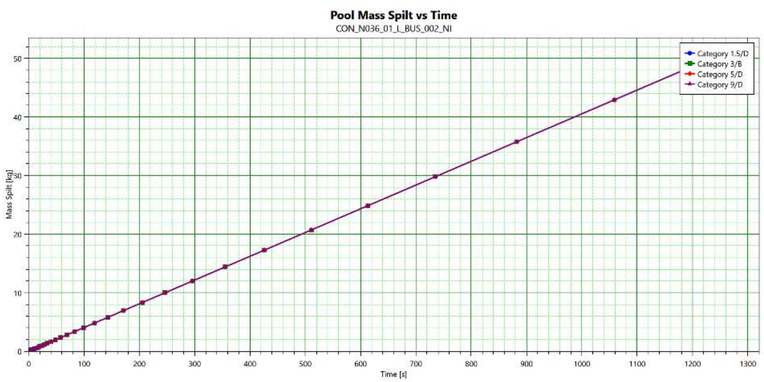
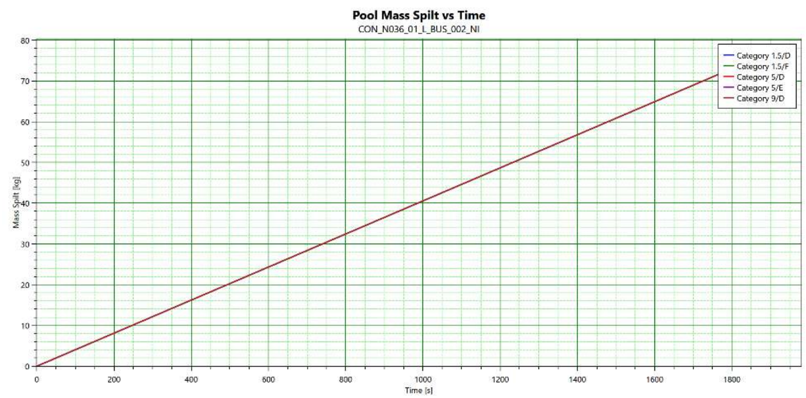
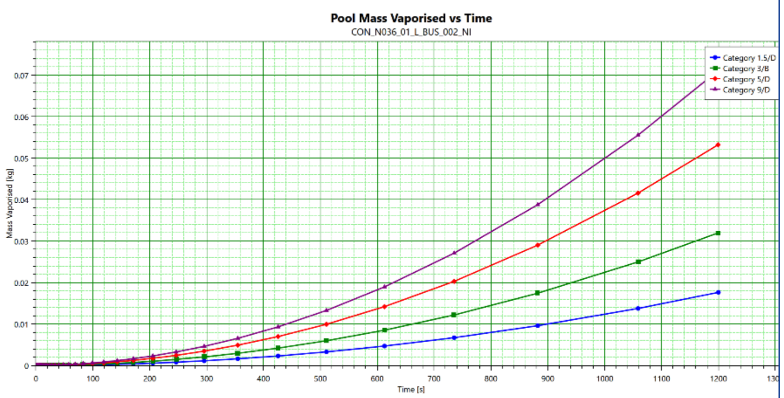
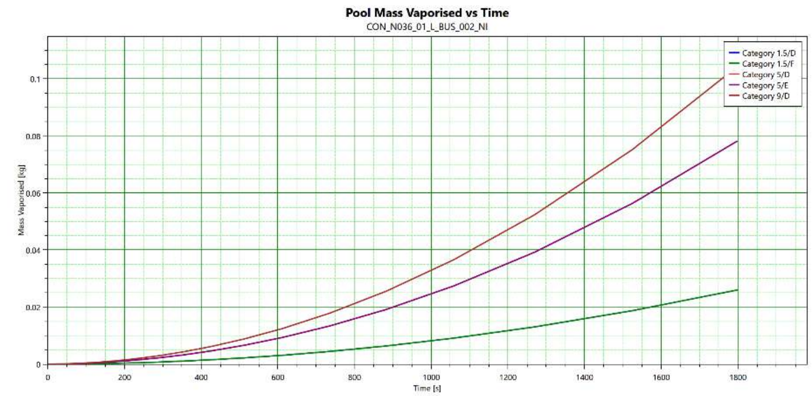
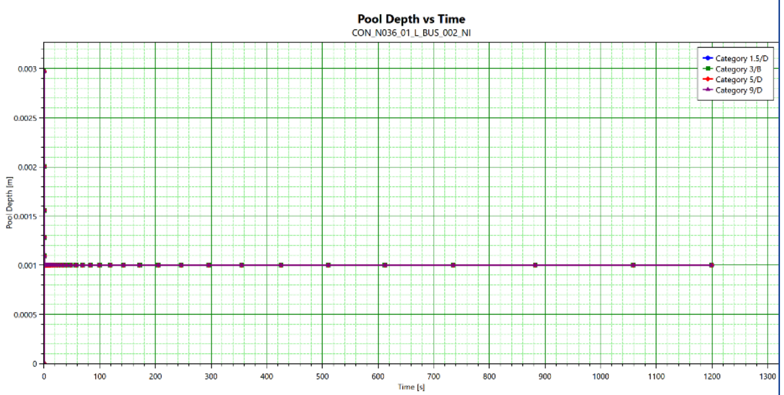
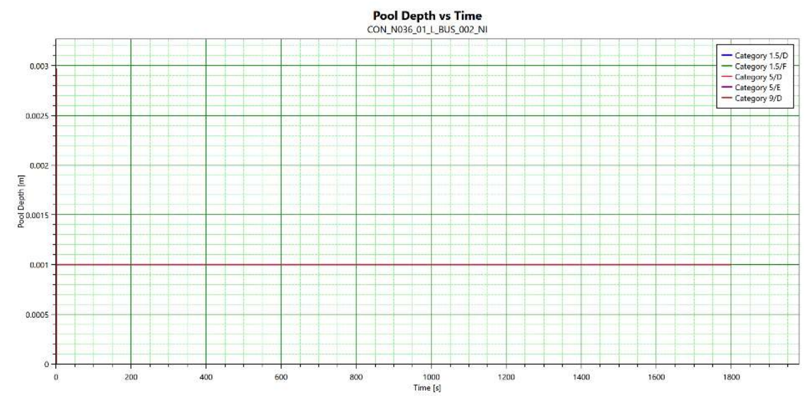
	Day	Night
Pool Mass Remaining		
Mass Split		

	Day	Night
Mass Vaporised		
Pool Depth		

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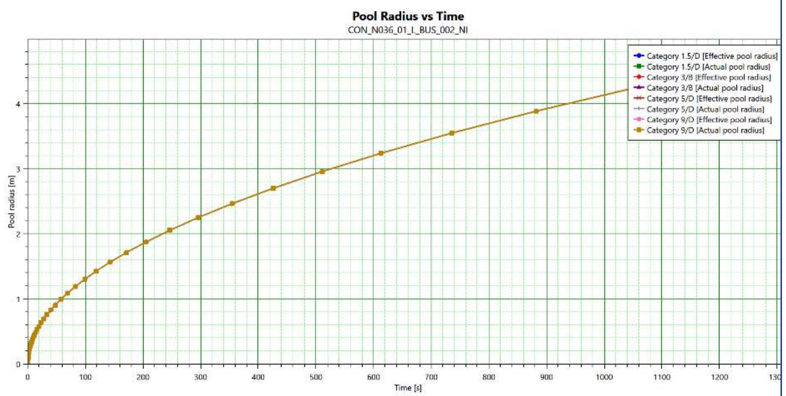
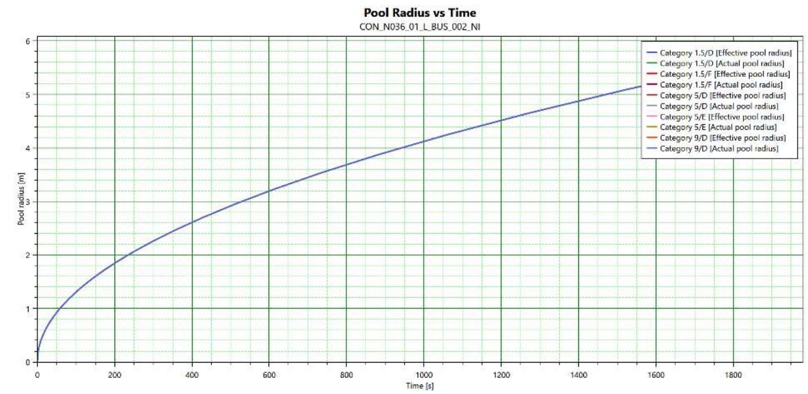
<tr><td>Pool Radius</td><td>
</td><td>
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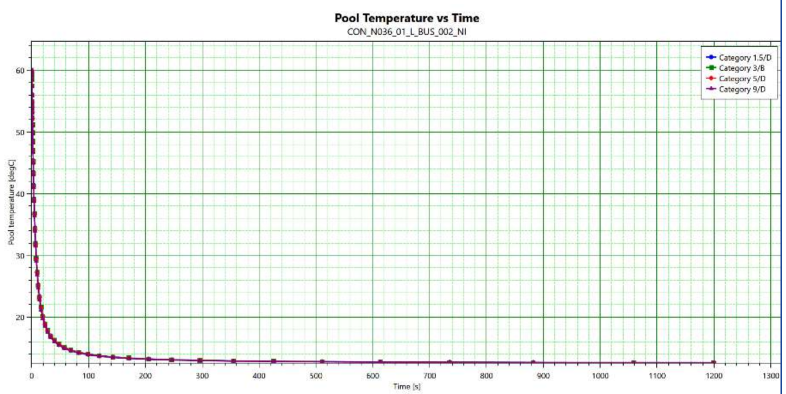
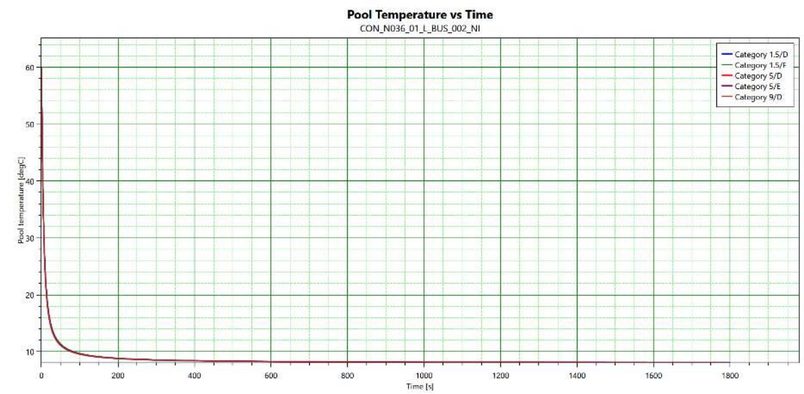
<tr><td>Pool Temp</td><td>
</td><td>
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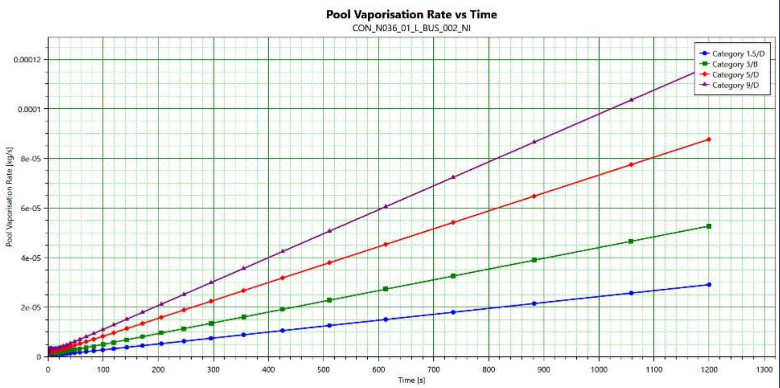
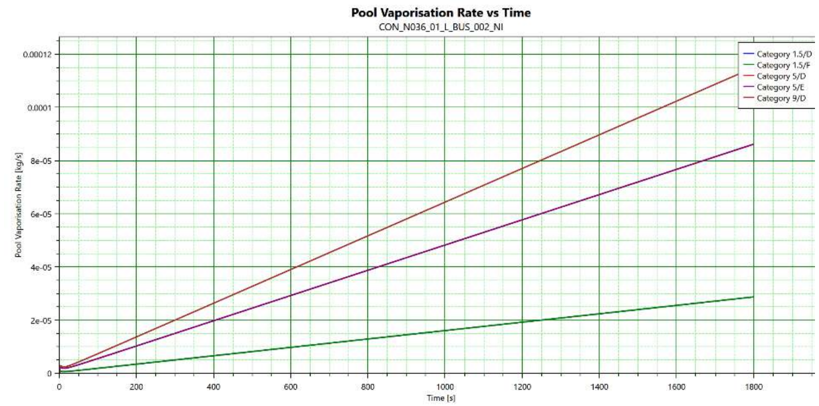
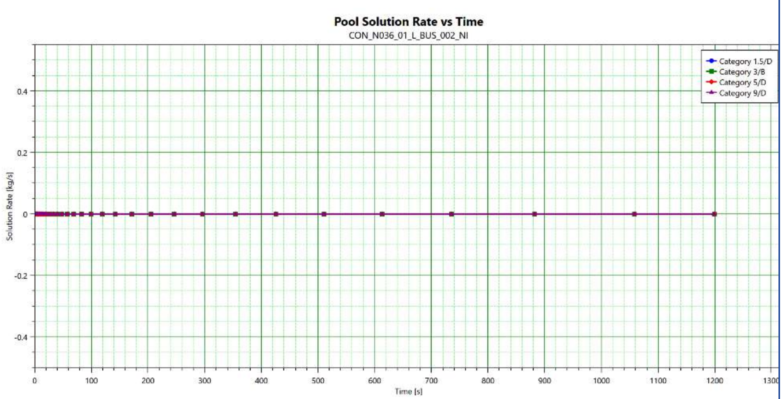
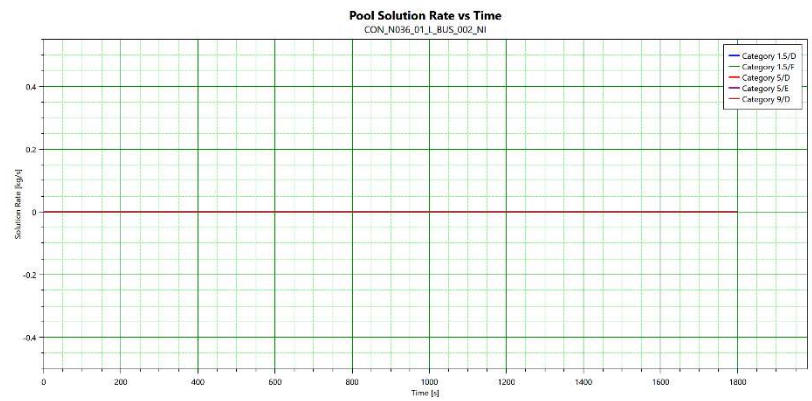
	Day	Night
Pool Vaporisation Rate		
Solution Rate		

