# Modelling and measuring the weathering and bioavailability of fuel spills in polar marine environments, and assessment of the applicability of fuel dispersants

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## Statement of Authenticity

I hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, or substantial proportions of material which have been accepted for the award of any other degree or diploma at Macquarie University or any other educational institution, except where due acknowledgement is made in the thesis. Any contribution made to the research by others, with whom I have worked at Macquarie University or elsewhere, is explicitly acknowledged in the thesis. I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.

#### Konstantinos Kotzakoulakis

#### Abstract

Shipping activity is increasing continuously in Antarctica in the last couple of decades. During the 2014/2015 summer season 191 tourist expeditions visited Antarctica carrying 36,702 passengers in addition to the illegal fishing activity and shipping related to research station support operations. Recent incidents such as the stranding of Akademik Shokalskiy on 25 December 2013, the grounding of the MS Nordkapp at Deception Island on 30 January 2007 and the fire aboard the Nisshin Maru in February 2007, which was carrying approximately 1000 tonnes of heavy fuel oil, have highlighted the risk of a major fuel spill in the Antarctic waters. Currently, much needed data on the behaviour of these fuels in the Antarctic marine environment in order to plan response measures is missing.

The three fuels that are used in the Australian Antarctic Territory are the Special Antarctic Blend (SAB), the Marine Gas Oil (MGO) and the Intermediate Fuel Oil 180 (IFO-180). During this study we examined the rate of weathering and the path to bioavailability of these fuels to the Antarctic marine biota. The main mechanism of weathering for SAB and MGO in the Antarctic marine environment is evaporation with 80% of SAB and 33% of MGO evaporated in 6 days and 30 days respectively. Both SAB and MGO are pure distillates consisting of hydrocarbons in the range of C<sub>10</sub>-C<sub>15</sub> and C<sub>7</sub>-C<sub>26</sub> respectively which explains the fast evaporation rate. IFO-180 is a heavy fuel consisting of around 90% residual distillation fuel (Bunker C) and less than 10% light distillate. It was found that the loss from evaporation during the first 30 days is 7% which corresponds to the majority of the added distillate and then evaporation almost stops. These results show that the majority of both MGO and IFO can persist in the Antarctic marine environment for long periods of time and response measures such as mechanical recovery or treatment methods need to be considered.

The main path to bioavailability of these fuels is through dissolution in the seawater column. For SAB and MGO, the main groups of components that are becoming bioavailable are benzenes, nathphalenes,

phenols, indanes, tetralins and biphenyls whereas for IFO-180 except for the aforementioned groups that are present we also identified some smaller amounts of heavier bioavailable groups such as the fluorenes, phenanthrenes, anthracenes and dibenzothiophenes that are entering the water column. Due to the slower rate of evaporation under Antarctic conditions the dissolution time window is extended and the potentially dissolved amount of hydrocarbons larger in comparison to more temperate regions. This is an additional reason for response measures to be deemed necessary.

We examined the efficiency of a suite of six chemical dispersants under Antarctic conditions in combination with the MGO and IFO-180 as well the Kuwait crude oil since it is used by the Australian Maritime Safety Authorities as a reference for dispersant certification purposes. The order of efficiency was determined for the Antarctic and sub-Antarctic temperatures of 0°C and 5°C. Additionally, we examined the Kuwait crude oil and the IFO-180 on an extended temperature range from 0°C to 22°C in order to study the effects of temperature on the efficiency of the dispersants. An interesting observation during this study was that heavy fuels seem to exhibit a logarithmic relationship between the viscosity and the dispersant efficiency due to the temperature change. A second observation was the change in the dispersant efficiency order at different temperatures, as it appears that each dispersant is affected to a different degree by the temperature change.

During the study of the evaporation mechanism an effort has been made to construct a mathematical model that can predict the rates of evaporation of the different fuels at the Antarctic temperatures. The result of this effort was the successful development of a general model that takes into account the diffusion forces and the concentration gradient in the body of the fuel and can predict the evaporation rate of the fuels but also of other complex mixtures and crude oils in a wide range of temperatures and can be applied in different regions. Additionally, and for the needs of this model a new correlation had to be developed that can predict the viscosity of the weathering fuel or crude oil based on the average boiling

iv

point, the density and the prevailing temperature. Further work is underway in order to incorporate the prediction of the dissolution rate into the model.

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vi

# Table of Contents

A	Aim an	d objectives of the research project	1
1.	Intro	oduction	2
1	l.1.	The Antarctic ecosystem	2
1	L.2.	The risk of fuel spills	6
1	L.3.	Other biological stressors of the Antarctic environment1	1
1	L.4.	Areas that require scientific input1	4
1	l.5.	Possible response options to a fuel spill in Antarctic waters1	6
1	l.6.	References	5
2.	The	fate and bioavailability of fuel spills in polar marine environments2	8
2	2.1	Introduction	0
2	2.2	Materials, methods and calculations3	3
	2.2.	1 Materials 3	3
	2.2.2	2 Analytical Methods	4
	2.2.3	3 Estimation of the evaporation parameters3	6
	2.2.4	4 Measurement of hydrocarbon solubility3	9
	2.2.	5 Measurement of dissolution rate and dissolution constants	0
	2.2.	6 Measurement of hydrocarbon depletion4	7
	2.2.	7 Measurement uncertainty and experimental errors4	7
2	2.3	Results and discussion4	9
	2.3.	1 Fuel characterisation results	9
	2.3.2	2 Characterisation of the aromatic fraction of the fuels and the corresponding WAFs5	5
	2.3.3	Evaporation of the three fuels at polar and temperate marine conditions	2
	2.3.4	4 Dissolution under polar versus temperate marine conditions	8
	2.3.	5 Partitioning of hydrocarbons between the gas and water phases after an oil spill7	6
	2.3.	6 Natural dispersion of a fuel spill into the water column	1
	2.3.	7 Fate of dissolved hydrocarbons in seawater8	3
2	2.4	Conclusions9	1
2	2.5	References9	4
A	Appen	dix 2A. Detailed composition and dissolution parameters9	7
3.	A ge	eneral evaporation model for crude oils and complex hydrocarbon mixtures	1
3	3.1	Introduction	4

3.2	Theory and methodology	
3.2	1 Molecular diffusion model	
3.2	2 Evaporation rate R calculation	
3.3	Materials and experimental methodology.	
3.3	1 Fuels and mixtures	
3.3	2 Experimental methods	
3.4	Results and discussion	
3.4	1 Synthetic mixtures	
3.4	2 Fuels used in the Australian Antarctic Territory.	
3.4	3 Crude oils	
3.4	4 Prediction of the fluid's physical properties.	
3.4	5 Interplay between evaporation and diffusion on individual components	137
3.5	Conclusions	
3.6	References	
Apper	ndix 3A. Pseudo-component properties' calculations	
3A.	1. Vapour pressure calculation.	
3A.	2. Effective carbon number (ECN) of pseudo components and distillation cuts	147
3A.	3. Boiling point of pseudo components and distillation cuts.	148
3A.	4. Average molar mass of pseudo components and distillation cuts	149
3A.	5. Average molar volume of pseudo components and distillation cuts	150
3A.	6. Density of pseudo components and distillation cuts.	152
3A.	7. Gas phase diffusion coefficients calculation.	153
3A.	8. Liquid phase diffusion coefficients calculation	
4. A g	eneral viscosity correlation for crude oils	158
4.1	Introduction	159
4.2	Data and methodology	
4.2	1 Data	
4.2	2 Viscosity	163
4.2	3 Specific Gravity	
4.3	Results and discussion	
4.4	Conclusions	
4.5	References	

5. Comparative study of the effectiveness of 6 dispersants under polar conditions on the fuels used in								
the Australian Antarctic Territory181								
5.1 Introduction	33							
5.2 Fuel properties and environmental conditions that affect dispersibility	35							
5.3 Previous studies on the dispersion efficiency of medium and heavy fuels	€							
5.3.1 The 1993-1997 North Sea field trials	<del>)</del> 3							
5.3.2 2003 North Sea field trial	<del>)</del> 5							
5.3.3 Previous wave tank studies on IFO-180 and IFO-380	<del>)</del> 6							
5.3.4 Previous Laboratory Tests on IFO-180 and IFO-380	<del>)</del> 9							
5.4 Materials and methods	)6							
5.4.1 Fuels	)6							
5.4.2 Standards and reagents	)8							
5.4.3 Methods	)9							
5.4.4 Gas chromatography and analytical procedure21	11							
5.5 Results and discussion	12							
5.6 Conclusions	24							
5.7 References	26							
6. Summary and conclusions	29							
6.1. Fuel characteristics and environmental conditions.	29							
6.2. The evaporation process	<u>29</u>							
6.3. Modelling the evaporation process	30							
6.4. Predicting the viscosity of weathered fuel	31							
6.5. Evaporation rates and prediction accuracy for the three fuels.	31							
6.6. The dissolution process	33							
6.7. Modelling the dissolution process	34							
6.8. Partitioning among the fuel, seawater and atmosphere	34							
6.9. Natural dispersion and depletion of dissolved compounds	35							
6.10. Applicability of chemical dispersion under Antarctic conditions	35							
6.11. Further investigation	37							
6.12. References	38							
Appendix. Assessing fuel spill risks in polar waters: Temporal dynamics and behaviour of								
hydrocarbons from Antarctic diesel, marine gas oil and residual fuel oil								

#### Chapter 1.

#### Aim and objectives of the research project

The overall aim of this research project was to provide the necessary scientific input on the physicochemical processes responsible for the weathering of fuel spills in order to assist with risk assessment and response planning for the scenario of a fuel spill in the Antarctic marine environment. The identified areas include (1) the evaporation process, responsible for the majority of fuel mass loss at the initial stages of weathering, (2) the dissolution process, responsible for the bioavailability of the more soluble, toxic compounds to the marine biota living in the water column, and (3) the dispersion process, both natural and chemically-enhanced, as a possible response measure, but also to examine environmental concerns due to the additional amount of fuel compounds bioavailable to the marine organisms. Finally, (4) the fate of the dissolvable compounds once they enter the water column was another area that required investigation. The objectives for these areas of study were:

- To fully characterise the chemical composition of the fuels used in the Australian Antarctic Territory (ATT) and the corresponding water accommodated fraction (WAF).
- To provide experimental data on the evaporation rate under Antarctic conditions of the fuels used in the AAT and to use the experimental data for the construction of prediction formulas and evaporation models for the fuels used in the AAT.
- To measure the water solubility and the dissolution rates of the soluble compounds of the fuels and to develop prediction formulas of the dissolution rates at different spill scenarios under Antarctic conditions.

- To assess the efficiency of a large suite of chemical dispersants under Antarctic conditions on the fuels used in the AAT and to investigate the effect of environmental conditions and fuel properties such as water temperature and fuel viscosity on the efficiency of the dispersants.
- To experimentally measure the rate of depletion of the dissolved compounds in the water column and use this data in order to identify the possible processes responsible for the depletion.

## Introduction

#### 1.1. The Antarctic ecosystem

The Antarctic Treaty System is a group of agreements, including the Protocol on Environmental Protection to the Antarctic Treaty, put in place with the goal of regulating the activities in Antarctica and protecting the Antarctic Environment (Treaty, 1959). The Antarctic environment is home to a unique ecosystem of organisms living under extreme environmental conditions. The Antarctic terrestrial flora and fauna are limited due to the extreme climatic conditions. The combination of freezing temperatures, low precipitation, limited areas with exposed soil, poor quality of soil and limited sunlight inhibit the growth of extensive vegetation. Most of the Antarctic continent is covered by permafrost or snow, leaving less than 1% of ground available to plants. There are no trees or higher plants in continental Antarctica, and only two species of flowering plans are found in the Antarctic Peninsula (Figure 1.1).



Figure 1.1. Overview map of Antarctica with the Antarctic Peninsula magnified. The peninsula is located at the west, north-west side of the continent and exhibits the highest terrestrial biodiversity.

The Antarctic flora is mostly made up by lower plants such as mosses (Figure 1.2), liverworts, lichens and fungi. There are about 100 species of mosses, 25 species of liverworts, 300-400 species of lichen and 20 species of macro-fungi. Most of these species are found in the Antarctic Peninsula and in the coastal regions around the edge of the Antarctic continent (Survey, 2016b).



Figure 1.2. A typical endemic moss turf (*Schistidium antarctici*) found near Casey Station in the Australian Antarctic Territory (Photo: Sharon Robinson).

Similarly the continental fauna is limited to small animals predominantly living in areas of vegetation, with the largest diversity found in the Antarctic Peninsula. The largest endemic land animal of the continental Antarctica is a flightless midge (*Belgica antarctica*) at 2-6 mm long and is the only insect in that region (Zoology, 2009). Micro-arthropods can be found in areas of vegetation predominantly around the edge of the Antarctic continent (Figure 1.3), while in the continental cold deserts simple food webs exist consisting mainly of nematodes (Survey, 2016a).



Figure 1.3. This Antarctic springtail (*Cryptopygus antarcticus*) is one of the most successfully adapted arthropods to survive the extreme Antarctic terrestrial conditions. Although only 1-2mm in length, it is one of the largest animals on the Antarctic mainland. Its body accumulates antifreeze compounds allowing it to survive temperatures below -25°C (Survey, 2016a).

In contrast to the limited biodiversity of the Antarctic terrestrial environment, the Antarctic marine environment accommodates a large range of extraordinary and diverse creatures (Figure 1.4). In 2005, a major international investigation started recording the distribution and abundance of Antarctica's vast marine biodiversity, the Census of Antarctic Marine Life (CAML). By 2010 the CAML census had identified more than 6,000 different species living in or on the Antarctic sea floor, with more than half of these being unique to the Antarctic continent (CAML, 2010).



Figure 1.4. The Antarctic sea floor is home to an extraordinary and diverse range of unique marine creatures (Photo: Andrew Tabor).

#### 1.2. The risk of fuel spills.

The marine life around the coastline of Antarctica is exposed to freezing temperatures and ice coverage for most of the year. This unique ecosystem is the result of millions of years of adaptation to the freezing and stable conditions of the Antarctic waters. Antarctic marine organisms grow slowly, have long generation times, low metabolic rates and low levels of activity (Peck, 2005). The slow metabolic rate renders these organisms vulnerable to the presence of toxic pollutants such as petroleum fuel spills induced by anthropogenic activity.

Marine traffic around the Antarctic coastline have been steadily increasing over the last 15 years (Figure 1.5) (IAATO, 2009). During the 2015/2016 summer season 39,037 tourists visited Antarctica, in addition to illegal fishing activity and shipping related to research station support operations (IAATO, 2016).





Figure 1.5. The trend of tourism in Antarctica during the period 1992-2007 (IAATO, 2009). A rapid increase has been observed over the last 15 years. By the 2015-2016 summer season the number of tourists reached 39,037 (IAATO, 2016).

The southern ocean and the waters around Antarctica pose an increased risk for shipping accidents compared to shipping routes in other parts of the world. Cyclonic storms travel eastward around the continent and frequently become intense because of the temperature contrast between ice and open ocean. The ocean area from about latitude 40° south to the Antarctic Circle has the strongest average winds found anywhere on Earth, because winds blow around the entire globe unimpeded by any land mass (US Government, 2017). Icebergs occur especially in May to October, but can also occur at any time of year throughout this part of the ocean, make the area even more dangerous. The continental shelf has a floor of glacial deposits varying widely over short distances, posing an additional shipping hazard. In winter the ocean freezes outward to 65° south in the Pacific sector and 55° south in the Atlantic sector, lowering surface temperatures well below 0° Celsius. These extreme conditions combined with the

remoteness of the region make emergency response operations dangerous for the response personnel, as well technically and financially challenging.

The risk of a major accidental fuel release related to a marine incident is steadily increasing, as has been highlighted by recent incidents such as the stranding of the *Akademik Shokalskiy* on 25 December 2013, the grounding of the *MS Nordkapp* at Deception Island on 30 January 2007, the sinking of the MS Explorer on 23 November 2007 (Figure 1.7), and the fire aboard the *Nisshin Maru* in February 2007. The latter was carrying approximately 1000 tonnes of heavy fuel oil. In April 2009, in an effort to reduce the risk of shipping accidents and protect the Antarctic environment, the signing parties to the Antarctic Treaty agreed to impose binding restrictions on the size of cruise ships that can land passengers in Antarctica. The new mandatory restrictions limit the ships that can visit landing sites to no more than 500 passengers, restrict landings to one vessel at a time per site, and limit passengers on shore to 100 at a time (Press, 2009). As a result of these restrictions the increase in tourism appear to be slowing down over the last 5-6 years.



Figure 1.6. The shipping routes followed by the research and resupply vessels during the 2013-2014 season in Australian Antarctic Territory. The traffic hotspots around the research stations and glaciers are visible where fuel spill incidents are more likely to occur. Map created by the Australian Antarctic Division.

The Antarctic Treaty System prohibits commercial mineral and petroleum production in the Antarctic Treaty Territory, so as a result the sources of possible petroleum spills are limited to fuels used for propelling marine vessels and fuels for the energy needs of Antarctic research stations.

The main shipping routes in Antarctica connect the land-based research stations and other coastal points of interest such as major glacial formations to the ports that expedition and support vessels depart from. For the expeditions to the Australian Antarctic Territory (AAT) and the Australian research stations the main departing port is located in Hobart, Tasmania. In Figure 1.6, the main shipping routes are presented that were followed by ships visiting Antarctica during the 2013-2014 season. The main destination points are Macquarie Island, the Casey, Davis and Mawson research stations, as well as the ice shelves and glaciers around the coast of the AAT. These are the hotspots for possible fuel spills because the vessels approach the coastline to refuel the research stations or study the glaciers. In Figure 1.6 the route of the *Akademik Shokalskiy* is visible when it was trapped by ice while approaching the Mertz Glacier.

In 2010, the International Maritime Organisation amended the protocol relating to the international convention for the prevention of pollution from ships in response to concerns over the potentially high ecological impact from a heavy fuel spills in the Antarctic marine environment. As a result, the heaviest fuel that is now allowed in Antarctic Treaty waters is Intermediate Fuel Oil 180 (IFO-180) (IMO, 2010). The fuels investigated in the present study are the ones used in the Australian Antarctic Territory (AAT). These fuels include a light diesel named Special Antarctic Blend (SAB), an intermediate Marine Gas Oil (MGO) and the heaviest allowed fuel, the IFO-180.



Figure 1.7. The sinking of MS Explorer on 23 November 2007 after she hit an iceberg in the Bransfield Strait close to the Antarctic Peninsula (Photo: Associated Press).

## 1.3. Other biological stressors of the Antarctic environment

In addition to fuel spills, scientists have identified a number of processes already in action that are disturbing the sensitive balance and are stressing the Antarctic marine biota.

The Western Antarctica and the Antarctic Peninsula are amongst the fastest warming regions on Earth due to global warming caused by greenhouse gas emissions. Surface temperatures in these areas have risen almost 3°C in the past 50 years with a rate 10 times faster than the average global rate (Figure 1.8) (SCAR, 2009). A number of species are being negatively affected, including the Antarctic krill, a keystone

species of the Antarctic marine ecosystem (Vacchi et al., 2012), the Adelie penguins and other species that breed on the ice (CAML, 2010).



Figure 1.8. The average surface warming rate in degrees Celsius per decade for the period of 1957-2008. Western Antarctica and the Antarctic Peninsula are warming 10 times faster than the average global rate (SCAR, 2009). (Photo: NASA).

Ocean acidification caused by the increased uptake of CO<sub>2</sub> from the Earth's atmosphere is another process that are causing adverse effects on a number of species. Such effects are depressing the metabolic rates of jumbo squid, depressing the immune response of blue mussel, and enhancing the dissolution rate of calcareous material deposited by calcifying organisms, thus threatening their survival (Solomon et al., 2011). Unregulated fishing in the Southern Ocean as well as illegal and unreported fishing in the Antarctic treaty area are adversely affect the sustainability of the marine food web. Exploitation of the Patagonian Toothfish was unregulated in the Southern Ocean, so as a result five to six times more Patagonian Toothfish was caught than in the regulated fishery in the late 1990s to early 2000s, nearly causing a collapse of the stock in the Southern Ocean. Thanks to the Commission for the Conservation of Antarctic Marine Living Resources (CCAMLR), since 2005 illegal fishing of Patagonian Toothfish has decreased by 95%. CCAMLR estimates that currently 90% of the illegal fishing has shifted to Antarctic Toothfish instead of Patagonian Toothfish (CCAMLR, 2010; Miller et al., 2010).

Increased solar ultraviolet radiation due to the ozone layer depletion and the ozone hole located over Antarctica (Figure 1.9) has decreased the phytoplankton productivity by as much as 15%, and has started corrupting the DNA of some fish species (Smith and Prezelin, 1992). Additionally, larger mammals such as seals and whales appear to suffer from diseases associated with solar UV radiation (similar to human diseases from this cause), such as severe skin burns and ocular cortical cataracts (Tevini, 1993; Thomas, 2010).



Figure 1.9. From 21-30 September 2006 the average area of the ozone hole above Antarctica reached 27.45 million square kilometres, the largest ever observed. Image created from satellite data, with purple colour indicate the least ozone and green the most (NOAA, 2006). (Photo: NASA).

# 1.4. Areas that require scientific input

The necessary data on the fate and bioavailability of petroleum fuels to marine organisms are very limited due to the unique Antarctic conditions. There are many processes that take place during the weathering of a fuel in the marine environment, including evaporation, dissolution, dispersion, photolysis, biodegradation and spreading (Figure 1.10).



Figure 1.10. Weathering processes acting on an oil spill in the marine environment (National Research Council, 2014).

Evaporation is one of the main processes responsible for the majority of the fuel loss during the initial stages of weathering, and affects the availability of hydrocarbons to the marine biota by removing them from the fuel-water interface. Although dissolution and natural dispersion cause only a small fraction of the fuel loss during weathering, these are the two processes responsible for the transfer of fuel components into the water column and thus the availability of the fuel to marine organisms. Presently, the majority of the literature data on the properties of fuel compounds including vapour pressures,

aqueous solubility and partition coefficients between the different phases refer to more temperate conditions (Mackay et al., 2006).

Existing empirical correlations and models predicting the weathering processes such as the evaporation and dissolution rates of fuels spills were developed from experimental data performed at temperate conditions (Fingas, 2010), and their predictions could exhibit high deviations from the Antarctic weathering rates. Additionally, the fate of the dissolved fuel compounds after they have entered the seawater column is largely unknown. The persistence of these compounds under Antarctic marine conditions and their depletion rate determines the exposure time of the marine biota. Currently, there are no published measured depletion rates of fuel compounds under Antarctic conditions. The concerned authorities need to have the necessary scientific input on the possible impact of such an event, the rates of natural attenuation following the event, and the effectiveness of a possible human intervention in order to plan response and remediation measures in case of a fuel spill.

#### 1.5. Possible response options to a fuel spill in Antarctic waters

In most of the countries with coastlines there are emergency plans and regulations in place for the incident of an oil spill in the marine environment. For the areas that fall under the Australian Government's jurisdiction, including the Australian Antarctic Territory, the National Plan for Maritime Environmental Emergencies provides the policies and the guidance for the actions necessary in order to minimise the marine pollution from oil spills (AMSA, 2017). In summary, the plan is characterised by three distinct phases:

<u>Response phase.</u> During the response phase information gathering, monitoring and spill modelling is initiated. Net environmental benefit analysis is undertaken in accordance with local regulations for making

the best choices to minimise the oil spill impacts on environmental and community values. The feasible response options are evaluated and the response actions are re-evaluated.

<u>Damage assessment phase.</u> The assessment measures the cost of restoring or replacing the damaged environmental and community values. This cost includes the interim value loss until the complete restoration is complete and the cost of the assessment itself. Environmental and community values include the water and shoreline habitat, cultural and historic values, food organisms and water for human consumption, wildlife contact surfaces, amenity and safety of beaches and structures and local or regional affected businesses.

<u>Restoration or recovery phase.</u> This starts when the required endpoints for the clean-up activities have been reached. These endpoints define when environmental harm has been minimised and the potential for natural rehabilitation towards pre-spill ecological conditions has been maximised. In this phase the restoration monitoring is initiated, and if required additional restoration activities are carried out until the contamination levels reach the pre-spill baseline levels and the environmental and community values have been restored. This phase gathers and incorporates lessons learned into future policies, plans and good practice guides. In addition to the National Plan, the Australian Maritime Safety Authority (AMSA) in collaboration with the Commonwealth Scientific and Industrial Research Organisation (CSIRO) have published the Oil Spill Monitoring Handbook that provides a detailed presentation of the oil spill response phases and the actions of each phase (CSIRO, 2016).

Below we present some of the response options available to the emergency response team. One environmentally friendly response option to a fuel spill is mechanical recovery of the fuel from the marine environment as soon as possible, so as to remove as much as possible. The presence of ice fragments operate as natural barriers that limit the spreading of the spill, compared to an open sea scenario. Furthermore, the low temperature of the Antarctic environment reduces the evaporation rate of fuels

17

and thus the overall weathering rate. New Zealand authorities experimented with the efficiency of mechanical recovery in ice-covered waters using brush-drum skimmers and found that they can positively process ice and recover oil in an efficient manner (NZ, 2012). They concluded that mechanical recovery in Antarctic waters is possible, with efficiency similar to open sea when there are large ice floes but efficiency is expected to drop in the presence of small ice floes and slush ice. In another case study, the successful mechanical recovery of over 50% of heavy fuel oil (IFO-380) was reported under extremely cold and difficult conditions in south Norway after the grounding of a ship at Godafoss in 2011 (Figure 1.11). The ship was carrying 500 tons of IFO-380 fuel when it grounded. One hundred and twelve tons of heavy fuel leaked during the first few hours after grounding into a sea containing large amounts of ice at -2°C and with the air temperature at -20°C. The pumps designed to operate with heavy fuel were unable to perform due to the extremely high viscosity of the IFO-380 at that temperature. Instead conventional grabs were successfully used to remove the oil from the booms. Hot water and steam proved very important in order to solve problems with frozen connections, pipes, hoses and ice clogged boat engine cooling systems (Bergstrøm, 2012).



Figure 1.11. Confinement of discharged IFO-380 fuel with booms during the Godafoss accident (Photo: Swedish Coast Guard).

However, the remote location and the vast area around the Antarctic continent makes the transport and maintenance of such equipment technically and financially challenging. Additionally, the extremely cold conditions pose a risk to the response personnel and a challenge to the effective operation of the equipment. Other alternative response options that involve transport and maintenance of lighter equipment and a smaller number of response personnel are the in-situ burning of the fuel spill (Figure 1.12) and the use of chemical dispersants to disperse the fuel from the water surface into the water column.

In-situ burning has been tested in field experiments performed by the New Zealand maritime authorities in cold waters with the presence of ice; burn efficiency was measured above 90% (NZ, 2012). During these tests fire resistant booms and chemical herders were proven effective for the confinement of the oil spill. In-situ burning was proven effective on both free floating oil in ice and oil collected in the fire resistant booms.

There are certain advantages to consider in favour of in-situ burning in the Antarctic marine environment. The presence of ice can operate as a natural barrier containing the fuel spill and preventing further spreading. The cold environmental conditions reduce the rate of weathering as discussed earlier, creating a larger window of opportunity for the emergency authorities to respond. In-situ burning requires lighter equipment to be transported and fewer emergency personnel on site compared to mechanical recovery. It rapidly removes large amounts of fuel and greatly reduces the fuel volume that requires disposal. Depending on the type of fuel in-situ burning can achieve high efficiency rates (Fingas, 2014; Fingas et al., 2000b) (Table 1.1). Finally, due to the logistical challenges of the Antarctic Environment it may be the only viable response option (ASTM, 2014).



Figure 1.12. In-situ burning experiment of fuel oil in ice covered waters (Photo: SINTEF).

Disadvantages of in-situ burning include the creation of large smoke plumes in the atmosphere and burn residues on the water surface that later can sink to the sea bed if not collected. There are concerns over the toxicity of the burn products, although studies have shown that usually the concentrations of toxic secondary products are low (Fingas et al., 1996; Fingas et al., 2005; Fingas et al., 2000a; Lemieux et al., 2004). These secondary products include (Fingas, 2010):

- Particulate matter, especially from diesel fuels, which can exceed human health concern levels.
- Polyaromatic hydrocarbons (PAHs) are elevated in the burn residue.
- Dioxins and dibenzofurans are produced when chlorine-containing organic compounds are burned.
- Carbonyl compounds (aldehydes, ketones, esters, acetates and acids) are formed from the incomplete burning of fuel compounds.
- Sulphuric acid is formed when SO<sub>2</sub> produced during the burning process reacts with water.
- CO<sub>2</sub> produced by the fire can be 500 ppm near the burn, but presents no danger to humans.
- CO is usually below or at the detection level, and poses no risk to humans.

Another disadvantage of in-situ burning is that a spill need to be of a certain thickness in order to ignite. This minimum thickness is in the range of 0.5 - 3 mm, depending on the type of fuel. Furthermore, in-situ burning usually requires containment with booms in order to be achieved. Additionally some fuels are difficult to ignite and require primer to be used. The burning characteristics of various fuels are summarised in Table 1.1.

				<b>Burning Rate</b>	Sootiness	Efficiency
Fuel	Burnability	Ease of Ignition	Flame Spread	(mm/min)	of Flame	Range (%)
			rapid - through			
Gasoline	very high	very easy	vapours	3.5-4	medium	95-99
Diesel Fuel	high	easy	moderate	3-3.7	very high	90-98
	h: - h			252	Lev.	00.00
Light Fuel Oli	nign	medium	moderate	2.5-3	IOW	80-90
Heavy Fuel Oil	very low	difficult, add primer	slow	2.5.2.8	low	40-70
Lube Oil*	very low	difficult, add primer	slow	2	medium	40-60
Wasta Oil		difficult add arimar	alour	2 2 5		15 50
waste Oli	very low	difficult, add primer	SIOW	2-2.5	medium	15-50
Emulsified Oil	low	difficult, primer, high heat	slow	1 to 2	low	40-80

Table 1.1. Burning characteristics of various types of fuels (Fingas, 2014). \*(Fingas et al., 2000b)

The SAB fuel falls between the gasoline and diesel categories with an expected burning efficiency of 90 to 99% (Table 1.1). Although SAB is lighter than a standard diesel fuel, it is missing the light end components found in a gasoline fuel. The MGO is a marine diesel and it will fall under the diesel category with an expected burning efficiency of 90 to 98%. Finally, the IFO-180 is a heavy fuel consisting of more than 90% residual fuel. As such it will fall under the category of heavy fuel oil with an expected burning efficiency of 40 to 90%.

The efficiency results in Table 1.1 show that burning removes a significant amount of the spill for all types of fuel. Although there is limited information regarding in-situ burning in Antarctic waters, tank tests have shown that oil spills can be burned effectively at air temperatures from -11 to 23°C and water temperatures from -1 to 17°C (Tennyson, 1994). Other environmental conditions that need to be taken into account are wind velocity and sea state. Generally, an oil spill can be successfully ignited and burned at wind velocities below 20 m/s and wave heights below 1m (ASTM, 2014).

The use of dispersants to treat a fuel spill in polar or sub-polar conditions could provide an additional response measure. Dispersants contain chemicals compounds with one hydrophilic and one hydrophobic end in their molecule (Figure 1.13). They attach on the water-oil interface and reduce the interfacial tension between the two. As a result the oil spill breaks into small droplets that disperse into the water column. The aim is to remove the oil from the water surface that poses higher risk of reaching coastal areas and harming wildlife and transfer it to a large water volume that will quickly reduce the concentration to levels below concern. Due to the higher area to volume ratio of the dispersed droplets compared to the surface oil spill they are biodegraded faster by bacteria living in the water column.



Dioctyl sodium sulphosuccinate (DOSS)

Figure 1.13. An example of an active ingredient (surfactant) of a dispersant formulation. Other compounds that are part of the dispersant formulation are solvents that improve viscosity and promote solubility in oil.

Areas that are not recommended for dispersant use are coastal areas with shallow water columns and areas with limited water renewal, since the use of dispersants can lead to high concentrations of fuel compounds in the water column that can harm marine life. There is contradictory information in regards to the efficiency of dispersants, especially on heavy fuels such as the IFO-180. Some national response guidelines characterise heavy fuels such as the IFO-180 as non-dispersible (ESD, 1999). However, field trials conducted in the North Sea (Colcomb et al., 2005; Lunel, 1995; Lunel et al., 1997) have indicated that it is possible to partially disperse Medium Fuel Oils (MFO) and IFO-180 under favourable conditions. Furthermore, wave tank tests (Li et al., 2010; Trudel et al., 2005) and laboratory dispersability tests (Crosbie et al., 1999; Sorial, 2006; Srinivasan et al., 2007; Stevens and Roberts, 2003) have strengthened this argument by reporting results of the successful dispersion of IFO-180 and the heavier IFO-380. Unfortunately, most of these results were carried out at water temperatures of 15°C, with very limited results reported at water temperatures as low as 5°C (Srinivasan et al., 2007; Stevens and Roberts, 2003). Additionally, most of the efficiency tests of the aforementioned studies were performed using a single dispersant (Corexit 9500), with very little data on other dispersants. Thus there is lack of data on the efficiency of various dispersants under Antarctic conditions on the fuels used in the Antarctic Treaty area and the Australian Antarctic Territory.

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# The fate and bioavailability of fuel spills in polar marine environments.

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## Statement of authors' contribution

This Chapter is to be submitted soon to Marine Pollution Bulletin. This paper has been formatted to conform to the font and referencing style adopted in this thesis. Sections, Figures, Tables and Equations included within the text are prefixed with the chapter number.

I am the primary author (90% of the effort). I designed and performed the evaporation rate, water solubility, dissolution rate and dispersion experiments. Kathryn Brown performed the depletion experiment. I performed the analyses of the samples from all the aforementioned experiments on the gas

chromatograph coupled with flame ionisation detector, mass spectrometer detector and on the two dimensional gas chromatograph coupled with time of flight mass spectrometer. I processed and interpreted all the data derived from the measurements. I wrote and designed the structure of the paper. All co-authors carefully reviewed and provided feedback and valuable refinements on the final version of the manuscript, and approved it for submission and publication. Neither this manuscript nor one with similar content under our authorship has been published or is being considered for publication elsewhere, except as described above.

#### Abstract

The marine environment on the coast line of Antarctica harbours a unique ecosystem of marine organisms living under extreme conditions. Antarctic marine life is already stressed by the extreme conditions, so is particularly vulnerable to pollutants induced by anthropogenic activity such as accidental release of fuel spills from marine vessels and resupply operations of research stations. The increased marine traffic during recent years caused by growing tourism, research and support operations and illegal fishing in the Antarctic waters have increased the risk of a fuel spill incident along the Antarctic coast line. The required data on the fate and bioavailability of fuel spills in the Antarctic marine environment is largely missing. In this study the weathering rates and the partition ratios were examined for Special Antarctic Blend (SAB), Marine Gas Oil (MGO) and Intermediate Fuel Oil 180 (IFO-180), the three fuels used in the Australian Antarctic Territory. Specifically, the main focus was on the evaporation and dissolution rates of the fuels, since evaporation is the process responsible for the majority of the weathering loss, while dissolution determines the bioavailable fraction of the fuel. Other processes considered were natural dispersion of the fuels into the water column, and depletion of the hydrocarbons from the water column, which also need to be known in order to estimate the duration that the marine biota are exposed to the pollutants. The results show that evaporation is the process most influenced by the Antarctic conditions, with initial evaporation rates 3.5, 3.5 and 4.1 times slower for IFO-180, MGO and SAB respectively, compared to more temperate conditions. The slower evaporation rate allows more hydrocarbons to enter the water column, since the solubility and dissolution rates are affected to a lesser degree by the Antarctic conditions. Specifically, 105.8%, 79.9% and 63.2% greater masses of hydrocarbons are expected to enter the water column from SAB, MGO and IFO-180 fuel spills, respectively, in comparison to the same fuel spills under more temperate conditions. Once the polluted water drifts away from the spill, the dissolved hydrocarbons' depletion rates have been measured to exceed those expected from evaporation from the water column, indicating that other processes such as oxidation of hydrocarbons accelerate the depletion.

## 2.1 Introduction.

The Antarctic marine environment is home to a unique ecosystem of marine organisms living under extreme environmental conditions. The marine life around the coastline of Antarctica is exposed to freezing temperatures and ice coverage for most of the year. One of the effects of the extreme conditions on these organisms is the slower metabolic rate compared the marine organisms in more temperate regions (Gillooly et al., 2001). The slow metabolic rate renders these organisms vulnerable to the presence of toxic pollutants such as petroleum fuel spills induced by anthropogenic activity. Although the Antarctic Treaty is in place with the goal of keeping this pristine ecosystem protected, the risk of a major accidental fuel release is steadily increasing, as has been highlighted by recent incidents such as the stranding of the Akademik Shokalskiy on 25 December 2013, the grounding of the MS Nordkapp at Deception Island on 30 January 2007, and the fire aboard the Nisshin Maru in February 2007. The latter was carrying approximately 1000 tonnes of heavy fuel oil. These accidents are the result of the increasing marine traffic around the Antarctic coastline, mainly due to growing tourism, illegal fishing activity and research and resupply operations in support of the Antarctic research stations (IAATO, 2015).