Table A39 Results for Bunkering spill of MGO, 23 mm hole, day/night

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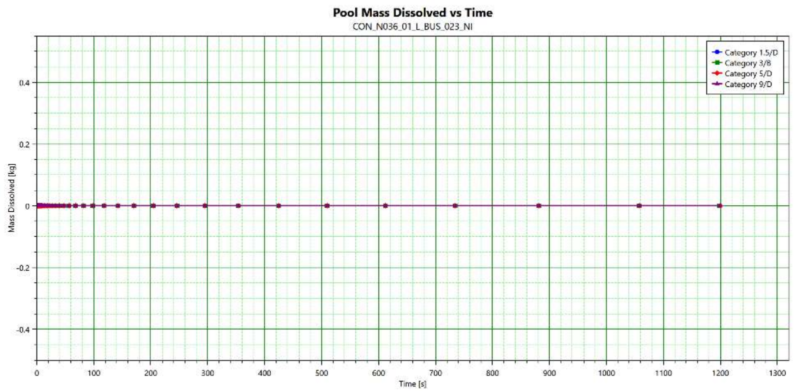
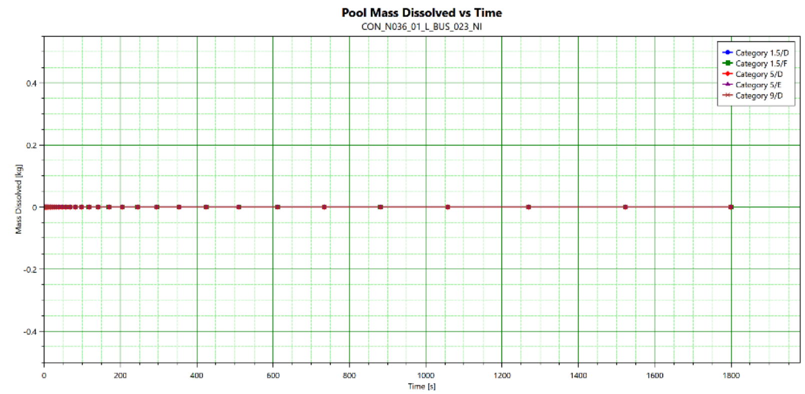
<tr><td>Pool Mass Dissolved</td><td>
</td><td>
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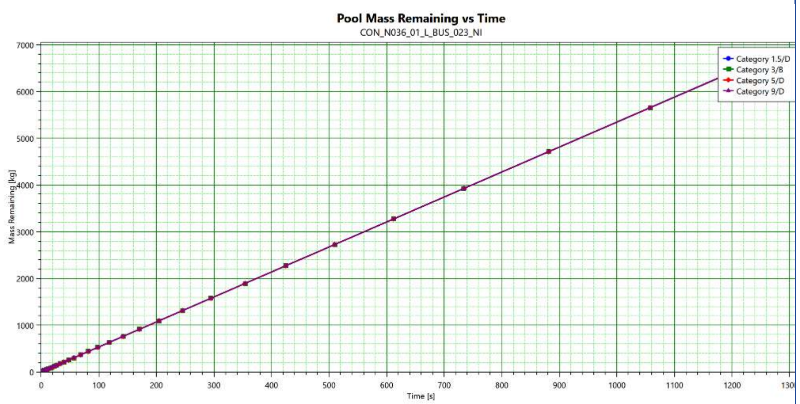
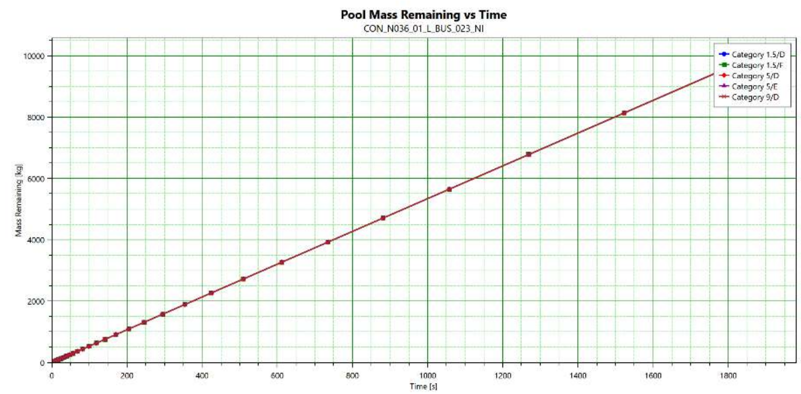
<tr><td>Pool Mass Remaining</td><td>
</td><td>
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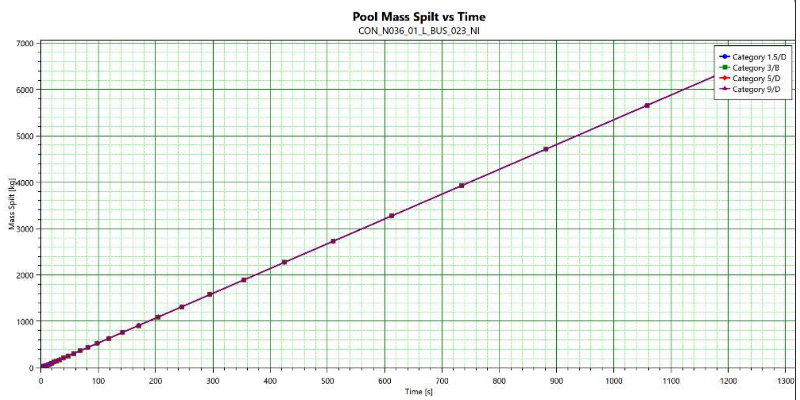
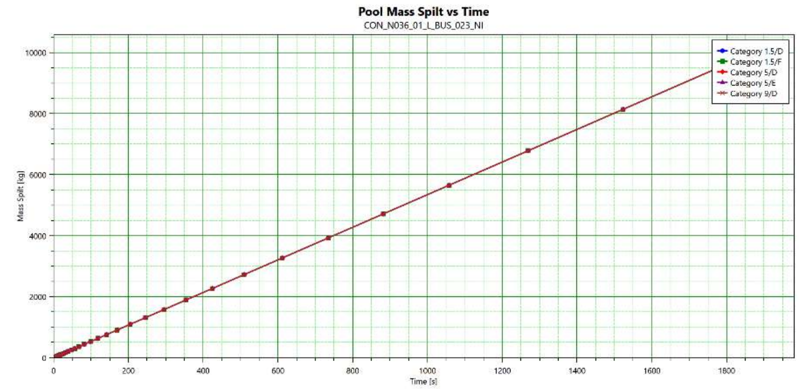
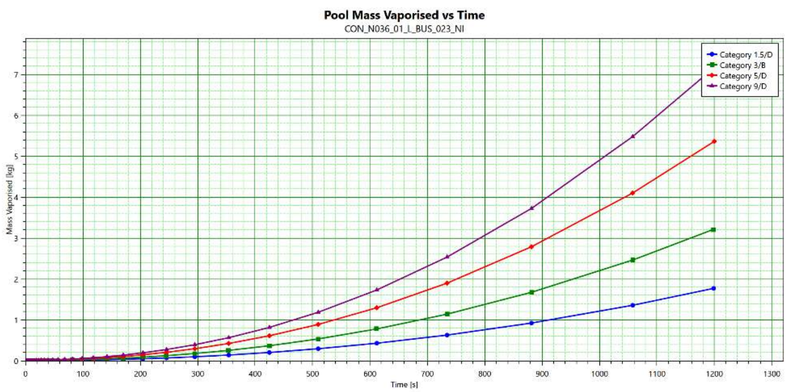
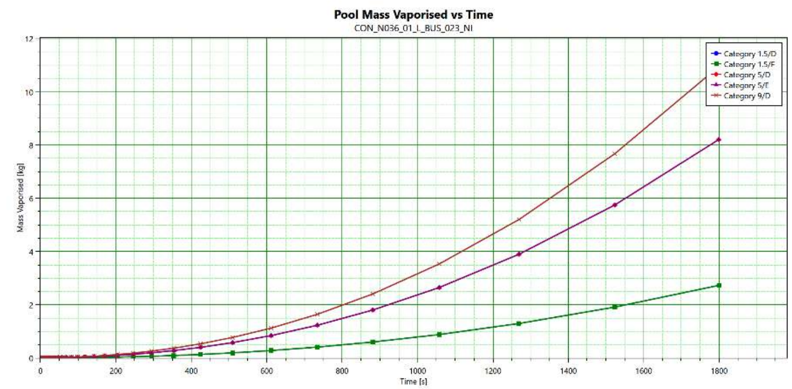
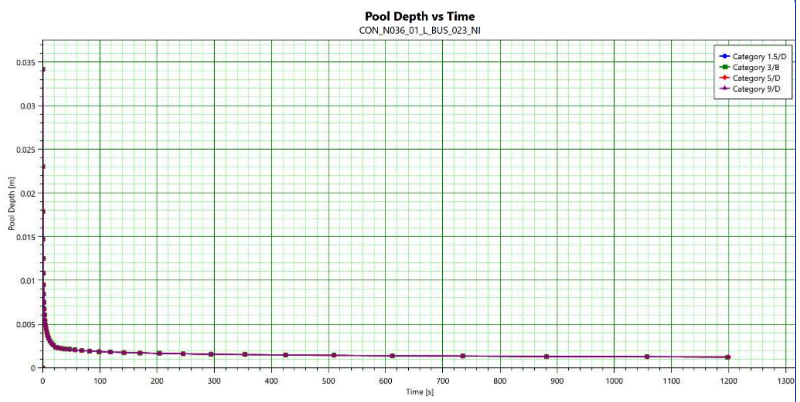
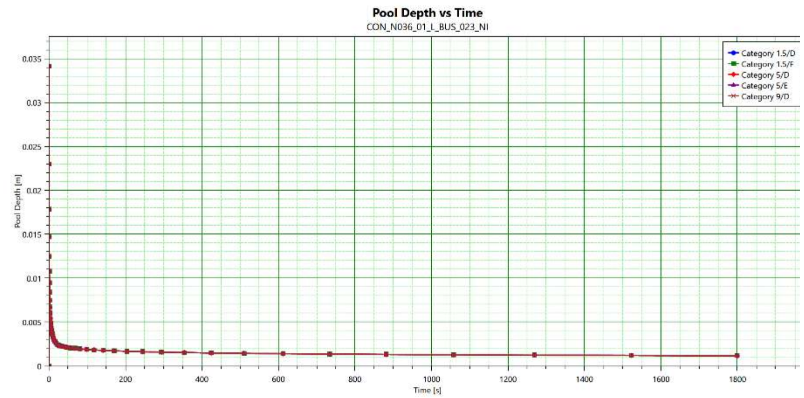
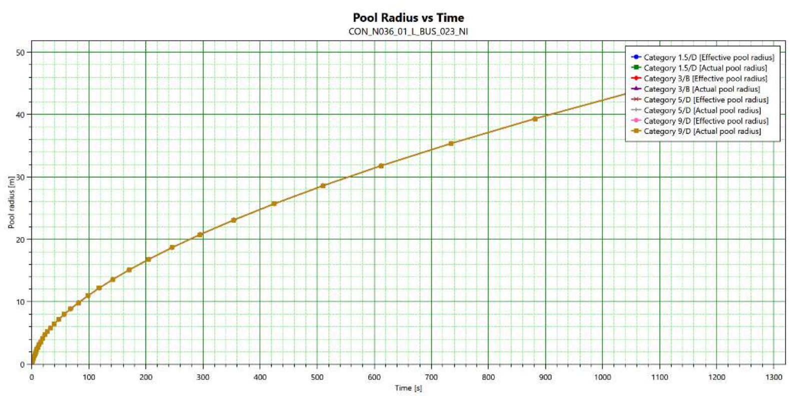
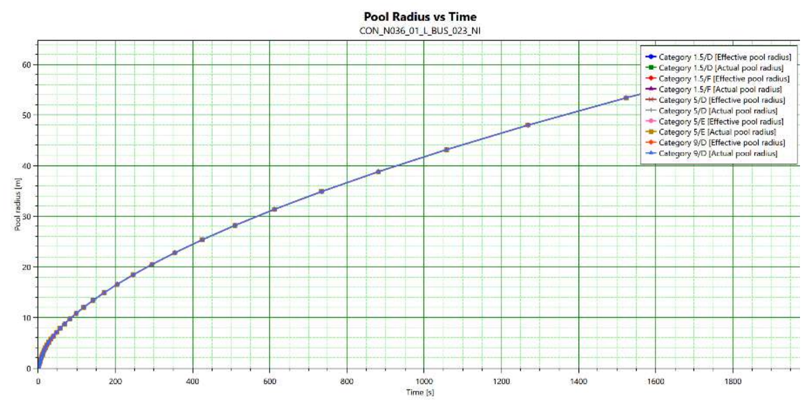
	Day	Night
Mass Split		
Mass Vaporised		