The necessary data on the fate and bioavailability of petroleum fuels to marine organisms are very limited due to the unique Antarctic conditions. These are many processes that take place during the weathering of a fuel in the marine environment, including evaporation, dissolution, dispersion, oxidation, photolysis, biodegradation and spreading (Fingas, 2010). Evaporation is one of the main processes responsible for the majority of the fuel loss during the initial stages of weathering and affects the availability of hydrocarbons to the marine biota by removing them from the fuel-water interface. Presently, the majority of the literature data including vapour pressures, fuel evaporation rates, empirical correlations and evaporation models refer to more temperate conditions (Fingas, 2010; Mackay et al., 2006).

Although dissolution and natural dispersion cause only a small fraction of the fuel loss during weathering, these are the two processes responsible for the transfer of fuel components into the water column and the availability of the fuel to marine organisms. Similarly to evaporation, the available literature data on aqueous solubility, water partition coefficients and dissolution rates of hydrocarbons refer to more temperate conditions (Mackay et al., 2006). Finally, additional information is required on the depletion of hydrocarbons once they have entered the water column, since the persistence of these pollutants determines the exposure time of the marine biota.

Recently, a new technique has been developed initially from Arey et al. (2005) and subsequently improved by Nabi et al. (2014) for the estimation of the environmental partitioning properties for fuel hydrocarbons and other nonpolar environmental contaminants with the use of comprehensive two dimensional gas chromatography. The estimated properties include liquid vapour pressures, aqueous solubilities and airwater partition coefficients in a total of 11 estimated properties. The technique involves the calculation of two dimensional retention indices and the mapping of the two dimensional chromatogram with multiple contours assigning estimated values for each property. The technique is automated and fast since it involves the identification of only a few n-alkanes as reference components, before estimating the partition properties for all the other components detected in the chromatogram. This present study used a different approach where the majority of the components of the fuel have been manually identified and assigned partition properties measured experimentally or extrapolated from measured values in an effort to reach the highest possible accuracy.

The aim of this study was to address some of these unknowns, with more emphasis on the evaporation and dissolution rates of the fuels used in the Australian Antarctic Territory (AAT). Additionally, the partitioning of the fuel components between the fuel, the seawater and the atmosphere were investigated at both Antarctic and more temperate conditions. The effect of salinity on dissolution was also examined since the influx of fresh water from melting ice can alter the seawater salinity. Due to the high solubility of the aromatic hydrocarbons in seawater, the aromatic fraction of these fuels is the main source of the water accommodated fraction (WAF). For this reason, the detailed composition of both the aromatic fraction and the WAF produced by the three fuels was determined and the solubility of the main hydrocarbons present in the WAF was measured experimentally. Finally, an initial attempt was made to determine the depletion rates of the different types of dissolved hydrocarbons in order to identify the main processes responsible for their depletion.

## 2.2 Materials, methods and calculations

#### 2.2.1 Materials

The three fuels used in the present study are Special Antarctic Blend (SAB) diesel, Marine Gas Oil (MGO) and Intermediate Fuel Oil 180 (IFO-180). The SAB is a light distillate with a very narrow boiling point distribution especially formulated for cold climates. The volatile hydrocarbons have been removed from this fuel and it consists of a narrow distribution of hydrocarbons between C<sub>9</sub> and C<sub>15</sub> (this study). It is used in the AAT to power the stations' generator sets, to provide heat through boilers, and to run plant and equipment including the station incinerators and vehicles (Committee, 2011). Due to the large quantities used and transported, it is the most important fuel examined in this study. The MGO is a marine gas oil that consists exclusively of distillate without any addition of distillation residue. It consists of a broad distribution of hydrocarbons in the range C<sub>7</sub> to C<sub>26</sub> and is used in the AAT by marine vessels, including the Aurora Australis icebreaker, to power the main engines and generator sets, to provide propulsion and general services to the vessels such as power and heating (Bryson, 2002, updated 2014). The third fuel is the Intermediate Fuel Oil 180 (IFO-180). This is a widely used blend, generally containing less than 10% distillate, the remaining 90% being a heavy residual fuel (Bunker C) and with a boiling range reaching well over 700°C (ETC, 2015). It is used by large ships and it is the heaviest fuel oil now allowed in Antarctic Treaty waters.

The synthetic sea salt "Instant Ocean" (Aquarium Systems) was used to prepare water with a salinity equal to 34.5‰ by adding 34.5 g of synthetic sea salt to deionised water (Millipore filtration system) to prepare a total of one litre of solution.

Four internal standards of analytical grade were used for the quantification of the fuel and WAF samples analysed by the gas chromatograph. These standards were cyclooctane, 1,4-dichlorobenzene, tetracosane-d50 and bromoeicosane. The internal standards were added into dichloromethane to prepare a concentration of 5 μg/mL for each of the internal standards. This dichloromethane solution with the internal standards was used for the extraction of the WAF samples as well as for the preparation of the spiked fuel samples.

A synthetic standard mixture containing aromatic hydrocarbons of analytical grade at known quantities diluted in normal dodecane was prepared in order to accurately measure their partition coefficient and solubility. These values were used for comparison with the values obtained from the fuel solubility measurements as well as with values from the literature. The molar composition of the synthetic fluid was 0.31% benzene, 0.95% toluene, 1.92% o-xylene, 0.53% 1,2,4-trimethylbenzene, 0.98% tertbutylbenzene, 0.57% naphthalene, 0.96% 2-methylnaphthalene, and 1.88% 2-ethylnaphthalene, with the balance being normal dodecane.

### 2.2.2 Analytical Methods

Initially, the density and the kinematic viscosity of the three fuel samples were measured. The densities were determined gravimetrically by measuring the weight of either 50 mL or 100 mL of each fuel sample in a volumetric flask at the desired temperature, using a high precision (5 decimal places of a gram) mass balance (AND GR-202). The density of each fuel was measured at two temperatures, at 0 °C and at 15°C. All materials were brought to the desired temperature (±0.1°C) before the measurement in an incubator (Binder KB-115). The kinematic viscosities were determined with glass capillary viscometers immersed in a temperature regulated bath (Julabo F12).

The three fuels were fractionated into aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds by a liquid chromatographic column packed with activated silica gel and the fractions were collected for chromatographic analysis. The fractionation was performed by flowing in sequence two bed volumes of n-hexane, n-hexane/dichloromethane (4:1 v/v) and methanol/dichloromethane (1:1 v/v) through the column in order to elute the aliphatic, aromatic and polar fractions. The fractions were then

spiked by adding a known amount of internal standard and stored at -35 °C until the chromatographic analysis.

The composition of all samples was determined with three types of analysis: gas chromatography coupled with flame ionisation detector (GC-FID), gas chromatography coupled with mass spectrometry (GC-MS) and two dimensional gas chromatography coupled with time-of-flight mass spectrometry (GCxGC ToF-MS). Each technique provided certain advantages and combined together a high accuracy on the determined composition. The GC-FID (Agilent 6890N) was used to obtain the quantification of the pseudo component groups since it provides practically equal response for all hydrocarbons (Tong and Karasek, 1984). Then the GC-MS (Agilent 5975B) with the same GC configuration produced identical chromatograms where the different groups of isomers (n-alkanes, iso-alkanes, cycloalkanes, and aromatic hydrocarbons) were identified and their relative quantity was determined inside each pseudo component. Finally the GCxGC ToF-MS (Agilent 7890A GC, LECO Pegasus 4D ToF MS) was utilised to separate the unresolved complex mixture (UCM) in the heavier samples such as the IFO-180 fuel and the corresponding WAF.

The configuration of the GC for both the GC-FID and GC-MS analysis was as follows. The injection volume was 1  $\mu$ L splitless injection into a programmable temperature vaporisator (PTV) injector. The initial PTV temperature was 40 °C for 0.1 min., which was then increased to 310°C at a rate of 150°C/min. until the end of the run. The GC oven temperature program had an initial temperature of 30°C for 8 min., which was then increased to 310°C at a rate of 30°C for 8 min., which was then increased to 310°C at a rate of 4°C/min. The final time at maximum temperature was 30 min. The column used was a J&W DB5MS 5% polarity, with dimensions of 60 m length, 0.25 mm ID, and 0.25  $\mu$ m film thickness, with a constant flow of 1.3 mL/min of helium carrier gas, creating a velocity of 30 cm/sec.

35

The configuration of the GCxGC ToF-MS was as follows. The injection volume was 1 µL splitless injection into a split/splitless injector at 310°C constant temperature. The GC oven temperature program had an initial temperature of 35°C for 4 min., which was then increased to 300°C at a rate of 3°C/min. The final time at the maximum temperature was 25 min. The first column was a J&W DB5MS 5% polarity, with dimensions of 60m length, 0.25mm ID, and 0.25 µm film thickness, and the second column was a Restek Rxi-017 polar column with dimensions of 1.5m length, 0.25mm ID, and 0.25 µm film thickness, with a constant flow of 1.5 mL/min of helium carrier gas creating a velocity of 35 cm/sec. The modulation period was set to 4 seconds, and used a consumable-free system.

## 2.2.3 Estimation of the evaporation parameters

Kotzakoulakis and George (in prep.) (Chapter 3) performed a series of evaporation experiments on the three fuels under polar and temperate conditions in order to establish the evaporation curves of each fuel and develop an evaporation prediction model based on the pseudo-component composition. The detailed methodology and experimental setup for the evaporation measurements is given in Section 3.3.2 of Chapter 3. Each pseudo component was assigned an effective carbon number (ECN) according to the methodology developed by Snape et al. (2005), based on the ratio of n-alkanes, iso-alkanes, cycloalkanes, and aromatic components in each pseudo group. There is available data in the literature (Ruzicka and Majer, 1994) for the estimation of the vapour pressure of all normal hydrocarbons up to n-C<sub>20</sub> based on the Cox Equation in the form:

$$\ln\left(\frac{p_{sat}}{p_o}\right) = \left(1 - \frac{T_o}{T}\right)e^{\left(A_o + A_1 T + A_2 T^2\right)}$$
(2.1)

where  $p_{sat}$  and T are the vapour saturation pressure (KPa) at temperature T (K), T<sub>o</sub> and p<sub>o</sub> are the boiling point (K) at atmospheric pressure  $p_o = 101.325$  KPa, and A<sub>0</sub>, A<sub>1</sub>, and A<sub>2</sub> are the three experimentally determined parameters retrieved from the literature. The ECN of each carbon group and the Cox Equation were used to estimate the vapour pressure of all pseudo-components in each fuel according to the procedure described by Kotzakoulakis and George (in prep.) (Chapter 3).

Mackay and Matsugu (1973) have correlated the vapour pressure of a fuel oil or crude oil to the evaporation rate by taking into account the wind velocity, the temperature and the length of the spill downwind. This correlation can also be used to estimate the evaporation rates of the pseudo-components in a hydrocarbon mixture if we replace the vapour pressure of the oil ( $P_v$ ) with the partial pressure of the pseudo-component ( $p_i$ ). If we assume that the volatile hydrocarbons behave similarly to ideal gases at atmospheric pressure, then according to Dalton's Law of partial pressures and Raoult's Law, the partial pressure of a pseudo-component is equal to  $p_i=P_{Vi} * x_i$ , and the Mackay and Matsugu (1973) correlation for the molar evaporation rate of each pseudo-component thus becomes:

$$R_i = 4.82 \times 10^{-3} D_{i,Air}^{2/3} \nu^{-0.67} V^{0.78} L_D^{-0.11} \frac{P_{Vi} x_i}{R_G T}$$
(2.2)

where  $D_{i,Air}$  is the diffusion coefficient of component i in air (m<sup>2</sup> s<sup>-1</sup>), v is the kinematic viscosity of air (m<sup>2</sup> s<sup>-1</sup>), V is the air velocity (m s<sup>-1</sup>) at 10 m above the surface of the spill, L<sub>D</sub> is the equivalent diameter of the spill (m), P<sub>Vi</sub> is the vapour pressure of the component i in the mixture (Pa), x<sub>i</sub> is the molar fraction of component i, R<sub>G</sub> is the universal gas constant (Pa m<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup>), and T is the temperature (K). For the calculation of the diffusion coefficients D<sub>i,Air</sub> in air, we have used the Lennard-Jones collision integrals method as described by Kim and Monroe (2014).

Furthermore we can extract some more useful information by knowing the vapour pressures and the pseudo-component composition. Specifically, it is simple to calculate the evaporation coefficient K<sub>ev</sub> and another evaporation constant Q<sub>ev</sub> that are independent of specific conditions such as the wind velocity and the spill length, and can be applied easily under any given conditions. The same molar evaporation

rate  $R_i$  of Equation 2.2 can be expressed with the evaporation rate coefficient  $K_{ev}$  as follows (Riazi and Edalat, 1996):

$$R_i = -\frac{1}{A}\frac{dn}{dt} = K_{ev}(C_g - C_{\infty})$$
(2.3)

where A is the evaporation area (m<sup>2</sup>), dn/dt is the rate of evaporating moles per unit of time (s),  $C_g$  is the concentration of component i in the gas phase at the air-liquid interface in (mol/m<sup>3</sup>), and  $C_{\infty}$  is the concentration of component i in the gas phase at infinite distance from the spill, which can be assumed to be equal to zero. If we can also assume that the volatile hydrocarbons behave similarly to ideal gases at atmospheric pressure, then we can replace the term  $P_{Vi}x_i/R_GT$  of Equation 2.2 with  $C_g$ . Then we can derive the evaporation rate coefficient  $K_{ev}$  from Equation 2.3 to be equal to:

$$K_{ev} = \frac{R_i}{C_g} = 4.82 \times 10^{-3} D_{i,Air}^{2/3} v^{-0.67} V^{0.78} L^{-0.11}$$
(2.4)

The evaporation coefficient  $K_{ev}$  is independent of the concentration of the pseudo-component I and has the advantage that it can be used at any stage of the weathering process to calculate the evaporation rate if wind velocity and spill dimensions remain the same.

The wind velocity and the spill dimensions are two variables that change frequently, while the water temperature is much more stable over long periods of time. For this reason it is useful to calculate another quantity that is constant for a specific pseudo group but independent of these two variables, as this simplifies the calculation of the evaporation rate. This quantity can be called constant Q<sub>ev</sub> and can be extracted from Equation 2.4 and is equal to:

$$Q_{ev} = 4.82 \times 10^{-3} D_{i,Air}^{2/3} v^{-0.67} \frac{P_{Vi}}{R_G T}$$
(2.5)

Now having calculated the constant Q<sub>ev</sub> at a specific temperature for all the pseudo-components of a fuel, we can easily calculate the evaporation rate at any stage of the weathering process and under any environmental conditions, assuming that the seawater temperature remains the same. We only need to know the current wind velocity V, the length of the spill L, and the molar fraction of the pseudocomponent i:

$$R_i = Q_{ev} V^{0.78} L^{-0.11} x_i \tag{2.6}$$

The total evaporation rate of the whole fuel will be given by the sum of the rates of the pseudocomponents:

$$R_{fuel} = \sum R_i \tag{2.7}$$

#### 2.2.4 Measurement of hydrocarbon solubility

The solubility of individual hydrocarbons as well as that of hydrocarbon groups was measured for the three fuels and the synthetic standard mixture at different temperatures and salinities. For the solubility measurement the apparatus used was a set of four small, 60 mL separation funnels, and an orbital shaker (Grant PSU-20i) with 20 mm rotational diameter and adjustable rotation speed. The complete equilibration apparatus and materials were preconditioned at the desired temperature ±0.1°C and the procedure was performed in a temperature controlled environment (Binder KB-115).

56 mL of synthetic seawater was poured into the 60 mL separation funnel, followed by 4 mL of the sample, leaving a minimum of headspace in order to avoid evaporation of the volatile hydrocarbons. The funnel was placed upright on the orbital shaker and agitated at 180 rpm for 1 hour. This rotation speed was selected because it provides fast agitation but without breaking the sample into droplets. The agitation time was determined after a series of equilibration tests with varying agitation times from 10 min. to 2 hours. It was found that equilibration was achieved at around 30 min., and the hydrocarbon concentration remained constant over longer agitation times. After the agitation was complete the sample was left to settle for another hour until possible small sample droplets resurfaced. 25 mL of water was then collected from the bottom of the funnel for hydrocarbon extraction.

The water samples were extracted by adding 2 mL of extraction mix to the 25 mL water sample inside a 40 mL glass vial with a Teflon screw top. They were then vigorously agitated with a vortexer (TerraUniversal BenchMixer XL, BR19-29) at 2000 rpm for 15 min. At the end of the agitation the sample was left to settle for 30 min., and then the extraction mix was transferred into 2 mL autosampler vials with disposable glass pipettes and stored at -35°C until the chromatographic analysis.

## 2.2.5 Measurement of dissolution rate and dissolution constants

The apparatus used for the measurement of the dissolution rate of hydrocarbons was a 5 L glass aspirator bottle with a glass stopcock near the bottom and a magnetic stirrer with electronic adjustable stirring rate. The rate measurements were performed in a temperature controlled environment (Binder KB-115) at the desired temperature ±0.1°C. The following procedure was repeated for each fuel type.



Figure 2.1. Experimental determination of the dissolution rate of four fuel hydrocarbons (sum of xylenes, 1,2,4-trimethylbenzene, naphthalene, 2-methylnaphthalene). A common dissolution constant  $C_d$  for all hydrocarbons of a fuel under the specific conditions can then be calculated based on these four rates.

For the measurement of the dissolution rate, 4 L of synthetic seawater was poured into the aspirator bottle followed by 200 mL of fuel. The dissolution experiment was performed at 0°C with the stirring rate set to 200 rpm, which created a vortex less than 20% of the height of the water column. Small water

aliquots of 25 mL were collected from the bottom of the aspirator bottle at regular intervals for chromatographic analysis and determination of the concentration of hydrocarbons in the water. These experimental data points were plotted and fitted with a curve of the type  $C_i = C_{eq} (1 - e^{-kt})$ , where  $C_{eq}$  is the equilibration concentration of the compound i that describes the temporal progression of the concentration  $C_i$  (Schwarzenbach et al., 2003), as show in Figure 2.1. The tangent line at the beginning of the curve gave the initial dissolution rate when the concentration of hydrocarbons in the water is close to zero, as would be expected in a real case scenario in the open sea.

The slope of the tangent line is equal to the concentration increase for the first hour of the experiment, and the molar dissolution rate  $R_d$  can be calculated from the formula:

$$R_d = \frac{C_i}{Mw_i} \frac{V}{A} \frac{1}{t}$$
(2.8)

where  $C_i$  is the measured concentration of hydrocarbon i in g/m<sup>3</sup>, Mw<sub>i</sub> is the molar mass of hydrocarbon i, V is the volume of the water column in m<sup>3</sup>, A is the fuel-water interface area in m<sup>2</sup>, and t is the time in s required to reach concentration  $C_i$ .

After the molar dissolution rate is established, the dissolution rate coefficient  $K_d$  can be calculated from formula 2.9 (Riazi and Edalat, 1996) and the saturation concentration is given from equation 2.10 (Schluep et al., 2001):

$$R_d = -\frac{1}{A}\frac{dn}{dt} = K_d (C_{eq} - C_{\infty}) \qquad or \qquad K_d = \frac{R_d}{(C_{eq} - C_{\infty})}$$
(2.9)

With

$$C_{eq} = S_i x_i \tag{2.10}$$

where dn is the number of moles dissolved during the time period dt, A is the fuel-water interface area,  $C_{eq}$  is the equilibration concentration of the component in the water phase,  $S_i$  is the water solubility of the component i,  $x_i$  is the molar fraction of the component i in the fuel, and  $C_{\infty}$  is the concentration of the component in the water phase at infinite distance from the interface, which can be assumed to be equal to zero.

These experimental  $K_d$  values were compared with values obtained from the empirical correlation published by the U.S. Department of Interior (1987) for calculating the coefficient  $K_d$ . The correlation is as follows:

$$K_d = 0.035 \left(\frac{uL}{v}\right)^{0.8} \left(\frac{v}{D_f}\right)^{0.33} \frac{D_f}{L}$$
 (2.11)

where u is the water velocity under the spill, L is the length of the spill in the direction of the water velocity, v is the kinematic viscosity of the seawater, and  $D_f$  is the diffusion coefficient of the compound in the water phase.

The velocity u refers to the relative velocity of water in relation to the oil spill, and not the absolute water velocity. For the calculation of this quantity either measurement of the absolute water velocity of the current under the oil spill is required, or this parameter must have been previously constrained. Then

from this value, the observed drifting velocity of the oil spill needs to be subtracted. Because such information or the equipment to measure the water velocity may not be available, Riazi and Edalat (1996) proposed the use of an approximate value of 0.27m/s, which is considered to be a typical velocity of water movement at sea.

Equation 2.11 suggests that the only property specific to an individual compound is the diffusion coefficient D<sub>f</sub>, and all the remaining parameters are related to the environmental conditions and the geometric characteristics of the spill which are common for all the compounds of a spilled fuel. A common dissolution constant Cd<sub>exp</sub> can then be derived by multiplying each experimentally measured K<sub>d</sub> value with the quantity D<sub>f</sub><sup>-0.66</sup> of the specific compound to eliminate the contribution of D<sub>f</sub>. The required diffusion coefficients can be calculated with the Hayduk-Laudie correlation. By applying this calculation for each measured compound one should arrive at the same experimental diffusion constant Cd<sub>exp</sub> that is independent of the properties of the dissolved compounds:

$$Cd_{exp} = K_{di} D_{fi}^{-0.66}$$
 (2.12)

where  $K_{di}$  is the measured dissolution rate coefficient for compound i and  $D_{fi}$  the corresponding diffusion coefficient for the same compound.

These experimental constants can then be compared with the equivalent correlation constant  $Cd_{cor}$  derived from Equation 2.11 if we omit the term  $D_{f}$ :

$$Cd_{cor} = 0.035 \left(\frac{uL}{v}\right)^{0.8} \left(\frac{v}{1}\right)^{0.33} \frac{1}{L}$$
 (2.13)

Additionally, it is possible to calculate another quantity that simplifies the calculation of the dissolution rate when the environmental conditions change. The experimentally determined dissolution rate coefficient K<sub>d</sub> determined by Equation 2.9 is specific to the experimental conditions. The mole fraction, the water current velocity and the length of the spill are expected to change during the weathering process. In order to calculate a dissolution constant independent of these parameters we need to remove the contribution of these parameters from the experimentally determined dissolution coefficient K<sub>d</sub>. By equating the experimental coefficient K<sub>d</sub> with the right side of Equation 2.11 we can remove the contribution of spill length L and water velocity u according to Equation 2.14. We can call this new quantity dissolution constant Q<sub>d</sub>:

$$Q_{di} = K_d S_i \frac{L^{0.2}}{u^{0.8}}$$
(2.14)

The constant Q<sub>di</sub> is independent of the geometric characteristics of the spill and the water velocity and is applicable to any spill at the specific temperature. Once the dissolution rate coefficients K<sub>d</sub> have been determined experimentally for a specific set of conditions, the constant Q<sub>di</sub> can be calculated from Equation 2.14. Then constant Q<sub>di</sub> can be used to calculate the molar dissolution rate R<sub>di</sub> of each pseudocomponent at any given spill conditions by applying the new water velocity u and spill length L at the down current direction as follows:

$$R_{di} = Q_{di} \frac{u^{0.8}}{L^{0.2}} x_i \tag{2.15}$$

where  $x_i$  is the molar fraction of the component i.

Finally, the total molar dissolution rate of the whole fuel will be given by the sum of the dissolution rates of all pseudo-components:

$$R_{d fuel} = \sum R_{d i} \tag{2.16}$$

Another parameter that affects the dissolution rate of fuel compounds in the water column is the wind velocity. Wind causes wave action and movement of the water underneath the spill. Furthermore, as the wind velocity increases, the wave action disperses fuel droplets into the water column, thus accelerating the dissolution process. The greater the wind velocity is, the more the dissolution rate is increased. Previous investigations have measured the effect of the wind velocity on the air-water exchange for compounds with high Henry's law constants such as O<sub>2</sub> and CO<sub>2</sub>. Several empirical correlations have been developed for the calculation of the water-side transfer velocity in relation to wind velocity, as summarised by Schwarzenbach et al. (2003). Some investigations have used these air-water exchange correlations in oil spill boundary layer models in order to estimate the transfer velocity and the dissolution rate of oil components (Arey et al., 2007; Gros et al., 2014). However, there are a few considerations that constrain the accuracy of these correlations when used with oil spills. The oil layer that is interposed between the water and the gas phases changes the surface tension of the water and interferes with the direct air-water exchange, as demonstrated by Jähne et al. (1987). Furthermore, these correlations have been developed for gas compounds with high Henry's law constants. In this study, the experimental dissolution

rates were measured in the lab without the incorporation of wind above the fuel spill, and as such the reported results do not include the wind effect on the dissolution rate.

#### 2.2.6 Measurement of hydrocarbon depletion

To measure dissolved hydrocarbon depletion from a water body involves the experimental measurement of the composition of hydrocarbons in the water phase over time after the water has lost contact with the fuel spill. This experiment is designed to measure the rate of hydrocarbon depletion from the water phase under polar conditions. The required volume (8 L) of WAF was prepared according to the ecotoxicology protocol developed by Singer et al. (2001) and modified by Barron and Ka'aihue (2003). Natural seawater was filtered (0.5 µm) before it was used for the preparation of the WAF. The WAF was poured into a series of open 500 mL jars and placed in a temperature controlled cabinet at 0°C. The cabinet was lit with fluorescence light for the duration of the test. Duplicate samples were collected at predetermined time intervals, starting at time zero to determine the initial and the subsequent compositions of the depleting WAF. Additionally, a portion of the fresh WAF at time zero was stored in an air tight container without a gas cap in order to determine the depletion of dissolved hydrocarbons while excluding evaporation and oxidation processes. The collected water samples were spiked with internal standard, extracted with dichloromethane and stored in a freezer until the chromatographic analysis on GC-FID and GC-MS. The full details of the procedure can be found in Brown at al. (2016).

#### 2.2.7 Measurement uncertainty and experimental errors

The estimation of the vapour pressures with the Cox equation was performed by applying the factor values recommended by Ruzicka and Majer (1994) for the hydrocarbon range between n-hexane and n-eicosane. The comparison of the equation's estimated values with the published experimental data from the literature shows an error of <3%. For the measurement of the evaporation rates the uncertainty of

the hotwire anemometer was always <4%. The uncertainty of the temperature incubator was ±0.1°C which corresponds to an error in the evaporation rate of approximately 1%. The propagation of these errors lead to an uncertainty for the evaporation rate of less than 9%.

For the measurement of solubility duplicate pairs were analysed for the three types of fuels and the solubility standard mixture. The experimental uncertainty did not exceed 5% for the components, with water solubilities more than 100  $\mu$ g/L and 12% for the components with lower solubility. The uncertainty of the temperature incubator of ±0.1°C corresponds to practically no change in the solubility of the examined hydrocarbons. Finally there is an uncertainty of 5% in the rotational speed of the magnetic stirrer. The propagation of these errors lead to an uncertainty in the estimation of the dissolution rate of approximately 13% for the components with a solubility higher than 100  $\mu$ g/L, and 25% for the components with lower solubility.

Finally, the dissolution to evaporation ratios can carry an accumulated error of up to 27%.

## 2.3 Results and discussion

## 2.3.1 Fuel characterisation results

The initial molar composition and physical properties of the three fresh fuels are shown in Tables 2.1-2.3. As shown by its composition (Figure 2.2, Table 2.1), SAB is a very light distillate with a narrow molecular weight range, and its physical properties are least affected by the polar conditions. Both density and viscosity remain low at 0°C, and importantly most of the volatile fraction below C<sub>10</sub> has been removed from this distillate.



Figure 2.2. Gas chromatogram of fresh SAB fuel. SAB is a very narrow distillate consisting of  $C_9-C_{15}$  hydrocarbons.

Sample:	Special Antarctic Blend (SAB)					
Physical properties			Density:		Viscosity	
Temperature °C			g/cm³		mPa s	
	0		0.806		2.26	
	15		0.795		2.07	
Composition			Mole %			
	N-					
СN	alkanes	Isoalkanes	Cycloalkanes	Aromatics	Total	
С8	0.05	0.02	0.02	0.01	0.11	
С9	0.48	0.33	0.28	0.26	1.34	
C10	4.51	2.88	2.39	1.73	11.5	
C11	9.84	7.56	6.27	3.30	27.0	
C12	9.69	8.89	6.56	7.05	32.2	
C13	4.61	6.82	5.03	3.06	19.5	
C14	0.84	1.67	1.23	3.07	6.81	
C15	0.08	0.13	0.11	0.80	1.13	
C16	0.03	0.03	0.02	0.10	0.18	
C17	0.03	0.01	0.00	0.03	0.06	
C18	0.02	0.01	0.01	0.04	0.08	
C19	0.02	0.00	0.00	0.01	0.03	
C20	0.01	0.00	0.00	0.02	0.04	
C21	0.01	0.00	0.00	0.01	0.02	
C22	0.01	0.00	0.00	0.00	0.01	
C23	0.00	0.00	0.00	0.00	0.00	
C24	0.00	0.00	0.00	0.00	0.00	
C25+					0.00	

Table 2.1. Physical properties and molar composition of fresh SAB fuel. The physical properties of SAB do not change significantly under polar conditions.

The composition of MGO (Table 2.2; Figure 2.3) reveals a fluid with a much wider molecular weight distribution than SAB, with its composition reaching  $C_{25}$ . Despite this broad chemical distribution its physical properties indicate a relatively light fluid. With a temperature drop from 15°C to 0°C there is a ~50% increase in the viscosity of MGO, but this is still very low (6.21 mPa s). One of the reasons for this low viscosity is that MGO containing more volatile components < $C_{10}$  than SAB.



Figure 2.3. The gas chromatogram of fresh MGO fuel, showing it is composed of a wide range of hydrocarbons from  $C_7$  to  $C_{25}$ .

Sample	Marine Ga	as Oil			
Physical properties		Density:	Viscosity		
Temperatu	Temperature °C		g/cm <sup>3</sup>		mPa s
	0		0.839		6.21
	15		0.829		4.15
Composition			Mole %		
	N-				
CN	alkanes	Isoalkanes	Cycloalkanes	Aromatics	Total
C7	0.00	0.00	0.01	0.00	0.02
C8	0.17	0.28	0.67	0.12	1.24
С9	0.63	0.62	0.95	0.35	2.54
C10	1.34	1.47	1.74	0.93	5.49
C11	2.42	2.08	2.41	1.12	8.04
C12	3.10	2.66	3.18	1.88	10.8
C13	2.68	3.33	3.11	1.96	11.1
C14	2.43	3.04	2.99	2.48	10.9
C15	2.33	3.03	2.80	2.44	10.6
C16	1.99	2.68	2.56	1.85	9.08
C17	1.70	2.68	2.31	1.46	8.16
C18	1.10	2.02	1.60	1.18	5.91
C19	0.97	1.99	1.37	0.85	5.18
C20	0.70	1.26	1.12	0.66	3.75
C21	0.47	0.95	0.80	0.43	2.65
C22	0.31	0.65	0.55	0.28	1.79
C23	0.18	0.45	0.38	0.15	1.17
C24	0.11	0.29	0.24	0.09	0.74
C25+					0.83

Table 2.2. Molar composition and physical properties of MGO fuel. Its viscosity remains low, even at polar seawater temperatures.

The IFO-180 fuel consists of more than 90% residual oil and this is obvious in its chemical composition (Table 2.3; Figure 2.4). IFO-180 has a large  $>C_{25}$  fraction and a wide molecular weight distribution extending down to C<sub>8</sub>. This is due to the addition of a small amount (<10%) of light fuel, often MGO, during manufacture of IFO-180, in order for it to meet the viscosity requirements (ESD, 1999; Wikipedia, 2016).

Its physical properties and especially its viscosity are affected greatly by low polar temperatures. An increase of viscosity by 500% is observed when chilling it from 15°C to 0°C, and it reaches a very viscous value of almost 13,000 cSt at 0°C in its fresh state. This viscosity makes IFO-180 very adhesive and difficult to clean from anything that it comes in contact with, making it dangerous for wildlife as an environmental pollutant.



Figure 2.4. Gas chromatogram of fresh IFO-180 fuel. A large proportion of this heavy fuel is  $>C_{25}$ , and is not eluted from the capillary column. The slight rise in the baseline is due to a small unresolved complex mixture (UCM), which is not present in SAB or MGO.

Sample:	Intermedia	Intermediate Fuel Oil (IFO)						
Physical properties		Density:	Density:					
Temperature °C		g/cm³	g/cm <sup>3</sup>					
	0		0.963		12926			
	15		0.952		2605			
Composition			Mole %					
СN	N-alkanes	Isoalkanes	Cycloalkanes	Aromatics	Total			
С7	0.00	0.00	0.00	0.00	0.00			
С8	0.01	0.02	0.09	0.04	0.16			
С9	0.09	0.10	0.20	0.19	0.58			
C10	0.22	0.35	0.41	0.39	1.37			
C11	0.36	0.44	0.46	0.37	1.62			
C12	0.56	0.65	0.75	0.64	2.60			
C13	0.79	1.14	1.02	0.74	3.69			
C14	1.23	1.66	1.67	1.43	5.98			
C15	1.43	2.41	2.34	2.33	8.51			
C16	1.23	2.06	1.88	2.81	7.98			
C17	0.98	1.98	1.50	2.38	6.85			
C18	0.85	2.37	1.31	2.01	6.54			
C19	0.76	1.79	1.13	1.71	5.38			
C20	0.58	1.16	0.96	1.48	4.18			
C21	0.42	0.90	0.72	1.09	3.12			
C22	0.29	0.68	0.51	0.75	2.23			
C23	0.20	0.55	0.39	0.48	1.62			
C24	0.15	0.47	0.31	0.28	1.21			
C25+					36.36			

Table 2.3. Physical properties and molar composition of fresh IFO-180 fuel. Polar seawater temperatures cause a drastic increase in the viscosity of this fuel. The composition shows a heavy fuel with 36.36% molar fraction  $>C_{25}$ .

#### 2.3.2 Characterisation of the aromatic fraction of the fuels and the corresponding WAFs

The aromatic fraction of a fuel is the main contributor of dissolved hydrocarbons into seawater if it is spilled, due to the higher aqueous solubility of aromatic hydrocarbons compared to other hydrocarbon types (McAuliffe, 1966). Therefore it is important to understand the detailed composition of the aromatic fraction of the three fresh fuels, and also the aromatic composition of the resulting WAFs after seawater has equilibrated with each fuel. Identifying and quantifying the majority of individual compounds present in the WAF and the corresponding compounds in the fuels is a challenging task especially for the IFO-180 due to the large number of heavier hydrocarbons and NSO compounds. A large number of these compounds have similar retention times in the chromatographic column and overlap or co-elute creating an Unresolved Complex Mixture (UCM) when analysed on a single dimension gas chromatograph as can be seen in Figure 2.7. A combination of different identification and quantification techniques was used in order to complete this task.

The mass spectrum of overlapping compounds found outside the UCM was deconvoluted with the automated mass spectral deconvolution and identification system (AMDIS version 2.71) software for all three fuels. The deconvoluted spectra were then imported into the OpenChrom chromatography and mass spectrometry software (version 1.1.0 'Diels'), were the areas of the deconvoluted compounds were extracted from the initial area of the overlapping peaks according to the abundances of the deconvoluted spectra. The identification of the deconvoluted spectra was performed by matching the unknown spectra with the NIST MS Search software to the spectra of two mass libraries (NIST 05 and Wiley 9). The library identification was then verified and common errors were corrected, such as the identification of two separate peaks under the same name, by calculating the linear retention indices of all the compounds and comparing them with the NIST Retention Index Library (version 2011).

The deconvolution of the UCM in the IFO-180 WAF was performed by two dimensional gas chromatography, time of flight mass spectrometry (GC x GC – ToF MS). The compounds were separated

55

on the first non-polar column according to their boiling point and on the second highly polar column according to their polarity (Figures 2.8-2.9). A similar methodology was followed for the identification of the compounds. Following the spectral library search and identification (Libraries NIST 05 and Wiley 9), the compounds were verified and occasionally corrected according to their linear retention Index order on the NIST Retention Index library. Table 2.4 summarises the aromatic composition of the three fresh fuels, and their resultant WAFs.

					Water Accommodated			
	Fuel				Fraction			
	Concentration g/L				Concentration µg/L			
Total Aromatic Content 286 147 154		154		2,790	3 <i>,</i> 560	6,610		
Group Name	IFO-180	MGO	SAB		IFO-180	MGO	SAB	
Benzenes	6.85	33.7	75.2		538	2,310	2,620	
Naphthalenes	16.5	6.14	32.0		178	268	2,070	
Phenols	0.00	0.00	0.00		43.0	80.6	1,030	
Benzothiophenes	4.82				22.8			
Dibenzothiophenes	0.51				1.5			
Indanes	2.93	8.69	17.6		45.2	178	385	
Indenes	1.91	1.90			3.5	1.2		
Tetralins	8.23	41.3	5.51		32.8	204	165	
Biphenyls	1.01	2.47	0.64		5.7	14.3	30.2	
Acenaphthene	0.01				0.6			
Fluorenes	0.53				2.2			
Anthracenes + Phenanthrenes	0.17				0.3			
Other hydrocarbons	155	32.8	13.6		151	125	55.6	
Other NSO compounds	87.7	19.8	9.9		1,770	373	252	

Table 2.4. Composition of the aromatic fraction of the three fresh fuels and the resulting WAFs. The IFO-180, due to its heavier composition, produces a WAF fraction with heavier polyaromatic hydrocarbons and NSO compounds. Detailed compositional breakdowns of each aromatic group are given in Appendix 2A, Tables 2A.1 and 2A.2. "Benzenes" means benzene and the various alkylated benzene isomers; etc. SAB in equilibrium with seawater creates a WAF with the highest concentration of aromatic hydrocarbons (Table 2.4; Figure 2.5). Compared to the other two WAFs, SAB WAF contains higher concentrations of benzenes, but also an order of magnitude higher concentrations of naphthalenes and phenols. The MGO WAF contains similar amounts of benzenes to the SAB WAF, but much lower concentrations of the other types of aromatic hydrocarbons (Table 2.4; Figure 2.6). The IFO-180 WAF contains less aromatic hydrocarbons of all types, but the ratio of heavier aromatic hydrocarbons to volatile aromatic hydrocarbons is much higher (Table 2.4; Figure 2.7 and 2.8). Additionally, it contains benzothiophenes and dibenzothiophenes, which the other WAFs do not contain, and a large amount of heavier nitrogen, sulphur and oxygen (NSO) containing organic compounds of unknown toxicity. These heavier aromatic hydrocarbons and NSO compounds tend to reside longer in the water column due to their low air to water partition coefficient and cause longer exposure and bioaccumulation in the marine biota (Booth et al., 2007). A summary of the compositional differences of the three WAF fractions is given in Figure 2.10.



Figure 2.5. Gas chromatogram of the WAF produced by SAB fuel. Benzenes and naphthalenes are the two dominant hydrocarbon groups dissolved in the seawater.



Figure 2.6. Gas chromatogram of the WAF fraction produced by the MGO fuel. Compared to SAB it has a higher ratio of light benzenes to heavier naphthalenes.



Figure 2.7. Gas chromatogram of the WAF produced by the IFO-180 fuel. It is characterised by a large number of compounds especially heavier aromatic hydrocarbons and NSO compounds that create an Unresolved Complex Mixture (UCM).



Figure 2.8. Two dimensional total ion chromatogram of the IFO-180 WAF acquired by GCxGC ToF MS. The IFO-180 WAF contains heavier aromatic hydrocarbons and NSO compounds that create an Unresolved Complex Mixture (UCM) on one dimension GC-MS, and these can mostly be resolved by two dimensional gas chromatography.



Figure 2.9. Two dimensional chromatographic map of the location of the different hydrocarbon and NSO groups in the IFO-180 WAF. A large amount of heavy NSOs are present in the IFO-180 WAF that are absent from the other two fuels.



Figure 2.10. Compositional comparison of the WAFs produced by the three fuels. The SAB WAF has the highest concentration of benzenes and naphthalenes, whereas the IFO-180 WAF has the lowest concentration of light aromatic hydrocarbons, but the highest concentration of NSO compounds.

## 2.3.3 Evaporation of the three fuels at polar and temperate marine conditions

The evaporation parameters of each pseudo component up to  $C_{25}$  are presented in Tables 2.5-2.7 for the SAB, MGO and IFO-180 fuels, respectively. These parameters were calculated according to the methodology outlined in Section 2.2.3. The Tables include the evaporation rate coefficient K<sub>ev</sub> and the molar evaporation rate R<sub>ev</sub> for a case study of a hypothetical fuel spill with 100 m length downwind and a wind velocity of 7m/s. The rates were calculated for both 0°C and 20°C.
Sample:	Special Antar	ctic Blend (SA	В)							
	Evaporation	parameters at	0°C			Evaporation	parameters at	20°C		Rate ratio
CN	Pv (Pa)	Q <sub>ev</sub>	K <sub>ev</sub>	R <sub>ev</sub>	CN	Pv (Pa)	Q <sub>ev</sub>	K <sub>ev</sub>	R <sub>ev</sub>	20°C / 0°C
Pseudo-C8	8.73E+02	1.05E-03	7.50E-03	3.13E-06	Pseudo-C8	2.79E+03	3.14E-03	7.55E-03	9.39E-06	3.0
Pseudo-C9	2.86E+02	3.30E-04	7.20E-03	1.22E-05	Pseudo-C9	1.04E+03	1.12E-03	7.25E-03	4.14E-05	3.4
Pseudo-C10	6.95E+01	7.60E-05	6.83E-03	2.40E-05	Pseudo-C10	2.96E+02	3.04E-04	6.88E-03	9.62E-05	4.0
Pseudo-C11	1.79E+01	1.88E-05	6.53E-03	1.39E-05	Pseudo-C11	8.95E+01	8.79E-05	6.58E-03	6.52E-05	4.7
Pseudo-C12	5.61E+00	5.70E-06	6.34E-03	5.04E-06	Pseudo-C12	3.19E+01	3.04E-05	6.39E-03	2.69E-05	5.3
Pseudo-C13	1.42E+00	1.39E-06	6.10E-03	7.45E-07	Pseudo-C13	9.51E+00	8.72E-06	6.14E-03	4.68E-06	6.3
Pseudo-C14	5.39E-01	5.23E-07	6.06E-03	9.80E-08	Pseudo-C14	4.03E+00	3.67E-06	6.11E-03	6.88E-07	7.0
Pseudo-C15	1.78E-01	1.72E-07	6.02E-03	5.31E-09	Pseudo-C15	1.52E+00	1.37E-06	6.06E-03	4.25E-08	8.0
Pseudo-C16	3.94E-02	3.62E-08	5.73E-03	1.78E-10	Pseudo-C16	3.96E-01	3.42E-07	5.78E-03	1.68E-09	9.4
Pseudo-C17	8.21E-03	7.19E-09	5.46E-03	1.25E-11	Pseudo-C17	9.78E-02	8.04E-08	5.51E-03	1.40E-10	11.2
Pseudo-C18	2.65E-03	2.30E-09	5.42E-03	4.98E-12	Pseudo-C18	3.62E-02	2.95E-08	5.47E-03	6.39E-11	12.8
Pseudo-C19	5.63E-04	4.68E-10	5.19E-03	4.08E-13	Pseudo-C19	9.08E-03	7.09E-09	5.23E-03	6.19E-12	15.2
Pseudo-C20	1.81E-04	1.49E-10	5.16E-03	1.68E-13	Pseudo-C20	3.34E-03	2.60E-09	5.20E-03	2.91E-12	17.4
Pseudo-C21	4.05E-05	3.22E-11	4.97E-03	1.67E-14	Pseudo-C21	8.84E-04	6.61E-10	5.01E-03	3.44E-13	20.5
Pseudo-C22	2.92E-06	2.13E-12	4.57E-03	4.22E-16	Pseudo-C22	8.99E-05	6.19E-11	4.61E-03	1.22E-14	29.0
Pseudo-C23	7.66E-07	5.48E-13	4.47E-03	5.00E-17	Pseudo-C23	2.75E-05	1.85E-11	4.51E-03	1.69E-15	33.8
Pseudo-C24	2.01E-07	1.41E-13	4.37E-03	1.28E-17	Pseudo-C24	8.42E-06	5.54E-12	4.41E-03	5.06E-16	39.4
C25 plus	5.28E-08	3.62E-14	4.28E-03	1.60E-18	C25 plus	2.58E-06	1.66E-12	4.32E-03	7.32E-17	45.9
Fuel	19.74	2.15E-05	6.39E-03	5.91E-05	Fuel	87.60	8.89E-05	6.43E-03	2.44E-04	4.1

Table 2.5. The evaporation parameters of the pseudo-components and the whole SAB fuel at 0°C and 20°C. Pv = vapour pressure,  $Q_{ev} = an$  evaporation constant. The evaporation rate coefficients  $K_{ev}$  and molar evaporation rates  $R_{ev}$  correspond to the case scenario of a 100 m long spill with a wind velocity of 7m/s. In the last column the rate ratio shows that at 20°C the molar evaporation rate of pseudo-components is 3 to 45.9 times greater than at 0°C, with an average rate ratio for the whole SAB fuel of 4.1.

The constant Q<sub>ev</sub> values presented in Tables 2.5-2.7 are independent of the wind velocity and the spill dimensions. These take into account the vapour pressure and are specific for the given seawater temperature. The Q<sub>ev</sub> values simplify the calculation of the molar evaporation rate using Equation 2.6, such that only the parameters that are expected to change during the weathering are required. Those parameters are the wind velocity, the spill length downwind and the molar fraction of the specific pseudo-component. These evaporation parameters have been incorporated into an oil-spill evaporation model developed by Kotzakoulakis and George (in prep.) (Chapter 3) that takes into account the diffusion forces

inside the body of the oil phase and the concentration gradient that develops between the surface and

the inner part of the spill.

Sample:	Marine Gas C	Dil (MGO)								-
	Evaporation	parameters at	0°C			Evaporation	parameters at	20°C		Rate ratio
CN	Pv (Pa)	Q <sub>ev</sub>	K <sub>ev</sub>	R <sub>ev</sub>	CN	Pv (Pa)	Q <sub>ev</sub>	K <sub>ev</sub>	R <sub>ev</sub>	20°C / 0°C
Pseudo-C8	8.72E+02	1.05E-03	7.53E-03	3.56E-05	Pseudo-C8	2.83E+03	3.20E-03	7.58E-03	1.08E-04	3.0
Pseudo-C9	2.36E+02	2.71E-04	7.15E-03	1.89E-05	Pseudo-C9	8.90E+02	9.57E-04	7.20E-03	6.67E-05	3.5
Pseudo-C10	6.36E+01	6.96E-05	6.83E-03	1.05E-05	Pseudo-C10	2.79E+02	2.86E-04	6.88E-03	4.31E-05	4.1
Pseudo-C11	1.63E+01	1.71E-05	6.53E-03	3.78E-06	Pseudo-C11	8.37E+01	8.21E-05	6.57E-03	1.82E-05	4.8
Pseudo-C12	5.36E+00	5.45E-06	6.34E-03	1.62E-06	Pseudo-C12	3.08E+01	2.93E-05	6.39E-03	8.74E-06	5.4
Pseudo-C13	1.42E+00	1.39E-06	6.11E-03	4.22E-07	Pseudo-C13	9.46E+00	8.70E-06	6.16E-03	2.65E-06	6.3
Pseudo-C14	3.99E-01	3.79E-07	5.94E-03	1.14E-07	Pseudo-C14	3.07E+00	2.75E-06	5.98E-03	8.26E-07	7.2
Pseudo-C15	1.07E-01	9.89E-08	5.76E-03	2.88E-08	Pseudo-C15	9.62E-01	8.33E-07	5.81E-03	2.43E-07	8.4
Pseudo-C16	2.71E-02	2.42E-08	5.58E-03	6.04E-09	Pseudo-C16	2.85E-01	2.39E-07	5.62E-03	5.96E-08	9.9
Pseudo-C17	6.73E-03	5.82E-09	5.40E-03	1.30E-09	Pseudo-C17	8.28E-02	6.73E-08	5.44E-03	1.51E-08	11.6
Pseudo-C18	1.87E-03	1.58E-09	5.28E-03	2.56E-10	Pseudo-C18	2.67E-02	2.12E-08	5.32E-03	3.44E-09	13.4
Pseudo-C19	4.73E-04	3.89E-10	5.13E-03	5.54E-11	Pseudo-C19	7.92E-03	6.11E-09	5.17E-03	8.71E-10	15.7
Pseudo-C20	1.26E-04	1.01E-10	5.01E-03	1.04E-11	Pseudo-C20	2.45E-03	1.85E-09	5.05E-03	1.90E-10	18.3
Pseudo-C21	3.25E-05	2.54E-11	4.89E-03	1.85E-12	Pseudo-C21	7.38E-04	5.44E-10	4.93E-03	3.95E-11	21.4
Pseudo-C22	8.46E-06	6.48E-12	4.78E-03	3.18E-13	Pseudo-C22	2.24E-04	1.61E-10	4.82E-03	7.93E-12	24.9
Pseudo-C23	2.15E-06	1.61E-12	4.67E-03	5.16E-14	Pseudo-C23	6.69E-05	4.70E-11	4.71E-03	1.51E-12	29.2
Pseudo-C24	5.59E-07	4.09E-13	4.57E-03	8.29E-15	Pseudo-C24	2.03E-05	1.40E-11	4.61E-03	2.83E-13	34.1
C25 plus	4.52E-08	3.18E-14	4.40E-03	7.26E-16	C25 plus	2.18E-06	1.44E-12	4.44E-03	3.29E-14	45.3
Fuel	22.33	2.58E-05	5.85E-03	7.09E-05	Fuel	84.35	9.06E-05	5.90E-03	2.49E-04	3.5

Table 2.6. The evaporation parameters of the pseudo-components and the whole MGO fuel at 0°C and 20°C. Pv = vapour pressure,  $Q_{ev} = an$  evaporation constant. The evaporation rate coefficients  $K_{ev}$  and the molar evaporation rates  $R_{ev}$  correspond to the case scenario of a 100m long spill with a wind velocity of 7m/s. In the last column the rate ratio shows that at 20°C the molar evaporation rate of pseudo-components is 3 to 45.3 times greater than at 0°C, with an average rate ratio for the whole MGO fuel of 3.5.

In Figure 2.11 the experimentally measured evaporation amounts (blue symbols) are presented for the three fuels at 0 °C and 15°C. In addition the evaporation curves predicted by the evaporation model are plotted(red continuous lines), which exhibit a high correlation factor to the experimental data. This correlation indicates that the model and stimulated evaporation parameters are close to the real

evaporation parameters. The vapour pressures of each pseudo-component for all three fuels are given in

Tables 2.5-2.7.

Sample:	Intermediate Fuel Oil 180 (IFO-180)									
	Evaporation	parameters at	0°C			Evaporation p	parameters at	20°C		Rate ratio
CN	Pv (Pa)	Q <sub>ev</sub>	K <sub>ev</sub>	R <sub>ev</sub>	CN	Pv (Pa)	Q <sub>ev</sub>	K <sub>ev</sub>	R <sub>ev</sub>	20°C / 0°C
Pseudo-C8	1.20E+03	1.49E-03	7.74E-03	6.64E-06	Pseudo-C8	3.73E+03	4.34E-03	7.79E-03	1.94E-05	2.9
Pseudo-C9	3.92E+02	4.66E-04	7.42E-03	7.46E-06	Pseudo-C9	1.39E+03	1.55E-03	7.47E-03	2.48E-05	3.3
Pseudo-C10	1.04E+02	1.18E-04	7.05E-03	4.43E-06	Pseudo-C10	4.32E+02	4.58E-04	7.10E-03	1.72E-05	3.9
Pseudo-C11	2.40E+01	2.56E-05	6.68E-03	1.14E-06	Pseudo-C11	1.16E+02	1.17E-04	6.73E-03	5.21E-06	4.6
Pseudo-C12	6.81E+00	7.02E-06	6.44E-03	5.02E-07	Pseudo-C12	3.81E+01	3.69E-05	6.49E-03	2.64E-06	5.3
Pseudo-C13	1.71E+00	1.70E-06	6.19E-03	1.72E-07	Pseudo-C13	1.12E+01	1.05E-05	6.24E-03	1.06E-06	6.2
Pseudo-C14	4.96E-01	4.78E-07	6.01E-03	7.86E-08	Pseudo-C14	3.75E+00	3.39E-06	6.06E-03	5.57E-07	7.1
Pseudo-C15	1.36E-01	1.27E-07	5.84E-03	2.98E-08	Pseudo-C15	1.19E+00	1.05E-06	5.89E-03	2.45E-07	8.2
Pseudo-C16	3.92E-02	3.58E-08	5.71E-03	7.86E-09	Pseudo-C16	3.95E-01	3.40E-07	5.76E-03	7.45E-08	9.5
Pseudo-C17	1.04E-02	9.21E-09	5.56E-03	1.74E-09	Pseudo-C17	1.22E-01	1.02E-07	5.60E-03	1.92E-08	11.0
Pseudo-C18	2.69E-03	2.32E-09	5.40E-03	4.18E-10	Pseudo-C18	3.69E-02	3.00E-08	5.45E-03	5.40E-09	12.9
Pseudo-C19	7.00E-04	5.92E-10	5.27E-03	8.75E-11	Pseudo-C19	1.12E-02	8.92E-09	5.32E-03	1.32E-09	15.1
Pseudo-C20	1.81E-04	1.50E-10	5.17E-03	1.72E-11	Pseudo-C20	3.41E-03	2.65E-09	5.21E-03	3.04E-10	17.7
Pseudo-C21	4.75E-05	3.83E-11	5.03E-03	3.29E-12	Pseudo-C21	1.03E-03	7.82E-10	5.08E-03	6.72E-11	20.4
Pseudo-C22	1.27E-05	1.00E-11	4.93E-03	6.16E-13	Pseudo-C22	3.22E-04	2.39E-10	4.97E-03	1.47E-11	23.8
Pseudo-C23	3.21E-06	2.47E-12	4.81E-03	1.10E-13	Pseudo-C23	9.51E-05	6.89E-11	4.85E-03	3.06E-12	27.9
Pseudo-C24	7.78E-07	5.85E-13	4.69E-03	1.94E-14	Pseudo-C24	2.72E-05	1.92E-11	4.73E-03	6.37E-13	32.8
C25 plus	1.42E-18	7.36E-25	3.24E-03	7.36E-25	C25 plus	1.09E-15	5.32E-22	3.28E-03	5.31E-22	722.1
Fuel	6.33	7.44E-06	4.78E-03	2.05E-05	Fuel	23.72	2.59E-05	4.83E-03	7.12E-05	3.5

Table 2.7. The evaporation parameters of the pseudo-components and the whole IFO-180 fuel at 0°C and 20°C. Pv = vapour pressure,  $Q_{ev}$  = an evaporation constant. The evaporation rate coefficients  $K_{ev}$  and the molar evaporation rates  $R_{ev}$  correspond to the case scenario of a 100m long spill with a wind velocity of 7m/s. In the last column the rate ratio shows that at 20°C the molar evaporation rate of pseudo-components is 2.9 to 722.1 times greater than at 0°C, with an average rate ratio for the whole IFO-180 fuel of 3.5. In particular these rates indicate that the heavy  $C_{25+}$  residue of the IFO-180 practically stops evaporating at 0°C.

The SAB fuel is a narrow distillate with a large majority of its components  $<C_{15}$  (Figure 2.2; Table 2.1). Evaporation is the main weathering process until the SAB fuel is completely evaporated, which happens after 4 days at 15°C (Figure 2.11B). Even under polar conditions at 0°C the SAB fuel will eventually evaporate completely, but at a slower rate so taking approximately two weeks (Figure 2.11A). MGO fuel is also a pure distillate but it has a much wider distribution of components, with some components  $>C_{25}$  (Figure 2.3; Table 2.2). Under polar conditions at 0°C evaporation of MGO fuel progresses reasonably fast until ~30% of its mass is lost in the first 10 days (Figure 2.11A), but evaporation then slows down until it practically stops after 3 months, at which time about half of its mass is lost (Figure 2.12A). Even at 15°C, the MGO fuel is not expected to evaporate completely, with 35% mass residue persisting after 3 months (Figure 2.12B). Other slower processes are expected to continue the weathering of MGO such as



Figure 2.11. The experimentally determined evaporation extent (blue symbols) of the three fuels (SAB, MGO and IFO-180) at (A) polar (0°C) and (B) temperate (15°C) environmental conditions, and the predicted evaporation curves (red lines) derived from the evaporation model developed by Kotzakoulakis and George (in prep.) (Chapter 3).



Figure 2.12. Long term prediction for the evaporation of the MGO and IFO-180 fuels at (A) polar (0°C) and (B) temperate (15°C) environmental conditions. The prediction was performed by using the evaporation parameters presented in this work, in conjunction with the evaporation model developed by Kotzakoulakis and George (in prep.) (Chapter 3). The predicted evaporation curves (red lines) are in good agreement with the experimental data (blue symbols) for both temperatures.

oxidation, photolysis and biodegradation, but further investigation is required in order to determine the rates of these processes under polar conditions.

The IFO-180 fuel is the heaviest of the three fuels (Figure 2.4; Table 2.3), with more than 90% of its mass being distillation residue (Bunker C), with the rest being a blended distillate such as MGO fuel. It weathers very slowly, with evaporation being the fastest process. However, evaporation is only responsible for 4% mass loss during the first 10 days under polar conditions (0°C; Figure 2.11A). Evaporation then progresses at an even slower rate, until it has lost all the light distillate (8-10%) from its mass over the first three months (Figure 2.12A). At this time the viscosity of IFO-180 fuel has reached 188,063 mPa s (model predicted value), and evaporation practically stops. At 15°C, the IFO-180 lose its 8-10% distillate at a moderate rate over the first 10 days (Figure 2.11B). Evaporation then continues at a slower rate, with about 20% of its mass being lost after three months (Figure 2.12B). Therefore residual IFO-180 is expected to persist in the marine environment for many years.

Both these measured and predicted evaporation rates for the SAB, MGO and IFO-180 fuels are referring to an ice-free water surface, which is usually the case during the summer season resupply operations at Antarctic bases. In the case of a significant percentage of ice coverage, where portions of the fuel spill could be trapped under the ice, the evaporation rate is expected to be slower.

# 2.3.4 Dissolution under polar versus temperate marine conditions

The aromatic fraction of a fuel is the main contributor to the hydrocarbons that dissolve into a water column. This is because the aqueous solubility of aromatic hydrocarbons are roughly two orders of magnitude higher than the equivalent straight chain hydrocarbons, due to the polarity of their molecule induced by the aromatic ring (McAuliffe, 1966). The water molecule has a permanent dipole and interacts with the quadrupole moment of the aromatic ring, with non-covalent polar- $\pi$  interaction increasing the solubility of aromatic hydrocarbons (Anslyn and Dougherty, 2006). In the current work the solubility of individual aromatic hydrocarbons as well as aromatic groups was measured experimentally at different temperatures and salinity conditions in order to determine the effect of the polar conditions on the solubility of the fuels (Section 2.2.4). A synthetic standard mixture was also used for this purpose as it contains only nine analytical standards whose concentration and physical properties are well defined. The solubilities at 0°C and 20°C with zero and 34.5‰ salinity are presented in Table 2.8 for the synthetic standard mixture and the WAF of SAB fuel.

68

Temperature (°C)	0	0	20		
Salinity (‰)	0	34.5	34.5		
				Salinity	Temperature
				effect	drop effect
Standard Compound		S (mg/L)		(%)	(%)
Benzene	1660	1520	1440	-8.5	5.3
Toluene	599	489	445	-18.4	9.8
o-Xylene	223	175	154	-21.9	13.1
1,2,4-Trimethylbenzene	67	50	44	-25.7	13.9
tert-Butylbenzene	39	29	24	-24.6	22.3
Naphthalene	165	135	149	-18.4	-9.3
2-Methylnaphthalene	44	32	38	-26.5	-16.5
2-Ethylnaphthalene	13	9	11	-28.6	-15.4
SAB Compound		S (mg/L)		(%)	(%)
Benzene, C <sub>2</sub> -alkyl-	214	154	137	-27.8	12.5
Benzene, C <sub>3</sub> -alkyl-	70.5	51.2	45.3	-27.3	13.2
Benzene, C <sub>4</sub> -alkyl-	27.5	19.2	16.2	-30.5	18.1
Benzene, C₅-alkyl-	10.9	7.4	5.7	-32.0	30.6
Benzene, C <sub>6</sub> -alkyl-	5.4	3.4	2.0	-36.2	73.4
Naahthalana	102	96.0	07.7	16.2	12.0
Naphthalene mathul	20.0	00.0 20.4	97.7	-10.2	-12.0
Naphthalene, methyl-	35.8	28.4	33.0	-20.8	-13.9
Naphthalene, C <sub>2</sub> -alkyl-	15.2	11.4	12.4	-25.1	-7.6
Naphthalene, C <sub>3</sub> -alkyl-	13.4	5.1	3.0	-61.6	74.2
Indane	141	103	96.5	-27.1	6.4
Indane, methyl-	25.8	18.6	17.3	-28.0	7.4
Indane, C <sub>2</sub> -alkyl-	13.8	10.0	9.0	-27.0	11.7
Indane, C <sub>3</sub> -alkyl-	8.1	5.2	4.0	-35.9	30.0
Tatualia	46.0	24.0	24.4		1 4
	40.8	34.8	34.4 10.9	-25.0	1.4
i etralin, methyl-	15.9	11./	10.8	-26.4	ბ.ხ
Biphenyl	36.8	27.6	32.3	-24.8	-14.5

Table 2.8. The effect of temperature and salinity on the solubility (S; mg/L) of aromatic components detected in the water accommodated fraction of SAB, and in a standard synthetic mixture. The salinity effect is the percentage change in solubility between zero and 34.5‰ salinity. The temperature drop effect is the percentage change in solubility when dropping the temperature from 20°C to 0°C.

The percentage change in solubility between zero and 34.5‰ salinity is presented as the salinity effect. Similarly, the percentage change in solubility when dropping the temperature from 20°C to 0°C is presented as the temperature drop effect. The temperature change from a temperate to a polar marine environment can have different effects on the solubility of various aromatic components (Table 2.8). Specifically, all hydrocarbons with a single aromatic ring, such as the benzenes, indanes and tetralins have increased solubility under polar conditions, as opposed to hydrocarbons with two aromatic rings such as the naphthalenes and biphenyls for which their solubility drops under polar conditions (Economou et al., 1997; Tsonopoulos, 2001). This experimental observation can be explained by thermodynamics. It is generally accepted that the heat of solution incorporates two effects, the positive heat of cavitation and the negative heat of interaction between the hydrocarbon and the water (Tsonopoulos, 2001). At the temperature where the solubility of the hydrocarbon reaches a minimum  $(T_{min})$ , the two effects cancel each other, and at higher temperatures the heat of cavitation becomes the dominant effect. T<sub>min</sub> has been measured experimentally to be 291 K (17.9°C) for alkylbenzenes (Bohon and Claussen, 1951; Gill et al., 1976), whereas for alkylnaphthalenes T<sub>min</sub> has been estimated to be below the freezing point of water (Economou et al., 1997). As a result the solubility of alkylbenzenes increases as the temperature drops to  $0^{\circ}$ C, because this temperature is <T<sub>min</sub>. In contrast, the solubility of alkylnaphthalenes continues to decrease as the temperature drops to 0°C, since this temperature is still >T<sub>min</sub> (Figure 2.13).



Figure 2.13. The fitted curves to experimental data for (A) alkylbenzenes (Tsonopoulos, 2001) reveal a solubility minimum at 291 K, whereas (B) the curves of alkylnaphthalenes indicate a minimum below the freezing point of water (Economou et al., 1997).

Another observation is the increased solubility effect caused by the temperature change as the degree of alkylation increases. As shown in Table 2.8, the more alkylated benzenes exhibit a greater percentage solubility increase at polar compared to temperate conditions than less alkylated benzenes. In addition, more alkylated naphthalenes exhibit a larger percentage solubility decrease at polar compared to temperate conditions than less alkylated naphthalenes exhibit a larger percentage solubility decrease at polar compared to temperate conditions than less alkylated naphthalenes (except for C<sub>3</sub> alkylnaphthalenes, which appear to be anomalous data).

The effect of increased salinity reduces the solubility of all the hydrocarbons detected in the WAF. This "salting-out" effect was initially investigated by Sechenov (1889) who concluded that the relationship between the solubility and the salt concentration is given by Equation 2.17:

$$\log\left(\frac{S_0}{S}\right) = K_S C \tag{2.17}$$

where  $S_0$  is the solubility in pure water, S is the solubility in water with salt concentration C (mol/L), and  $K_s$  is the Sechenov coefficient for the specific salt-nonelectrolyte pair.

Later Gordon and Thorne (1967) demonstrated that the effect of multiple salts on the solubility is additive, meaning that the total  $K_S$  for sea salt can be calculated from the coefficients  $K_S$  of the component salts using the Equation:

$$\log S = \log S_0 - C_S \sum_{i=1}^n N_i K_{Si}$$
 (2.18)

where S and S<sub>0</sub> are as in Equation 2.17,  $C_S$  is the sum of the individual salt molarities,  $N_i$  is the mole fraction of the ith salt component in the sea salt, and  $K_{Si}$  is the Sechenov coefficient of the ith salt component.

A similar trend as for temperature can be observed regarding the effect of degree of alkylation on salinity. More alkylated benzenes exhibit a greater percentage solubility drop due to increased salinity than less alkylated benzenes (Table 2.8). This trend is the same for all types of hydrocarbons detected in the WAF, and the standard aromatic hydrocarbons, irrespective of the number of aromatic rings contained in the molecule. Additionally, Eganhouse and Calder (1976) concluded that Sechenov coefficients are not affected by co-solutes, meaning that for a given nonelectrolyte-salt pair, the salting-out percentage will be the same regardless of the presence or not of other nonelectrolytes. The dissolution rates of the three fuels were measured experimentally by determining the rate of dissolution of individual components, as is demonstrated in Figure 2.1, and then a common dissolution rate constant  $Cd_{exp}$  was deduced for all the components of the fuel according to the procedure described in Section 2.2.5. The equivalent correlated constants ( $Cd_{cor}$ ) were then calculated by Equation 2.13 for comparison purposes. Table 2.9 shows the comparison between the experimentally determined constants ( $Cd_{exp}$ ) and  $Cd_{cor}$  from the empirical correlation 13 for the three fuels SAB, MGO and IFO-180. Due to the measuring uncertainty of the rotational speed difference between the two phases ( $\Delta$ RPM), the  $\Delta U_{linear}$  and  $Cd_{cor}$  values are given as a range rather than a fixed value. Nevertheless, the results indicate an agreement between the experimental and the correlated dissolution constants for all three fuels. Furthermore, the low RSD% values show that  $Cd_{exp}$  is indeed independent of the compound used to measure it, and is common for all compounds of the fuel for the specific experimental conditions.

$Cd_{exp}$	RSD%	ΔRPM	$\Delta U_{\text{linear}}$	Cd <sub>cor</sub>
5.79	7.3	20-40	0.12-0.24	4.76-8.30
6.65	5.9	20-40	0.12-0.24	4.76-8.30
8.03	6.9	30-50	0.18-0.31	6.59-9.92
	Cd <sub>exp</sub> 5.79 6.65 8.03	Cd <sub>exp</sub> RSD%   5.79 7.3   6.65 5.9   8.03 6.9	Cd <sub>exp</sub> RSD%   ΔRPM     5.79   7.3   20-40     6.65   5.9   20-40     8.03   6.9   30-50	Cd <sub>exp</sub> RSD%   ΔRPM   ΔU <sub>linear</sub> 5.79   7.3   20-40   0.12-0.24     6.65   5.9   20-40   0.12-0.24     8.03   6.9   30-50   0.18-0.31

Table 2.9. Comparison of experimental dissolution constants ( $Cd_{exp}$ ) with the correlated constants ( $Cd_{cor}$ ) from Equation 2.13. RSD% is the relative standard deviation of  $Cd_{exp}$  for the values obtained from the four hydrocarbons shown in Figure 2.1,  $\Delta$ RPM is the difference in rotational speed between the water phase and the fuel phase, and  $\Delta U_{linear}$  is the average linear velocity difference between the water and fuel phase.

Another quantity that is derived from the dissolution rate calculations is the dissolution constant Q<sub>di</sub>. This constant is specific to each pseudo-component and seawater temperature, and is independent of the water current velocity, spill dimensions and degree of weathering. It simplifies the calculation of the dissolution rates at any point of the weathering process, because only a knowledge of the water current velocity, spill length and pseudo-component molar fraction of the spill is required in order to calculate the molar dissolution rate according to Equation 2.15.

The solubility (S) and Q<sub>di</sub> were calculated for the three fuels analysed in this study, and all the compounds and compound groups detected in the WAFs produced from these fuels (Table 2.10; Appendix 2A Table 2A.2). The dissolution parameters differ for the same hydrocarbon group (e.g. benzenes) among the three fuels. This can be explained by the different ratios of lighter to heavier hydrocarbons found in the specific groups among the fuels. For example, MGO fuel contains a higher amount of low molecular weight benzenes in its benzene group, compared to the SAB and IFO-180 fuels, and as a consequence exhibits the highest solubility of the three fuels for this group. Solubility differences of individual hydrocarbons among the fuels can be explained by the presence of co-solutes, which can have both positive and negative effects on the solubility of the hydrocarbon in question. As shown by Eganhouse and Calder (1976), who experimented with ternary and quaternary systems of aromatic hydrocarbons and water, the presence of naphthalene can increase the solubility of biphenyl, while in the case of biphenyl and phenanthrene the co-solution effect causes a mutual solubility reduction. The interaction of co-solutes in a complex mixture such as a fuel involving hundreds of compounds, so is much more complex and difficult to predict. Experimental results indicate that the solubilities of hydrocarbons in such a fuel mixture are dependent on the composition of the fluid. Finally, some compounds that would normally be solids in pure form under these experimental or environmental conditions, such as naphthalene, can be dissolved in a liquid mixture of other hydrocarbons, and these behave as supercooled liquids. This liquid state causes them to exhibit enhanced solubility compared to the pure solid phase (Vadas et al., 1991).

Dissolution parameters at 0°	С					
Sample:	IFO-180		MGO		SAB	
Compound Group	S (mg/L)	Q <sub>d</sub> (m s <sup>-1/2</sup> )	S (mg/L)	Q <sub>d</sub> (m s <sup>-1/2</sup> )	S (mg/L)	Q <sub>d</sub> (m s <sup>-1/2</sup> )
Benzenes	48	2.54E-06	67	5.35E-06	50	4.27E-06
Naphthalenes	8	3.25E-07	34	2.27E-06	47	3.74E-06
Indanes	13	6.10E-07	18	1.18E-06	16	1.24E-06
Tetralins	5	1.91E-07	5	2.63E-07	21	1.63E-06
Biphenyls	4	1.55E-07	5	2.55E-07	28	1.87E-06
Phenols	1,870	9.35E-05	2,110	1.52E-04	2,410	1.95E-04
Benzothiophenes	8	2.95E-07				
Aromatic fraction	19	3.35E-07	43	2.06E-06	48	3.69E-06
Fuel	6	1.00E-07	8	3.73E-07	13	8.29E-07

Table 2.10. The measured solubility (S) and dissolution constant Q<sub>di</sub> for the three fuels and the main hydrocarbon groups detected in their WAFs under polar conditions (0°C). A detailed breakdown of the solubilities and dissolution quantities for all the isomers in each hydrocarbon group is given in Appendix 2A Table 2A.2.

#### 2.3.5 Partitioning of hydrocarbons between the gas and water phases after an oil spill

The partitioning of certain hydrocarbons between the gas and water phases is now presented for two hypothetical fuel spills, one under polar conditions and one under temperate conditions. The hypothetical conditions for the two spills were a wind velocity of 7 m/s (25 km/h), a water current velocity of 0.27 m/s (1 km/h), a spill down-current length of 100 m, seawater salinity of 34.5‰, and seawater temperatures of 0°C and 20°C. Although the selection of the conditions for the spill at 0°C is intended to be close to a realistic scenario of a limited fuel leak during the refuelling of the Casey research station under favourable environmental conditions, it is nevertheless arbitrary and it is intended to serve as an example of the use of the experimental dissolution data together with the presented equations for the calculation of the weathering rates. Exactly the same equations and procedure can be used for a spill under different condition. Furthermore, the comparison of the two identical spills at 0°C and 20°C and their weathering rate ratios are valid even for spills of different dimensions, wind velocity and water current velocity, as long they are common for both spills and the comparison scenario is between 0°C and 20°C.