	Day	Night
Pool Depth		
Pool Radius		

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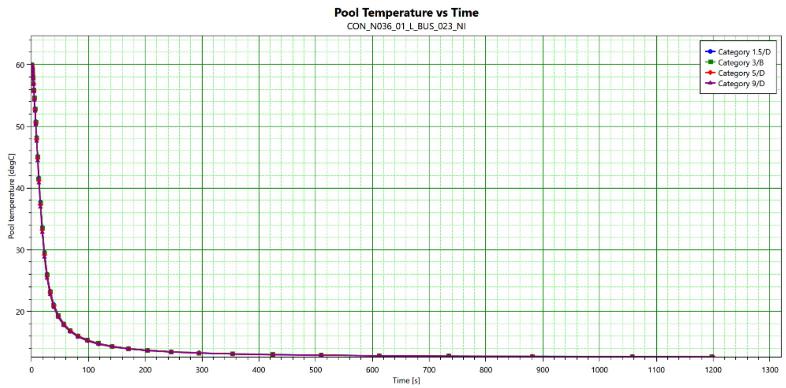
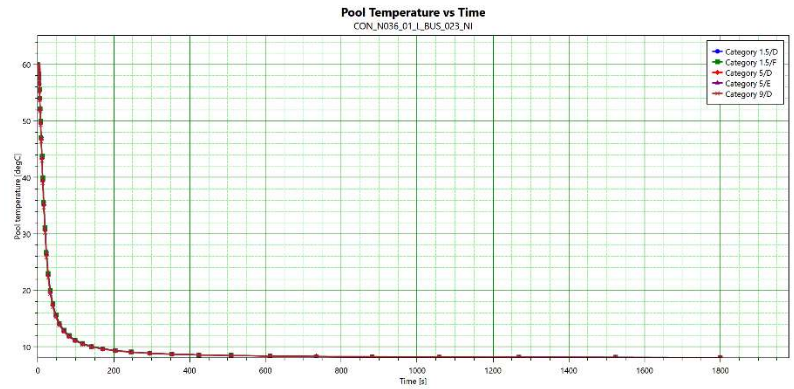
<tr><td>Pool Temp</td><td>
</td><td>
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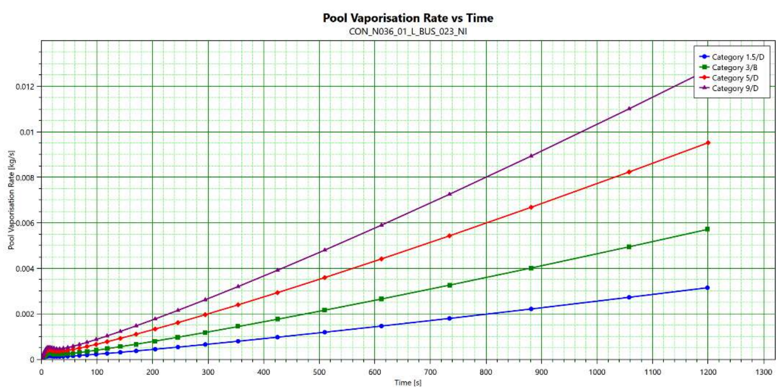
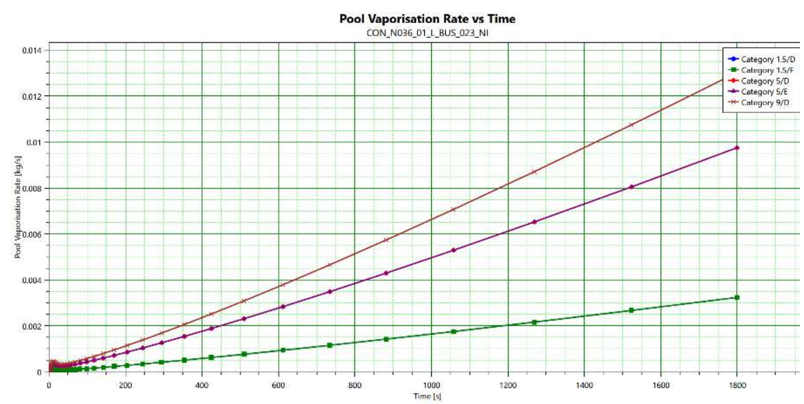
<tr><td>Pool Vaporisation Rate</td><td>
</td><td>
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<table>
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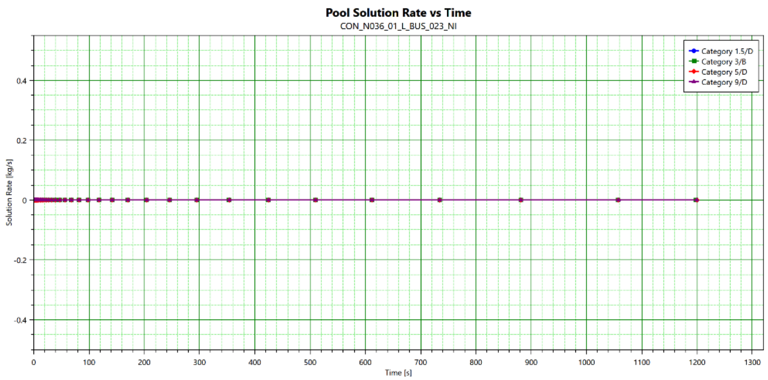
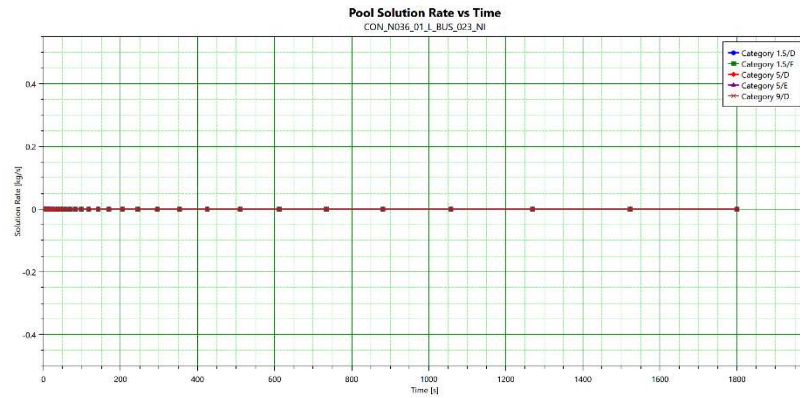
<tr><td>Solution Rate</td><td>
</td><td>
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Table A40 Results for Bunkering spill of MGO, 219 mm hole, day/night