The three fuels types were used for this experiment, and in addition the synthetic standard mixture was also used, due to its well-known properties and precise composition made of analytical standards. The solubilities and molar dissolution rates of the three fuels and the standard mixture were determined experimentally at 0°C and 20°C with the lab apparatus as described in the Section 2.2.4 and 2.2.5. The dissolution constant Q<sub>di</sub>, which is independent of water velocity and spill length, was then calculated from Equation 2.14. The dissolution rate coefficient (K<sub>d</sub>) and the dissolution rate (R<sub>d</sub>) could then be calculated for the water velocity and the spill length of the two hypothetical spills using Equations 2.9 and 2.15, respectively. The evaporation parameters partial pressure (p<sub>i</sub>), evaporation rate coefficient (K<sub>ev</sub>) and molar evaporation rate (R<sub>ev</sub>) were calculated for the two hypothetical spills as described in Section 2.2.3 using Equations 2.1, 2.2 and 2.4. Table 2.11 lists all the evaporation and dissolution parameters for the two hypothetical spills based on data from the synthetic standard, as well as the percentage change of the

evaporation and dissolution rates caused by the temperature difference between the two spills. Table

2.12 shows the same information based on the three fuels.

Sample:	Synthetic Standard									
	Evapo	ration param	eters at 0°C	Evapo	ration parame	eters at 20°C	Rate change %			
Compound	p <sub>i</sub> (Pa)	K <sub>ev</sub> (m/s)	R <sub>ev</sub> (mol/s m <sup>2</sup> )	p <sub>i</sub> (Pa)	K <sub>ev</sub> (m/s)	R <sub>ev</sub> (mol/s m²)	20°C → 0°C			
Benzene	1.08E+01	9.15E-03	4.35E-05	3.06E+01	9.21E-03	1.16E-04	-62.4			
Toluene	8.61E+00	8.45E-03	3.20E-05	2.77E+01	8.51E-03	9.66E-05	-66.8			
o-Xylene	3.31E+00	7.88E-03	1.15E-05	1.26E+01	7.93E-03	4.10E-05	-72.0			
1,2,4-Trimethylbenzene	2.50E-01	7.45E-03	8.20E-07	1.07E+00	7.50E-03	3.30E-06	-75.1			
tert-Butylbenzene	9.69E-02	7.15E-03	3.05E-07	5.18E-01	7.20E-03	1.53E-06	-80.1			
Naphthalene	2.82E-02	8.38E-03	1.04E-07	1.44E-01	8.41E-03	4.98E-07	-79.1			
2-Methylnaphthalene	1.05E-02	7.92E-03	3.65E-08	6.46E-02	7.95E-03	2.11E-07	-82.7			
2-Ethylnaphthalene	7.76E-03	7.54E-03	2.57E-08	5.16E-02	7.57E-03	1.60E-07	-84.0			
N-dodecane	1.63E+00	6.82E-03	4.89E-06	1.08E+01	6.84E-03	3.04E-05	-83.9			
	Pv (Pa)			Pv (Pa)						
Synthetic Standard	24.73	6.90E-03	9.32E-05	83.58	6.93E-03	2.89E-04	-67.8			
	Disso	lution parame	eters at 0°C	Dissol	ution parame	ters at 20°C	Rate change %			
Compound	S (mg/L)	K <sub>d</sub> (m/s)	R <sub>d</sub> (mol/s m <sup>2</sup> )	S (mg/L)	K <sub>d</sub> (m/s)	R <sub>d</sub> (mol/s m <sup>2</sup> )	20°C → 0°C			
Benzene	1,520	1.88E-06	1.11E-07	1,440	3.93E-06	2.21E-07	-49.6			
Toluene	489	1.73E-06	8.73E-08	445	3.63E-06	1.66E-07	-47.5			
o-Xylene	175	1.62E-06	5.12E-08	154	3.39E-06	9.46E-08	-45.9			
1,2,4-Trimethylbenzene	50	1.53E-06	3.37E-09	44	3.21E-06	6.19E-09	-45.5			
tert-Butylbenzene	29	1.46E-06	3.12E-09	24	3.06E-06	5.34E-09	-41.5			
Naphthalene	135	1.59E-06	9.56E-09	149	3.32E-06	2.20E-08	-56.6			
2-Methylnaphthalene	32	1.50E-06	3.25E-09	38	3.14E-06	8.14E-09	-60.1			
2-Ethylnaphthalene	9	1.43E-06	1.64E-09	11	2.99E-06	4.05E-09	-59.6			
N-dodecane	0	1.22E-06	2.44E-11	0	2.55E-06	5.10E-11	-52.2			
Synthetic Standard	26	1.74E-06	2.70E-07	24	3.64E-06	5.26E-07	-48.7			

Table 2.11. The effect of temperature on the evaporation and dissolution rate of aromatic hydrocarbons, based on the synthetic standard. The evaporation parameters are partial pressure ( $p_i$ ), evaporation rate coefficient ( $K_{ev}$ ) and molar evaporation rate ( $R_{ev}$ ). The dissolution parameters are solubility (S), the dissolution rate coefficient ( $K_d$ ), and the dissolution rate ( $R_d$ ). Both the evaporation and dissolution rates decrease when the temperature drops from 20°C to 0°C, with the evaporation rate exhibiting a larger drop than the dissolution rate.

	Evap	oration param	neters at 0°C	Evapo	oration parame	eters at 20°C	Rate change %
Fuel	p <sub>i</sub> (Pa)	K <sub>ev</sub> (m/s)	R <sub>ev</sub> (mol/s m <sup>2</sup> )	p <sub>i</sub> (Pa)	K <sub>ev</sub> (m/s)	R <sub>ev</sub> (mol/s m <sup>2</sup> )	20°C → 0°C
SAB	19.7	6.39E-03	5.91E-05	87.6	6.43E-03	2.44E-04	-75.8
MGO	22.3	5.85E-03	7.09E-05	84.3	5.90E-03	2.49E-04	-71.5
IFO-180	6.3	4.78E-03	2.05E-05	23.7	4.83E-03	7.12E-05	-71.3
	Disso	olution param	eters at 0°C	Disso	Rate change %		
Fuel	S (mg/L)	K <sub>d</sub> (m/s)	R <sub>d</sub> (mol/s m <sup>2</sup> )	S (mg/L)	K <sub>d</sub> (m/s)	R <sub>d</sub> (mol/s m <sup>2</sup> )	20°C → 0°C
SAB	12.6	1.47E-06	1.16E-07	12.1	3.08E-06	2.32E-07	-50.2
MGO	8.2	1.30E-06	5.21E-08	7.6	2.71E-06	1.02E-07	-48.7
IFO-180	5.7	9.08E-07	1.40E-08	5.8	1.90E-06	2.99E-08	-53.1

Table 2.12. The effect of temperature on the evaporation and dissolution rates of the three fuels. The evaporation parameters are partial pressure ( $p_i$ ), evaporation rate coefficient ( $K_{ev}$ ) and molar evaporation rate ( $R_{ev}$ ). The dissolution parameters are solubility (S), the dissolution rate coefficient ( $K_d$ ), and the dissolution rate ( $R_d$ ). The temperature drop affects the evaporation rate to a greater degree than the dissolution rate for all three fuels.

Based on the synthetic standard the evaporation and dissolution processes slow down when temperature drops from 20°C to 0°C, but the evaporation rate drop is greater than the dissolution rate drop for the whole fluid (-67.8% and -48.7% respectively; Table 2.11). Equation 2.2 for the calculation of the evaporation rate reveals that the parameters affected from the temperature drop are vapour pressure, air viscosity and vapour diffusion coefficient. Both vapour pressure and diffusion coefficient decrease and they affect the evaporation rate negatively while the decrease of air viscosity affects the evaporation rate positively. Similarly, from the calculation of the dissolution rate (Equations 2.9-2.11), the parameters that are affected from the temperature drop are solubility, water viscosity and component diffusion coefficient in water. Both water viscosity and diffusion coefficient affect the dissolution rate negatively while for di-aromatic hydrocarbons, the solubility increases and the effect is negative.

Another observation is that as the carbon number of the component increases the amount of reduction in the evaporation rate increases significantly, in contrast to the reduction in the dissolution rate, which remains almost constant for all the components. Again this is the result of the vapour pressure decreasing faster than the solubility at higher carbon numbers when the temperature decreases.

The results in Table 2.12 reveal a similar pattern for the whole fuels. When the temperature drops from 20°C to 0°C, the evaporation rate drops by -75.8%, -71.5% and -71.3% for the SAB, MGO and IFO-180 fuels, respectively. Despite that the decrease of air viscosity has a positive effect on the evaporation rate, the vapour pressure and diffusion coefficient decrease cause the overall evaporation rate to drop.

Similarly, the dissolutions rate of the whole fuels drop by -50.2%, -48.7% and -53.1% for SAB, MGO and IFO-180, respectively, despite the increase of the solubility of SAB and MGO and the practically constant solubility of IFO-180. The overall dissolution rate drop is due to the higher seawater viscosity and slower diffusion coefficient at 0°C, as discussed earlier.

These observations explain the results presented in Table 2.13 which summarise the ratios of dissolved moles to evaporated moles at 0°C and 20°C, and the % ratio change. Although the weathering process progresses slower in polar conditions, the percentage of moles ending up in the water phase is greater at 0°C than at 20°C for all hydrocarbons, as well as for the whole fuels. The absolute amount of fuel dissolution into the water at 0°C is only a small fraction of the total fuel evaporated, equal to 1.96% for SAB, 0.734% for MGO and 0.685% for IFO-180. However, this is significantly larger than the equivalent amounts at 20°C, by 105.8% for SAB, 79.9% for MGO and 63.2% for IFO-180. The lighter SAB fuel was found to exhibit the greatest increase in dissolved to evaporated ratio (105.8%), with the ratio reaching 1.96% when the temperature is reduced from 20°C to 0°C, making it the most bioavailable and potentially toxic fuel of the three. SAB is the most widely used fuel in the AAT, and is transported by sea and transferred with hoses from ship to shore in large volumes, so statistically has the highest probability of

being the fuel involved in a fuel spill. In contrast to the negative environmental effects that dissolution has on the water column, it has a positive counter-effect on the water surface and the coastline. Although the percentage of mass removed from the surface by dissolution is in the order of 1-2‰, it still reduces the amount of contamination on the surface and on the beaches that emergency personnel would have to respond to. Furthermore, since dissolution preferentially removes the more toxic aromatic fraction of the fuel, it also reduces the toxicity of the remaining residue on the surface that wildlife would have been exposed to.

Finally, it is noted that these partition results refer to ice-free water surfaces, and in the case of a significant percentage of ice coverage, parts of the fuel spill may be trapped under the ice. In this case the evaporation rate is expected to practically stop under the ice, which would create prolonged contact of the spill with the water surface, driving higher amounts of hydrocarbons into the water column by dissolution, and hence making them bioavailable. These results indicate that the impact of a fuel spill under Antarctic conditions would likely be greater compared to the impact of an identical spill under more temperate conditions.

			Ratio change
Temperature (°C)	0	20	%
Compound	Dis/Evap	Dis/Evap	20°C → 0°C
Benzene	2.56E-03	1.91E-03	34.0
Toluene	2.73E-03	1.72E-03	58.4
o-Xylene	4.46E-03	2.31E-03	93.2
1,2,4-			
Trimethylbenzene	4.11E-03	1.88E-03	119
tert-Butylbenzene	1.02E-02	3.49E-03	193
Naphthalene	9.20E-02	4.42E-02	108
2-Methylnaphthalene	8.91E-02	3.86E-02	131
2-Ethylnaphthalene	6.36E-02	2.52E-02	152
			Ratio change
Temperature (°C)	0	20	%
Fluid	Dis/Evap	Dis/Evap	20°C → 0°C
Synthetic Standard	2.90E-03	1.82E-03	59.4
SAB	1.96E-03	9.51E-04	106
MGO	7.34E-04	4.08E-04	79.9
IFO-180	6.85E-04	4.20E-04	63.2

Table 2.13. Distribution ratios (dissolution/evaporation) between the gas phase (atmosphere) and the aqueous phase (seawater) for individual hydrocarbons, the synthetic standard mixture, and the SAB, MGO and IFO-180 fuels. The "Ratio change %" column indicates the percentage increase of moles ending up in the aqueous phase due to the temperature drop. Under polar conditions the mole percent in seawater increases for all individual hydrocarbons examined, as well as for the whole fuels.

# 2.3.6 Natural dispersion of a fuel spill into the water column

Dispersion is another process that contributes to the weathering of spilled fuel in the marine environment. Natural dispersion takes place when the wave energy is large enough to break the oil spill into droplets of such size that they can be suspended in the water column and driven away from the main body of the spill. Although the creation of microdroplets have been observed in low energy oil spill-water mixing systems, such as the WAF preparation technique with the slow stirring method (Redman et al., 2012) and the wave tank test under non-breaking wave mixing regime (Li et al., 2010), the concentration of these microdroplets are at trace levels, in the order of few µg/L. For natural dispersion to be effective and have droplet concentrations in the order of a few percent, high energy mixing is required such as when there are winds strong enough to create breaking waves (Li et al., 2010). The percentage of oil that can be naturally dispersed can vary greatly, and depends on the oil spill chemical composition, the physical properties of the oil, and the environmental conditions (Fingas, 2010; Lunel, 1995). Kotzakoulakis et al. (in prep.) (Chapter 5) have investigated the dispersion of fuel spills under polar conditions with and without the use of chemical dispersants, and they have summarised the parameters that control the effectiveness of dispersion. In a polar marine environment the low temperatures cause the oil into droplets more difficult and the dispersion less effective. Additionally, the possible presence of ice fragments have a damping effect on the waves, reducing even further the effectiveness of dispersion.

For the SAB, MGO and IFO-180 fuels that are used in the AAT, Kotzakoulakis et al. (in prep.) (Chapter 5) measured their dispersibility under Antarctic marine conditions (seawater at 0°C, 34.5‰ salinity and breaking waves energy) to be equal to 2% mass loss for IFO-180, and 4% mass loss for MGO. The dispersibility of SAB fuel could not be measured reliably because it is a very narrow distillation cut that evaporates rapidly, even under Antarctic conditions (Figure 2.11). It should be noted that these dispersibilities were measured according to the Baffled Flask Test (BFT) Protocol at 200 rpm orbital agitation (Sorial et al., 2004) that corresponds to breaking wave mixing energy. The BFT test is a small scale lab technique, so the results can only be taken as a qualitative indication of the magnitude of dispersion. Nevertheless, as shown by Kaku et al. (2006) the rheological characteristics of the BFT test can recreate the three dimensional turbulent flow of the breaking waves and produce a droplet size range

82

similar to that observed in actual field trials at sea. In conclusion, the measured dispersibilities indicate that only a minor fraction of these fuels can be expected to disperse under Antarctic conditions, so natural dispersion cannot be regarded as a major mechanism of weathering for these fuels.

#### 2.3.7 Fate of dissolved hydrocarbons in seawater

There are several processes that take place in the seawater leading to the depletion of the dissolved hydrocarbons. A fraction of the dissolved hydrocarbons will evaporate from the water surface according to their Henry's Law constant or water to air partitioning coefficient (Schwarzenbach et al., 2003). Depending on the intensity of the incident light and presence of oxygen in the water column, direct and indirect photo-oxidation may occur (National Research Council, 2003). Because few petroleum hydrocarbons absorb light efficiently, most photo-oxidation reactions occur indirectly. Dissolved polycyclic aromatic hydrocarbons degrade to relatively stable quinones (Sigman et al., 1998). Light absorbing natural organic matter, such as humic and fulvic acids, can play a role in catalysing the indirect photolysis of PAH. Microbial oxidation or biodegradation occurs on the oil-water interface and on the dissolved hydrocarbons. There are two main pathways to aerobic degradation. The first is utilising the detoxification enzymatic mechanism to oxidise the PAH to smaller more water soluble molecules that can be excreted by cells. The second pathway is aerobic respiration where energy in the form of adenosine triphosphate (ATP) is generated from the breakdown of hydrocarbons (National Research Council, 2003). Finally, anaerobic degradation has been measured in areas of low oxygen by sulphate- and iron- reducing bacteria (Coates et al., 1996). The environmental conditions such as oxygen concentration, temperature and salinity as well as the physical properties of the oil can greatly influence the rate of biodegradation. In polar marine environments, low temperature causes oil viscosity to increase and dissolution rate to decrease, limiting available hydrocarbons to microbes. Additionally, the evaporation rate decrease of light and toxic hydrocarbons can be detrimental to microbes. Finally, the low temperature affects the cellular

83

enzymatic activity with the rate of enzymatic activity becomes approximately half for every 10°C of temperature drop (National Research Council, 2003). The combined effect is reduced rate of biodegradation in cold marine environments that can be important factor in the risk assessment of fuel spills in the Antarctic marine environment.

A depletion-over-time test was performed in order to measure the rate of depletion, and possibly to identify the main process responsible for the majority of the loss under polar conditions. The test was performed according to the procedure outlined in Section 2.2.6. The depletion test results are presented for each compound group detected in the WAF produced from contact with SAB fuel under polar conditions (Table 2.14; Figure 2.14).

Time (days)	0	0.25	1	2	3	7	7 sealed
Compound group	Concent	ration (µg/	L)				
Benzenes	1,270	869	448	139	47	0	1,210
Naphthalenes	1,430	942	498	166	66	0	1,300
Phenols	236	245	273	264	257	188	227
Indanes	135	97	45	13	4	0	140
Tetralins	60	41	21	9	4	1	58
Biphenyls	35	24	12	2	2	0	32
Total	3,170	2,220	1,300	593	379	189	2,970
	Ratio to	initial cond	entration				
Benzenes	1.00	0.68	0.35	0.11	0.04	0.00	0.95
Naphthalenes	1.00	0.66	0.35	0.12	0.05	0.00	0.91
Phenols	1.00	1.04	1.16	1.12	1.09	0.80	0.96
Indanes	1.00	0.72	0.33	0.10	0.03	0.00	1.04
Tetralins	1.00	0.68	0.35	0.14	0.06	0.01	0.97
Biphenyls	1.00	0.69	0.35	0.05	0.05	0.00	0.93
Total	1.00	0.70	0.41	0.19	0.12	0.06	0.94

Table 2.14. Results and ratios to the initial composition from the experimental depletion of dissolved compounds from a SAB WAF over time



Figure 2.14. Comparison of the relative depletion trends of the compound groups detected in the SAB WAF.

The results demonstrate that all types of compounds in the SAB WAF deplete rapidly from the water phase, the only exception being the phenols (Table 2.14). The ratios to the initial concentration show that the relative depletion rates are almost identical for all the compound types other than phenols (Figure 2.14). In order to evaluate the contribution of different processes to the overall depletion we can perform certain calculations based on theory and previous empirical results. The expected evaporation rate can be determined by applying Deacon's boundary layer model (1977). The exchange velocity for a component i on the water side of the interface (u<sub>iw</sub>) is given by the expression:

$$u_{iw} = constant (Sc_{iw})^{-2/3}$$
 for  $Sc_{iw} > 100$  (2.19)

where Sc<sub>iw</sub> is the Schmidt number, equal to v<sub>i</sub>/D<sub>i</sub> (kinematic viscosity/diffusion coefficient).

By utilising known  $CO_2$  velocities as a reference, the unknown "constant" can be removed by creating a ratio of the two expressions in Equation 2.19:

$$u_{iw} = \left(\frac{Sc_{iw}}{Sc_{CO2}}\right)^{-2/3} u_{CO2}$$
(2.20)

For the test conditions at 0°C and no wind, the values are  $u_{CO2} = 0.65 \times 10^{-3}$ ,  $Sc_{CO2} = 1,910$ , and  $Sc_{iw}$  for 1,2,4-trimethylbenzene and 1-methylnaphthalene are 5,529 and 5,552 respectively. The resulting  $u_{iw}$  values for 1,2,4 trimethylbenzene and 1-methylnaphthalene are 3.20 x  $10^{-4}$  and 3.19 x  $10^{-4}$  cm/s, respectively.

Similarly, the exchange velocity for a component i on the air side of the interface (u<sub>ia</sub>) can be calculated by using water vapour as a reference, and the empirical correlation developed by Mackay and Yeun (1983):

$$u_{H20 a} = 0.2 u_{10} + 0.3 \tag{2.21}$$

and

$$u_{ia} = \left(\frac{D_{ia}}{D_{H20 a}}\right)^{2/3} u_{H20 a} \tag{2.22}$$

where  $u_{H2Oa}$  is the exchange velocity of the water vapour on the air side of the interface in cm/s,  $u_{10}$  is the wind velocity at 10 m height from the water surface in m/s,  $D_{ia}$  is the diffusion coefficient of component i in air (cm<sup>2</sup>/s), and  $D_{H2Oa}$  is the diffusion coefficient of the water vapour in air (cm<sup>2</sup>/s).

For the given test conditions the values are  $u_{H20} = 0.3$  cm/s,  $D_{ia} = 0.0717$  cm<sup>2</sup>/s for 1,2,4-trimethylbenzene and  $D_{ia} = 0.0783$  cm<sup>2</sup>/s for 1-methylnaphthalene, and  $D_{H2O a} = 0.222$  cm<sup>2</sup>/s. The resulting  $u_{ia}$  for 1,2,4trimethylbenzene and 1-methylnaphthalene are 0.141 and 0.150 cm/s, respectively. To find the overall transfer velocity u<sub>i aw</sub> of a component i through the interface we use Equation 2.23 as the inverse of the transfer velocities that can be interpreted as the layer resistance (Schwarzenbach et al., 2003):

$$\frac{1}{u_{i\,aw}} = \frac{1}{K_{i\,aw}\,u_{ia}} + \frac{1}{u_{iw}} \tag{2.23}$$

where  $K_{iaw}$  is the partition constant between the air and water phase; and the other parameters remain the same as Equations 2.20 and 2.22.

From the mass conservation principle we can deduce Equation 2.24, which connects the overall transfer velocity to the geometric characteristics of the water container:

$$V dC_i(t) = u_{i aw} A C_i(t) dt \qquad (2.24)$$

where V is the volume of the container in  $cm^3$ ,  $C_i(t)$  is the concentration of component i as a function of time,  $u_{i aw}$  is the overall transfer velocity in cm/s and A is the area of the surface of the water. By solving the differential Equation we find the exponential Equation that describes the concentration of the component i over time:

$$C_i(t) = C_0 e^{-\frac{uA}{V}t}$$
 (2.25.*a*) or  $C_i(t) = C_0 e^{-\frac{u}{h}t}$  (2.25.*b*)

where  $C_0$  is the initial concentration at time zero, h is the depth of the container, and the rest parameters as in Equation 2.24. When the container has a constant cross sectional area on the vertical axis, such as a cylindrical container, then Equation 2.25.a simplifies to Equation 2.25.b. This theoretical concentration decrease caused by the evaporation process is plotted in Figure 2.15 for 1,2,4-trimethylbenzene and 1methylnaphthalene against the corresponding depletion data for the same compounds.



Figure 2.15. Comparison of the experimental depletion over time data against the theoretical concentration decrease caused by evaporation for 1,2,4-trimethylbenzene and 1-methylnaphthalene.

The theoretical evaporation rate of 1,2,4-trimethylbenzene is only slightly slower than the observed depletion rate of benzenes, with only a 7% difference between the experimental exponent (-1.30x10<sup>-5</sup> s<sup>-1</sup>) and the theoretical exponent (-1.21x10<sup>-5</sup> s<sup>-1</sup>) from Equation 2.25. In contrast, the exponent of the theoretical evaporation rate of 1-methylnaphthalene (-6.11x10<sup>-6</sup> s<sup>-1</sup>) is roughly half that of the observed depletion rate of naphthalenes (-1.25x10<sup>-5</sup> s<sup>-1</sup>). This observation indicates that the main depletion process for the more volatile benzenes is likely to be the evaporation, while for other less volatile groups such as naphthalenes there is a significant input from other processes that are resulting in a faster depletion than from the expected evaporation rate.

The last column 7 *sealed* in Table 2.14 presents the concentration of the main compound groups detected in the SAB WAF after it was sealed from air for 7 days with a minimum gap cap. The *ratio to initial*  *concentration* for the same column is in the range of 1.04 to 0.91 which indicates a 0-9% loss, with an average ratio of 0.94 or 6% loss for the sum of compounds. This result reveals that sealing not only prevents the evaporation process, but also that the depletion contribution from other processes such as oxidation, photolysis and biodegradation is absent when there is no oxygen available, or at least strongly reduced. This is an indication that absence of oxygen stops the depletion and that oxidation may be the next most prominent process after evaporation. Further investigation is required in order to fully identify the contributors to the compound depletion processes.

The persistence of phenols at almost the same concentration level for the duration of the depletion experiment (Figure 2.14) can be explained by the non-covalent dipole-dipole interaction between the phenol polar molecules and the water polar molecules that restricts the evaporation process (Anslyn and Dougherty, 2006). This is an additional indication that evaporation is the main process of depletion.

## 2.4 Conclusions

All three SAB, MGO and IFO-180 fuels that are used in the Australian Antarctic Territory were characterised for their composition and physical properties at polar and temperate conditions. The vapour pressure, evaporation rate coefficient and evaporation constant were determined for each pseudo component of the three oils. With these information, the evaporation rate of the three fuels was calculated for any given wind velocity and spill dimensions at polar or temperate conditions.

By examining the weathering rates from the different processes it is apparent that evaporation is responsible for the majority of mass loss for all three fuels during the initial stages of weathering at both polar and temperate conditions. The rate of evaporation is greatly affected by the low polar temperatures. Specifically for the SAB, MGO and IFO-180 fuels the initial evaporation rates are 4.1, 3.5 and 3.5 times slower at 0°C than at 20°C, respectively. For SAB fuel evaporation remains the main weathering process until it is completely evaporated, even at polar conditions, since it is a narrow distillate with a large majority of its components <C15. MGO fuel is also a pure distillate but it has a much wider distribution of components, with some components >C25. Under polar conditions at 0°C evaporation progresses fast until  $\sim$ 30% of its mass is lost in the first 10 days, but then slows down until it practically stops after 3 months with 50% mass loss. Other slower processes are expected to continue the weathering of MGO such as oxidation, photolysis and biodegradation, but further investigation is required in order to determine the rates of these processes under polar conditions. The IFO-180 is the heaviest of the three fuels with more than 90% of its mass being distillation residue (Bunker C), with the rest (8-10%) being a distillate such as MGO. IFO-180 weathers very slowly, with evaporation being the fastest process but responsible for only 4% of mass loss during the first 10 days at polar conditions. Evaporation then continues at a slower rate, with about 8-10% of its mass being lost after three months. At this time the viscosity of IFO-180 has reached 188,063 mPa s and evaporation practically stops. Further investigation is needed, especially for IFO-180, in order to determine the rate of weathering caused by other processes such as oxidation,

biodegradation and photolysis, as the processes examined in this study indicate that a spill of IFO-180 can persist in the Antarctic marine environment for many years.

The evaporation coefficients that were determined have been incorporated into an oil-spill evaporation model developed by Kotzakoulakis and George (in prep.) (Chapter 3) that takes into account the diffusion forces inside the body of the oil phase, and the concentration gradient that develops between the surface and the inner part of the spill. This concentration gradient is higher in more viscous fuels such as the IFO-180, and results in slower evaporation compared to a homogeneous fuel phase. The predictions of the oil-spill evaporation model are in close agreement with experimental evaporation data from fuels and crude oil at both polar and temperate conditions.

The aromatic fraction of a fuel is the main contributor of hydrocarbons dissolved in the water phase, as expected, due to the polarity of these molecules induced by the aromatic ring. The detailed composition of the aromatic fraction of the three fuels and the water accommodated fraction derived from the three fuel was determined, and the solubility of each hydrocarbon type in the aromatic fraction was measured experimentally. Salinity lowers the solubility of hydrocarbons both at polar and temperate conditions, which is known as the "salting-out" effect. This effect becomes stronger for every type of hydrocarbon as the degree of alkylation increases. The near zero temperatures of the polar marine environment exhibit variable effects on the solubility of hydrocarbons. Solubilities of monoaromatic hydrocarbons at 0°C are higher than those at 20°C, while solubilities of diaromatic hydrocarbons are lower at 0°C than at 20°C. Additionally, the dissolution rate constants and the dissolution rates for all hydrocarbon groups detected in the water accommodated fraction were experimentally determined for all three fuel types. The information provided herein facilitates the determination of the dissolution rates of the three fuels for any wind velocity and spill size at polar or temperate conditions.

The dissolution of hydrocarbons into the water phase accounts for a minor fraction of the mass loss due to weathering of the fuels, which at 0°C is equal to 1.96‰, 0.734‰ and 0.685‰ of that attributed to evaporation for the SAB, MGO and IFO fuels, respectively. The dissolution rate at 0°C is roughly half of that at 20°C for all three fuels. Despite this, the absolute amount of hydrocarbons that are dissolved in the water column at 0°C is 105.8%, 79.9% and 63.2% higher than that at 20°C for SAB, MGO and IFO-180, respectively, because the evaporation rate drop is roughly double that of dissolution. This is an important observation since the dissolved hydrocarbons together with the dispersed ones are responsible for the bioavailability of the fuel spill to the marine organisms living in the water column. This observation, combined with the slower metabolic rate of the Antarctic marine organisms compared to those in temperate regions, highlights the necessity for measurements of the toxicity of the WAFs produced by the three fuels to the Antarctic organisms.

Other weathering processes that may affect Antarctic fuel spills were also examined, including natural dispersion and the depletion of hydrocarbons from the water column. It was found experimentally using the baffled flask test that natural dispersion under polar conditions can only account for a minor loss of fuel spills, in the range of 2% mass loss for the MGO and 4% for the IFO-180. Results from the hydrocarbon depletion test indicate that although evaporation from the water surface is the main depletion process, other processes accelerate the depletion of hydrocarbons from the water column, with oxidation being probably the second most effective process. Further investigation is needed in order to determine the rate of depletion caused by other processes.

93

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Appendix 2A. Detailed	composition	and	dissolution	parameters
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		Fuel		Water	Accommod	ated Fraction
	IFO-180	MGO	SAB	IFO-180	MGO	SAB
	C	oncentrati	on g/L	C	oncentratio	on μg/L
Total Aromatic Content	286.0	146.9	154.4	2,793	3,557	6,608
Detailed breakdown						
Benzene	0.00	0.01	0.00	25.7	99.8	0.0
Benzene, methyl-	0.06	0.92	1.76	118.6	486.1	51.2
Benzene, C <sub>2</sub> -alkyl-	0.30	2.15	1.22	170.9	708.0	352.4
Benzene, C <sub>3</sub> -alkyl-	0.66	6.49	13.70	116.0	637.3	1,168
Benzene, C <sub>4</sub> -alkyl-	1.09	8.13	26.04	67.2	277.5	743.8
Benzene, C <sub>5</sub> -alkyl-	1.81	7.67	29.36	34.2	87.7	293.9
Benzene, C <sub>6</sub> -alkyl-	1.59	5.92	3.16	5.3	17.5	13.4
Benzene, C <sub>7</sub> -alkyl-	0.44	1.78		0.3	0.0	
Benzene, C <sub>8</sub> -alkyl-	0.54	0.39				
Benzene, C <sub>9</sub> -alkyl-	0.24	0.17				
Benzene, C <sub>10</sub> -alkyl-	0.12	0.08				
Naphthalene	0.14	0.76	9.45	38.5	152.1	1,267
Naphthalene, methyl-	0.86	1.65	18.64	57.6	91.2	744.1
Naphthalene, C <sub>2</sub> -alkyl-	2.87	1.51	3.94	49.8	19.9	57.6
Naphthalene, C <sub>3</sub> -alkyl-	7.11	1.51	0.00	30.6	5.0	0.0
Naphthalene, C <sub>4</sub> -alkyl-	4.72	0.72		1.6	0.0	
Naphthalene, C <sub>5</sub> -alkyl-	0.75			0.4		
Phenol, methyl-	0.00	0.00	0.00	0.9	3.6	28.8
Phenol, C <sub>2</sub> -alkyl-	0.00	0.00	0.00	18.6	34.3	484.3
Phenol, C <sub>3</sub> -alkyl-	0.00	0.00	0.00	16.3	29.7	422.4
Phenol, C <sub>4</sub> -alkyl-	0.00	0.00	0.00	6.4	12.9	93.7
Phenol, C <sub>5</sub> -alkyl-	0.00			0.9		
Benzothiophene	0.00			1.2		
Benzothiophene, methyl-	0.04			3.3		
Benzothiophene, C <sub>2</sub> -alkyl	0.39			10.1		
Benzothiophene, C <sub>3</sub> -alkyl	1.55			8.0		
Benzothiophene, C <sub>4</sub> -alkyl	1.74			0.2		
Benzothiophene, C <sub>5</sub> -alkyl	1.10			0.0		

continued	Fuel			Water Accommodated Fraction	
	IFO-180	MGO	SAB	IFO-180 MGO	SAB
Dibenzothiophene	0.08			1.3	
Dibenzothiophene, methyl-	0.20			0.2	
Dibenzothiophene, C <sub>2</sub> -alkyl-	0.21			0.0	
Dibenzothiophene, C <sub>3</sub> -alkyl-	0.03			0.0	
1H-Indene, 2,3-dihydro	0.02	0.22	0.40	7.1	70.2
1H-Indene, 2,3-dihydro-methyl-	0.15	1.31	6.20	13.0	174.1
1H-Indene, 2,3-dihydro-C <sub>2</sub> -alkyl-	0.68	2.38	9.47	18.9	130.3
1H-Indene, 2,3-dihydro-C <sub>3</sub> -alkyl-	0.70	2.77	1.54	5.2	10.0
1H-Indene, 2,3-dihydro-C <sub>4</sub> -alkyl-	0.90	0.94		0.9	
1H-Indene, 2,3-dihydro-C <sub>5</sub> -alkyl-	0.32	1.07		0.2	
1H-Indene, 2,3-dihydro-C <sub>6</sub> -alkyl-	0.17			0.0	
1H-Indene, C <sub>2</sub> -alkyl-	0.00	0.29		1.4	
1H-Indene, C <sub>3</sub> -alkyl-	0.05	0.05		0.0	
1H-Indene, C <sub>4</sub> -alkyl-	0.37	0.37		1.7	
1H-Indene, C₅-alkyl-	1.49	1.19		0.4	
Tetralin	0.07	0.61	2.01	7.4	106.1
Tetralin, methyl-	0.41	3.63	3.50	12.2	56.0
Tetralin, C <sub>2</sub> -alkyl-	2.13	14.70	0.00	11.4	3.1
Tetralin, C₃-alkyl-	2.46	13.93		1.8	
Tetralin, C <sub>4</sub> -alkyl-	3.05	8.38		0.0	
Tetralin, C <sub>5</sub> -alkyl-	0.12	0.07		0.0	
	0.05	0.47	0.64		22.0
Biphenyl Bishawd, westkul	0.05	0.17	0.64	2.2	22.9
Biphenyl, metnyl-	0.24	0.67	0.00	3.1	1.2
Bipnenyi, C <sub>2</sub> -aikyi-	0.64	1.45		0.4	
Biphenyl, C <sub>3</sub> -alkyl-	0.09	0.18		0.0	
Acenaphthene	0.01			0.6	
	0.00				
9H-Fluorene	0.06			1.0	
9H-Fluorene, methyl-	0.22			1.2	
ун-Fluorene, C <sub>2</sub> -alkyl-	0.26			0.0	
Anthracene + Phenanthrene	0.04			0.3	
Anthr. + Phenan, methyl-	0.09			0.0	
Anthr. + Phenan, C <sub>2</sub> -alkyl-	0.05			0.0	

Table 2A.1. Detailed compositions of the aromatic fraction of the three fresh fuels (SAB, MGO and IFO-

180) used in the Australian Antarctic Territory (AAT), and the resulting WAFs of these three fuels.
| Dissolution parameters at 0°C         |             |                                       |                |                                       |                 |                                       |  |  |
|---------------------------------------|-------------|---------------------------------------|----------------|---------------------------------------|-----------------|---------------------------------------|--|--|
| Sample:                               | IFO-180     |                                       | MGO            |                                       | SAB             |                                       |  |  |
| Compound                              | S (mg/L)    | Q <sub>d</sub> (m s <sup>-1/2</sup> ) | S (mg/L)       | Q <sub>d</sub> (m s <sup>-1/2</sup> ) | S (mg/L)        | Q <sub>d</sub> (m s <sup>-1/2</sup> ) |  |  |
| Benzene                               | 1,518       | 1.69E-04                              | 1,518          | 2.38E-04                              | 1,518           | 2.61E-04                              |  |  |
| Benzene, methyl-                      | 489         | 4.27E-05                              | 489            | 6.00E-05                              | 489             | 9 6.60E-05                            |  |  |
| Benzene, C <sub>2</sub> -alkyl-       | 159         | 1.13E-05                              | 143 1.42E-05   |                                       | 154 1.68E-05    |                                       |  |  |
| Benzene, C <sub>3</sub> -alkyl-       | 56          | 3.33E-06                              | 48             | 4.01E-06                              | 51              | 4.68E-06                              |  |  |
| Benzene, C₄-alkyl-                    | 22          | 1.10E-06                              | 19             | 1.33E-06                              | 19              | 1.49E-06                              |  |  |
| Benzene, C₅-alkyl-                    | 7           | 3.25E-07                              | 7              | 4.26E-07                              | 7 5.01E-07      |                                       |  |  |
| Benzene, C <sub>6</sub> -alkyl-       | 1           | 5.45E-08                              | 2 1.06E-07     |                                       | 3 2.04E-07      |                                       |  |  |
| Naphthalene                           | 90 5.18E-06 |                                       | 106            | )6 8.51E-06                           |                 | 7.62E-06                              |  |  |
| Naphthalene, methyl-                  | 25          | 1.23E-06                              | 32             | 2.21E-06                              | 28              | 2.15E-06                              |  |  |
| Naphthalene, C <sub>2</sub> -alkyl-   | 7           | 3.04E-07                              | 8              | 5.04E-07                              | 11 7.49E-07     |                                       |  |  |
| Naphthalene, C₃-alkyl-                | 2           | 7.25E-08                              | 2              | 1.21E-07                              | 5               | 2.98E-07                              |  |  |
| Indane                                | 132         | 8.32E-06                              | 95             | 8.41E-06                              |                 | 1.00E-05                              |  |  |
| Indane, methyl-                       | 30          | 1.59E-06                              | 30             | 2.22E-06                              | 19              | 1.53E-06                              |  |  |
| Indane, C <sub>2</sub> -alkyl-        | 11          | 4.92E-07                              | 11             | 7.37E-07                              | 10              | 7.11E-07                              |  |  |
| Indane, C <sub>3</sub> -alkyl-        | 6           | 2.24E-07                              | 4              | 2.38E-07                              | 5               | 3.20E-07                              |  |  |
| Tetralin                              | 36          | 1.92E-06                              | 38             | 2.86E-06                              | 35              | 2.89E-06                              |  |  |
| Tetralin, methyl-                     | 12          | 5.35E-07                              | 13             | 8.63E-07                              | 12              | 8.35E-07                              |  |  |
| Tetralin, C <sub>2</sub> -alkyl-      | 5           | 2.01E-07                              | 3              | 1.77E-07                              | 4               | 2.53E-07                              |  |  |
| Tetralin, C <sub>3</sub> -alkyl-      | 1           | 4.62E-08                              | 1              | 2.53E-08                              | 1               | 4.96E-08                              |  |  |
| Biphenyl                              | 19          | 8.10E-07                              | 25             | 1.54E-06                              | 28              | 1.87E-06                              |  |  |
| Biphenyl, methyl-                     | 6           | 2.22E-07                              | 7              | 3.52E-07                              | 6 3.65E-07      |                                       |  |  |
| Biphenyl, C <sub>2</sub> -alkyl-      | 2           | 6.78E-08                              | 1 2.84E-08     |                                       | 1 6.80E-08      |                                       |  |  |
| Phenol, methyl-                       | 25,900      | 1.89E-03                              | 25,900         | 2.66E-03                              | 25,900 2.93E-03 |                                       |  |  |
| Phenol, C <sub>2</sub> -alkyl-        | 6,050       | 3.67E-04                              | 6,050 5.16E-04 |                                       | 6,050 5.67E-04  |                                       |  |  |
| Phenol, C <sub>3</sub> -alkyl-        | 1,761       | 9.08E-05                              | 1,761          | 1.28E-04                              | 1,761 1.40E-04  |                                       |  |  |
| Phenol, C₄-alkyl-                     | 579         | 2.58E-05                              | 579            | 3.64E-05                              | 579             | 3.99E-05                              |  |  |
| Phenol, C <sub>5</sub> -alkyl-        | 189         | 7.39E-06                              |                |                                       |                 |                                       |  |  |
| Benzothiophene                        | 127         | 7.13E-06                              |                |                                       |                 |                                       |  |  |
| Benzothiophene, methyl-               | 36          | 1.74E-06                              |                |                                       |                 |                                       |  |  |
| Benzothiophene, C <sub>2</sub> -alkyl | 11          | 4.60E-07                              |                |                                       |                 |                                       |  |  |
| Benzothiophene, C <sub>3</sub> -alkyl | 4           | 1.47E-07                              |                |                                       |                 |                                       |  |  |
| Benzothiophene, C <sub>4</sub> -alkyl | 1           | 4.10E-08                              |                |                                       |                 |                                       |  |  |

Table 2A.2. Detailed dissolution parameters for all the hydrocarbon types found in the WAFs produced by the SAB, MGO and IFO-180 fuels used in the Australian Antarctic Territory (AAT). S is the experimentally measured solubility of the compounds at 0°C. The constant  $Q_{di}$  is independent of the water current velocity and spill size, and simplifies the calculation of the dissolution rate by applying Equation 2.15.

# A general evaporation model for crude oils and complex hydrocarbon mixtures

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## Statement of authors' contribution

This Chapter is an article in review with *Environmental Modelling & Software*. This paper has been formatted to conform to the font and referencing style adopted in this thesis. Section, Figures, Tables and Equations included within the text are prefixed with the chapter number.

I am the primary author (95% of the effort). I conceptualised and developed the evaporation model. I verified the model predictions and calculated the statistical deviations based on the evaporation experimental presented in Chapter 2. I wrote and designed the structure of the paper. The co-author carefully reviewed and provided feedback and valuable refinements on the final version of the manuscript, and approved it for the submission (5%). Neither this manuscript nor one with similar content under our authorship has been published or is being considered for publication elsewhere, except as described above.

### Abstract

There are numerous models in the literature for predicting the evaporation of crude oils and other petroleum hydrocarbon mixtures, but these are based almost exclusively on the boundary layer model or empirical correlations.

The model presented in this study is the first to combine molecular diffusion and boundary layer theory to simulate the evaporation process. The information required are the density and the distillation data or the composition of the fluid. If viscosity or aromaticity is available the prediction accuracy is improved. Environmental conditions and wind velocity are taken into account.

The model was tested with synthetic mixtures, petroleum fuels and crude oils with initial viscosities ranging from 2 to 13,000cSt. The tested temperatures varied from 0°C to 23.4°C and wind velocities from 0.3 to 3.8 m/s. There is close agreement between the predicted and experimental data for all the fluids, with correlation coefficients ranging from 0.959 to 1.000.

#### Nomenclature

#### Greek symbols

δ	gas boundary layer thickness (m)
v	kinematic viscosity of fluid (cSt)
ρ	density of fluid (g/cm <sup>3</sup> )

### Latin symbols

Co	initial concentration of a compound in the liquid (mol/m³)
C <sub>Lint</sub>	concentration of a compound on the surface of the liquid (mol/m <sup>3</sup> )

$C_{eq}$	equilibration concentration for the liquid phase (mol/m <sup>3</sup> )
D <sub>Air</sub>	diffusion coefficient of a compound in air (m <sup>2</sup> /s)
D <sub>bl</sub>	diffusion coefficient of a compound in the gas boundary layer (m <sup>2</sup> /s)
DL	diffusion coefficient of a compound in the liquid phase (m <sup>2</sup> /s)
н	heat radiation constant (W/m <sup>2</sup> K)
К	heat conductivity (W/m K)
K <sub>G/L</sub>	partition coefficient between the gas and liquid phase (non-dimensional)
L <sub>D</sub>	equivalent diameter of the spill (m)
Ls	length of the spill in the direction of the wind (m)
Lo	starting length of the spill (m)
Μ	evaporated moles of a compound per unit area (mol/m <sup>3</sup> )
Mm	molar mass (g/mol)
Mm <sup>s</sup>	molar mass of air and vapour mix above the spill (g/mol)
Mm∞	molar mass of air away from the spill (g/mol)
Mv	molar volume (cm <sup>3</sup> /mol)
pi	partial vapour pressure of a component of the mixture (Pa)
Ρ	total pressure over the spill (Pa)
P <sub>Im,Air</sub>	log-mean partial pressure of air (Pa)
Pv	vapour pressure of the pure compound (Pa)
R	evaporation rate of a compound (mol/s m <sup>3</sup> )
R <sub>G</sub>	universal gas constant (Pa m <sup>3</sup> /mol K)
R <sub>R</sub>	relative evaporation rate of a compound (mol/s m <sup>3</sup> )
Т	temperature (K)
t	time since the start of evaporation (s)
T <sub>0</sub>	temperature of the medium that the plane sheet is radiating to (K)

Tb	boiling temperature of a compound (K)
Ts	surface temperature of the plane sheet (K)
V	air velocity at 10 m above the surface of the spill (m/s)
VL	transfer velocity in the liquid phase (m/s)
x	vertical distance from the plane surface (m)
Xi	molar ratio of the component i in the mixture (dimensionless)

## 3.1 Introduction.

Hydrocarbon mixtures such as crude oils and petroleum products are complex fluids containing hundreds up to thousands of individual compounds (Neumann et al., 1981). Their composition can vary significantly, and they can contain high amounts of toxic and carcinogenic compounds such as polycyclic aromatic hydrocarbons (PAHs) that are dangerous to humans and to other organisms once they are released in the environment (Echols et al., 2015). Weathering is a general descriptive term for several processes occurring in the environment that alter the composition of crude oils and petroleum products both physically and chemically, resulting in altered properties and phase distributions of the mixtures after they are spilled (Fingas, 2010). These processes include evaporation, photooxidation, and biodegradation, as well as dispersion, dissolution and emulsification if the spill has occurred on a water surface. Of the aforementioned processes evaporation is the most important process in the case of crude oils and volatile hydrocarbon mixtures (Fingas, 2010), since it is responsible for the largest loss of mass, including the most toxic aromatic components during the initial stages of weathering. In order to estimate the exposure of biota in the environment to these chemicals we need to know the fate of the petroleum mixtures and their individual components once they are accidentally released in the environment (Engraff et al., 2011). Direct measurement of the changes occurring in an oil or fuel spill is impractical and extremely difficult most of the time. In these cases modelling is the most important tool we can use in our effort to assess risk and prepare a remediation strategy in advance. Evaporation is also known to be responsible for the alteration of oils, fuels and rock extracts when they are being prepared for analysis in geochemistry laboratories (Ahmed and George, 2004), but the extent of this has only been empirically measured and has not been modelled.

Modelling the evaporation process of a complex mixture such as a crude oil imposes great challenges, and in order to succeed we need to understand the mechanisms that control this process. Past efforts to model evaporation can be divided into two main categories: theoretical models, and empirical correlations.

Most of the theoretical models developed in the past have borrowed their theory from the existing formulations of water evaporation and the concept of a boundary layer forming at the interface of a liquid and gas phase (Fingas, 2010). These models are mainly from two areas of concern, firstly spills occurring in the workplace environment, either indoor or outdoor, and secondly spills occurring during production and transportation of petroleum and its products. Unfortunately previously developed evaporation models have had limited success in providing a general solution for all hydrocarbon mixtures that would be accurate and applicable under different environmental conditions. This inability of the models can be attributed to oversimplification of the modelled processes, and to assumptions that overlook the underlying evaporation mechanisms. One oversimplified assumption is that hydrocarbon mixtures can be treated as one pseudo-component having a single evaporation rate (Blokker, 1964; Brighton, 1985; Mackay and Matsugu, 1973; Stiver and Mackay, 1984). Other researchers followed a more detailed approach by assigning multiple evaporation rates to a number of pseudo-components, but made the inaccurate assumption that a boundary layer in the gas phase is the sole controlling mechanism of the evaporation process and that the liquid phase stays homogenous over the evaporation period (Leinonen

and Mackay, 1975; Payne et al., 1987; Yang and Wang, 1977). One exception to this assumption is the modification made to the Mackay and Matsugu model (1973) by Brown and Nicholson (1991) where they introduced a simple correction to the mass-transfer constant for the "thick skin" that develops on the oil surface as evaporation progresses. The most commonly used evaporation model today is that of Mackay and Matsugu (1973), including variants implemented by several researchers (Leinonen and Mackay, 1975; Yang and Wang, 1977), including those of Stiver and Mackay (1984) who suggested that the boundary layer is the sole controlling mechanism. In reality, in complex mixtures such as crude oils, a concentration gradient is formed between the surface and the inner body of the oil, and a dynamic controlling mechanism between diffusion forces and boundary layer regulation is introduced, depending on the composition of the fluid and the environmental conditions that can greatly alter the evaporation rate.

Recently, Arey et al. (2007) have developed a two-layer model that takes into account the diffusion-limited transfer in both the oil phase and the gas phase boundary layer. The model assigns discreet vapour pressures to a number of pseudo-components. The vapour pressures of the pseudo-components are derived from mapping a comprehensive two dimensional chromatographic analysis with contours of estimated values. The model is solved in small time increments to accommodate for the change in the oil properties. One limitation of this approach is that the oil layer is assumed to be homogeneous and there is no concentration gradient developed due to the diffusion resistance. A more sophisticated model was developed by Lemkau (2012) where the diffusion-limited transfer is taken into account in both the gas boundary layer and the oil layer that is described by a number of sub-layers. A similar approach to the previous mentioned model is followed where the model is solved in small time increments to accommodate for the change in the oil properties. Each of the sub-layers is described by the mathematics of a wall boundary layer. As the evaporation from the top layer progresses the concentration gradient. Although this approach accommodates for the concentration gradient.

diffusion-restricted transfer, the mathematical formulations describing the transfer through a wall layer do not agree with the mathematical formulations describing the transfer in a diffusive layer. Both of the aforementioned models have only been tested by simulating weathered oils of past oil spills and they have not been verified with controlled experiments where the experimental data from the progression of evaporation are available.

Some researchers followed a different approach by rejecting the boundary layer controlling mechanism and developed empirical Equations based on the observation that all naturally occurring hydrocarbon mixtures such as crude oils and their petroleum products follow either a logarithmic or an exponential type evaporation curve (Butler, 1976; Fingas, 1998). Although such empirical correlations can provide an approximate prediction since the empirical factors include the contribution from other controlling mechanisms, they are lacking the accuracy and flexibility of a detailed model sensitive to different environmental conditions.

The aim for this study was to develop an evaporation model that is generally applicable to any hydrocarbon mixture and to a wide range of environmental conditions. This was achieved by combining the theoretical principals of a boundary layer mechanism on the surface of a fluid with those of diffusion theory that describes the controlling process in the body of a fluid.

## 3.2 Theory and methodology.

#### 3.2.1 Molecular diffusion model.

During the evaporation of a complex hydrocarbon mixture such as a crude oil, there are two interdependent processes taking place: migration of material inside the body of the fluid, and evaporation of hydrocarbons from the surface of the fluid to the atmosphere. When there is no significant mechanical stirring in the liquid phase, such as the case of an oil spill on a calm water body, or a spill of fuel on a solid

surface, the migration of material inside the body of the fluid is mainly due to molecular diffusion (Crank, 1979). Understanding the kinetics of this process is crucial in order to predict the rate of evaporation of an oil spill.

Molecular diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motion (Crank, 1979). There is a direct analogy between molecular diffusion and the conduction of heat since both phenomena are due to random molecular motion. In fact, the majority of the theory of molecular diffusion has been adopted from the theory of conduction of heat (Crank, 1979). Conduction of heat in materials is a thoroughly investigated phenomenon and the mathematics governing this phenomenon have been extensively developed in previous studies. Carslaw and Jaeger (1959) present a wealth of mathematical solutions for the transport of heat for different scenarios that can be easily converted to equivalent diffusion scenarios. For this study we have adopted the mathematical formulations that describe the transport of heat in a plane sheet, where radiation of heat occurs from the surface of the plane sheet to another medium (Carslaw and Jaeger, 1959). This scenario is analogous to the transport of hydrocarbons in a fluid and the evaporation that occurs from the open surface to the atmosphere. The boundary conditions in the case of heat conduction and radiation are given by the Equation 3.1:

$$K \frac{\partial T}{\partial x} + H(T_S - T_0) = 0$$
 (3.1)

where K is the heat conductivity,  $\partial T/\partial x$  is the temperature gradient in the direction perpendicular to the radiation surface, H is the heat radiation constant, T<sub>s</sub> is the surface temperature of the plane sheet, and T<sub>0</sub> is the temperature of the medium that the plane sheet is radiating to.

For the diffusion and evaporation scenario, the evaporation mechanism is characterised by a diffusive layer where a concentration gradient is formed in the liquid phase in contact with a boundary layer in the gas phase of thickness equal to  $\delta$  where evaporation takes place (Figure 3.1).



Figure 3.1. Conceptual model of the diffusive layer of the liquid phase where a hydrocarbon is evaporating into the gas phase. A boundary layer of thickness  $\delta$  is formed in the gas phase in contact with the liquid phase. The concentration of the hydrocarbon in the liquid phase  $C_L$  is a function of the distance from the surface and the evaporation time. The ratio of the hydrocarbon's gas concentration at the interface  $C_{Gint}$ to the liquid concentration  $C_{Lint}$  at the interface is equal to the partition coefficient  $K_{G/L}$ . The diffusion coefficient in the liquid phase  $D_L$  is the lowest, followed by a higher diffusion coefficient in the boundary layer  $D_{bl}$ , and the highest diffusion coefficient is found in the gas phase  $D_G$ .

The gas layer above the boundary layer is characterised by a well-mixed gas phase due to the presence of wind, and the concentration of the evaporating component  $C_G$  is almost equal to zero. For the simplification of calculations we will assume it is zero. This condition means that equilibration between the gas and liquid phase will only be reached when the liquid concentration of the evaporating component reaches zero, or the liquid equilibration concentration  $C_{eq} = C_G/K_{G/L} = 0$ .

The interface conditions between the layers are described by Equation 3.2 (Crank, 1979):

$$D_L \frac{\partial C_L}{\partial x} - V_L (C_{Lint} - C_{eq}) = 0 \qquad (3.2)$$

with

$$V_L = \frac{D_{bl}}{\delta} K_{G/L} \tag{3.3}$$

where V<sub>L</sub> is the transfer velocity (m s<sup>-1</sup>) in the liquid phase, C<sub>Lint</sub> is the concentration of the compound on the surface of the liquid (mol m<sup>-3</sup>), C<sub>eq</sub> is the equilibration concentration for the liquid phase, K<sub>G/L</sub> is the partition coefficient between the gas and liquid phase (nondimentional) equal to  $\frac{C_{Gint}}{C_{Lint}}$ , D<sub>bl</sub> is the diffusion coefficient of the compound in the gas boundary layer (m<sup>2</sup> s<sup>-1</sup>),  $\delta$  is the boundary layer thickness (m), D<sub>L</sub> is the diffusion coefficient of a compound in the liquid phase (m<sup>2</sup> s<sup>-1</sup>) and  $\frac{\partial C}{\partial x}$  is the concentration gradient in respect to the depth axis in the liquid phase (mol m<sup>-3</sup> m<sup>-1</sup>).

The following quantities can be replaced with the dimensionless parameters L, T and X:

$$L = l V_L / D_L$$
  $T = D_L t / l^2$   $X = x / l$  (3.4)

where l is the depth of the liquid phase, t is the time since the start of the evaporation, and x is the vertical distance from the surface to a point in the liquid phase.

Then, the general solution for the concentration  $C_L$  of a component in the liquid phase with respect to its initial concentration  $C_0$  is given by Equation 3.5 (Crank, 1979):

$$\frac{C_L - C_0}{C_{eq} - C_0} = 1 - \sum_{n=1}^{\infty} \frac{2L \cos(\beta_n X)e^{(-\beta_n^2 T)}}{(\beta_n^2 + L^2 + L)\cos\beta_n}$$
(3.5)

with

$$\beta_n \tan \beta_n = L \tag{3.6}$$

where  $\beta_n$  are the positive roots of Equation 3.6,  $C_{ini}$  is the initial concentration of the homogeneous liquid, l is the depth of the liquid phase and  $C_{eq}$  is the required concentration of the compound on the surface of the liquid phase to reach equilibrium with the gas phase,

For the case where  $C_L$  is the surface concentration  $C_{Lint}$  at x = 0 and  $C_{eq}$  is equal to zero, since there is no build-up of concentration in the open air the solution simplifies to:

$$\frac{C_{Lint}}{C_0} = \sum_{n=1}^{\infty} \frac{2 L e^{(-\beta_n^2 T)}}{\beta_n^2 + L^2 + L}$$
(3.7)

The solution for the diffused moles  $M_t$  that have crossed one unit of area (m<sup>2</sup>) after time t is given by the Equation (Crank, 1979):

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2 L^2 e^{(-\beta_n^2 T)}}{(\beta_n^2 + L^2 + L)\beta_n^2}$$
(3.8)

where  $M_{\infty}$  is the diffused moles after infinite time that is equal to the initial moles of the component in the liquid phase since the equilibration concentration is equal to zero.

## 3.2.1.1 Heavy and viscous oils.

The number of terms we need to add to the summation series of Equation 3.7 in order to reach the desired accuracy depends on the values of the dimensionless parameters L and T. From the definition of L and T

(Equation 3.4) it is apparent that if the liquid phase is an oil of high viscosity and low diffusion coefficient  $D_L$  and creates a spill of large thickness I, then the parameter L becomes high and the parameter T becomes small. In this case the number of terms we need to add becomes high. During this study we had to calculate the roots and evaluate the series for up to 50 terms of Equations 3.7 and 3.8 for high viscosity fluids. This number of terms for every component and every time step leads to cumbersome calculations that require complex spreadsheets or dedicated software to be developed. An alternative is to use a simple solution for the similar scenario where the spill layer is considered of infinite thickness. This solution is only accurate for heavy and viscous oils where the diffusion and evaporation rates are very slow, so the resulting concentration gradient in the liquid layer is very high and effectively it behaves as a layer of infinite depth.

In this case, and for boundary conditions given by Equation 3.2, the solution takes the form (Crank, 1979):

$$\frac{C_L - C_0}{C_{eq} - C_0} = erfc \frac{x}{2\sqrt{D_L t}} - e^{hx + h^2 D_L t} erfc \left(\frac{x}{2\sqrt{D_L t}} + h\sqrt{D_L t}\right)$$
(3.9)

If  $C_L$  is the surface concentration  $C_{Lint}$  at x = 0 and  $C_{eq}$  is equal to zero, as in our model, the solution simplifies to:

$$\frac{C_{Lint}}{C_0} = e^{h^2 D_L t} erfc(h\sqrt{D_L t})$$
(3.10)

The moles that are crossing one unit area ( $m^2$ ), on the surface x=0 and C<sub>eq</sub> is equal to zero is given by the Equation (Crank, 1979):

$$M_t = -\frac{C_{Lint}}{h} \left( e^{h^2 D_L t} erfc \left( h \sqrt{D_L t} \right) - 1 + \frac{2}{\sqrt{\pi}} h \sqrt{D_L t} \right)$$
(3.11)

where  $h = V_L / D_L$  with  $V_L$  and  $D_L$  defined in Equation 3.2.

#### 3.2.1.2 Low or medium viscosity oils.

In the opposite case of a low or medium viscosity oil with high diffusion coefficients and a thin spill layer, the solution presented above with Equations 3.9 to 3.11 is not accurate, and only the original solution presented with Equations 3.5 to 3.8 can be used. In this case the first 4 to 5 terms provide high accuracy and the computations are much simpler. Although there are Tables in the literature with the roots of  $\beta$  for the Equation 3.6 for specific values of L, the model requires the roots of  $\beta$  for all calculated values of L during the evaporation simulation, and a solution on demand is required. The technique that was used in this study to accomplish this task was the iterative approximation of Newton-Raphson (Deuflhard, 2011). For every time step the first *n* successive roots where approximated until the iterative approximation provided the desired accuracy.

### *3.2.1.3 Complications due to multiple components evaporating simultaneously.*

The above solution is valid for a single component evaporating from a non-evaporating solvent, such that the total mass of the system and the surface concentration are not affected from other evaporating components. In the case of a complex mixture such as a crude oil, multiple components are evaporating simultaneously. The effect of this process is that the surface concentration of a specific component after time *t* appears higher than the one calculated from the above solution, due to the evaporation of other components from the surface of the mixture. To accommodate for this phenomenon we have introduced an additional quantity, the relative evaporation rate R<sub>R</sub>, that will replace the real evaporation rate R in our diffusion calculations. In effect R<sub>R</sub> determines if the evaporation rate of a specific component is higher or lower than the average evaporation rate of the fluid. If it is lower, then R<sub>R</sub> becomes negative, indicating that despite the evaporation of the component, the concentration of the component on the surface is increasing. If it is higher, then R<sub>R</sub> of the component is higher than the average and the surface

concentration of the component is decreasing. The formula for the calculation of  $R_R$  is given by Equation 3.12:

$$R_{Ri} = R_i - \sum_{1}^{n} R_k x_k$$
 (3.12)

where  $R_i$  is the evaporation rate of component i,  $R_k$  is the evaporation rate of each of the components in the mixture, n is the total number of components, and  $x_k$  is the molar fraction of each of the components in the mixture.

The introduction of  $R_R$  leads to two different mass transfer rates. The first describes the mass transfer rate inside the hydrocarbon mixture due to diffusion forces. This rate depends on the concentration gradient in the liquid phase and consequently on the relative evaporation rate  $R_R$  that describes the concentration on the liquid surface. The transfer velocity  $V_L$  that appears in the diffusion Equations 3.2-3.4 can be calculated from the relative evaporation rate  $R_R$  using the Equation:

$$V_L = \frac{R_R}{\left(C_S - C_{eq}\right)} \tag{3.13}$$

The second transfer rate is the rate of evaporation R from the surface of the liquid to the gas phase. We assume that for small time steps  $\Delta t$ , the surface concentration and the fluid properties remain constant and the calculation of the evaporated moles  $M_{\Delta T}$  per unit area for each (pseudo) component can be calculated from the Equation:

$$M_{\Delta t} = R \,\Delta t \tag{3.14}$$

The calculation of the evaporation rate R for each component is described in Section 3.2.2.

A second implication that arises from the fact that we have a complex mixture and not a non-evaporating solvent is that the total mass and the physical properties of the mixture change constantly as evaporation

progresses. We can use the solution presented above with Equations 3.5 to 3.8 for small time periods, if we assume that the properties of the fluid remain practically the same. However, for long time periods, the model needs to accommodate the changes in composition and physical properties such as the viscosity, the diffusion coefficients and the changing partial vapour pressures. Such a calculation for a complex mixture is impossible to be solved analytically, so a numerical, step-based solution has been devised.

The model is solved in small time steps. After each step the remaining mass, the new composition and the surface concentration are determined, as well as the values for the changing properties of viscosity, density, diffusion coefficients and evaporation rates. Next we calculate the equivalent time  $t_{j+1 \text{ start}}$  after the end of the time step j that is needed for each component in the slightly different resulting fluid to reach the same surface concentration as at the end of the previous step, starting from the same initial homogeneous concentration. To accomplish this we need to solve Equation 3.15 for  $T_{j+1 \text{ start}}$ . This Equation requires two separate sets of roots  $\beta$ , one for each side of the Equation, since the fluid parameters L and T for each step are different.

$$\frac{C_{Lint \ j \ end}}{C_0} = \frac{C_{Lint \ j+1 \ start}}{C_0} \Rightarrow \sum_{n=1}^{\infty} \frac{2 \ L_j \ e^{\left(-\beta_{n_j}^2 T_j\right)}}{\beta_{n_j}^2 + L_j^2 + L_j} = \sum_{n=1}^{\infty} \frac{2 \ L_{j+1} \ e^{\left(-\beta_{n_j+1}^2 T_{j+1 \ start}\right)}}{\beta_{n_j+1}^2 + L_{j+1}^2 + L_{j+1}}$$
(3.15)

Solving Equation 3.15 requires the utilisation of the iterative approximation of Newton-Raphson (Deuflhard, 2011). After we determine the time that the two fluids are at the same diffusive state we apply the additional time step  $\Delta T_{i+1}$  to the new fluid:

$$T_{j+1 end} = T_{j+1 start} + \Delta T_{j+1}$$
 (3.16)

The new time  $T_{j+1 \text{ end}}$  can now be used with Equation 3.7 to calculate the new surface concentrations of each component for the fluid with the updated properties at the end of the step j+1.

Note that in all Equations we use the dimensionless parameter T, instead of real time. Conversion to and from the real time is done by the expression in Equation 3.4.

In Figure 3.2 we present a flow diagram of our method for modelling the evaporation process in small time steps. The following are notes about this flow diagram. At Step 1, a pseudo-component composition or alternatively distillation cuts can be used. Compositional data (NINA) from gas chromatography-mass spectrometry (GC-MS) analyses and viscosity data are optional information that increase the accuracy of the model. At Step 9,  $t_{real}$  is the actual time of modelling and is calculated by adding the durations  $\Delta t_j$  of each time step up to the current step.



Figure 3.2. Flow diagram of the modelling process for complex hydrocarbon mixtures. Pseudo-component properties have the index i. NINA = normal, iso, naphthenic and aromatic hydrocarbon fractions.  $\rho$  = density of fluid, v = kinematic viscosity of fluid, ECNi = effective carbon number, Mmi = molar mass, Mvi = molar volume, Tbi = boiling temperature,  $\rho$ i = density, pi = partial vapour pressure, Ri = evaporation rate, D<sub>Gi</sub> = diffusion coefficient for gas phase, D<sub>Li</sub> = diffusion coefficient for liquid phase, Mi = moles evaporated, C<sub>Lint</sub>i = surface concentration,  $\Delta$ t<sub>i</sub> = duration of step j.

In the appendix 3A we present a series of calculations and techniques for estimating the pseudocomponent properties as well the bulk fluid properties shown on the flow diagram that are required for solving and updating the model as evaporation progresses.

#### 3.2.2 Evaporation rate R calculation.

In this Section we describe two different ways of calculating the evaporation rate R depending on the scale of the spill and the wind flow regime.

For the scenario of predicting the evaporation of a large scale spill in an open environment, such as an oil spill in the marine environment where turbulent wind flow is prevailing, the formula developed by Mackay and Matsugu (1973) is presented here, with the modification of using the partial pressures instead of the total vapour pressure since we have a mixture of (pseudo) components and not a single (pseudo) component:

$$R_i = 4.82 \times 10^{-3} D_{i,Air}^{2/3} \nu^{-0.67} V^{0.78} L_D^{-0.11} \frac{P_{Vi} x_i}{R_G T}$$
(3.17)

where  $D_{i,Air}$  is the diffusion coefficient of component i in air (m<sup>2</sup> s<sup>-1</sup>), v is the kinematic viscosity of air (m<sup>2</sup> s<sup>-1</sup>), V is the air velocity (m s<sup>-1</sup>) at 10m above the surface of the spill, L<sub>D</sub> is the equivalent diameter of the spill (m), P<sub>Vi</sub> is the vapour pressure of the pure component i (Pa), x<sub>i</sub> is the molar ratio of the component i in the mixture, R<sub>G</sub> is the universal gas constant (Pa m<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup>), and T is the temperature (K).

For the scenario of a small scale spill such as an accidental leak in an indoor workplace where a low wind velocity and laminar air flow is prevailing, the evaporation rates of each component are determined from the work of Nielsen et al (1995) based on the laminar boundary layer theory. The mass balance Equation for the evaporating compound is (Coulson et al., 1999):

$$\frac{\partial}{\partial x} \int_{0}^{l} C_{i} V(y) dy = -D_{i,Air} \left( \frac{\partial C_{i}}{\partial y} \right)$$
(3.18)

where  $C_i$  is the concentration of the compound in air, and V(y) is the air velocity at a distance y from the surface.

After integrating over the evaporation length and adding corrections for the air-vapour variable density and the bulk flow, the final expression that gives the evaporation rate of a pure organic compound takes the form (Nielsen et al., 1995):

$$R_{i} = 0.662 D_{i,Air}^{2/3} v^{-1/6} V^{1/2} \left[ \frac{(L_{S}^{3/4} - L_{o}^{3/4})^{2/3}}{L_{S} - L_{o}} \right] \frac{\ln \frac{Mm^{S}}{Mm^{\infty}}}{\frac{Mm^{S}}{Mm^{\infty}} - 1} \frac{P}{P_{lm,Air}} \frac{P_{Vi}}{R_{G}T}$$
(3.19)

and

$$P_{lm,Air} \cong \frac{P_{Vi}}{\ln \frac{P}{P - P_{Vi}}} \tag{3.20}$$

where  $D_{i,Air}$  is the diffusion coefficient of component i in air (m<sup>2</sup> s<sup>-1</sup>), v is the kinematic viscosity of air (m<sup>2</sup> s<sup>-1</sup>), V is the air velocity (m s<sup>-1</sup>), L<sub>s</sub> is the length of spill at the direction of wind (m), L<sub>o</sub> is the starting length (m), Mm<sup>s</sup> is the molar mass of air and vapour mix above the spill (g mol<sup>-1</sup>), Mm<sup>∞</sup> is the molar mass of air away from the spill (g mol<sup>-1</sup>), P is the total pressure over the spill (Pa), P<sub>Im,Air</sub> is the log-mean partial pressure of air (Pa), P<sub>Vi</sub> is the vapour pressure of compound i (Pa), R<sub>G</sub> is the universal gas constant (Pa m<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup>), and T is the temperature (K).

In order to use this calculation for the determination of the evaporation rate of individual components in a mixture like a crude oil we need to replace some of the quantities of Equation 3.19 with the equivalent quantities for a mixture. Therefore the vapour pressure ( $P_{Vi}$ ) in Equation 3.19 is replaced by the partial vapour pressure ( $p_i$ ) of the (pseudo) component, and the  $P_{Vi}$  in Equation 3.20 is replaced by the total vapour pressure ( $P_{V \text{ total}}$ ) of the mixture. Lastly, the air-vapour molar mass at the surface (Mm<sup>S</sup>) should include the contribution to the molar mass from the vapours of all the components, named Mm<sup>S</sup>. So for the case of a hydrocarbon mixture the evaporation rate of a component in the mixture is given by Equation 3.21.

$$R_{i\,mix} = 0.662 \, D_{i,Air}^{2/3} \, \nu^{-1/6} \, V^{1/2} \left[ \frac{(L^{3/4} - L_o^{3/4})^{2/3}}{L - L_o} \right] \frac{\ln \frac{Mm_T^2}{Mm^{\infty}}}{\frac{Mm_T^S}{Mm^{\infty}} - 1} \frac{P}{P_{lm,Air}} \frac{p_i}{RT}$$
(3.21)

~

$$P_{lm,Air} \cong \frac{P_{V \ total}}{\ln \frac{P}{P - P_{V \ total}}}$$
(3.22)

where  $p_i = P_V * x_i$  and  $x_i$  is the molar fraction of component i in the mixture.

In both scenarios we have assumed that the activity coefficients of the pseudo components inside the liquid mixture are equal to 1. This assumption is not far from the reality since fuels and crude oils consist mainly of hydrocarbons with small amounts of NSO polar compounds. The majority of hydrocarbons are predominantly normal and branched and therefor apolar with smaller amounts of aromatics and therefor monopolar compounds. When monopolar or apolar compounds are dissolved in a mixture of predominantly apolar compounds we can expect their activity coefficient to be close to 1 (Schwarzenbach et al., 2003).

### 3.3 Materials and experimental methodology.

### 3.3.1 Fuels and mixtures

Two synthetic mixtures, three fuels and two crude oils were used for the validation of the developed model.

The fuels used were a Special Antarctic Blend (SAB) diesel, a Marine Gas Oil (MGO) and an Intermediate Fuel Oil 180 (IFO-180). The SAB is a very light diesel fuel and mainly consists of  $C_9-C_{16}$  hydrocarbons (Snape et al., 2006). The MGO is a light marine fuel also known as Marine Diesel Oil (MDO) that conforms to the ISO 8217 Grade DMA specifications. Compared with the SAB, it has a broader  $C_7-C_{26}$  hydrocarbon distribution (ETC, 2015; Snape et al., 2006; Wang et al., 2003). Lastly, IFO-180 is a heavy and viscous marine fuel used by large marine vessels. It is a blend, generally containing less than 10% distillate with the remaining 90% being a heavy residual fuel (Bunker C) and with a boiling range going well over 700°C (ETC, 2015). All three fuels are used in the Australian Antarctic Territory for station and marine operations.