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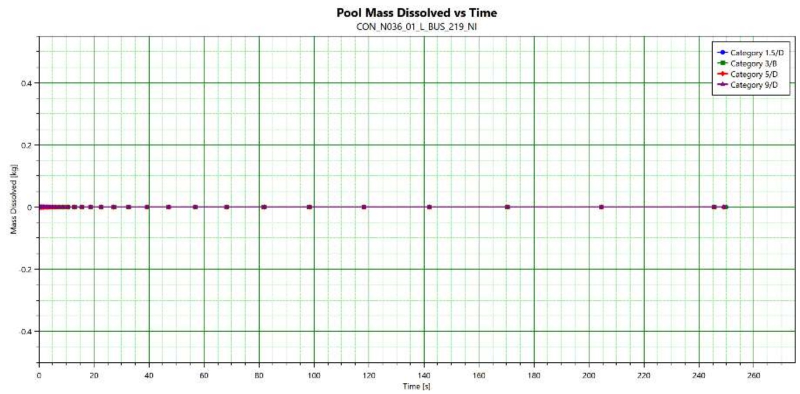
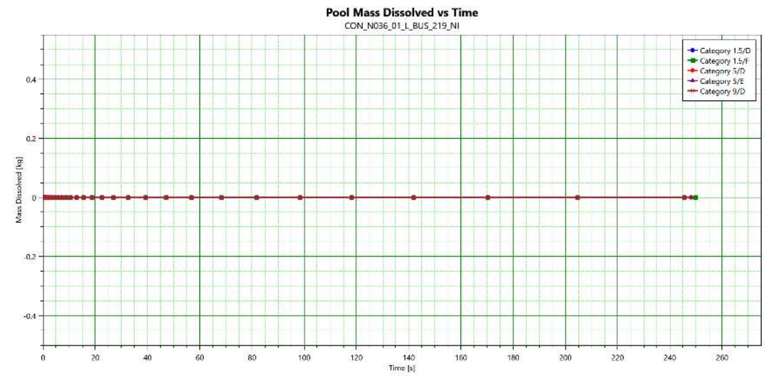
<tr><td>Pool Mass Dissolved</td><td>
</td><td>
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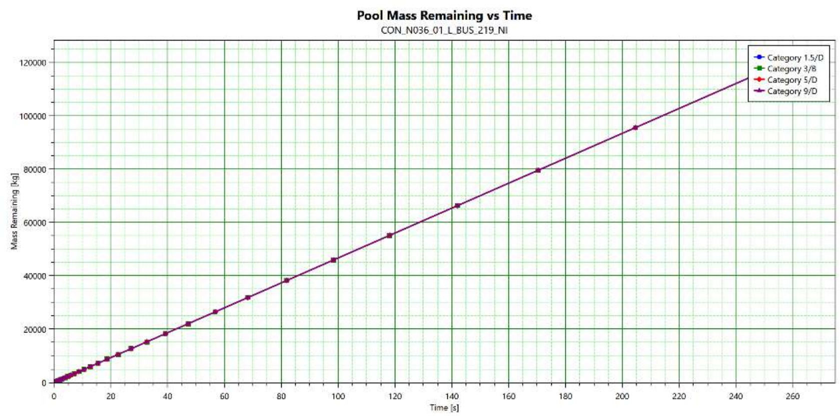
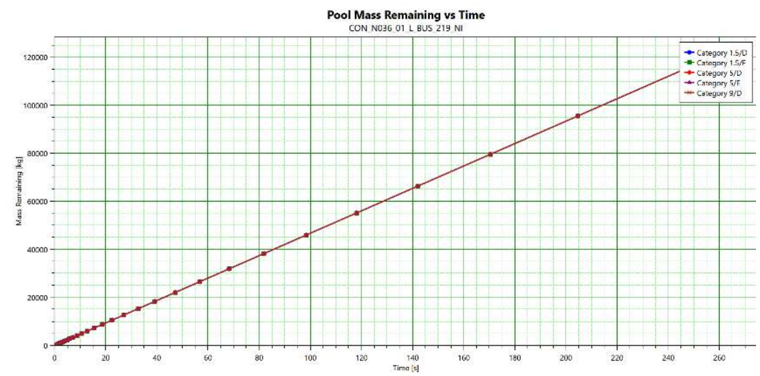
<tr><td>Pool Mass Remaining</td><td>
</td><td>
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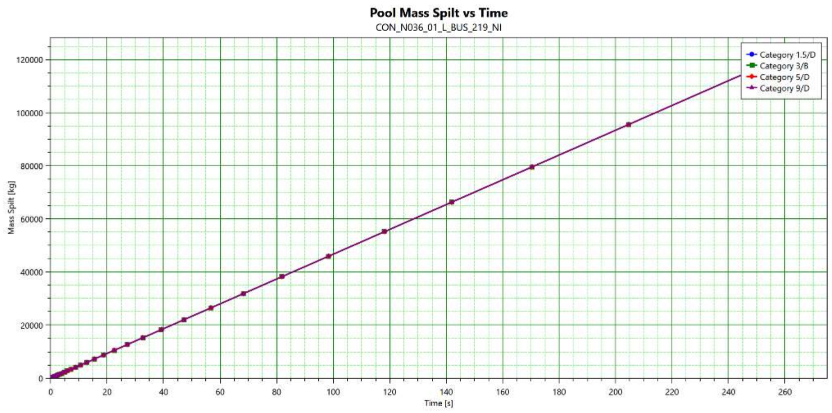
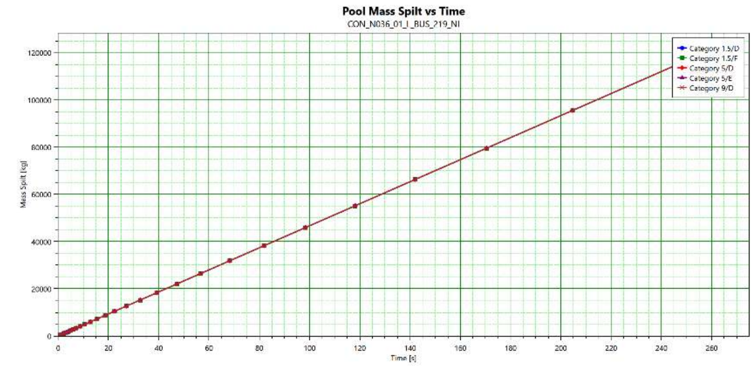
<tr><td>Mass Split</td><td>
</td><td>
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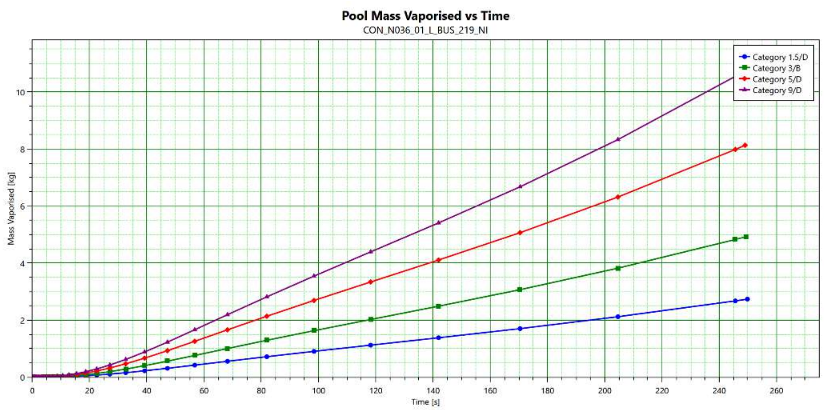
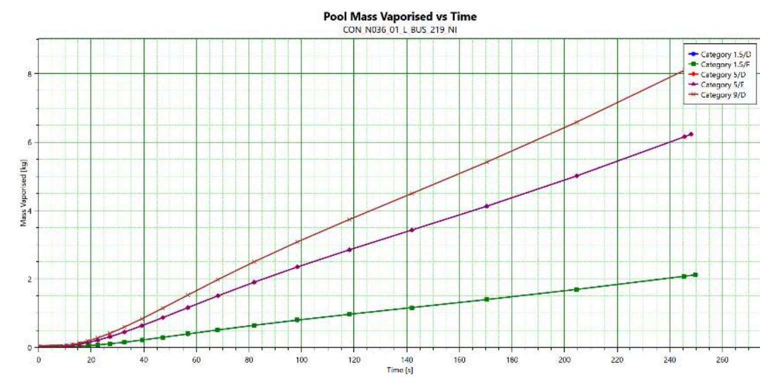
<tr><td>Mass Vaporised</td><td>
</td><td>
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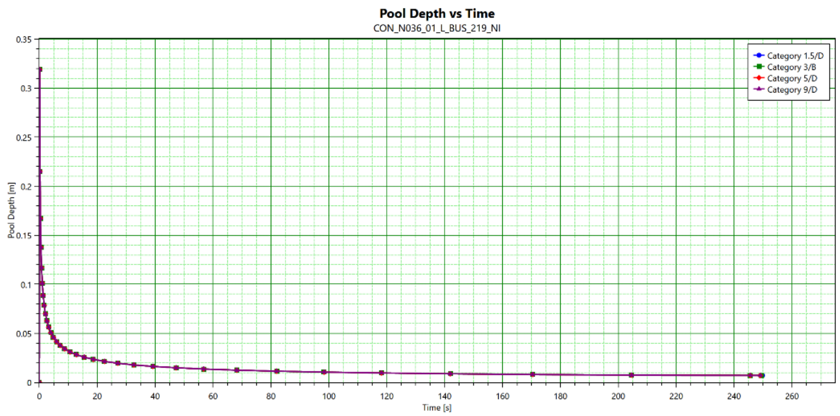
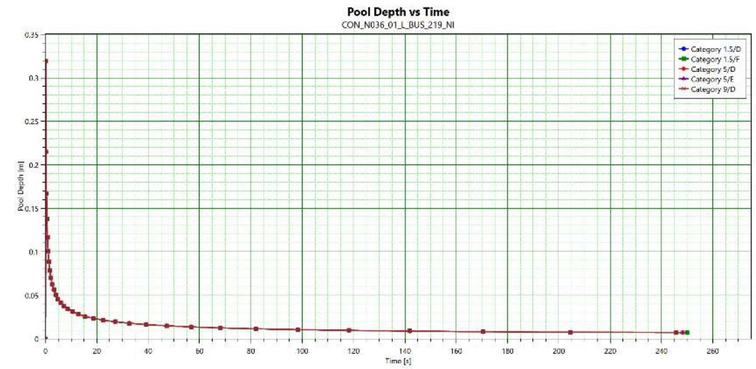
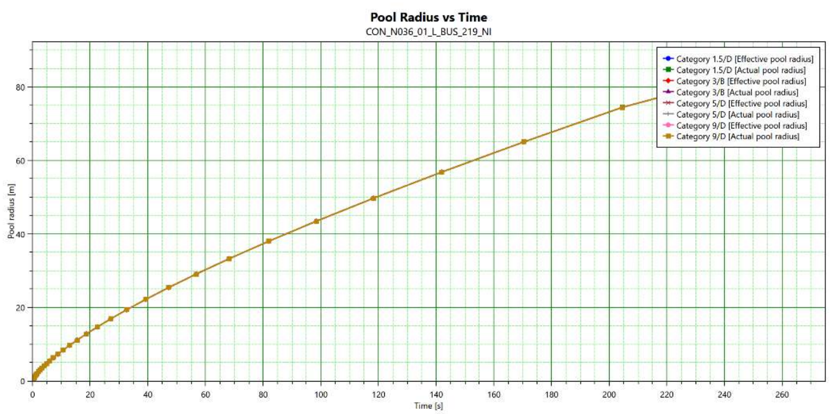
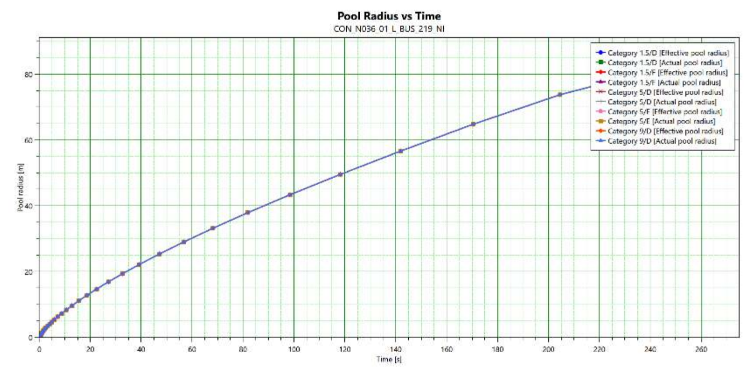
	Day	Night
Pool Depth		
Pool Radius		