Pure tert-butylbenzene and n-dodecane of analytical grade were used to prepare two synthetic mixtures. The first synthetic fluid (Fluid A) was a binary mixture of 5% by mass tert-butylbenzene dissolved in 95% n-dodecane. The second synthetic fluid (Fluid B) consists of 4% by mass tert-butylbenzene and 13% n-dodecane dissolved in 83% artificially weathered IFO-180 fuel. The artificial weathering of the IFO-180 fuel was performed on a hot plate with continuous magnetic stirring and a flow of nitrogen over the surface of the fuel. The heating was applied at a slow rate over a period of eight hours, starting from 70°C and ramping up to 140°C until the 8% mass loss was achieved. The artificially weathered IFO-180 had lost essentially all its volatile components, and provided a highly viscous fluid to test the theoretical concept of the model (Figure 3.3).



Figure 3.3. GC-FID chromatograms of IFO-180 A. before and B. after the artificial weathering to a mass loss of 8%. The carbon numbers of n-alkanes are shown by n-Cxx, the shaded grey area is the unresolved complex mixture.

Additionally, two crude oils were included in the validation experiments since they exhibit different evaporation behaviour and produce a "logarithmic" shape evaporation curve. These are the Kuwait crude oil (ETC, 2015) and the Alberta ASMB reference 4 crude oil (ETC, 2015). Both oils have a wide hydrocarbon distribution with large amounts of volatile components and a significant amount of non-volatile heavy residue.

#### 3.3.2 Experimental methods.

The fuel samples were characterised by measuring the density, the viscosity and the mass fractions of aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds. The densities were determined gravimetrically by measuring the weight of either 50 mL or 100 mL of each fuel sample in a volumetric flask at the desired temperature, using a high precision (5 decimal places of a gram) mass balance (AND GR-202). The viscosities were determined with glass capillary viscometers immersed in a temperature regulated bath (Julabo F12). The fractionation of each sample into aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds was performed with a liquid chromatographic column packed with activated silica gel. Two bed volumes of normal hexane, normal hexane/dichloromethane (4:1 v/v) and methanol/dichloromethane (1:1 v/v) were flowed through the column in sequence in order to elute the aliphatic, aromatic and polar fractions. The fractions were then quantified by adding a known amount of internal standard and analysed by GC-MS.

The composition of all samples was determined by GC-MS and gas chromatography coupled with flame ionisation detector (GC-FID). At predetermined time intervals during the evaporation experiments, the weathered fuel was sub-sampled for analysis on the GC-MS and GC-FID. Two microliters of sample (from about 8 mL; ~0.03 %) were removed, and the weathering fuel was weighed before and after the sub-sample removal so that the evaporation curve could be corrected for the removal of this mass. Not all of the measured properties were used for the modelling of the evaporation. Only the GC-FID composition, the aliphatic/aromatic hydrocarbon ratio and the density of the samples were used. The weathered

compositions of the samples were used for verification of the predicted mass loss of individual pseudocomponents in the model against the measured ones.

The evaporation experiments were performed according to the setup shown in Figure 3.4 in a temperature controlled environment (Binder KB-115).



Figure 3.4. Experimental setup for the controlled evaporation of complex hydrocarbon mixtures.

Roughly 8 mL of fuel was placed in a 3 mm deep rectangular polystyrene dish with dimensions 125 mm x 65 mm, which created a layer of fuel about 1 mm deep. The dish was placed at mid-height of the tunnel on the extended middle glass blade, as shown on Figure 3.4. The weight of the fuel was measured initially and periodically as the evaporation experiment progressed using the high precision weight balance. The wind velocity could be regulated by adjusting the wind-tunnel's fan revolution rate, and was measured with a high precision (0.01 m/s accuracy) hot-wire anemometer (TES model 1340). The anemometer was

placed directly above and behind the sample so as to measure the mid-height wind velocity in the tunnel. The samples were tested under different wind (0.3m/s and 2m/s) and temperature (0°C and 15°C) conditions. The duration of the experiments is shown in Table 3.1, and ranged from 5 to 16 days. Additionally 2 samples, the IFO-180 (IFO-3 LT) and MGO (MGO 3 LT), were used for long duration evaporation experiments (77 days) in order to study the performance of the model on highly evaporated samples.

Table 3.1 summarises the physical properties and the test conditions for all the hydrocarbon fluids used for the validation of the model.

Sample	Density (g/cm <sup>3</sup> )		Viscosity (cSt)		Duration (days)	Evaporated mass (%)		Temperature (°C)	Wind (m/s)	R <sup>2</sup>	AAD (%)
	start	end <sup>2</sup>	start	end <sup>2</sup>		experimental	model prediction	I			
Fluid A	0.767	0.762	2.7	2.6	5.3	28.0	26.2	1.0	2.0	0.999	0.99
Fluid B	0.937	0.959	1,554	14,246	6.0	12.4	11.6	1.0	2.1	0.997	1.31
SAB 1	0.795	0.881	2.6	35	4.9	99.5	98.8	15.0	2.0	0.998	5.15
SAB 2	0.806	0.883	2.8	19	8.3	85.4	88.3	0.0	0.3	0.996	9.61
MGO 1	0.829	0.848	5.0	9.7	7.9	40.4	39.7	15.0	2.0	1.000	3.22
MGO 2	0.839	0.856	7.4	18	10.6	27.6	28.6	0.0	0.3	0.990	6.19
MGO 3 LT <sup>1</sup>	0.829	0.855	5.0	13	77.1	63.1	64.0	15.0	0.3	0.993	8.57
IFO 1	0.952	0.970	2,736	13,510	10.0	13.1	11.4	15.0	2.0	0.999	13.11
IFO 2	0.963	0.969	13,423	53,354	16.1	4.8	4.8	0.0	0.3	0.976	17.13
IFO 3 LT <sup>1</sup>	0.952	0.975	2,736	32,267	77.2	18.0	16.9	15.0	0.3	0.993	8.81
Kuwait	0.869	0.913	25	323	11.0	32.1	30.4	15.0	1.9	0.999	3.41
Alberta	0.839	0.935	5.3	104	1.4	41.4	40.7	23.4	3.8	0.959	5.77
<sup>1</sup> Long term ev	aporation ex	periment									

<sup>2</sup>Model predicted value at the end of the experiment

Table 3.1. Summary of the physical properties and experimental conditions for all the tests fluids. For

sample descriptions see Section 3.3.1.

The Average Absolute Deviation (AAD) was calculated as the average percentage of deviation from the

measured evaporated mass for all the data points:

$$AAD\% = \frac{\sum_{i=1}^{n} \frac{|m_{pr} - m_{exp}|}{m_{exp}}}{n} \times 100$$
(3.23)

where  $m_{exp}$  is the experimentally determined evaporated mass,  $m_{pr}$  is the predicted mass, and n is the number of experimental data point.

The R<sup>2</sup> is the square of the Pearson product moment correlation coefficient between all the experimental evaporation measurements for a specific sample and the corresponding model prediction data.

## 3.4 Results and discussion

The comparison between the data from the performed evaporation tests and the predicted evaporation results from the model described in Section 3.2.1 are presented here for the synthetic mixtures, the three fuels used in the Australian Antarctic Territory, and the two crude oils. The presented experimental data from the evaporation tests were performed in the laboratory with the experimental setup presented in Section 3.3.2 (Figure 3.4) and are characterised by low wind velocities in the range of 0.3 to 2 m/s and a linear wind flow regime. For this reason, the evaporation rates of the pseudo components of the fluids were estimated with equations 3.21 and 3.22 (Nielsen et al., 1995). There is a need for field tests in an open sea environment in order to fully evaluate the model under higher wind velocities and turbulent wind flow regimes. For that scenario the evaporation rates of the individual pseudo components would have to be estimated with equation 3.17 (Mackay and Matsugu, 1973). Presently, all model predictions presented in this work have used the Nielsen et al. (1995) evaporation rates.

### 3.4.1 Synthetic mixtures

Fluid A consists of two analytical standards, tert-butylbenzene and n-dodecane, and hence its properties are well known (Table 3.1). Additionally, the fluid has a very low viscosity of 2.7 cSt at 1°C, and the effect of diffusion is minimal. The main controlling mechanism for this fluid is expected to be the boundary layer. Fluid B is a mixture of tert-butylbenzene, n-dodecane and weathered IFO-180. This fluid has viscosity of 1554 cSt at 1°C and diffusion forces are expected to play a significant role in controlling the evaporation process. Fluid A lost 28.0 % mass due to evaporation in 5.3 days, whereas Fluid B lost 12.4% in 6.0 days (Figure 3.5). For both fluids the model prediction was accurate, with an AAD of 1% and 1.3% respectively. Both synthetic mixtures are not characterised by the typical skewed Gaussian distribution that a natural crude oil possesses, but have arbitrary quantities of volatile components that an empirical evaporation correlation would have failed to predict. In contrast, the model presented here can give successful predictions on synthetic mixtures of arbitrary component concentrations. Additionally, the high viscosity of the IFO in Fluid B creates a steep concentration gradient in the fluid that reduces the evaporation rate and was successfully predicted.



Figure 3.5. Prediction of evaporation from the model versus experimental mass loss data due to evaporation of two synthetic hydrocarbon mixtures for 6 days. Fluid A is a low viscosity binary mixture of tert-butylbenzene and n-dodecane, and Fluid B is a high viscosity mixture of tert-butylbenzene, n-dodecane and weathered IFO-180 fuel.

#### 3.4.2 Fuels used in the Australian Antarctic Territory.

Next we present the results of three very different fuels used in the Australian Antarctic Territory for the needs of the research stations and shipping operations. All fuels have been tested at 0°C and 15°C as well as at two wind velocities (0.3m/s and 2.0m/s) (Figure 3.6). There is good agreement between the experimental data and the predictions of the model (all R<sub>2</sub> values >0.99, except for IFO-180 at 0°C where  $R^2 = 0.976$ ). The AAD for the SAB fuel was 5.15% and 9.61% at 15°C and 0°C respectively, the AAD for the MGO fuel was 3.22% and 6.19% at 15°C and 0°C respectively, and for the viscous IFO-180 the AAD was 13.11% and 17.13% at 15°C and 0°C respectively (Table 3.1). The IFO-180 exhibits higher AADs for two reasons. Firstly, a high viscosity creates greater uncertainty with the estimation of the diffusion coefficients in the model. Secondly, the very low amounts of evaporated mass over the course of the experiment (Figure 3.6) exacerbated experimental and analytical errors. For example a measured evaporated mass of 0.60% and a predicted evaporated mass of 0.66% create an absolute deviation of 10%.

Another observation regarding the SAB model predictions is that straight segments start to appear at the late stages of the evaporation curve (Figure 3.6). This phenomenon can be explained by the grouping of the fuel components into pseudo components. When the majority of the volatile components have been depleted and only two or three pseudo components remain, effectively only a single pseudo component contributes to the mass loss at this stage which results in a constant evaporation rate and creates a straight evaporation curve segment.

128



Figure 3.6. Model prediction versus experimental mass loss data due to evaporation for the three fuels at different conditions. The first fuel is the highly viscous IFO-180 used by large marine vessels, the second is a medium viscosity Marine Gas Oil (MGO) and the third is the light Special Antarctic Blend (SAB) diesel. A, results at 15°C temperature and 2.0 m/s wind velocity; B, results at 0°C and 0.3 m/s.

We also performed long-term evaporation tests on the MGO and IFO, where each evaporation experiment was run for 77 days in order to examine if the predictions of the model continue to be accurate when a considerable portion of the fluid has been lost. The results of these long-term tests are plotted against the model predictions in Figure 3.7, which shows that even at advanced stages of the evaporation process the model predictions remain accurate. The AAD for the MGO fuel was 8.57% and for the IFO-180 was 8.81%, and the respective correlation coefficients for the MGO and IFO are both 0.993. These findings are in line with the expected performance of the model, since the mathematical calculations take into account the changes of the fluid's composition and physical properties, as well as other parameters such as the change in the geometric characteristics of the fuel spill, and the depth of the fuel phase as the evaporation process progresses.



Figure 3.7. Prediction of long-term evaporation from the model versus experimental mass loss data due to evaporation for MGO and IFO-180. Predictions from the model appear to remain accurate when a large portion of the fluid has been evaporated.

Another observation from the long-term evaporation experiment is the improved performance of the model regarding the evaporation prediction of the IFO-180. The slow evaporation of IFO exacerbates errors, so when a long term test is performed there is considerable evaporated mass and these errors are minimised.

We also present a comparative graph of the model predictions for the evaporation of IFO-180 at 0°C versus a prediction based on the vapour pressures of the pseudo components alone (Figure 3.8). It can be seen that evaporation rates are overestimated by the latter, since this prediction does not take into account the compositional gradient formed inside the fluid due to the slow diffusion rate of viscous fluids such as the IFO-180.



Figure 3.8. Comparison between the predictions for the evaporation of IFO-180 from the present model and a prediction based only on the partial vapour pressures assuming homogenous composition across the fluid.

We have included below (Video 1) a video presentation of the long term evaporation experiment of the MGO fuel. The video shows the loss of the light hydrocarbon fraction as the evaporation progresses through a series of chromatograms from GC-MS recorded during the experiment. The corresponding predicted and experimental data for each chromatogram are also presented.



Video 1 Caption 1. Video demonstration of the evaporation progression over time and the comparison between the experimental and the predicted data. The video can be seen at:

https://www.youtube.com/watch?v=nU8PdmE0O6w

## 3.4.3 Crude oils

Finally we evaluated the performance of the model on crude oils with quite different molecular weight distribution characteristics compared with the three fuels. A Kuwait crude oil was used that is characterised by a wide boiling point distribution with large amounts of volatile components and equally large amounts of heavier residue.



Figure 3.9. Prediction of evaporation from the model versus experimental mass loss data due to evaporation of the Kuwait crude oil.

The predicted evaporation curve is plotted against the experimental data in Figure 3.9 and shows different evaporation behaviour comparing to all the previously tested hydrocarbon fluids. Initially, the Kuwait crude oil has a rapid evaporation rate, due to the large amounts of volatile compounds, followed by a fast deceleration of the evaporation rate due to the presence of large amounts of heavy residue, giving rise to a characteristic "L" shaped evaporation curve. Despite this different behaviour compared with the fuels, the evaporation model matches the experimental data with high accuracy. The correlation factor was 0.999, with the model data almost perfectly matching the experimental evaporation profile, and the AAD was 3.41%.

The second crude oil tested was the Alberta Sweet Mixed Blend Reference 4 (ASMB). This crude oil was selected to demonstrate the efficiency of the model when only distillation data is available. The evaporation experiment was performed by Fingas (1998) and the distillation data for this crude oil was retrieved from the Environment Canada oil properties database (ETC, 2015). The temperature of the evaporation was 23.4°C and the wind velocity was 3.8 m/s, and other details of the experiment are available in the publication (Fingas, 1998). In this paper Fingas (Fingas, 1998) claims that crude oils cannot be accurately predicted by boundary layer controlled models, a claim that is partially correct since in this work we have shown that there is an interplay between the air boundary layer and the diffusion controlling processes. The predicted evaporation curve against the experimental results for the Alberta ASMB crude oil are shown in Figure 3.10.



Figure 3.10. Prediction of evaporation from the model based on distillation data only for the ASMB crude oil versus experimental mass loss data published by Fingas (1998) due to evaporation of the ASMB crude oil.
This result shows that there is a small drop in the accuracy of the model prediction, with a correlation coefficient of 0.959 and the AAD equal to 5.77%. This drop in the accuracy of the model is expected when only distillation data is available. Despite this, the prediction is close to the experimental data and it shows that the concept on which the model is based is correct.

## 3.4.4 Prediction of the fluid's physical properties.

The combination of successful evaporation predictions from the model on a range of hydrocarbon mixtures with different characteristics ranging from synthetic mixtures to fuels and crude oils indicates the general applicability of the developed model and its high accuracy on all the tested fluids. This general applicability of the model is an expected outcome, since its predictions are based on theoretical calculations that take into account the processes that take place both in the body of the fluid and on its surface. Table 3.1 summarises the characteristics of the tested fluids and the range of properties that the developed model has been tested on. In addition to the prediction of the evaporation behaviour the model also provides information on a number of physical properties of the tested fluid. This is possible because the numerical calculations continuously update the changing composition and physical properties of the fluid caused by the progression of evaporation. In Figure 3.11 we present the predictions for four physical properties as the evaporation progresses for two of the fuels, namely the average molecular weight, the average boiling point, the kinematic viscosity, and the density of the fluid. The evolution of these physical properties are only the predicted values from the model. The evaporation experiments could not be replicated with large enough volumes of fuel in order to measure the physical properties during the evaporation process, due to the absence of a large-scale controlled environment. However, values obtained from artificial weathering of two fuels (MGO, IFO-180) on a heating plate under different conditions indicate that the predicted values are a good approximation. For example, after the artificial weathering of IFO-180 to 8% mass loss this fluid had a density and viscosity at 0°C equal to 0.977

135

g/cm<sup>3</sup> and 105,400 cSt respectively, while the predicted values for the same mass loss from the model were 0.973 g/ cm<sup>3</sup> and 99,500 cSt respectively (Figure 3.11). Consequently, these model predictions are not verified, but they can indicate the order of magnitude of the physical properties of the residual fuel and provide a qualitative prediction of the effect of the evaporation on its physical properties.



Figure 3.11. Predicted evolution of the average molar mass (A) and average boiling temperature (B) of the MGO fuel during the evaporation process over 30 days. Predicted evolution of the kinematic viscosity (C) and density (D) of the IFO-180 fuel during the evaporation process over 30 days.

3.4.5 Interplay between evaporation and diffusion on individual components.

Finally, the developed model can give us a detailed insight on the effects of the interplay between evaporation and diffusion on the individual components. The changes in the concentration profiles of seven pseudo-components on the surface in relation to the concentration in the body are shown on Figure 3.12. The lines represent individual pseudo-components and their value over time (6.5 days) shows whether they are being enriched or depleted on the surface of the fluid. Values >1 indicate enrichment of the component on the surface, due to faster average evaporation of the fluid, and values <1 indicate components on the surface that evaporate faster than the average of the fluid. Other information provided from the graph is when the line becomes horizontal an equilibrium is being established between the diffusion velocity and the evaporation velocity (Figure 3.12). As predicted by the mathematics of Equation 3.2, there is a specific concentration gradient value for each component where the diffusion velocity equals that of the evaporation velocity. For more volatile components the gradient has to be greater in order to match the evaporation velocity, whereas for less volatile components the ratio of the two concentrations on the graph approaches unity.



Figure 3.12. Surface to body concentration ratios versus time of individual pseudo components (C<sub>8</sub> to C<sub>14</sub>).

The ability of the model to calculate the equilibration concentration and the combined velocity of evaporation can be used in order to determine the influence of each process on the overall evaporation rate, as well as the influence of the environmental conditions on the diffusion–evaporation equilibrium. The relationship of the velocity of each process to the combined velocity is given by Equation 3.24 (Schwarzenbach et al., 2003):

$$\frac{1}{v_{tot}} = \frac{1}{v_{Napl}} + \frac{1}{v_{air}K_{air/fluid}}$$
(3.24)

where  $v_{air} = \frac{D_{bl}}{\delta}$ , with  $D_{bl}$  the diffusion coefficient of the boundary layer, and  $\delta$  the thickness of the boundary layer. K<sub>air/fluid</sub> is the equilibration coefficient between the gas and the liquid phase, and  $v_{Napl} = \frac{D_L}{l}$ , with  $D_L$  the diffusion coefficient in the liquid phase, and I the thickness of the liquid layer. The resulting

graphs (Figures 3.13-3.15) demonstrate the effect of wind velocity, temperature and fluid composition on the dominating process of the diffusion–evaporation interplay.



Figure 3.13 The effect of modelled variable wind velocity (A, 0.3 m/s; B, 5 m/s) on the two processes (diffusion and vapour pressure) controlling the overall velocity of evaporation for nine pseudocomponents ( $C_6-C_{14}$ ) of the IFO-180 fuel.

From Figure 3.13 it is apparent that the volatile components are predominantly controlled by diffusion, whereas the heavier components are mainly controlled by vapour pressure. Equation 3.24 shows that this phenomenon is explained by the influence of each process on the combined velocity. The slower of the two velocities influences the combined velocity to a greater extent. Volatile components having high vapour pressures are restricted by the slower diffusion process, while the opposite is true for the heavier components with slow evaporation rates. Greater wind velocity appears to have a moderate effect on this interplay by shifting the balance of the intermediate  $C_8$ - $C_{10}$  pseudo-components to a more diffusion-dominated control since it is increasing the evaporation rate.



Figure 3.14. The effect of variable temperature on the modelled interplay between diffusion and vapour pressure controlling the overall velocity of evaporation. The graphs are based on the predictions at  $15^{\circ}$ C (A) and  $0^{\circ}$ C (B) for the nine pseudo-components of IFO-180.

Figure 3.14 reveals a large degree of influence of the temperature on the controlling process of evaporation. At 15°C the pseudo-components over C<sub>9</sub> are predominantly controlled by vapour pressure, but at 0°C the pseudo-components up to C<sub>13</sub> are mainly controlled by diffusion. This pronounced effect of temperature is especially strong for IFO-180, since the drop of temperature from 15°C to 0°C increases its viscosity by an order of magnitude, thus affecting the diffusion coefficients according to Equation 3A.8 (in the appendix 3A), while the vapour pressures only drop by approximately 50%. The temperature effect is less pronounced for MGO and SAB since the viscosity change due to the temperature drop is much smaller for light fuels.

Lastly, composition is an important factor in the balance between the evaporation controlling processes. Composition determines to a great degree the viscosity of the fluid and the diffusion coefficients of its components. This is illustrated by Figure 3.15, where for the same environmental conditions, the pseudo components up to  $C_{14}$  of the heavier IFO-180 fuel are predominantly controlled by diffusion. In contrast, only the first few pseudo components up to  $C_8$  in the light SAB fuel are partially controlled by diffusion. The components of the medium molecular weight MGO fuel as expected exhibit an intermediate behaviour (Figure 3.15).



Figure 3.15. The effect of variable molecular composition on the degree that diffusion controls the overall velocity of evaporation for the three fuels, as shown on 11 pseudo-components ( $C_6-C_{16}$ ).

## 3.5 Conclusions

Based on comparison of the evaporation experiments performed so far with the model's predictions we can conclude the following:

- The evaluation of the developed evaporation model shows that the evaporation behaviour of all types of hydrocarbon mixtures tested experimentally have been successfully predicted with high accuracy. The evaporation curves of two synthetic hydrocarbon mixtures with varying viscosity that do not exhibit the typical skewed Gaussian component distribution of crude oils were successfully predicted. The evaporation curves of three fuels and two crude oils with initial viscosities ranging from 2 cSt to over 13,000 cSt were also predicted successfully with high accuracy. These experimental results indicate the general applicability of the model for any type of hydrocarbon mixture that behaves as a Newtonian fluid.
- The evaporation model presented here can be used in a wide range of environmental conditions and regions, since it incorporates calculations for environmental temperature, pressure and wind velocity.
- The model requires a minimum amount of information in order to give predictions. Only partial
  distillation data or gas chromatography composition and density are required, since all other
  properties of the fluid can be modelled. In cases where more information is available, such as the
  viscosity or the aromatic hydrocarbons content of the fluid, then the accuracy of the model
  predictions is increased.
- In addition to the evaporation curve, the presented model continuously predicts the progression
  of the chemical composition and the physical properties of the fluid during evaporation, including
  density, viscosity, the average boiling temperature, and the average molecular mass.
- Because it continuously updates the chemical composition and the physical properties of the weathering fluid, it can easily be incorporated as an autonomous module into a comprehensive

oil spill forecasting software suite such as the ADIOS (Automated Data Inquiry for Oil Spills) (Lehr et al., 2002) or other similar suite.

 Finally, there is a need for large scale evaporation experiments in order to evaluate the model for large spill scenarios, since all the evaluation experiments used in this work were performed within the constraints of the laboratory apparatus and low ≤ 2m/s wind velocities. Additionally, since convection is not included in the model calculations, the accuracy of the predictions is expected to drop as higher wind velocities will cause breaking waves and mechanical stirring.

This is the first time that a general theoretical model has been developed for complex hydrocarbon mixtures such as viscous crude oils and fuels, that takes into account the interplay between the diffusion and the boundary layer controlling mechanisms. Although the operation of the model requires numerous calculations, the required input data are minimal and the provided predictions show high accuracy.

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## Appendix 3A. Pseudo-component properties' calculations

In this appendix we propose a series of calculations for estimating the properties of the pseudo components or distillation cuts as well as the estimation of the bulk properties of the mixture that are required to be updated after each time step in order to run the model simulation.

#### 3A.1. Vapour pressure calculation.

The vapour pressure of each (pseudo) component in the mixture is calculated by a Cox Equation of the type:

$$\ln\left(\frac{p_{sat}}{p_{o}}\right) = \left(1 - \frac{T_{o}}{T}\right)e^{(A_{o} + A_{1}T + A_{2}T^{2})}$$
(3A.1)

where  $p_{sat}$  and T are the vapour saturation pressure (KPa) at temperature T (K), T and  $p_o$  are the boiling point (K) at atmospheric pressure  $p_o = 101.325$  KPa, and  $A_0$ ,  $A_1$ , and  $A_2$  are the three experimentally determined parameters, which are constants for each single component.

Ruzicka and Mayer (1994) have determined the required experimental parameters for the calculation of the vapour pressure for all n-alkanes from n-pentane to n-eicosane. For the case of pseudo components the Effective Carbon Number (ECN) is estimated for each type of hydrocarbon in the group, as explained in the Section 3A.2, and then the vapour pressure for the ECN of each subgroup is calculated. Since most of the times the calculated ECN is not an integer number, the procedure we use to estimate the vapour pressure is to calculate the vapour pressure for all the integer carbon numbers (CNs) from 5 to 20 with the Cox Equation for the desired temperature, and then interpolate for the non-integer ECNs. The interpolation is done with a fitted curve of the form Pv=a\*exp(b\*CN) which gives the best fit to the Cox vapour pressures as shown in Figure 3A.1.



Figure 3A.1. Example of interpolation curve fitted to the Cox calculated vapour pressures versus carbon number.

After the vapour pressures are estimated for each hydrocarbon type, the pseudo-component or distillation cut vapour pressure is calculated as the sum product of the mole fraction by the vapour pressure of each subgroup.

3A.2. Effective carbon number (ECN) of pseudo components and distillation cuts. For the cases when the fluid molar composition is grouped into pseudo-components, we can refine the ECN of the group by applying a statistical average CN to each type of hydrocarbon in the group. For example, the  $C_{12}$  pseudo-component, defined by GC-MS analysis starting just after the retention time of *n*-undecane and ending with *n*-dodecane, includes hydrocarbons of lower carbon numbers than  $C_{12}$ . We apply the statistical average CNs for each type of hydrocarbon as they have been estimated by Snape et al. (2005) as follows. For the iso-hydrocarbons (branched open chain), we assign 0.4 CN lower than the current pseudo-component. For example, for the  $C_{12}$  pseudo-component we assign 11.6. For naphthenic hydrocarbons (one saturated ring), we assign 0.9 CN lower than the current pseudo-component. For example, for the C<sub>12</sub> pseudo-component we assign 11.1. For polynaphthenic hydrocarbons (two or more saturated rings), we assign 1.4 CN lower, for monoaromatic hydrocarbons 1 CN lower, and for polyaromatic hydrocarbons 1.7 lower than the current pseudo-component. The sum product of the molar fraction of each type of hydrocarbon in the pseudo-component by its assigned CN gives the ECN of the whole pseudo-component.

In the case of a distillation cut we linearly interpolate the mid-point boiling temperature of the cut with the boiling temperatures of the two normal hydrocarbons before and after the mid-point of the cut (Equation 3A.2):

$$ECN = N_i + \frac{T_{b \ mid} - T_{b \ Ni}}{T_{b \ N(i+1)} - T_{b \ Ni}}$$
(3A.2)

where  $N_i$  is the carbon number of the normal before the mid-point,  $T_{b mid}$  is the mid-point temperature,  $T_b$ <sub>Ni</sub> is the boiling temperature of the normal before the mid-point, and  $T_{b N(i+1)}$  is the boiling temperature of the normal after the mid-point.

3A.3. Boiling point of pseudo components and distillation cuts. The boiling point of the pseudo component is related to the ECN as described in Section 3A.2. Initially, we construct a graph of boiling points of normal hydrocarbons from the literature (Mackay et al., 2006) versus the normal hydrocarbons CN and fit a polynomial curve to the points. Then we calculate the boiling point of the pseudo-components by solving the polynomial Equation for the ECN that we calculated earlier.



Figure 3A.2. Example of estimating the boiling point of pseudo components. For the case of a distillation cut, the mid-point boiling temperature of the cut is used.

#### 3A.4. Average molar mass of pseudo components and distillation cuts.

In the cases where the breakdown of the fluid into different hydrocarbon types is available, such as normal-, iso-, naphthenic and aromatic hydrocarbons, we use the ECN of each hydrocarbon type to calculate the molecular mass of that type by the corresponding formula. In the previous example of pseudo-component C<sub>12</sub>, the ECN of the naphthenic hydrocarbons was equal to 11.1 and the molar mass (mm) of the subgroup will be given by the standard formula:

$$mm = n(C + 2H) \tag{3A.3}$$

where n is the ECN for naphthenic hydrocarbons, equal to 11.1 for pseudo-component  $C_{12}$ .

The same process is followed for all the subgroups of the pseudo-component by using the specific formulas for each hydrocarbon type. Once the molar masses of all subgroups are calculated the average

molar mass of the pseudo-component is given by the sum product of the molar fraction of each subgroup by its molar mass.

For the case of a distillation cut the same process is followed, with the only difference being the ECN of all subgroups of the specific cut are the same as discussed in Section 3A.2.

3A.5. Average molar volume of pseudo components and distillation cuts.

The molar volume of each pseudo group is calculated by following the Schotte method (Schotte, 1992) as it is the most accurate method available in the literature, and utilises the ECN for each hydrocarbon type as described earlier. Although the Schotte method was developed for individual compounds with integer numbers of carbons, we can conveniently use it for estimating the statistical average molar volume of each subgroup by using the ECN, which can be a non-integer number of carbons. The Schotte formula for calculating the molar volume  $V_b$  of a component at its boiling temperature, is given by Equation 3A.4:

$$V_b = 0.32 L (L-1) + \sum A_j G_j$$
 (3A.4)

where L is the chain length adjusted according to the Schotte rules, A<sub>j</sub> is the number of j groups, and G<sub>j</sub> is the volume that each j group occupies.

The rules for the calculation of hydrocarbon chains are as follows:

- Side groups with less than three C atoms are not counted.
- Side groups are counted as one-half of the number of C atoms if there are more than two in the side group.
- A ring is counted as one.
- A fused ring segment is not counted, e.g. L= 1 for naphthalene.

The group volumes that are relevant only to hydrocarbons are given in Table 3A.1.

j	Group	Gj	
1	CH <sub>4</sub>	37.97	
2	-CH₃	27.38	
3	-CH <sub>2</sub> -	19.02	
4	>CH-	12.79	
5	>C<	7.66	
6	=CH <sub>2</sub>	24.45	
7	=CH-	15.05	
8	=C<	7.77	
9	≡CH	20.91	
10	≡C-	9.89	
11	=C=	10.34	
12	=CH- in ring	15.52	
13	=C< in ring	9.12	
Increments for ring			
14	3- and 4-membered ring	5.05	
15	5- and 6-membered ring	3.33	
16	Fused ring segment	2.56	
17	Second 6-membered ring	7.12	

Table 3A.1. Each index j on Table 3A.1 identifies a specific hydrocarbon group with volume contribution G<sub>j</sub> used for the determination of the molar volume in Equation 3A.4. Hyphens indicate a bond with another carbon atom. Groups in a ring should be included individually. Additionally the ring volume as a whole is indicated at the bottom of the Table.

If information is available on the breakdown of the pseudo components or distillation cuts into normal, branched, naphthenic, polynaphthenic, aromatic and polyaromatic subgroups from GC-MS, we calculate separate molar volumes for each subgroup. We select a characteristic hydrocarbon for each subgroup that has the closest carbon number to the ECN of that subgroup and calculate the molar volume, and then we multiply that molar volume with the ratio of the ECN to the hydrocarbon's carbon number. For example in pseudo-tetradecane, the corresponding polyaromatic has 12.3 ECN. We select a dimethylnaphthalene with 12 carbon atoms, calculate the molar volume with the Schotte method equal

to 190.25, and multiply by 12.3/12 to get an estimated molar volume of 195.01 for the polyaromatic subgroup.

If this information is not available we recommend the use of the statistical averages of 56.2% by mass alkanes and 27.5% by mass aromatic hydrocarbons, as has been established from the liquid column separation of 113 crude oils from variable locations around the world (ETC, 2015). Since there are no polyaromatic hydrocarbons below the molecular weight of pseudo-dodecane, the molar volume of the aromatic subgroup will be based only on monoaromatics. For pseudo-dodecane and high molecular weights, where there is no information on the mono-polyaromatic distribution an average molar volume of the two is assigned.

The molar volume of the pseudo-component is then calculated as the sum-product of the molar fraction of each subgroup by its molar volume.

#### 3A.6. Density of pseudo components and distillation cuts.

The density is calculated by utilising the molar volume and the molar mass of pseudo components or distillation cuts. Since the molar volume calculated by the Schotte method (Schotte, 1992) for each component refers to the boiling temperature, we need to convert this density to the environmental temperature. We have developed a simple formula that fits with high accuracy the boiling points for the complete range of volatile hydrocarbons, alkanes and aromatics. The conversion is given in Equation 3A.5:

$$\rho_i = \frac{mm_i}{V_{bi}} (1 + A \,\Delta T) \qquad (3A.5)$$

where mm<sub>i</sub> and V<sub>bi</sub> are the molar mass and the molar volume of the pseudo-component (i), A is the contraction factor equal to 1.354 x  $10^{-3}$ , which was calculated by fitting the literature data for the hydrocarbon range from hexane to eicosane, and  $\Delta T$  is the temperature difference between the boiling

point of the pseudo-component or distillation cut to the environmental temperature that the evaporation takes place in Kelvin.

Table 3A.2 presents the calculated densities using Equation 3A.5 and the experimentally measured densities from the literature (Mackay et al., 2006) for the hydrocarbons in the range of interest.

	Density @ 20°C		
Compound	calculated	experimental	Error%
benzene	0.876	0.877	-0.1
1,4-dimethylnaphthalene	1.028	1.017	1.1
n-hexane	0.654	0.659	-0.8
n-heptane	0.679	0.684	-0.8
n-octane	0.699	0.703	-0.5
n-nonane	0.716	0.718	-0.3
n-decane	0.730	0.730	-0.1
n-undecane	0.741	0.740	0.1
n-dodecane	0.751	0.749	0.2
n-tridecane	0.759	0.757	0.3
n-tetradecane	0.765	0.763	0.3
n-pentadecane	0.771	0.768	0.3
n-hexadecane	0.775	0.773	0.2
n-heptadecane	0.778	0.778	0.0
n-octadecane	0.780	0.782	-0.2
n-nonadecane	0.783	0.785	-0.4
n-eicosane	0.784	0.789	-0.5

Table 3A.2. Comparison of calculated densities at 20°C by utilising the Schotte molar volume method and Equation 3A.5 with measured experimental densities from the literature (Mackay et al., 2006) and the corresponding error.

3A.7. Gas phase diffusion coefficients calculation.

The gas phase diffusion coefficients for the (pseudo) components are calculated by utilising the Lennard-

Jones collision integrals and the interpolation Equation 3A.6 developed by Kim and Monroe (2014).

$$\Omega^{(l,s)} = A^{(l,s)} + \sum_{k=1}^{6} \left[ \frac{B_k^{(l,s)}}{(T^*)^k} + C_k^{(l,s)} (\ln T^*)^k \right]$$
(3A.6)

with

$$T^* = \frac{T}{\varepsilon_{AB}/k}$$
 and  $\varepsilon_{AB}/k = 1.15 \sqrt{T_{B(A)} T_{B(B)}}$ 

where  $A^{(l,s)}$ ,  $B_k^{(l,s)}$ ,  $C_k^{(l,s)}$  are experimental coefficients defined by Kim and Monroe (2014). The accuracy of this method is within 0.007%.

Then the diffusion coefficient in air can be calculated with the Wilke and Lee (1955) Equation 3A.7:

$$D_{AB} = \left[ 3.03 - \left( 0.98 / M_{AB}^{1/2} \right) \right] 10^{-3} \frac{T^{3/2}}{P M_{AB}^{1/2} \sigma_{AB}^2 \Omega^{(l,s)}}$$
(3A.7)

with

$$M_{AB} = \frac{2}{1/M_A + 1/M_B}$$

and

$$\sigma_{AB} = \frac{1.18(V_A + V_B)}{2} = 0.59(V_A + V_B)$$

where  $M_A$  is the molar mass of the air,  $M_B$  is the molar mass of the pseudo-component,  $V_A$  is the molar volume of the air,  $V_B$  is the molar volume of the pseudo-component, T is the atmospheric temperature (Kelvin), and P is the pressure (Pascal).

3A.8. Liquid phase diffusion coefficients calculation.

The diffusion coefficients of each component in a mixture are estimated by employing the following relationship between the solvent viscosity and the solute's diffusion coefficient (Funazukuri et al., 1994):

$$\frac{D_{12}}{T} = a \,\eta^{\beta} \qquad (3A.8)$$

where  $D_{12}$  is the binary diffusion coefficient of solute in the solvent,  $\eta$  = the dynamic viscosity of the solvent, and  $\alpha$ ,  $\beta$  = experimentally determined constants.

Funazukuri et al. (1994) experimented with a variety of organic solvents and solutes, mainly hydrocarbons, and correlated the constants  $\alpha$  and  $\beta$  to the solute's molar volume V<sub>b</sub> at its normal boiling point:

$$\alpha = 3.718 \times 10^{-19} V_b^{-1.246}$$
(3A.9)  
$$\beta = -1.981 V_b^{0.1072}$$
(3A.10)

In order to solve Equation 3A.8 we need to estimate the initial viscosity of the fluid, and the viscosity after every time step since the evaporation process affects this value. To accomplish this we have developed a simple and effective correlation based on Walther's Equation (1931).

$$\ln\left[\ln(v+0.8)\right] = a_1 + a_2\ln(T) \tag{3A.11}$$

where v is the kinematic viscosity (cSt), T is the temperature (K), and  $\alpha_1$  and  $\alpha_2$  are experimentally defined factors.

When a single viscosity measurement  $v_0$  is available at a specific temperature, the viscosity at a different temperature can be estimated by replacing  $\alpha_1$  with the double logarithm of the known viscosity measurement. In this case Equation 3A.11 becomes:

$$\ln\left[\ln(\nu + 0.8)\right] = \ln\left[\ln(\nu_o + 0.8)\right] + a_2 \ln\left(\frac{T}{T_o}\right)$$
(3A.12)

Kotzakoulakis and George (in prep., submitted) have correlated the values of factors  $\alpha_1$  and  $\alpha_2$  to the 50% mid-boiling point T<sub>b</sub> and the specific gravity (SG) of a crude oil, based on the data made available from the Environment Canada oil properties database (ETC, 2015). The database includes 137 fully characterised crude oils with 254 viscosity measurements at different temperatures. The resulting correlations for the two factors are shown below:

$$a_1 = 14.69T_b^{0.0684}SG^{0.267} \tag{3A.13}$$

$$a_2 = 3.682$$
 (3A. 14)

The final correlation takes the form:

$$\ln\left[\ln(\nu+0.8)\right] = 14.69T_b^{0.0684}SG^{0.267} + 3.682\ln(T)$$
(3A.15)

Using the correlation in Equation 3A.15 we can estimate the viscosity of the mixture, and then Equation 3A.8 is used to produce the diffusion coefficients for each component.

The calculations presented in this appendix can be used after each time step to update the model as the evaporation simulation progresses.

# A general viscosity correlation for crude oils

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## Statement of authors' contribution

This Chapter is an article in review with *Fluid Phase Equilibria*. This paper has been formatted to conform to the font and referencing style adopted in this thesis. Sections, Figures, Tables and Equations included within the text are prefixed with the chapter number.

I am the primary author (95% of the effort). I conceptualised and developed the viscosity correlation. I verified the correlation predictions and calculated the statistical deviations. I wrote and designed the structure of the paper. The co-author carefully reviewed and provided feedback and valuable refinements on the final version of the manuscript, and approved it for the submission (5%). Neither this manuscript nor one with similar content under our authorship has been published or is being considered for publication elsewhere, except as described above.

#### Abstract

A general correlation has been developed for the prediction of the kinematic viscosity of crude oils based on the Walther Equation (1931). The correlation was developed in order to improve on the accuracy of existing correlations and to assist the creation of oil spill weathering models, reservoir models and other models where the knowledge of viscosity of uncharacterised crude oils is required. The data used to build the correlation consist of measurements from 137 crude oils from various locations around the world, with 254 viscosity measurements taken at two temperatures, 0°C and 15°C, resulting in kinematic viscosity values ranging from 2 cSt to 9,000,000 cSt. The correlation requires only the 50% weight boiling point temperature (T<sub>b</sub>) and the specific gravity (SG) of the oil as inputs. When compared to the best performing published correlations that require the same inputs on the same set of crude oils, the new correlation outperforms them, with an average absolute deviation (AAD) of 52.9%, compared to 101% AAD and 218% AAD for the Aboul-Seoud and Moharam (1999) and Mehrotra (1995) correlations, respectively.

## 4.1 Introduction

The viscosity of a crude oil is the property that describes its resistance to movement, mainly due to collisions, electrostatic forces and hydrogen bonding between its molecules that are moving in different velocities and directions (Mehrotra et al., 1996). It is an important property used in reservoir modelling (Orbey and Sandler, 1993), design of production and transportation equipment, as well as in the design of processing facilities in crude oil refineries (Mendes et al., 2005). Additionally, in the case of an accidental release of crude oil during its production or transportation, viscosity plays an important role on the impact and the fate of the oil spill and consequently on the response measures. Modelling the

weathering processes of an oil spill requires knowledge of the viscosity of the fluid. As weathering progresses, the composition as well as the physical properties of the fluid, including viscosity, are changing constantly and a method is required to estimate viscosity since initial values are no longer valid. The incentive of this study was to develop an accurate method of estimating crude oil viscosity that would provide the necessary input to such oil spill weathering model. Crude oils are complex mixtures consisting of thousands of components of different type such as aliphatic, naphthenic and aromatic hydrocarbons, as well as other polar compounds containing heteroatoms (nitrogen, sulphur and oxygen). Therefore a purely theoretical prediction of crude oil viscosity is extremely difficult.

There are numerous published predictive models and correlations for the estimation of the liquid (kinematic) viscosity of crude oils and hydrocarbon mixtures. Typically they can be categorised into two groups, theoretical models or empirical correlations (Mehrotra et al., 1996). Theoretical models are usually more accurate but they are more complex and require a better characterisation of the oil including parameters such as critical properties, chemical composition, acentric factor or other similar properties which in many cases are not available. Empirical correlations are typically simpler and only require a few basic parameters such as mid-boiling point temperature and specific gravity of the oil, or alternatively a single viscosity measurement, in order to extrapolate the viscosity to a different temperature. Most of the empirical correlations are based in some form on one of the three Equations developed by Vogel (1921), Walther (1931) or Andrade (1934), respectively. Aboul-Seoud and Moharam (1999) have summarised the most popular correlations with their respective accuracies in predicting the kinematic viscosity of unknown oil fractions, as shown in Table 4.1.

Correlation	Equation type	Input data	% AAD
Amin and Madox (1980)	Andrade (1934)	T <sub>b</sub> , SG	37.22
Beg et al. (1988)	Andrade (1934)	T <sub>b</sub> , SG	7.40
Dutt (1990)	Vogel (1921)	T <sub>b</sub>	6.31
Mehrotra (1995)	Walther (1931)	Ть	5.00
Aboul-Seoud and Moharam (1999)	Walther (1931)	T <sub>b</sub> , SG	3.05
Puttagunta et al. (1992)	Walther (1931)	v @ 37.8°C	1.59
Aboul-Seoud and Moharam (1999)	Walther (1931)	ν	1.47

Table 4.1. Comparison of frequently used empirical viscosity correlations (Aboul-Seoud and Moharam, 1999). Where  $T_b = 50\%$  weight boiling point temperature; SG = specific gravity; v = viscosity; AAD = average absolute deviation.

The comparison made by Aboul-Seoud and Moharam (1999) was based on 45 undefined fractions of 13 crude oils from which 316 viscosity measurements were available at different temperatures. It is evident that the correlations based on the Walther Equation (1931) are the best performers, based on their lower average absolute deviation (AAD). The Aboul-Seoud and Moharam (1999) and Mehrotra (1995) correlations are the best when no viscosity measurement is available, while the Aboul-Seoud and Moharam (1999) correlation is the best when a single viscosity measurement is available. Additionally the latter correlation is more flexible since it does not require the viscosity measurement to be taken at a specific temperature, whereas the Puttagunta et al. (1992) correlation requires the viscosity to be measured specifically at 37.8°C.

While these correlation results are apparently accurate with 5% or less AAD, they are only referring to narrow petroleum fractions of 83°C to 125°C boiling range (Beg et al., 1988). When these correlations

were tested during this study against 254 viscosity measurements from 137 crude oils containing a full range of components from different locations around the world their performance was significantly lower, at 101% AAD for the Aboul-Seoud and Moharam (1999) correlation, and 218% AAD for the Mehrotra (1995) correlation. The objective of this study was to develop or improve the existing correlations, without increasing the need for more detailed input parameters, so that a better predictive tool was available, especially for whole crude oils.

### 4.2 Data and methodology

#### 4.2.1 Data

The data used in this study were obtained from the Environment and Climate Change Canada (Emergencies Science and Technology Division) oil properties database (ETC, 2015). The database contains the properties of around 450 oils and petroleum products.

Due to the requirements of this study only the oils with available distillation, density and viscosity data were used. This amounted to a total of 137 crude oils from multiple locations around the world. Only petroleum crude oils and petroleum products were used in this study, which excluded vegetable, synthetic, catalytic and other types of oils available in the database (ETC, 2015). Crude oils with non-Newtonian fluid behaviour were also excluded from this study since their apparent viscosity is dependent on the applied shear rate, and this would have introduced errors in the correlation. Experimental viscosity data for these oils were available at two temperatures, 0°C and 15°C. The range of each property of the qualified set of crude oils is summarised in Table 4.2.

Ranges of oil properties	
No of crude oils	137
Average $T_b$ range (K)	357 – 884
Specific Gravity range	0.806 -1.024
Kinematic viscosity range (cSt)	2.5 - 8,800,000

Table 4.2. Summary of the range of crude oil properties. Where  $T_b = 50\%$  weight boiling point temperature.

A subset of 12 crude oils with 20 viscosity measurements, covering the whole viscosity range for two temperatures (0°C and 15°C), was excluded from the development of the correlation so that the subset could be used as unknown crude oil samples for the verification of the efficiency of the new correlation. The methodology that was followed in this study is presented below.

## 4.2.2 Viscosity

Puttagunta et al. (1992) and Aboul-Seoud and Moharam (1999) have shown that the effect of temperature on viscosity can be correlated very accurately by Walther's Equation:

$$\ln[\ln(\nu + 0.8)] = a_1 + a_2 \ln(T) \tag{4.1}$$

When a single viscosity measurement is available at a specific temperature, the viscosity at a different temperature can be estimated by replacing  $a_1$  with the double logarithm of the known viscosity (Aboul-Seoud and Moharam, 1999). In this case the Equation 4.1 becomes:

$$\ln\left[\ln(v+0.8)\right] = \ln[\ln(v_o+0.8)] + a_2 \ln(T/T_o)$$
(4.2)

Using a complete set of known viscosities, Aboul-Seoud and Moharam (1999) estimated the value of  $a_2$  to be equal to -3.7, predicted with an AAD equal to 1.47%. This factor has also been confirmed in the current study, with a small adjustment to be equal to -3.682 as discussed below in the results Section.

All previous studies presented in Table 4.1 that do not require a viscosity measurement, require the 50% mid-boiling point ( $T_b$ ) of the complete crude oil as an input to the viscosity correlation. In this study we have tested the mid-boiling point and the weight average  $T_b$  of the crude oil, since the latter describes the skewed distribution of boiling points in a crude oil better than the mid-point. The calculation of the weight average requires a detailed description of the complete distillation curve to be known, and preferably the full True Boiling Point (TBP) distillation curve. Since these data are rarely available we describe a method in the Appendix 4A for constructing the complete distillation curve from the partial distillation data that are usually available. The same technique can be used to find the 50% mid-boiling point for heavy oils when the distillation have stopped before the 50% point.

#### 4.2.3 Specific Gravity

The next input parameter in the correlation presented in this study is the specific gravity. Again a different approach have been adopted for this input comparing to the previous developed correlations (Aboul-Seoud and Moharam, 1999; Amin and Maddox, 1980; Mehrotra, 1995). Instead of entering the specific gravity at the temperature of the predicted viscosity, the specific gravity at a constant reference temperature is used, specifically at 15°C for both oil and water. The reference water density at 15°C has been taken equal to 0.999099 g/cm<sup>3</sup>. This approach has been selected because the role of specific gravity is to characterise the oil in combination with the T<sub>b</sub>. So for oils with the same average boiling temperature T<sub>b</sub> but different amounts of aliphatic, aromatic and polar compounds, the difference in specific gravity is correlated to this difference in composition. If the specific gravity input of the same oil is changed for different temperatures then this correlations fails, and the correlation factors cannot be maintained at a constant value. The effect of the temperature is already described in the correlation by the term a<sub>2</sub>ln(T) of Equation 4.1. As discussed in the results Section, density change due to a temperature change has a negative effect on the efficiency of the correlation.

The second deviation from previous correlation methods that is related to the way specific gravity is used is in the addition of a separate exponent to describe the degree of influence of the density. Aboul-Seoud and Moharam (1999) correlation added the density as an additional input in order to improve the accuracy of the previous correlations, but kept it under the same exponent as the 50% mid-point T<sub>b</sub>. Since T<sub>b</sub> and specific gravity are two different measures we expect the degree of influence of specific gravity to be significantly different to that of T<sub>b</sub>, so an individual exponent was assigned to each input parameter. Although an extra factor was added to the correlation, the total number of factors was kept the same by eliminating an extra factor that existed in both previous Walther-type correlations (Aboul-Seoud and Moharam, 1999; Mehrotra, 1995).

Another point that makes the new correlation described here significantly different is that it has been fitted directly to a large set of viscosity data from whole crude oils. Both the Aboul-Seoud and Moharam (1999) and Mehrotra (1995) correlations that use Walther Equation (1931) have been fit to narrow distillation cuts originating from a small number of crude oils, and although they predict very accurately those cuts, when tested on whole oils the variation is much larger. For this study we had access to a large amount of crude oil viscosity data covering a wide range of viscosities, so the new correlation was developed on the actual crude oils.

## 4.3 Results and discussion

Initially, the temperature factor  $a_2$  was determined by fitting Equation 4.2 to the full set of crude oils with viscosity measurements at two different temperatures, 15°C and 0°C (Figure 4.1). The best fit for the temperature factor  $a_2$  was calculated by minimising the sum of squared errors with the iterative solver provided in LibreOffice. The temperature factor  $a_2$  was found to be equal to -3.682, with a Pearson's correlation factor ( $R^2$ ) equal to 0.996.



Figure 4.1. Estimation of the temperature factor  $a_2$  from measured viscosities at two temperatures. The predicted values at 0° were obtained from Equation 4.2 by using the measured viscosity at 15°C and calculating the value of  $a_2$  that best fits the measured viscosity at 0°C.

Next, complete distillation curves were constructed for the 137 crude oils in the database (ETC, 2015) with available distillation data. The Riazi distribution model (1989) (Appendix 4A) was used to fit the distillation data of all the crude oils with high degree of accuracy. The average Pearson's R<sup>2</sup> correlation factor was found to be equal to 0.988, and the standard deviation was 0.011 (Table 4.3).

Distillation data details	
Number of crude oils	137
Weight average T <sub>b</sub> range (K)	357 - 884
50% $T_b$ range (K)	358 - 873
Average distillation curve correlation (R <sup>2</sup> )	0.988
Correlation Standard Deviation (SD)	0.0112

Table 4.3. Summary of weight average  $T_b$  and 50%  $T_b$  ranges for the 137 crude oils.

The calculated average  $T_b$  and 50% mid-point  $T_b$  for each of the 137 crude oils together with the corresponding specific gravities were used as input parameters to Walther's Equation 4.1 in order to estimate the parameter  $a_1$  and fit the 254 viscosity measurements from these crude oils at two different temperatures, 15°C and 0°C. The hypothesis that the weight average  $T_b$  would better describe the boiling point distribution of the crude oil was not confirmed, with the AAD for the weight average  $T_b$  equal to 63.8%, in comparison to 55.6% AAD for the 50% mid-point  $T_b$ . Using the combination of weight average  $T_b$  and mid-point  $T_b$  by taking the mean value of the two resulted in a better accuracy of 58.8% AAD than weight average  $T_b$  alone, but still not better than the mid-point  $T_b$  alone. Still, the results are very close and the weight average  $T_b$  can be used to verify the prediction of the mid-point  $T_b$ . Additionally, the knowledge of the full distillation range with the Riazi distribution model (1989) can be used to calculate the 50% mid-point  $T_b$  for heavy oils when the distillation data do not reach the 50% mark.

Next we examined the effect of having a constant reference temperature for the specific gravity (method 1) in comparison to measuring the specific gravity at the viscosity prediction temperature (method 2). When we compared the results from two different temperatures, at 15°C and 0°C, method 1 provided more accurate and evenly distributed results at both temperatures with a 5% lower AAD, while having 2% and 10% deviation between the overestimated and underestimated samples for the two temperatures. Method 2 showed a 5% higher AAD, while having 30% higher deviation for the underestimated samples at 15°C and 26% higher deviation for the overestimated samples at 0°C. In other words, method 2 tends to always underestimate the viscosity at higher temperatures and overestimate the viscosity at lower temperatures. The final form of Walther's Equation 4.1 that gives the best results is obtained by following the constant reference temperature for SG (method 1) and is shown below by Equations 4.3 and 4.4.

The resulting expression for the parameter a<sub>1</sub> is shown by 4.3:

$$a_1 = 14.69T_b^{0.0684} SG^{0.267} \tag{4.3}$$

The complete correlation takes the form:

$$\ln\left[\ln(\nu+0.8)\right] = 14.69T_b^{0.0684}SG^{0.267} - 3.682\ln(T) \tag{4.4}$$

Where:

T<sub>b</sub> = the 50% mid-boiling point;

SG = the specific gravity at 15°C for both oil and water densities.

If the mean of weight average  $T_b$  and mid-point  $T_b$  is used then the term  $a_1$  is 14.85Tb<sup>0.0667</sup>SG<sup>0.274</sup>. If the weight average  $T_b$  alone is used then the term  $a_1$  is 15.46Tb<sup>0.0607</sup>SG<sup>0.288</sup>.

The comparative results on the complete set of crude oils (Table 4.4) show that the worst performer is Mehrotra (1995) correlation with an AAD equal to 218%. However, this correlation is the simpler one since

it only requires one input value, the 50%  $T_b$  of the oil. Aboul-Seoud and Moharam (1999) correlation exhibits more than double the accuracy with an AAD equal to 101%, but requires both the 50% mid-point  $T_b$  and the specific gravity as inputs. The correlation developed in this study based on both the 50% midpoint  $T_b$  and the specific gravity as inputs exhibits 4 times and 2 times respectively the accuracy of the two former correlations, with an AAD equal to 55.6%. For the case that only the mid-boiling point  $T_b$  is available we tried to improve the fit of Mehrotra (1995) correlation using the complete set of data and succeeded in reducing the AAD by 19% from 218% to 199%, or approximately 10% of the total error as shown in Table 4.4. In this case Mehrotra (1995) correlation becomes:

$$\ln[\ln(\nu + 0.8)] = 7.014T_b^{0.178} - 3.682\ln(T)$$
(8)

Prediction temperature °C:	15	0	Both
Number of crude oils:	136	118	254
	% AAD	% AAD	% AAD
Inputs: T <sub>b</sub> , SG			
Aboul-Seoud and Moharam (1999)	67.4	141	101
This work	46.6	66.3	55.6
<u>Input: T<sub>b</sub> only</u>			
Mehrotra (1995)	145	306	218
This work	136	274	199

Table 4.4. Summary of the statistics of the three correlations.

Figures 4.2A and 4.2B are a graphical comparison between the two correlations that require both  $T_b$  and specific gravity as inputs, and Figures 4.2C and 4.2D are a comparison between the correlations with only  $T_b$  as the input. The central blue diagonal line indicates the match between predicted and measured

values, and the two red external lines indicate the position of 10 times higher or lower values than the measured one. In both cases the improvement in population density and closer distribution around the central line is apparent when comparing the previous correlations (Aboul-Seoud and Moharam, 1999; Mehrotra, 1995) with this work. Additionally, comparison of Figures 4.2B and 4.2D clearly demonstrates the improved accuracy of the prediction when both  $T_b$  and specific gravity as used as inputs.

Predictions of the three correlations, (Aboul-Seoud and Moharam, 1999; Mehrotra, 1995) and this work, to the subset of 12 completely unknown crude oils from ETC (2015) with 20 viscosity measurements (Section 4.2.1) are shown in Figure 4.3. As described earlier, Mehrotra (1995) correlation is using T<sub>b</sub> only as an input, while Aboul-Seoud and Moharam (1999) and the present work use both the T<sub>b</sub> and SG as inputs. By unknown we mean that these crude oils have not been used during the development of the correlation, and there is no advantage for the correlation of the present study against the other two. The graph shows that the same trend exists as for the larger set of samples. The predictions of the correlation from this work are more evenly distributed and closer to the central line, with an AAD of 34.7%, while the Aboul Seoud and Moharam (1999) and the Mehrotra (1995) correlations have much higher AADs (127% and 214%, respectively). These results on the 12 unknown samples confirm the accuracy that was observed on the previous large set of crude oils.


Figure 4.2 Predicted versus measured viscosity, for (A) and (B) correlations with  $T_b$  and SG inputs, and (C) and (D) correlations with Tb only input. Correlations are for (A) Aboul-Seoud and Moharam (1999), (C) Mehrotra (1995), and (B and D) this work.



Figure 4.3. Comparison of the three correlations on the subset of 12 unknown crude oils. The AADs were found to be equal to 214%, 127% and 34.7% for Mehrotra (1995), Aboul-Seoud & Moharam (1999) and this work, respectively.

## 4.4 Conclusions

A new simple and effective general correlation for the prediction of crude oil viscosity has been successfully developed. When compared to the previously published Walther Equation-type correlations the new correlation provides the following advantages:

- The new correlation provides 4 times better predictions than the Mehrotra (1995) correlation and 2 times better predictions than the Aboul-Seoud and Moharam (1999) correlation, based on 254 viscosity measurements of 137 crude oils from a variety of locations around the world with viscosities ranging from 2 cSt to 8,800,000 cSt.
- The new correlation has applied a different influence factor to the boiling point and specific gravity term by assigning a separate exponent to the specific gravity. At the same time the number of inputs and complexity of the correlation has been kept at the previous level by eliminating one factor that existed in the previous correlations that was found to not be necessary.
- The new correlation has eliminated the need to measure the specific gravity of the crude oil at the temperature of the viscosity prediction, by always using the reference specific gravity of the crude oil at 15°C that is usually already available.
- In this work the Mehrotra (1995) correlation was modified and its accuracy was improved by 10% for the cases when only the boiling point is available.

The present study also describes an easy and effective method based on the Riazi distribution model (1989) to estimate the mid-boiling point and the average boiling point of crude oils for cases where only incomplete distillation data are available.

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## Appendix 4A The Riazi distribution model

Riazi (1989; 1997) developed a distribution model for multiple properties of the uncharacterised fractions of oils. He tested the new model on 68 fully characterised oils from various locations and found the AAD for the boiling point prediction equal to 0.56%. Nedelchev et al. (2011) verified the Riazi distribution model for the boiling point properties of 33 crude oils where detailed true boiling point distillation data were available and found an excellent fit to the experimental data, with a correlation factor R<sup>2</sup> over 0.99. The Riazi distribution model is described by the Equations 4A.1 and 4A.2:

$$\frac{T_i - T_o}{T_o} = \left(\frac{A}{B} \ln\left(\frac{1}{1 - x_i}\right)\right)^{1/B}$$
(4A.1)

The linear form of Equation 4A.1 is:

$$Y = C_1 + C_2 X$$
 where  $Y = \ln\left(\frac{T_i - T_o}{T_o}\right)$  and  $X = \ln\ln\left(\frac{1}{1 - x_i}\right)$  (4A.2)

Where:

T<sub>o</sub> = initial boiling point in Kelvin;

T<sub>i</sub> = temperature at which i percent is distilled;

x<sub>i</sub> = volume or weight fraction of distillate;

A, B = constants to be determined from experimental data;

 $C_1 = intercept;$ 

 $C_2 = slope$ .

By plotting the terms Y and X from available partial distillation data the slope  $(C_2)$  and the intercept  $(C_1)$  can be determined.

The constants A and B are calculated from Equations 4A.3:

$$B = \frac{1}{C_2} \qquad A = Be^{C_1 B} \qquad (4A.3)$$

Then Equation 4A.1 can be solved to produce the complete distillation curve from which the missing weight average Tb of the distillation residue can be calculated. An example of the procedure showing the partial distillation data for the Sockeye crude oil, which is available on the Environment and Climate Change Canada oil properties database (ETC, 2015), is given in Table 4A.1.

Temperature	wt%
°C	distillate
40	0.4
60	0.4
80	1.5
100	3.3
120	5.1
140	7.1
160	9.2
180	11.3
200	13.2
250	18.9
300	24.7
350	30.9
400	36.8
450	43.3
500	50.1
550	57.3
600	63.5
650	69.2

Table 4A.1. Experimental distillation data for the Sockeye crude oil (ETC, 2015).

In Figure 4A.1 the terms Y and X from Equation 4A.2 are cross-plotted for the Sockeye crude oil (ETC, 2015), and the slope  $C_2 = 0.6061$  and intercept  $C_1 = 0.7001$  were established by the least sum of squared errors.



Figure 4A.1. Boiling point distribution of Sockeye crude oil, fitted using the Riazi distribution model with a correlation factor of R<sup>2</sup>=0.999.

The complete distillation curve can then be constructed by solving the Equations 4A.3 and 4A.1 for the full boiling range of Sockeye crude oil, as shown in Figure 4A.2, and the weight average  $T_b$  is determined from the relationship:

$$T_{b \ average} = \sum_{i=1}^{n} \Delta x_i \times T_{bi} \tag{4A.4}$$

$$\Delta x_i = x_i - x_{i-1} \tag{4A.5}$$

Where:

 $T_{bi}$  = mid-point boiling temperature of mass fraction  $\Delta x_i$ . For example, if  $\Delta x_{90} = x_{90} - x_{89}$ , then  $T_{bi}$  is the result of Equation 4A.1 for  $x_{89.5} = 0.895$ ;

x<sub>i</sub> = cumulative mass fraction i;

n = number of mass fractions.

By splitting the whole oil into 100 equal mass fractions of 1% increment, each  $\Delta x_i$  is equal to 1%. In order to calculate the average boiling point of, for example, the Sockeye crude oil distillation residue where the distillation is stopped at 69% mass or x = 0.69, we need to solve for:

$$T_{b \ residue} = \frac{\sum_{i=69}^{100} \Delta x_i \times T_{bi}}{\sum_{i=69}^{100} \Delta x_i}$$
(4A.6)

Finally the average of the whole crude oil will be given by the Equation:

$$T_{b average} = x_{dist}T_{b dist} + x_{residue}T_{b residue}$$

*e.g.*  $0.69T_{b \ dist} + 0.31T_{b \ residue}$  for Sockeye crude oil (4A.7)

Where:

x<sub>dist</sub> = the mass fraction of the distillate;

 $T_{b \text{ dist}}$  = the average boiling point of the distillate, calculated with Equation 4A.6 for x<sub>i</sub> up to 0.69 directly from the distillation data. Naturally, there will not be 69  $\Delta x$  fractions, but as many as the distillation data provide.



Figure 4A.2. The complete TBP distillation curve of Sockeye crude oil, estimated using the Riazi distribution model.

# Comparative study of the effectiveness of 6 dispersants under polar conditions on the fuels used in the Australian Antarctic Territory

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## Statement of authors' contribution

This Chapter is to be submitted soon to Marine Pollution Bulletin. This paper has been formatted to conform to the font and referencing style adopted in this thesis. Figures and Tables included within the text are prefixed with the chapter number.

I am the primary author (95% of the effort). I designed and performed the dispersion experiments. I performed the analyses of the samples from the aforementioned experiments on the gas chromatograph coupled with flame ionisation detector and mass spectrometer detector. I processed and interpreted all

the data derived from the measurements. I wrote and designed the structure of the paper. All co-authors carefully reviewed and provided feedback and valuable refinements on the final version of the manuscript, and approved it for submission and publication. Neither this manuscript nor one with similar content under our authorship has been published or is being considered for publication elsewhere, except as described above.

## Abstract

Shipping activity has been increasing continuously in Antarctica over the last few years. During the 2014/2015 summer season 191 tourist expeditions visited Antarctica carrying 36,702 passengers, in addition to illegal fishing vessels and shipping related to research station support operations (IAATO, 2015). Recent incidents such as the stranding of Akademik Shokalskiy on 25 December 2013, the grounding of the MS Nordkapp at Deception Island on 30 January 2007, and the fire aboard the Nisshin Maru in February 2007, which was carrying approximately 1000 tonnes of heavy fuel oil, have highlighted the risk of a major fuel spill in Antarctic waters. Currently, much needed data on the behaviour of these fuels in the Antarctic marine environment in order to plan response measures are missing. In this study we examine the feasibility of using dispersants to combat a possible fuel spill in the Antarctic waters for the fuel types used in the Australian Antarctic Territory (AAT) and we extensively review the fuel properties and environmental conditions that affect dispersibility. A suite of six dispersants was tested in Antarctic and sub-Antarctic water temperatures, 0°C and 5°C respectively, against two fuels, the Marine Gas Oil (MGO) and the Intermediate Fuel Oil 180 (IFO-180), and a Kuwait crude oil. The results show that MGO can be successfully treated with dispersants at both temperatures, whereas the IFO-180 can only be partially dispersed in sub-Antarctic waters while it is still unweathered. The order of efficiency of the six dispersants has been identified for each type of fuel. The dispersibility of the IFO-180 and the Kuwait crude oil have been studied over an extended range of temperatures, from 0°C to 22°C in order to investigate the effect of temperature on the efficiency of dispersants and to identify possible trends. Finally, during this study it has been observed that the order of efficiency of the six dispersants varies with temperatures when applied to the same type of fuel. This finding highlights the need for assessing the efficiency of the dispersants at each temperature of interest, since each dispersant is affected to a different degree by a temperature change.

#### 5.1 Introduction.

In recent years, increased activity has been observed in polar and sub-polar regions. The melting of the Arctic ice cap as a result of climate change has made large parts of the Arctic accessible to marine vessels. The ever increasing demand for energy has also made these regions accessible for petroleum exploration, increasing the risk of an oil spill happening in these cold waters. Similarly, in recent years an increase in marine traffic has been observed in Antarctic waters, mainly due to the large number of tourists visiting Antarctica, as well as fishing and research vessels. In addition to the increased risk of a spill happening in these cold waters, the advancing of technology has made possible petroleum exploration in deep waters. The water temperature of the oceans, below the shallowest 100 m, drops fast to a minimum of around 4°C below 1000 m depth. This temperature is then maintained relatively constant due to the maximum density of water at 3.98°C. The risk of an accident in deep subsea petroleum wells was highlighted by the catastrophic failure of the blowout preventer of the Deepwater Horizon oilwell at 1500 m depth in the Gulf of Mexico in April 2010. During the emergency response effort, underwater dispersants injections were applied at the wellhead at 1500 m depth and at 4°C water temperature in order to prevent the leaked oil from reaching the water surface and the shoreline of the Gulf of Mexico. This led to the creation of large plumes that were neutrally buoyant and trapped at around 1100 m depth (Reddy et al., 2012). An unprecedented 4.9 million barrels of oil leaked into the Gulf of Mexico, and 2.9 million litres of dispersant were injected at the wellhead deep underwater with uncertain efficiency (Kujawinski et al., 2011; Peterson et al., 2012). This new scenario of underwater spill treatment with dispersants at cold temperatures further highlights the need for studying the efficiency of dispersants in cold waters.

Recent incidents in the Antarctic including the stranding of Akademik Shokalskiy on 25 December 2013, the grounding of the MS Nordkapp at Deception Island on 30 January 2007, and the fire aboard the Nisshin Maru in February 2007, which was carrying approximately 1000 tonnes of heavy fuel oil, have highlighted the risk of a major oil spill relating to a shipping incident in Antarctic waters. Shipping traffic in the Antarctic Treaty Area is growing rapidly, with 191 officially reported visits by tourist vessels in the 2014/2015 season (IAATO, 2015), in addition to voyages by national research programs and both legal and illegal fishing vessels. The risk of such spills occurring is clearly identified, particularly during fuel transfers from ship to shore and research station resupply activities. Despite this risk, the weathering and the fate of fuel spills in the Antarctic marine environment is largely unknown. Data regarding the behaviour of fuels is required in order to plan the response to an accidental fuel spill in Antarctica. The three main fuels that are used in the Australian Antarctic Territory are the Special Antarctic Blend (SAB) diesel, the Marine Gas Oil (MGO) and the Intermediate Fuel Oil 180 (IFO-180). The use of dispersants to treat a fuel spill in polar or sub-polar conditions could provide an additional response measure. There is contradictory information in regards to the efficiency of dispersants, especially on heavy fuels such as the IFO-180. Some national response guidelines characterise heavy fuels such as the IFO-180 as nondispersible (ESD, 1999). However, field trials conducted in the North Sea (Colcomb et al., 2005; Lunel, 1995; Lunel et al., 1997) have indicated that it is possible to partially disperse Medium Fuel Oils (MFO) and IFO-180 under favourable conditions. Furthermore, wave tank tests (Li et al., 2010; Trudel et al., 2005) and laboratory dispersibility tests (Crosbie et al., 1999; Sorial, 2006; Srinivasan et al., 2007; Stevens and Roberts, 2003) have strengthened this argument by reporting results of the successful dispersion of IFO-180 and the heavier IFO-380. Unfortunately, most of these results were carried out at water temperatures of 15°C, with very limited results reported at water temperatures as low as 5°C (Srinivasan et al., 2007; Stevens and Roberts, 2003). The aim of this study is to further investigate the feasibility of using dispersants at polar and sub-polar conditions at 0°C and 5°C respectively for the treatment of a possible oil spill in the Antarctic marine environment. The target fuels used were the MGO and IFO-180 fuels currently being used in the Australian Antarctic Territory, and a Kuwait crude oil that is used as a reference for the certification of dispersants by the Australian Maritime Safety Authorities (AMSA).

#### 5.2 Fuel properties and environmental conditions that affect dispersibility.

Previous studies have shown that there are a large number of factors that can affect the dispersibility of a fuel and the performance of a specific dispersant. These factors can be categorised into two distinct groups, the fuel properties and the environmental conditions. The term dispersibility is used by many authors interchangeably with the terms efficiency, effectiveness and efficacy and they all describe the mass percentage of a fuel that will be dispersed in the water column if it is treated with a specific dispersant at the given environmental conditions.

The chemical composition of the fuel is the most important of the properties that affect its dispersibility. Fingas et al. (2003) correlated 295 dispersibility data points to 29 oil properties. The dispersibility measurements were performed at 20°C with the swirling flask testing apparatus and the chemical dispersant used for this study was Corexit 9500. They concluded that aliphatic hydrocarbons up to  $C_{18}$  and polycyclic aromatic hydrocarbons (PAH) are readily dispersible. In contrast, aliphatic hydrocarbons > $C_{20}$  as well as resins and asphaltenes hinder dispersion. Other correlated properties included the content of naphthalenes, the total aromatic content, and physical properties such as viscosity, density, pour point and boiling point below 250°C. Figure 5.1 shows two of the developed correlations for saturate content and resins content. Using these correlated properties Fingas et al. (2003) developed 13 models of various complexity for estimating dispersion effectiveness. Since the dispersibility measurements were performed at 20°C and some of the physical properties used to construct the models such as density and viscosity were measured at 15°C, the developed models are tuned to predict the dispersibility at temperate conditions and not at polar conditions.



Figures 5.1. The correlations of saturates and resins content against the dispersibility of an oil (Fingas et al., 2003). Fingas et al. (2003) correlated 29 oil properties to the effectiveness of dispersion.

Beyond the chemical composition, physical properties of a fuel or oil such as viscosity and density are very important indicators of its dispersibility. In particular the viscosity of a specific oil can change drastically under different environmental conditions such as water temperature, while its chemical composition remains the same. Trudel et al. (2005) investigated the dispersibility of a suite of crude oils with viscosities ranging from 67 cP to 40,100 cP. The testing was performed on a large scale wave tank (OHMSETT) located at the National Oil Spill Response Test Facility, in Leonardo, New Jersey, USA. The viscosity was correlated successfully with the performance of a specific dispersant (Corexit 9500). It was concluded that oils in the range of 18,690 cP to 33,400 cP can experience limited chemical dispersion, while more viscous oils are non-dispersible. Figure 5.2 shows the correlation trend between dispersant effectiveness and oil viscosity.