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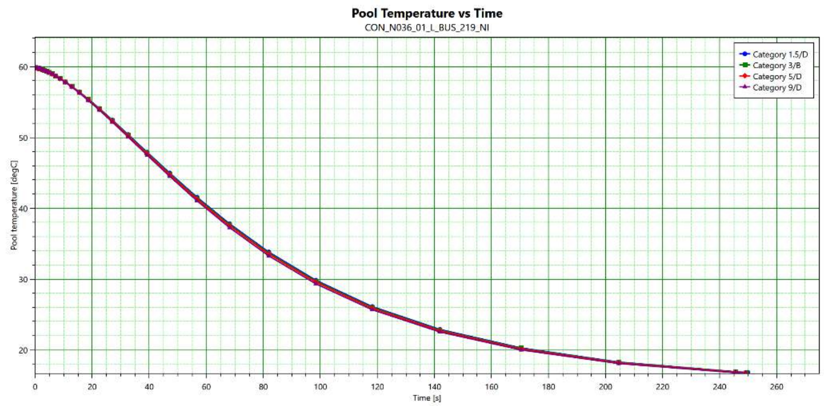
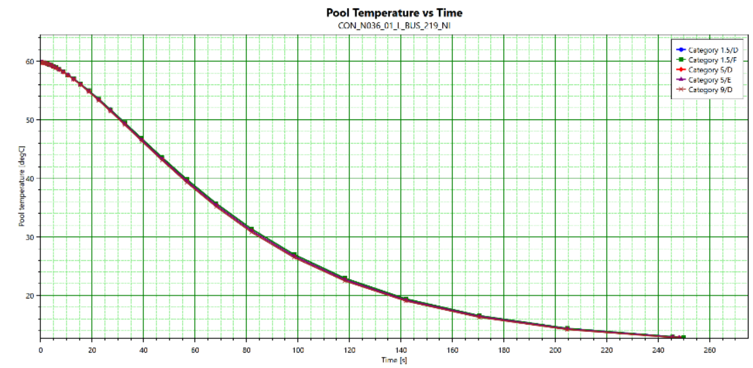
<tr><td>Pool Temp</td><td>
</td><td>
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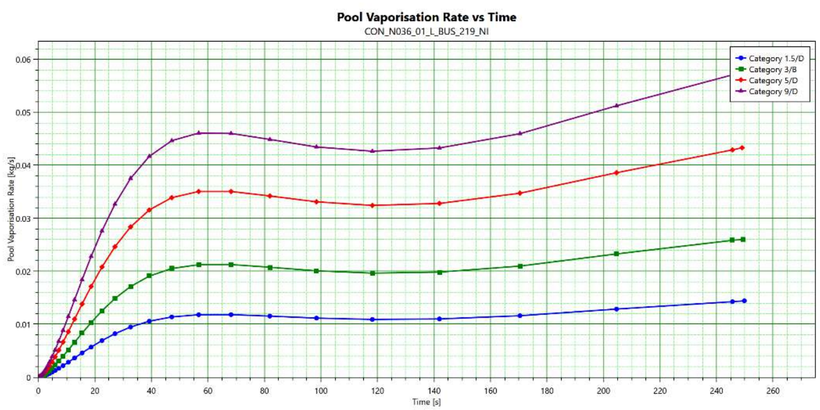
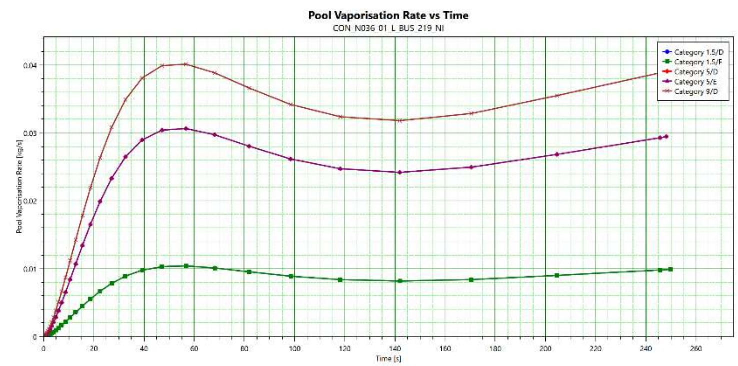
<tr><td>Pool Vaporisation Rate</td><td>
</td><td>
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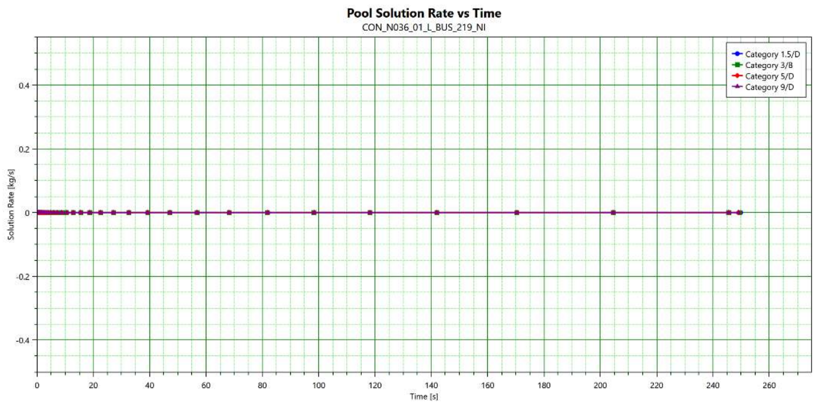
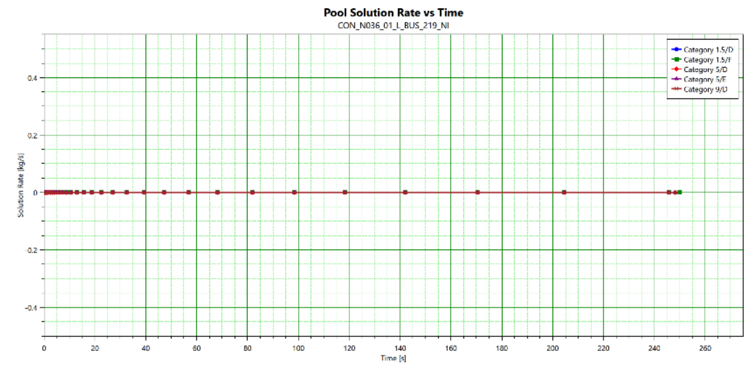
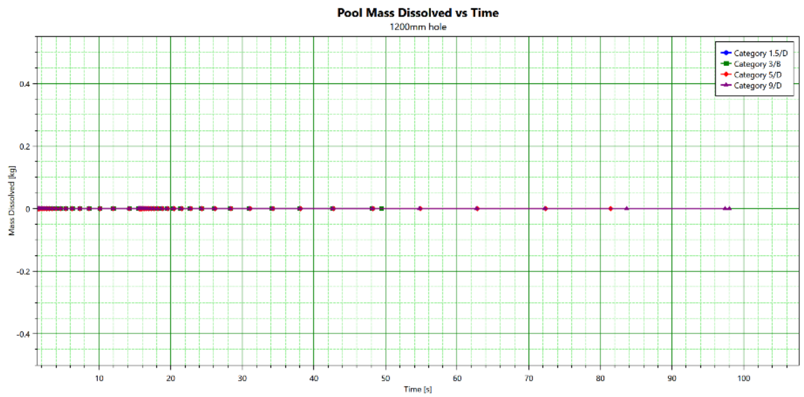
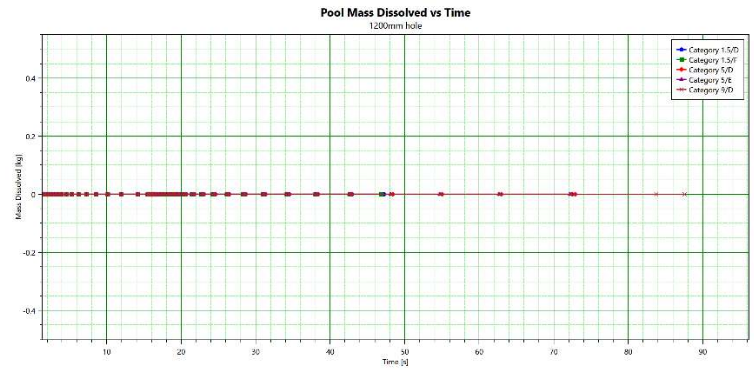
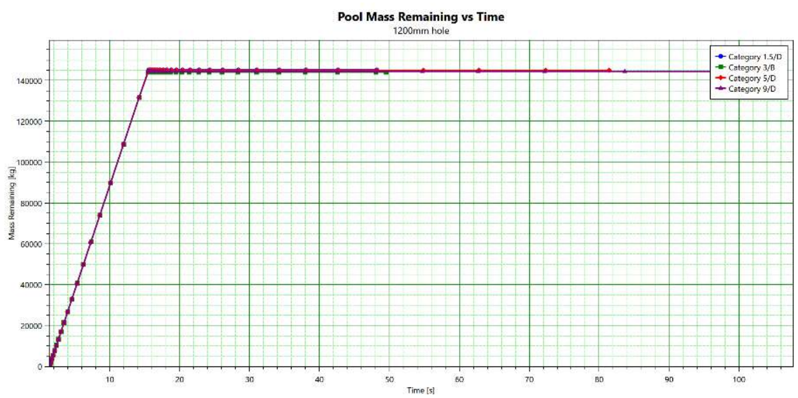
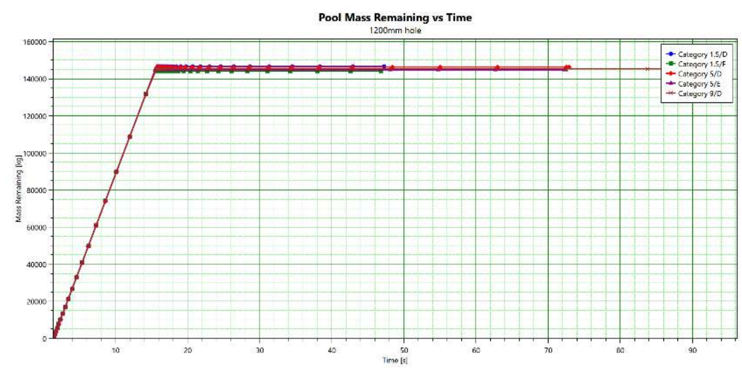
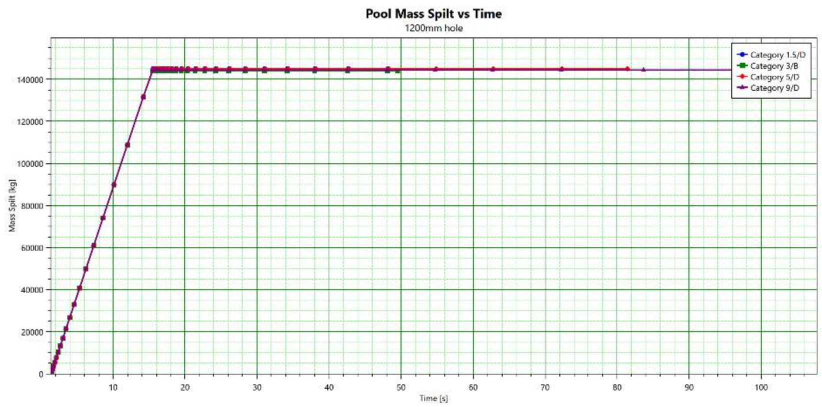
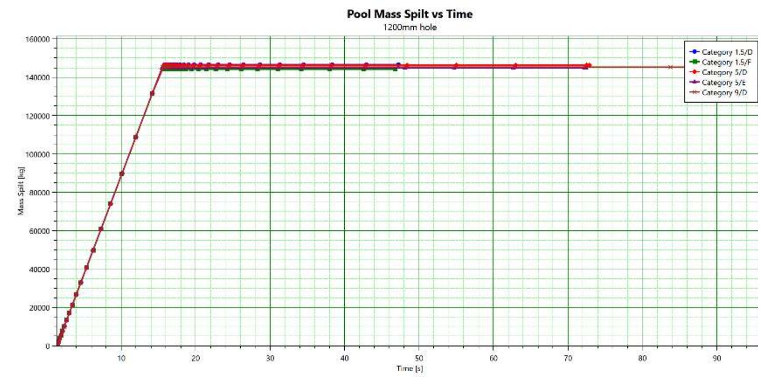
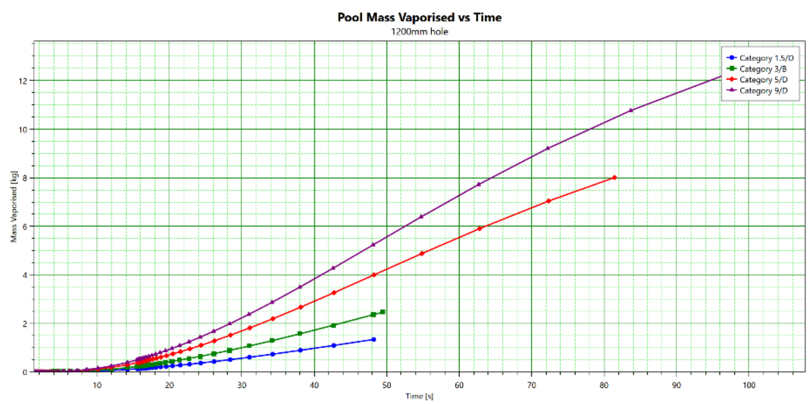
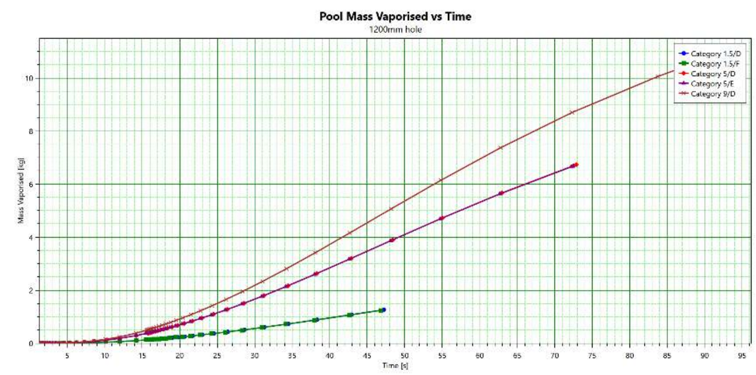
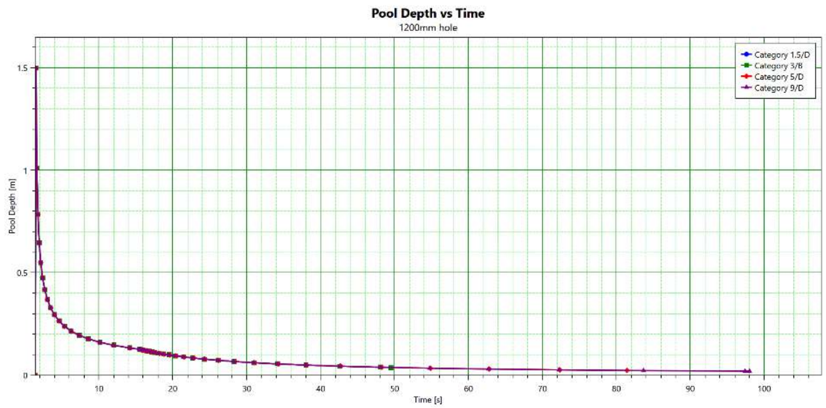
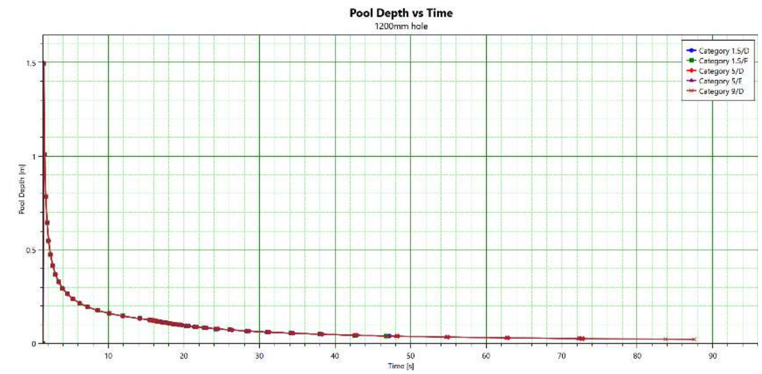
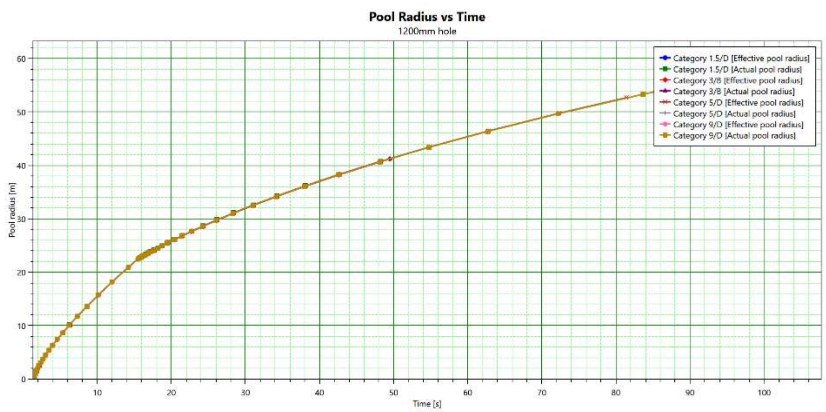
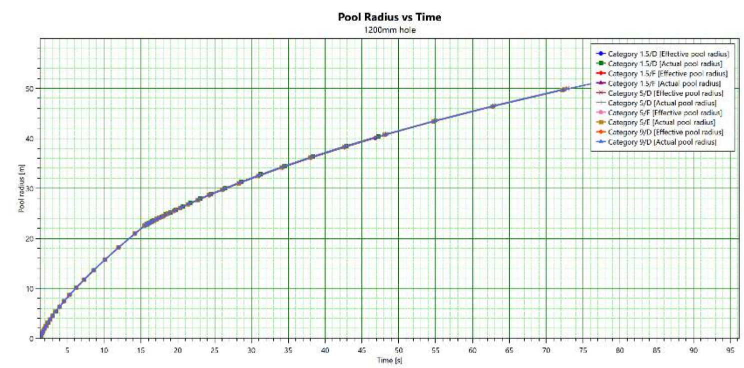
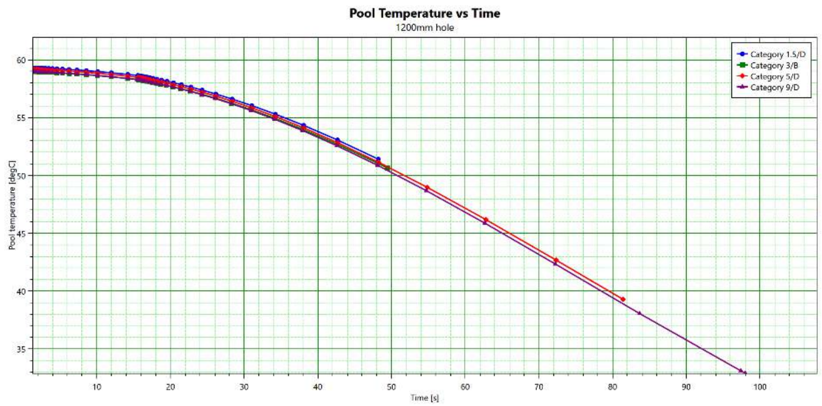
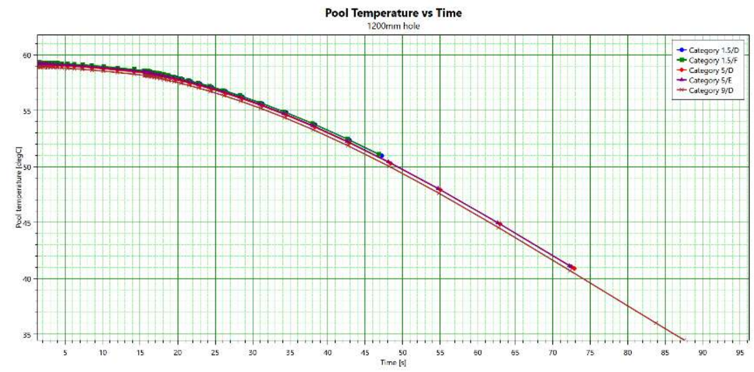
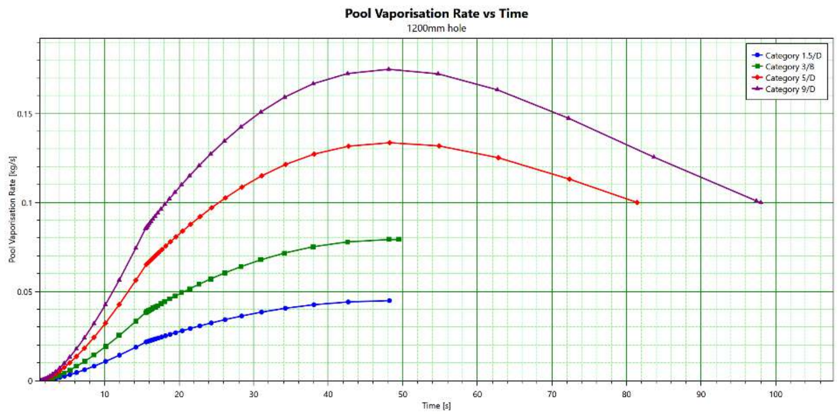
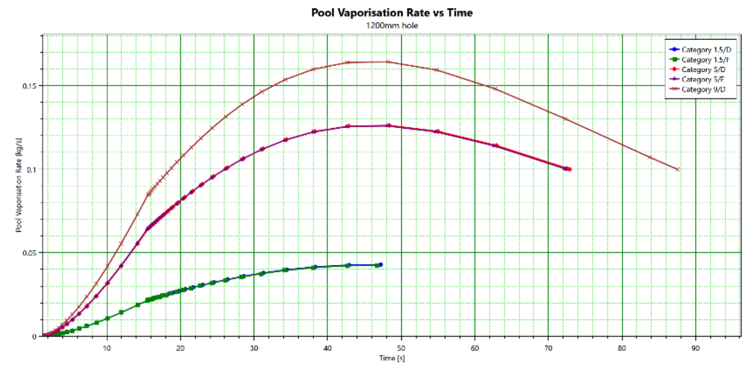
	Day	Night
Solution Rate		

Table A41 Results for Bunkering spill of MGO, 1200mm hole, day/night

	Day	Night
Pool Mass Dissolved		
Pool Mass Remaining		

	Day	Night
Mass Split		
Mass Vaporised		

	Day	Night
Pool Depth		
Pool Radius		

<table>
<tr><th></th><th>Day</th><th>Night</th></tr>
<tr><td>Pool Temp</td><td>
</td><td>
</td></tr>
<tr><td>Pool Vaporisation Rate</td><td>
</td><td>
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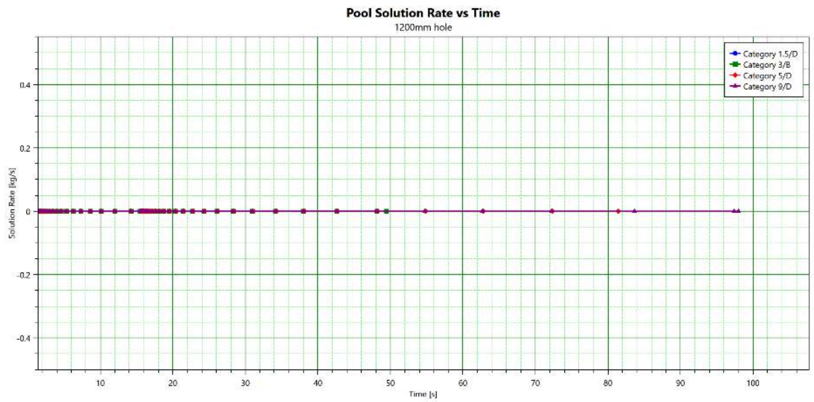
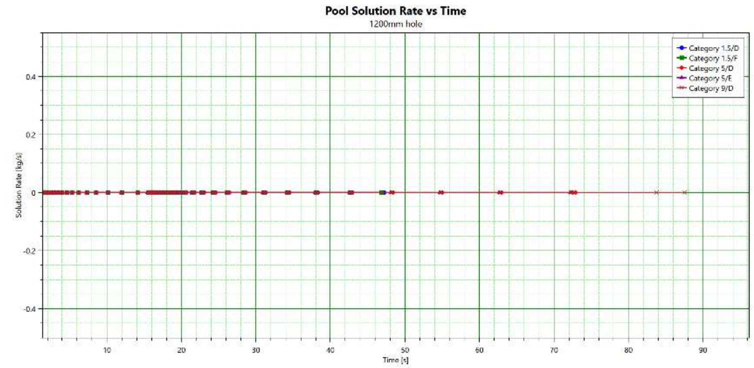
	Day	Night
Solution Rate		

7.7. Appendix 7

PHAST Modelling for ammonia Summary

This section presents a high-level summary of the PHAST modelling results shown above in Appendix 6. The presentation shows the graphical outputs for each scenario ranked (according to the scale below) lowest to highest in terms of the greatest value displayed by the parameter. Note that the scaling does not take into account whether is 'highest' or 'lowest' values are a relative positive or a negative for that determinand and further that the greatest value refers to the greatest value achieved over the time modelled and is not necessarily a start or end value.

Scale		
	(green)	Lowest
	(yellow)	
	(amber)	
	(orange)	Applicable to night scenarios
	(red)	Highest
	(blue)	All scenarios equal
	x	Weather condition not assessed under this scenario

Table A42 High-level summary of PHAST modelling for oil spills

Weather Conditions	Model output	Scenario							
		Day				Night			
		Bunkering scenario				Bunkering scenario			
		2 mm	23 mm	219 mm	1200 mm	2 mm	23 mm	219 mm	1200 mm
1.5D	Mass spilt								
5D	Mass spilt								
9D	Mass spilt								
3B	Mass spilt					x	x	x	x
5E	Mass spilt	x	x	x	x				
1.5F	Mass spilt	x	x	x	x				
1.5D	Pool depth								
5D	Pool depth								

Weather Conditions	Model output	Scenario							
		Day				Night			
		Bunkering scenario				Bunkering scenario			
		2 mm	23 mm	219 mm	1200 mm	2 mm	23 mm	219 mm	1200 mm
9D									
3B						x	x	x	x
5E		x	x	x	x				
1.5F		x	x	x	x				
1.5D	Pool radius								
5D									
9D									
3B						x	x	x	x
5E		x	x	x	x				
1.5F		x	x	x	x				
1.5D	Pool temperature								
5D									
9D									
3B						x	x	x	x
5E		x	x	x	x				
1.5F		x	x	x	x				
1.5D	Solution rate								
5D									
9D									
3B						x	x	x	x
5E		x	x	x	x				
1.5F		x	x	x	x				
1.5D	Mass dissolved								
5D									
9D									
3B						x	x	x	x
5E		x	x	x	x				
1.5F		x	x	x	x				
1.5D	Pool vaporisation rate								
5D									
9D									
3B						x	x	x	x
5E		x	x	x	x				
1.5F		x	x	x	x				
1.5D	Mass vaporised								
5D									
9D									
3B						x	x	x	x

Weather Conditions	Model output	Scenario							
		Day				Night			
		Bunkering scenario				Bunkering scenario			
		2 mm	23 mm	219 mm	1200 mm	2 mm	23 mm	219 mm	1200 mm
5E		x	x	x	x				
1.5F		x	x	x	x				
1.5D	Mass remaining								
5D									
9D									
3B						x	x	x	x
5E		x	x	x	x				
1.5F		x	x	x	x				

7.8. Appendix 8

Full descriptions of the impact of MGO on aquatic habitats

This section describes the the key impacts of an MGO spill on different aquatic habitats. It is noted that many studies do not necessarily differentititae between oil types and so the below section may also refer to HFO.

7.8.1. Rivers

Oil spills in or near rivers can have widepsread impacts because of connectivity and unidirectional flow will spread the pollutant to downstream sections of the system. As a result, it can spread into other environments such as wetlands. This can have short term and long term impacts on aquatic invertebrate and vertebrate fauna indirectly through disruptions in the food chain and directly by toxicity. Recovery is dependent upon a number of factors including the time of year, the availability of recolonizing forms, biological interactions and climate conditions[190].

7.8.2. Wetlands

The chemical composition of oil and its toxicity are not stable over time but change, in part, because of microbial processes; the primary biological means by which oil is degraded in wetlands. Microbial degradation activity in wetlands depends primarily on the type and concentration of petroleum hydrocarbons and environmental factors such as oxygen, nutrients such as nitrogen and phosphorus, salinity and pH. Surface waters and marsh sediments contain a high diversity of microorganisms. This rich diversity allows for maximum efficiency in resource (especially carbon) utilization and degradation; whether it is petrogenic or not—under changing environmental and nutrient-input conditions.

Polycyclic aromatic hydrocarbons (PAHs) are the most toxic contaminants and are relatively persistent in marshes. The highest levels generally occur below the sediment surface, where there is limited oxygen and a concomitant shift from aerobic to anaerobic bacterial taxa. In a heavily contaminated mangrove swamp for example, PAH concentrations increase with increasing substrate depth and decreasing oxygen content[191].

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[190] Kingston, P F. (2002). Long term environmental impact of oil spills, *Spill Science and Technology Bulletin*, 7(1-2): 53-61.
[191] Li CH Zhou HW Wong YS Tam NFY. (2009). Vertical distribution and anaerobic biodegradation of polycyclic aromatic hydrocarbons in mangrove sediments in Hong Kong, South China. Science of the Total Environment 407: 5772–5779

7.8.3. Estuaries

Estuaries and shallow bays act as sinks for sediment and associated particle-reactive contaminants[192] such as oil-based fuels. Aliphatic and polycyclic aromatic hydrocarbons are ubiquitous contaminants in estuaries, particularly those characterized by high urban and industrial development[193].

7.8.4. Coastal Waters

Oil slick trajectories can be controlled by prevailing winds and current eddies in coastal zone, with various levels of susceptibly at certain parts of the coastline. This is dependent upon the coastal morphology, exposure to wave action, uplifted wave cut platforms and coastal lagoons. Scattering and beaching of oil by strong currents can also occur with oil spills located further offshore. Saltmarshes and coastal lakes can draw water from foreshore areas polluted with oil, contaminating sub-surface aquifers and soil for a long time after the event.

Oil spills can cause disturbance to the food chain processes in coastal water regions and the interrelationship with fisheries, disrupting the seasonal migration rates as a result.

7.8.5. Coral reefs

The impact of an oil spill on coral reefs depends on the species and maturity of the coral (e.g., early stages of life are very sensitive to oil), as well as the means and level of exposure to oil. Exposing corals to small amounts of oil for an extended period can be just as harmful as large amounts of oil for a brief time.

Once oil comes into contact with corals, it can kill them or impede their reproduction, growth, behaviour and development. This will also impact on fish and aquatic invertebrates that rely on coral reefs as nursery grounds, shelter and feeding sites[194].

7.8.6. Mangroves

Oil spills pose a considerable threat to marine coastal ecosystems, particularly those present in the intertidal zone, such as mangroves. When oil is released into coastal waters,

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[192] D. Wang, C. Feng, L. Huang, J. Niu, Z.C. Shen. (2012). Historical deposition behaviors of PAHs in the Yangtze River estuary: role of the sources and water currents. Chemosphere. 90. Pp. 2020-2026

[193] D.R. Dudhagara, R.K. Rajpara, J.K. Bhatt, H.B. Gosai, B.K. Sachaniya, B.P. Dave. (2016). Distribution sources and ecological risk assessment of PAHs in historically contaminated surface sediments at Bhavnagar coast, Gujarat, India. Environ. Pollut. 213. pp. 338-346

[194] NOAA (2013). How Do Oil Spills Affect Coral Reefs? https://response.restoration.noaa.gov/about/media/how-do-oil-spills-affect-coral-reefs.html

it often deposits on surfaces exposed during tidal fluctuation. Oil deposits on the breathing roots, stems and surrounding sediments of mangroves. Once deposited, the oil sits on the surface asit adsorbs rapidly and effectively once in contact with the oleophilic surfaces[195].

7.8.7. Deep Sea

Almost all information on deep sea oils spills is derived from scientific research following the Deepwater Horizon (DWH) accident in the Gulf of Mexico (2010); the largest marine oil spill in history.

In the case of a deep-water blowout, as much as 50 % of spilled oil, consisting mainly of readily soluble hydrocarbons and essentially all of the discharged gas will be sequestered in deep-water plumes. Further, a large fraction of the oil that reaches the surface will end up back into the deep sea through sinking of marine oil snow[196].

7.8.8. Polar regions

Abiotic conditions in the polar regions including low temperatures, different ice types, strong wind and water turbulence influence the fate of oil spills. The physical characteristics of oil released in colder environments differ to those in temperate conditions, with wax components of the oil precipitating to form a gel-like consistency. The density of most heavy oils and petroleum products exceeds the density of ice at a temperature of ~ 0 °C[197]. This forms slicks that are thicker and resistant to flow. Consequently, this restricts diffusion of volatiles and with this, reduces the rate of evaporation. Ice can become oil infested if spills reach the marginal zones. Oil can be trapped within the ice through migration into brine channels or fissures and with this be transported over greater distances. Oil that remains on the surface will therefore, either rise towards the surface or be encapsulated in ice[198].

[195] Duke, N., Ellison, J., Burns, K. (1998). Surveys of oil spill incidents affecting mangrove habitat in Australia: a preliminary assessment of incidents, impacts on mangroves, and recovery of deforested areas. APPEA Journal 1998. Pp 646-654.

[196] Alves T M, Kokinaou E, Zodiatis G, Lardner R, Panagiotakis C and Radhakrishnan H. (2015). Modelling of oil in confined maritime basins: The case for early response in The Eastern Mediterranean Sea Journal of Environmental Management 206 350–399

[197] Efimov, S E; Tikhonov, R S. (2019). Experimental Study of Behaviour of Oil Spills in Ice Conditions, International science and technology conference Earth Science:1-5.

[198] Word J Q and *et al.* 2014 Environmental impacts of Arctic oil spills and Arctic spill response technologies: Literature review and recommendations (Arctic Oil Spill Response Technology Joint Industry Programme (JIP).

7.9. Appendix 9

This section describes the key impacts of an oil spill on different ecological receptors. It is noted that many studies do not necessarily differentititae between oil types and so the below section may also refer to HFO.

7.9.1. Bacteria

A case study of the Prestige oil tanker accident in 2002[199] describes the autochthonous bacterial community's response to an oil spill. The oil was a mixture of heavy crude oil consisting of polycyclic aromatic hydrocarbons, alkanes, asphaltenes and resins. Overall, the results evidenced biodegradation of the crude oil components mediated by natural bacterial communities, with a bias towards lighter and less substituted compounds. Notable observed changes at community level were the increased abundance of Alpha and Gammaproteobacteria, dominated by the groups Sphingomonadaceae, Rhodobacteraceae and Chromatiales in the supratidal and intertidal zones, whilst Gamma and Deltaproteobacteria were more relevant in subtidal zones.

However, there were insufficient nutrients to support the population increases post spill and the communities soon reverted to pre-spill levels.

7.9.2. Plankton

The impact of crude oil on marine organisms such as phytoplankton has not been studied as extensively as organisms at higher trophic levels and any reported impacts are noted to vary. Some studies[200,201,202] have demonstrated that crude oil can alter water conditions (e.g., chemical composition, food web interactions) to enhance phytoplankton growth and

[199] Acosta-González, A., Martirani-von Abercron, S. M., Rosselló-Móra, R., Wittich, R. M., & Marqués, S. (2015). The effect of oil spills on the bacterial diversity and catabolic function in coastal sediments: a case study on the Prestige oil spill. *Environmental science and pollution research international*, *22*(20), 15200–15214.

[200] Lee, R,F., Takahashi, M., Beers, J,R., Thomas, W,H., Seibert, D,L,R., Koeller, P., Green, D,R., Vernberg, F,J., Calabrese, A., Thurberg, F,P., Vernberg, W,B. (1977). Controlled ecosystems: Their use in the study of the effects of petroleum hydrocarbons on plankton, *Physiological Responses of Marine Biota to Pollutants*, Academic Press (pg.323-342)

[201] Elmgren, R., Vargo, G., Grassle, J., Heinle, D. Langlois, G., Vargo, S., Giesy, JPJr. (1980). Trophic interactions in experimental marine ecosystems perturbed by oil, Microcosms in Ecological Research, US Department of Energy(pg. 779-800)

[202] Ozhan, K., Miles, M,S., Gao, H., Bargu, S. (2014). Relative phytoplankton growth responses to physically- and chemically-dispersed South Louisiana sweet crude oil, Environmental Monitoring and Assessment, vol. 186 (pg. 3941-3956)

increase their biomass. However, some phytoplankton groups can play an active role in altering crude oil compounds in conjunction with microbial communities[203].

7.9.3. Macrophytes

Petroleum hydrocarbons ae known to affect plants chemically and physically[204]. Although plants can survive foulingvia leaf production, even relatively non-toxic oils can stress or kill plants if oil physically prevents plant gas-exchange. Plant sensitivity to fouling varies between species and among populations within a species, age of the plant, and season of the oil spill.

7.9.4. Invertebrates

Oil spills have complex and variable impacts on invertebrates. Several key invertebrate groups are described below[205].

Echinoderms can be particularly sensitive and oiling of nearshore habitats has resulted in mass die-offs and strandings. Early planktonic life stages exposed to oil may show impaired embryogenesis and larval growth.

Mollusks are highly sensitive and oil ingested by mussels and oysters during filter-feeding accumulates in their fatty tissues and may be retained on the gills. Mussels and oysters have a limited capacity to metabolize oil, which prolongs their exposure and negatively impacts feeding, growth, reproduction, embryo development and immune response. Snails and limpets in intertidal rocky shores and estuaries have shown high levels of mortality after oil spills and reduced recruitment of juveniles. Sublethal concentrations also impair their mobility, foraging behavior and reproduction.

High mortality rates have been associated with crustaceans and oil spills with large numbers becoming stranded on the shore. As many crustaceans burrow into sediment and feed on the surface, they are exposed to oil that combines to the surface layers of sediment. This chronic exposure can impair feeding, mobility, development and reproduction.

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[203] McGenity, T,J., Folwell, B,D., McKew, B,A., Sanni, G,O. (2012). Marine crude-oil biodegradation: A central role for interspecies interactions, Aquatic Biosystems, vol. 8

[204] Pezeshki, S., Hester, M., Lin, Q., Nyman, John. (2000). The effects of oil spill and clean-up on dominant US Gulf coast marsh macrophytes: A review. Environmental pollution

[205] Blackburn, M, C. A. S. Mazzacano, C. Fallon, and S. H. Black. (2014). Oil in Our Oceans. A Review of the Impacts of Oil Spills on Marine Invertebrates. 152 pp. Portland, OR: The Xerces Society for Invertebrate Conservation.

Polychaetes display complex and varied responses to oil pollution. Following oil spill induced die-offs of marine invertebrates, some polychaete species may increase in abundance, some will rapidly colonize damaged habitat and others suffer reduced populations.

7.9.5. Reptiles

Oil spills are known to impact on respiratory processes, skin and egg shell condition when turtles become heavily oil-covered or chronically exposed to oil. Oiled turtles are also known to have increased white blood cell counts, reduced red blood cell counts, increased numbers of immature red blood cells, acute inflammation of skin and mucosal surfaces[206]. Long term consequences of oil exposure are not well understood, but a high incidence of embryo deformity is known from turtle populations with chronic oil exposure[207]. Other long term indirect problems may include delayed mortality due to hindgut bacterial death in marine iguanas[208] and an increase in disease[209].

7.9.6. Fish

Typically, finfish either are unaffected by oil or are affected briefly because most oils float and routes of exposure to organisms living in the water column or on the ocean floor are typically very limited. Juvenile and adult finfish usually are more mobile, can be more selective in the foods they ingest and have a variety of enzymes that allow them to detoxify oil compounds. However, fish can be substantially affected in some circumstances, especially when oil spills occur in shallow or confined waters. The type of oil and the timing of the release influences the severity of impacts on fish

7.9.7. Birds

Mass mortality of seabirds is common after oil spills[210]. Seabirds are particularly vulnerable due to their distribution, foraging and breeding behaviour. Following a spill, seabirds come into contact with oil floating on the water's surface causing them to become smothered

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[206] Lutcavage M.E., Lutz P.L., Bossart G.D. Hudson D.M. (1995) Physiologic and clinicopathologic effects of crude oil on loggerhead sea turtles. *Archives of Environmental Contamination and Toxicology*, 28, 417–422.

[207] Bell B., Spotila J.R. Congdon J. (2006) High incidence of deformity in aquatic turtles in the John Heinz National Wildlife Refuge. *Environmental Pollution*, 142, 457–465.

[208] Wikelski M., Wong V., Chevalier B., Rattenborg N. Snell H.L. (2002) Galapagos Islands: marine iguanas die from trace oil pollution. *Nature*, 417, 607–608.

[209] Milton S., Lutz P. Shigenaka G. (2003) Oil toxicity and impacts on sea turtles. Pages 35–47 in G. Shigenaka (eds.) *Oil and Sea Turtles: Biology, Planning and Responses*. NOAA Ocean Service, Seattle, Washington.

[210] Castege, I.,Lalanne, Y.,Gouriou, Y.,Hemery, G.,Girin, M., D'Amico, F. (2007). Estimating actual seabird mortality at sea and relationship with oil spills: lessons from the "Prestige" oil spill in Aquitaine (France) Ardeola, 54 (2), pp. 289-307.

with oil and this can causemortality via suffocation[211]. Oil disrupts feather integrity displacing insulating air between feathers, leading to loss of water-proofing, thermal insulation and buoyancy. They become unable to dive or fly so they cannot forage to feed. Fat reserves become depleted and birds become severely hypothermic and emaciated, causing mortality[212]. The oil that is ingested from preening and feeding results in oral exposure to hydrocarbon chemicals present in oil. A significant proportion of these are toxic PAHs which, depending on the type of oil, degree of weathering and water content, can constitute up to 30 % of total hydrocarbons present[213].

7.9.8. Marine mammals

Marine mammals are potentially vulnerable to oil contamination, yet little is known about the effects of oil on either individuals or populations. In this regard, the 1989 Exxon Valdez oil spill in the nearshore waters of Alaska is unique. This spill of 11 million gallons of Prudhoe Bay crude oil resulted in the mortality of killer whales (*Orcinus orca)*, harbor seals (*Phoca vitulina)* and sea otters (*Enhydra lutris)*. The impacts on some nearshore communities and vulnerable subpopulations of marine mammals have lasted more than two decades[214].

7.9.9. Case Study – Milford Haven

Approximately 72,000 tonnes of light crude oil were released from the Sea Empress at the entrance to Milford Haven, South Wales over a seven-day period in February 1996. Natural factors (time of year, wind direction) coupled with effective clean-up at sea (through chemical dispersion) and on shore, minimised environmental impact. Nevertheless, there were adverse effects on fisheries and wildlife (particularly overwintering birds), tourism, and amenity.

7.9.9.1. Commercial fisheries

Soon after the spill, concentrations of hydrocarbons in seawater were elevated above background over a substantial area. Levels were particularly elevated in molluscs, but less so in crustaceans and some finfish. Contamination of edible intertidal seaweeds was mostly

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[211]Camphuysen, C.J., Leopold, M.F. (2004).The Tricolor oil spill: characteristics of seabirds found oiled in the Netherlands Atl Seabirds, 6 (3), pp. 109-128

[212] Piatt, J.F., van Pelt, T.I. (1997). Mass-mortality of guillemots (*Uria aalge*) in the Gulf of Alaska in 1993 Mar Pollut Bull, 34 (8), pp. 656-662

[213] I.A.R.C. (1989). Crude Oil Occupational exposures in petroleum refining; crude oil and major petroleum fuels IARC Monogr, 45 (1), pp. 119-158

[214] Helm, R., Costa, D., DeBruyn, T., O'Shea, T., Wells, R., Williams, T. (2015). Overview of Effects of Oil Spills on Marine Mammals.

on the surface rather than through tissue absorption. No attributable mortalities of commercial finfish, crustaceans or molluscs were recorded and spawning and recruitment remained successful. Though there is evidence that the immune competence of several species, such as mussels, was severely impaired through PAH exposure.

7.9.9.2. Plankton

There were no observed effects of the spill on phyto and zoo-plankton, with the exception of an absence of barnacle larvae in spring 1996 and a marked reduction on copepod egg viability in April 1996.

7.9.9.3. Invertebrates

Large numbers of dead or moribund molluscs (including cockles from a non-commercial area), starfish and urchins were washed ashore, both by the grounding and from further afield. Also, amphipods which are generally regarded as sensitive to oil pollution, disappeared from areas of the seabed. Polychaete worms were temporarily replaced by opportunistic worm fauna.

The mortality of limpets and other herbivorous gastropods was 'patchy', being especially prevalent in areas of fresh oil contamination.

7.9.9.4. Macrophytes

The above mortality of herbivorous gastropods contributed to prolific expansion of some species, notably fucoid seaweeds and *Enteromorpha*. Coralline red algae underwent an initial bleaching episode, though most areas had recovered by 1997. Saltmarsh communities were heavily impacted with slow recovery.

7.9.9.5. Birds

Around 7,000 oiled birds were collected from the shore and an unknown number died at sea. Of the 7,000, around half were rescued and released after aid. However, there is evidence that common guillemot *Urie aalge*, representing 23% of the rescued birds, died soon after their release.

The most abundant oiled bird (66%) was a sea-duck, the common scoter (*Melanitta nigra).* Of the 8,000 strong population in Carmarthen Bay, most washed ashore or died at sea. Additionally, the suitability of the bay as a feeding ground for this migrant was compromised adding to prolonged recovery time.

Census data of nesting sites in and adjacent to the affected area suggest that, with the exception of common guillemots and razorbills (*Alca torda*), success was not appreciably reduced. However, the number of common guillemots and razorbills declined by 13 and 7% respectively in 1996 and two colony sites underwent particularly prolonged recovery.

7.9.9.6. Marine mammals

The main nursey areas for grey-seal (*Halichoerus grypus*) populations were to the north-west of the affected oil spill area and the birthing period is in the autumn. Therefore, minimal affects were recorded. Cetacean sighting data suggests that there was no change to the frequency or distribution of their occurrence.