Figure 5.2. Correlation of the viscosity with the effectiveness of dispersion (Trudel et al., 2005).

Once fuel or oil has been released into the marine environment a number of processes take place, the combined effect of which is referred to as weathering. These processes include evaporation, emulsification, dissolution, natural dispersion, photo-oxidation, and biodegradation, with evaporation and emulsification having the fastest impact on the oil's properties and especially on the viscosity. Daling and Strøm (1999) used the results from three field trials on the North Sea to verify the SINTEF Oil Weathering Model (OWM) for predicting the effects of weathering on oil properties and most importantly on viscosity. Knowing the viscosity progression against the exposure time of oil on the sea surface is crucial for determining the time windows of opportunity for the chemical dispersion to be effective. Figure 5.3 demonstrates an example of the viscosity progression of a crude oil during field trials on the North Sea and the predicted viscosity curve from SINTEF's OWM model. This study shows that there is a time window of opportunity for the dispersion to be successful, beyond which the weathering state of the oil resists dispersion. Additionally, when testing the dispersibility of an oil, it has to be at a realistic weathering state taking into account the time required for the response mechanism to reach the spill.





The environmental conditions that affect dispersibility are the wave energy, the water temperature and the salinity of the water. Wave energy is important as it assists the dispersant to mix with the oil and break it into small droplets. Optimal effectiveness for chemical dispersion is achieved when breaking waves are prevailing (Li et al., 2010).

Fingas et al. (1995) have shown that there is a clear correlation between the effectiveness of dispersion, the energy state of the sea and the amount of dispersant applied (Figure 5.4). Generally, applying higher

amount of dispersant leads to more efficient dispersion, although environmental and economic implications have to be considered before releasing high amounts of dispersants into the environment.



Figure 5.4. The characteristic relationship between dispersion effectiveness, the sea energy state, and the dispersant to oil ratio (DOR) applied (Fingas, 2010). The dispersants used in this study were Corexit 9527 and Slickgone LTS and the effectiveness was measured at 20°C.

The water temperature and salinity of the sea play a significant role, especially in cold polar environments. Most dispersants are formulated to work best at typical sea salinity around 35‰, and as a result they tend to underperform when water salinity deviates far away from this typical value. During the polar summer there is significant fresh water influx into the sea from melting snow and ice. The salinity of the seawater could be lower in the case of an oil or fuel spill in a closed bay. Fingas et al. (1995) tested the dispersibility of Alberta Sweet Mixed Blend crude oil in water of various salinities using the dispersants Corexit 9527 and Enersperse 700 and found that the optimum performance was achieved at 40‰ to 45‰ water salinity. Lower and higher salinities led to sharp declines in the dispersant performance (Figure 5.5).



Figure 5.5. The effect of salinity on the performance of dispersants Corexit 9527 and Enersperse 700 (Fingas 2010).

The sea temperature has a strong effect on the dispersibility of fuels and crude oils. Temperature affects the physical properties of the oil such as the viscosity, the density and the phase of the oil when it falls below the pour point. These effects are even more pronounced on medium to heavy oils and heavy fuels where viscosity increases significantly at low temperatures (Kotzakoulakis and George, In prep.) (Chapter 4). Additionally, temperature can affect the efficiency of each dispersants to a different degree, as we shall present in the results of this study. In a study conducted by Alaska's National Marine Fisheries Service (Moles et al., 2001) the combined effect of temperature and salinity was studied on the dispersibility of Alaska North Slope (ANS) crude oil. The dispersants used were Corexit 9527 and 9500. At a constant

temperature of 10°C the performance drop due to a drop of salinity from 32‰ to 22‰ was found to be around 50% for both dispersants. The combined effect when dropping the temperature from 22°C to 3°C and the salinity from 32‰ to 22‰ was a drop of dispersant efficiency to around 1/3 of the original [16].

It is important to investigate the compatibility of each dispersant to the specific type of oil or fuel. Specific dispersants perform better when applied to different types of oils and under specific conditions. The characteristics of each oil are unique and there is no one best performing dispersant for all oils.

The efficiency of dispersion for a specific oil-dispersant pair is ultimately controlled by the degree the specific dispersant lowers the interfacial tension on the oil-water interface. Dispersants contain chemical compounds with one hydrophilic and one hydrophobic end in their molecule (Figure 5.6). They attach on the water-oil interface and reduce the interfacial tension between the two. As a result the oil spill breaks into small droplets that disperse into the water column. The more efficient a dispersant is on a specific oil, the more the interfacial tension between the oil and the water is reduced. A more effective dispersant will cause the oil to break into smaller droplets since the lower interfacial tension requires less energy for the oil to enter the water, compared to a less efficient dispersant were the opposite is true. Additionally, the smaller droplet sizes of an effective dispersant will have less buoyancy and they will resurface to a smaller degree in contrast to a less effective dispersant. Another advantage of the smaller droplet sizes is that they create higher area to volume ratios, and thus the oil is more accessible to bacteria living in the water column, leading to a faster biodegradation rate compared to larger droplets and oil that is floating on the sea surface.



Dioctyl sodium sulphosuccinate (DOSS)

Figure 5.6. An example of an active ingredient (surfactant) of a dispersant formulation. Other compounds that are part of the dispersant formulation are solvents that improve viscosity and promote solubility in oil.

## 5.3 Previous studies on the dispersion efficiency of medium and heavy fuels.

To date there is no standardised protocol for conducting dispersion field trials or wave tank tests. Fingas (2010) has published a set of dispersion testing guidelines to help investigators avoid commonly occurring mistakes such as the measurement of the surface oil only, the absence of mass balance calculation, the lack of control spill and the absence of realistic oil weathering period before the application of the dispersant. Recently, an effort has been initiated to produce standardised protocols for wave tank testing under the Arctic Oil Spill Response Technology Joint Industry Programme (JIP) (Faksness et al., 2013). The field and tank tests presented in this study do not follow the same efficiency testing protocols, so comparison of the results should take these differences into account.

Field trials are conducted in real conditions and they provide the most reliable dispersion assessment when a valid protocol is followed. The drawback of field trials is that they face technical challenges. It is extremely difficult with current technology to accurately measure the amount of oil dispersed in the sea's water column, and to determine the partitioning between surface oil, dispersed oil, evaporated oil and dissolved oil. In recent years the priority has shifted to wave tank tests in order to realistically simulate the field conditions. The controlled environment allows accurate measurements when valid testing protocols are followed. Lab tests can only give qualitative assessment of the relative performance of different dispersants and they are mainly used for regulatory purposes and for classifying the dispersants in order of effectiveness.

#### 5.3.1 The 1993-1997 North Sea field trials.

Between 1993 and 1997 a series of field trials were conducted in the North Sea (Lunel, 1995; Lunel et al., 1997). Dispersion experiments were conducted on Medium Fuel Oil (MFO) mixed with Gas Oil (GO) in a 50:50 ratio with a density of 0.922 g/cm<sup>3</sup>, and on IFO-180 fuel with a density of 0.970 g/cm<sup>3</sup>, as well as some other oils.

#### 5.3.1.1 The 1993-94 North Sea field trials

The 1993-94 North Sea field trials were performed using advanced technologies including remote sensing aircraft equipped with side-looking airborne radar (SLAR), video, ultraviolet, and infrared cameras in order to track the behaviour of surface slicks [4]. The test conditions were 15°C sea temperature and 3-14 m/s winds. The dispersed oil in the water column was measured with field fluorometers towed through the slicks at different depths (Table 5.1). These are the most reliable field results available due to the detailed testing protocol that was followed.

Year	Energy	Wind	Weathering	Dispersant	DOR	Dispersed %	Standard
	regime	velocity m/s	time				deviation
1993	Low	3	15 min	Control		0.8	0.7
	Low	5	15 min	Slickgone NS	1:20	8	4
	High	10	15 min	Control		2	0.7
	High	10	15 min	Slickgone NS	1:20	17	6
	High	10	15 min	1100X	1:20	10	4
	High	10	15 min	OSR-5	1:20	30	7
1994	High	7	8 hours	Control		4	2
	High	6	8 hours	Slickgone NS	1:5	16	7
	High	7	8 hours	Corexit 9527	1:5	26	10

Table 5.1. Effectiveness of four different dispersants on the MFO+GO 50:50 mixture (Lunel, 1995). DOR = dispersant to oil ratio.

## 5.3.1.2 The 1997 North Sea field trial

The 1997 AEA North Sea field trial investigated the feasibility of using chemical dispersion on the heavier IFO-180 fuel. Furthermore they wanted to investigate the effectiveness of dispersion after an extended period of one to two days weathering. The dispersants used in this study were Corexit 9500 and Slickgone NS.

The first dispersant application (Corexit 9500) was performed 4 hours after the release of the IFO-180 into the sea. The IFO-180 at the time was partially weathered and emulsified, with a viscosity in the range of 5,000–12,000 cP and a water content of 20–30%. This first dispersant application achieved partial dispersion of the weathered IFO-180. A second application was followed 23 hours after the release of the fuel in the sea. At this time the weathered IFO-180 viscosity exceeded 20,000 cP and the dispersant application did not succeed in further dispersing the fuel (Lunel et al., 1997). This field trial highlights the importance of applying the dispersant as early as possible during the "window of opportunity" as it is call, and before the fuel reaches a high degree of emulsification and weathering. In comparison the unweathered IFO-180 that was used in the present study has an initial viscosity of 13,423 cP at 0°C. When weathered to 8% mass loss the viscosity reached 82,559 cP at 0°C. This viscosity alone indicates a narrow window of opportunity, if the IFO-180 fuel is dispersible at all.

#### 5.3.2 2003 North Sea field trial

During June 2003 another field test was conducted in the North Sea using 3 different dispersants for the dispersion of IFO-180 and IFO-380. The field conditions were 15°C sea temperature with wind speeds varying between 4 and 8 m/s. The physical properties of the IFO-180 were a density of 0.970 g/cm<sup>3</sup> and a viscosity of 2,075 cP, and of the IFO-380 were a density of 0.983 g/cm<sup>3</sup> and a viscosity of 7,100 cP (Colcomb et al., 2005). The fuels were released into the sea unweathered and the dispersant was applied immediately before any weathering had taken place. During this test a visual ranking system was applied for the assessment of the dispersion efficiency. The system consisted of four rankings: Rank 1, no obvious dispersion; Rank 2, slow or partial dispersion; Rank 3, moderate to rapid dispersion; and Rank 4, very rapid and total dispersion. Three dispersants were tested, Agma DR-379, Superdispersant-25 and Corexit 9500 (Colcomb et al., 2005).

For the dispersion of IFO-180 at a dispersant to oil ratio (DOR) of 1:25 the Agma-379 efficiency and the Superdispersant-25 efficiency were assessed as Rank 2, whereas the Corexit 9500 efficiency was found to be in the range of Rank 3 to Rank 4. For the dispersion of IFO-380 at a DOR of 1:25 the Agma-379 efficiency was between Ranks 1 and 2, the Superdispersant-25 efficiency was equal to Rank 2, and the Corexit 9500 efficiency was between Ranks 1 and 2 (Colcomb et al., 2005).

This field trial was performed following a simple protocol. There were no remote sensing measurements or any other direct measurement to record the quantity of fuel on the surface or in the water column. According to the findings of this field trial the IFO-180 could be rapidly and totally dispersed in some cases

195

and even the heavier IFO-380 could be partially and slowly dispersed (Colcomb et al., 2005). This observation somewhat contradicting the previous field trials performed under similar conditions in the North Sea (1993-94, 1997), where the best dispersant efficiency on the lighter MFO+GO mixture dispersion was equal to 30% and IFO-180 dispersion proved to be challenging, with only partial dispersion during the first dispersant application and unsuccessful dispersion at the second application.

## 5.3.3 Previous wave tank studies on IFO-180 and IFO-380

Although the IFO-380 fuel is not used in the Australian Antarctic Territory it may be a good indicator for the rheological behaviour of IFO-180 at Antarctic conditions. IFO-380 has a viscosity in the range 7,000– 15,000 cP at 15°C, which is similar to IFO-180 viscosity at 0°C. Both fuels have Bunker C residual oil as the main fraction, with a small fraction of distillate added to meet the viscosity specifications of IFO-180 and IFO-380 (ESD, 1999). The light distillate added is evaporating quickly when spilled in the open sea, so the composition of IFO-180 could be very similar to IFO-380 after few hours of weathering. For this reason the dispersant efficiency of IFO-380 at 15°C could be a good indicator of the efficiency of IFO-180 in Antarctic conditions. This assumption would only be valid if both fuels have a Bunker C component from the same origin, because as shown below the IFO fuels from different sources have large variations in their composition and physical properties.

#### 5.3.3.1 The 2005 OHMSETT Wave Tank Tests

Dispersant efficiency tests were performed at OHMSETT on IFO-180 and IFO-380 at 15-16°C. The study was complementary to the 2003 North Sea field trials (Trudel et al., 2005). OHMSETT is the largest dispersant testing facility in the world, with a wave tank measuring 203 m long by 20 m wide and 3.4 m deep. Although these tests were conducted in a controlled environment, there was no direct

measurement of the water column fuel concentration. The effectiveness was calculated by recovering the surface oil and by assuming that the balance was dispersed (Table 5.2). There was no

			Dispersant Effectiveness %				
OHMSETT Tank Test			minus control				
Dispersant	Wave frequency	DOR nominal	IFO180	IFO380	IFO180	IFO380	
Control	35	0		30			
	33.3	0	26				
9500	35	1:50		58		28	
	33.3	1:50	84	34	58	4	
	30	1:50	21	26	<0	<0	
	30	1:25	36	13	10	<0	
SD25	33.3	1:50	45	53	19	23	
	33.3	1:50		29		<0	
	30	1:50	21	18	<0	<0	
	30	1:25		20		<0	
Agma	33.3	1:50	17	16	<0	<0	
	30	1:50	24		<0		

Table 5.2. Efficiency tests of dispersants Corexit 9500, SD25 and Agma DR379 (Trudel et al., 2005).

weathering time, which implies that in the case of a real spill, depending on the response time the dispersion effectiveness could be lower.

The dispersion efficiency of Corexit 9500 was 58% and SD25 was 19% on IFO-180 at 15°C. Corexit 9500 also performed better on IFO-380, achieving 28% dispersion efficiency against 23% for SD25.

## 5.3.3.2 2010 Bedford Institute Water Tank Tests

In 2010 tank dispersibility tests were conducted at the flow-through wave tank at the Bedford Institute of Oceanography in Nova Scotia, Canada (Li et al., 2010). The study's aim was to simulate the transport and dilution effects of ocean currents. The tests were conducted on IFO-180 at a range of temperatures

between 10°C and 17°C, and at two wave intensities, breaking and non-breaking waves. Corexit 9500 and SPC 1000 dispersants were assessed during this study (Li et al., 2010). The testing protocol incorporated direct measurements of the water column fuel concentration by collecting multiple samples from different locations and depths in the tank, and by measurement of the droplet-size distribution. The collected water samples were analysed by ultraviolet spectrophotometer adsorption for total petroleum hydrocarbon (TPH) concentrations.

Among the findings of this study was the ineffectiveness of both dispersants with non-breaking (lower energy) waves to disperse the IFO-180 fuel (Li et al., 2010). The dispersion was effective with breaking waves at temperatures over 14°C, with Corexit 9500 being the most effective dispersant. It was shown that dispersion of IFO-180 was very low at 10°C, even with breaking waves (Table 5.3). These findings demonstrate that temperature drastically affects the efficiency of the dispersants.

Dispersant	Wave energy	Temp °C	Control	Effectiveness %	minus control
Control	Regular waves	11.5	5		
		13.5	10		
		16	5		
	Breaker waves	10	15		
		12	15		
		14	20		
		17.5	20		
9500	Regular waves	10		3	<0
		10.5		3	<0
		15.5		6	1
	Breaker waves	9.5		3	<0
		10		19	4
		14		50	30
		15.5		95	75
SPC	Regular waves	12		3	<0
		12.5		6	<0
		16.5		10	5
	Breaker waves	10		6	<0
		13		25	10
		15.5		40	20
		17		50	30

Table 5.3. Detailed results on dispersants efficiency with IFO-180 from the 2010 Bedford Institute Water Tank Tests. Total efficiency at 10°C ranges from 6%-19% and chemical dispersion efficiency (minus the control) ranges from 0%-4% for the two dispersants (Li et al., 2010).

## 5.3.4 Previous Laboratory Tests on IFO-180 and IFO-380

Many laboratory tests have been developed over the years for dispersant efficiency testing. These tests incorporate simple protocols and are designed for fast screening of dispersants, and not to provide realistic dispersion efficiency expected in the field. Comparative studies between lab tests and field tests over the years have demonstrated that most of the laboratory tests overestimate the efficiency of the dispersants. Fingas (2010) has compiled the data from various laboratory techniques and correlated them with field results as shown in Table 5.4.

Effectiveness Results in Percent								
Oil Type	Dispersant	Field Test [16—17]	SF GC	SF CA	IFP	WSL Lab 1	WSL Lab 2	Exdet
Medium Fuel Oil	Corexit 9527	26	54	50	91	42	42	67
Medium Fuel Oil	Slickgone NS	17	49	46	94	29	23	50
Medium Fuel Oil	LA 1834/Sur	4	2	2	50	16	11	38
Forties Crude	Slickgone NS	16	47	65	95	28	25	60
Forties Crude	LA 1834/Sur	5	2	2	61	15	12	53
Correlation with field test (R <sup>2</sup> )				0.7	0.54	0.87	0.94	0.41
Ratio Lab test/field test				0.35	0.19	0.56	0.62	0.27

Legend: SF = Swirling Flask, GC = analysis by Gas Chromatography, CA = Colorimetric Analysis, IFP = French Institute for Petroleum test, WSL = Warren Springs Laboratory Test, EXDET - an Exxon test.

Table 5.4. Correlation between laboratory test and field test results (Fingas, 2010). The Warren Spring Laboratory (WSL) test produced the closest results to the field tests, with a high correlation factor. This lab test has been adopted by some countries including Australia and the UK as part of the certification process of new dispersants.

In recent years, in an effort to devise more valid and reproducible tests, new laboratory test designs have gained wider acceptance. The US Environmental Protection Agency have extensively tested and reviewed the Baffled Flask Test (BFT) in order to replace the Swirling Flask Test (SFT) (Sorial, 2006; Sorial et al., 2004; Srinivasan et al., 2007). Kaku et al. (2006) studied the flow dynamics and energy dissipation rate of these two laboratory techniques for estimating dispersant efficiency, and concluded that the BFT recreates the turbulent flow regime of the sea waves more efficiently.

#### 5.3.4.1 Laboratory test results on IFO-180 and IFO-380.

Sorial (2006) investigated the dispersibility of IFO-180 and IFO-380 using the BFT test at 16°C. He experimented with different agitation speed (150 rpm, 200 rpm, 250 rpm) and DORs (1:25, 1:50, 1:100) to determine the effects of different conditions on the dispersibility of these heavy fuels. The dispersants used were Corexit 9500 and Superdispersant 25. Later Srinivasan et al. (2007) expanded the investigation of the same fuels to include tests at the low temperature of 5°C and with one additional dispersant, the Agma DR379. In Table 5.5 we summarise the findings for the standard DOR of 1:25 and agitation speed of 200 rpm, as those are the recommended conditions for the BFT test (Sorial et al., 2004) and the most frequently applied DOR.

Fuel: IFO-180		DOR: 1:25		
Dispersant	Temperature °C	Efficiency %	RSD%	Reference
Control	16	2.7	5.9	1
C9500	16	76.6	2.4	1
SD25	16	79.5	1.6	1
Agma DR379	16	66.0	8.5	2
Control	5	3.3	0.6	2
C9500	5	35.6	4.7	2
SD25	5	52.9	4.1	2
Agma DR379	5	35.6	1.6	2
Fuel: IFO-380		DOR: 1:25		
Control	16	3.9	6.3	1
C9500	16	64.8	3.4	1
SD25	16	56.5	9.8	1
Agma DR379	16	48.4	3.7	2
Control	5	1.4	0.1	2
C9500	5	29.1	3.1	2
SD25	5	26.9	4.0	2
Agma DR379	5	30.0	4.8	2

Table 5.5. Summary of the dispersibility results for IFO-180 and IFO-380 using the BFT test at two temperatures (16°C and 5°C) for a suite of three dispersants (Sorial, 2006; Srinivasan et al., 2007).

The findings of the two studies are important because they provide an insight into the effects of temperature on the dispersibility of both IFO-180 and IFO-380 using the same dispersants (Sorial, 2006; Srinivasan et al., 2007). In most cases the temperature drop from 16°C to 5°C results in a reduction of the efficiency of the dispersants by roughly 50 percent for both fuels. Despite this efficiency drop the results indicate that at 5°C partial dispersion is still possible for both fuels.

A study conducted for the New Zealand Maritime Safety Authorities on the dispersibility of the heavy IFO-380 fuel used the Warren Spring Laboratory (WSL) testing apparatus (Stevens and Roberts, 2003). In this study a suite of six dispersants were tested on a variety of IFO-380 fuels of different origin. All dispersants were tested at 15°C and were classified in order of efficiency. Starting with the best performer the order was Corexit 9500, Slickgone EW, Corexit 9527, Slickgone LTSW, Tergo R40 and Gamlen OSD LT. It is significant to point out that the variation in efficiency of all the dispersants depended on the origin of the IFO-380. The efficiency of the best performer Corexit 9500 varied from 76% to as low as 30%. The best two performers (Corexit 9500 and Slickgone EW) were then tested on a range of temperatures from 15°C to 5°C on three IFO-380s of different origin. The results are summarised in Table 5.6.

IFO-380 Kee Lung	DOR: 1:25				
Temperature °C	15	10	5		
Viscosity mPa.s	2908	5166	31434		
Corexit 9500	66	59	37		
Slickgone EW	61	48	36		
IFO-380 Singapore		DOR: 1:25			
Temperature °C	15	10	5		
Viscosity mPa.s	13268	36515	208513		
Corexit 9500	62	49	5		
Slickgone EW	59	46	27		
IFO-380 Marsden Point		DOR: 1:25			
Temperature °C	15	10	5		
Viscosity mPa.s	7000	13200	19600		
Corexit 9500	24	29	7		
Slickgone EW	24	19	3		

Table 5.6. Summary of the dispersibility results for three IFO-380 of different origin using the WSL test at three temperatures and two dispersants (Stevens and Roberts, 2003).

These results show the effect of composition from the different origin of the fuels on dispersion efficiency. The IFO-380 originating from Singapore had the highest viscosity at 5°C (208,513 cP) and was 27% dispersed by Slickgone EW, while the IFO-380 from Masden Point had the lowest viscosity at 5°C (19,600 cP) but was only 3% dispersed using the same dispersant (Stevens and Roberts, 2003). Nevertheless, the experiments on two out of three IFO-380s indicate that they could be potentially be dispersible even at the low temperature of 5°C. Another interesting observation that was not included in the publication (Stevens and Roberts, 2003) is that two of the IFO-380s exhibit a perfect logarithmic relationship between dispersion efficiency and viscosity, as shown in Figure 5.7.



Figure 5.7. Efficiency of dispersion versus viscosity for three IFO-380s. The data is taken from Stevens and Roberts (2003). During this study a logarithmic trend has been identified between the dispersibility and the viscosity for two of the three IFO-380s (Figure 5.7.A). The third IFO-380 from Masden Point exhibits irregular dispersibility versus viscosity (Figure 5.7.B) that could be an indication of an erroneous measurement. Graph 5.7.A. demonstrates the effect of the viscosity alone on the dispersibility of the fuel. This is because the viscosity change is caused by the temperature change, while the composition of each fuel remains the same.

In another study undertaken for the Australian Maritime Safety Authority (AMSA), the dispersibility of IFO-180 and IFO-380 were studied at 15°C with the WSL apparatus (Crosbie et al., 1999). Various stages of evaporation of the IFO-180 were simulated by adding MGO to a Milford Haven IFO-380. A suite of 7 dispersants was tested on unemulsified IFO-380 and IFO-380 emulsified with 30% water. Starting with the best performer, the order of efficiency on unemulsified IFO-380 was Superdispersant 25, Corexit 9500, Slickgone LTSW, Slickgone NS, Ardrox 6120, Agma DR379 and Tergo R40. The first three dispersants achieved efficiencies over 50% at a DOR of 1:25, indicating that dispersion of IFO-380 is possible at 15°C. On the 30% emulsified IFO-380 the order starting from the best dispersant was Corexit 9500,

Superdispersant 25, Slickgone LTSW, Slickgone NS, Tergo R40, Ardrox 6120 and Agma DR379. Only the first two achieved efficiencies over 20% at a dispersant to emulsified oil ratio (DER) of 1:10, and only Corexit 9500 achieved an efficiency over 20% at a DER of 1:25. This is a clear indication that the "window of opportunity" for successful dispersion ends when a fuel/oil-water emulsion is formed with a water content over 30%.

Additional important information from this study was the effect of the simulated weathering on the dispersion efficiency. The simulated weathering was achieved by gradual evaporation and emulsification of the fuel (Crosbie et al., 1999). Table 5.7 shows the drop in efficiency with increasing evaporation with and without emulsification. The dispersant used for this test was Corexit 9500, one of the best performing dispersants in the previous test. The simulated evaporation loss dropped the dispersion efficiency from 95% for unweathered IFO-180 to 51% for the unemulsified IFO-380 fuel. For the 30% emulsified fuel, the efficiency dropped from 69% to 20%. Despite this drop the 36% dispersion efficiency of the emulsified IFO-180 with 8% simulated evaporation loss shows a significant potential for partial dispersion even at this stage of weathering.

DOR: 1:25	Temperature: 15°C						
IFO-180 loss%	0	2	4	8	IFO-380		
Viscosity mPa.s	2313	2633	3135	6008	13000		
Corexit 9500	95	86	74	86	51		
DER: 1:25		Temperatu	ıre: 15°C	Emulsion:	30% water		
IFO-180 loss%	0	2	4	8	IFO-380		
Viscosity mPa.s	10139	11511	13501	21873	26000		
Corexit 9500	69	N/A	55	36	20		

Table 5.7. The effect of evaporation and emulsification on the dispersion efficiency of heavy fuels (Crosbie et al., 1999).

## 5.4 Materials and methods

#### 5.4.1 Fuels

The fuels used in the present dispersibility study are SAB, MGO and the IFO-180. The MGO is a marine gas oil that consists exclusively of distillate without any addition of distillation residue. It contains a broad distribution of hydrocarbons in the range of C<sub>7</sub> to C<sub>26</sub>. Based on a laboratory evaporation experiment, one third of the fuel is expected to evaporate during the first month in the Antarctic marine environment with the remaining two thirds persisting for many months (Figure 5.8). MGO is used in the Australian Antarctic Territory (AAT) mainly by light marine vessels. The IFO-180 is a widely used blend, generally containing less than 10% distillate, the remaining 90% being a heavy residual fuel (Bunker C) and with a boiling range reaching well over 700°C (ETC, 2015). It is also used in the AAT by large ships and it is the heaviest fuel that is now allowed in Antarctic Treaty waters. It is expected to lose 7-8% of its mass during the first month in the Antarctic marine environment (Figure 5.8). The remaining residue could persist in the marine environment for years.

A third fuel that is used in the AAT is the SAB, which is a very light diesel fuel and mainly consists of  $C_9-C_{16}$  hydrocarbons. 80% of the SAB is expected to evaporate in the first 6 days after a spill in the Antarctic marine environment (Figure 5.8). Therefore the use of dispersants is not recommended, and it was not included in this study.


Figure 5.8. Experimental evaporation data for the three fuels used in the Australian Antarctic Territory (AAT). The SAB lost 80% of its mass during the first 6 days. The MGO lost 33% of its mass in one month and the IFO-180 lost only 7% of its mass after one month.

A Reference Kuwait crude oil was also included in this study for comparison reasons since it is used by the Australian Maritime Safety Authorities for regulatory purposes connected with dispersants, and the efficiency of the dispersants on this crude oil at low temperature is of great interest. This crude oil has a wide hydrocarbon distribution, starting at  $C_5$  and reaching well over  $C_{70}$ , containing large amounts of volatile components and a significant amount of non-volatile heavy residue.

The two fuels and the Kuwait crude oil were artificially weathered to remove the volatile fraction and stabilise them before the dispersibility tests. The artificial weathering was performed on a hot plate with continuous magnetic stirring and a flow of nitrogen gas over the surface of the fuel. Heating was applied at a slow rate over a period of few hours, starting from 70°C and ramping up to 140°C until the desired

mass loss was achieved. The mass fraction that was removed was 8% for the IFO-180, 16% for the MGO and 22% for the Kuwait crude oil.

The main properties of the two fuels and the crude oil before and after the artificial weathering are presented in Table 5.8.

Sample Name	Density g	/cm <sup>3</sup>	Viscosity cP	
	15 °C	0 °C	15 °C	0 °C
IFO-180	0.952	0.963	2605	12930
IFO-180 8% Loss	0.966	0.977	12000	80674
MGO	0.828	0.839	4.9	7.9
MGO 16% Loss	0.833	0.844	5.8	9.6
Kuwait Crude	0.869	0.880	21.6	45.5
Kuwait Crude 22% Loss	0.966	0.977	369	1396

Table 5.8. The properties of the fresh and artificially evaporated fuels and crude oil used in this study.

#### 5.4.2 Standards and reagents

The synthetic sea salt "Instant Ocean" (Aquarium Systems) was used to prepare water with a salinity equal to 34.5‰ by adding 34.5 g of synthetic sea salt to deionised water (Millipore filtration system) to prepare a one litre solution.

Four internal standards of analytical grade were used for the quantification of the extracted dispersed hydrocarbons. These were cyclooctane, 1,4-dichlorobenzene, tetracosane-d50 and bromoeicosane. The internal standards were used to prepare a solution in dichloromethane (DCM) containing 5  $\mu$ g/mL of each of the internal standards. This DCM solution with the internal standards was used for the solvent extraction of the hydrocarbons dispersed in the water.

A synthetic mix of alkanes from  $n-C_{11}$  to  $n-C_{36}$  and the internal standard compounds, all in known quantities, was used in order to determine the relative response factor (RRF) of each internal standard

against the n-alkanes. These RRFs of the internal standard compounds were then used for the guantification of the dispersed hydrocarbons.

#### 5.4.3 Methods

The density and the kinematic viscosity of the two fuels and the Kuwait crude oil were measured at different temperatures. The densities were determined gravimetrically by measuring the weight of either 50 mL or 100 mL of each fuel sample in a volumetric flask at the desired temperature, using a high precision (5 decimal places of a gram) mass balance (AND GR-202). The density of each fuel was measured at two temperatures, at 0 °C and at 15°C. All materials were brought to the desired temperature (±0.1°C) before the measurement in an incubator (Binder KB-115). The kinematic viscosities were measured with glass capillary viscometers immersed in a temperature regulated bath (Julabo F12). After the bath had stabilised at the desired temperature (±1°C), the viscometer with the sample inside was left to equilibrate for one hour before multiple measurements were performed. The viscosities of the three samples were determined for the range between 0 to 22°C.

150 mL screw cap baffled glass trypsinizing flasks (Wheaton – USA) with Teflon stopcocks attached on the side and near the bottom of the flask (Figure 5.9) are used for the Baffled Flask test. An orbital shaker (Grant PSU-20i) with 20 mm rotational diameter and adjustable rotation speed was used to agitate the water, oil and dispersant mixture. The complete dispersant test was performed in a temperature-controlled environment (Binder KB-115 incubator) at the described temperature ±0.1°C.



Figure 5.9. Trypsinizing glass flask with Teflon stopcock near the bottom used for the BFT test.

All materials and glassware were preconditioned inside the incubator at the desired testing temperature. 120 mL of artificial sea water are poured into each trypsinizing flask followed by 100  $\mu$ L of the tested fuel/oil. The fuel/oil was poured close to the surface of the water using a positive displacement pipette (Brand Transferpettor) with one 1 mL tip. Lastly 4  $\mu$ L of dispersant was added at the center of the simulated spill with an Agilent 10  $\mu$ L glass syringe (Agilent G5413) to create a DOR equal to 1:25. A DOR of 1:25 was used (1) because this is the recommended DOR by the dispersant manufacturers, (2) because this DOR is used in the majority of emergency responses to actual oil spills in the field, and (3) because the protocol for performing BFTs requires this DOR for comparability between studies.

The mixture was agitated for 10 minutes at 200 rpm orbital rotation speed. Following the agitation phase the flasks were removed from the mixer and left to settle for another 10 min. 2 to 3 mL of water were removed and discarded from the bottom stopcock of each flask. 30 mL of water was then collected from this stopcock, from which 25 mL was placed in a 40 mL glass vial with a Teflon cap for extraction. 1 mL of DCM extraction mix was added to each 40 mL vial containing the water samples, and these were placed on the vortex mixer where the mixture was agitated by creating a spinning vortex at 2000 rpm for 15 minutes. The samples were then left to settle and the DCM mixture was removed with a glass pipette and placed in 1.5 mL Agilent autosampler vials with Teflon screwcaps, and stored at -35°C until ready for analysis.

#### 5.4.4 Gas chromatography and analytical procedure

The collected samples were analysed on a gas chromatograph (GC) equipped with a flame ionisation detector (FID). The quantification of the dispersed oil was performed by integrating the recorded signal up to  $n-C_{20}$  and utilising the cyclooctane and 1,4-dichlorobenzene internal standards to quantify the mass of the dispersed oil below  $n-C_{20}$ , as described in Equations 5.1 and 5.2:

$$mass_{disp} = \frac{area_{(5.1)$$

$$Dispersed\% = \frac{mass_{disp}}{density_{oil}} \times \frac{1}{volume_{oil}} \times 100$$
(5.2)

Where mass<sub>disp</sub> is the dispersed mass of oil in the water column in mg, area<sub><C20</sub> is the integrated area below  $n-C_{20}$  in area counts, area<sub>STD</sub> is the integrated area of the internal standard in area counts, RRF<sub>STD</sub> is the relative response factor of the internal standard on the FID detector and is unitless, mass<sub>STD</sub> is the mass of internal standard in the DCM used for extraction in mg, fraction<sub><C20</sub> is the mass fraction of the components below  $n-C_{20}$  to the whole oil and is unitless, volume<sub>water</sub> is the total volume of water (120 mL,) volume<sub>extracted</sub> is the volume of water used for extraction (25 mL), volume<sub>Oil</sub> is the total volume of oil equal to 100  $\mu$ L, density<sub>Oil</sub> is the oil density in g/cm<sup>3</sup> and Dispersed% is the dispersant efficiency as the percent of volume dispersed.

The fraction<sub><C20</sub> in Equation 5.1 was calculated by preparing a solution of a known amount of oil in DCM, usually 1/300 mg/ $\mu$ L ratio for splitless injection, and then the solution was spiked with a known amount of internal standard, usually 5 x 10<sup>-3</sup> mg/cm<sup>3</sup> of internal standard in the whole solution. Analysis of this solution by GC-FID was used to calculate the fraction<sub><C20</sub> from Equation 5.3:

$$fraction_{(5.3)$$

Where massoil is the mass of oil added to the solution in mg.

The RRF of each internal standard was calculated from a standard solution containing the complete range of hydrocarbons from n-C<sub>11</sub> to n-C<sub>36</sub> as well as the four internal standards, all in known quantities. The response of the n-alkanes on the FID was taken as equal to one, and the relative response factor of each internal standard in relation to the n-alkanes was calculated by Equation 5.4:

$$RRF_{STD} = \frac{\frac{area_{THC}}{mass_{THC}}}{\frac{area_{STD}}{mass_{STD}}}$$
(5.4)

Where  $area_{THC}$  is the total area of the hydrocarbons in the solution, and  $mass_{THC}$  is the total mass of the hydrocarbons in the solution.

### 5.5 Results and discussion

All tests with the BFT technique were performed using the recommended 200 rpm revolution speed and 1:25 DOR according to the proposed protocol (Sorial et al., 2004). The results for the two fuels used in the AAT, the MGO and the IFO-180, are presented first at Antarctic and sub-Antarctic water temperatures (0°C and 5°C respectively). The MGO results presented in Table 5.9 are for the artificially weathered MGO with 16% mass loss of the lighter end of the fuel. For the heavier IFO-180 both results of the unweathered

and weathered up to 8% mass loss are presented in Tables 5.10 and 5.11, respectively. Results for the unweathered MGO are not presented because of the rapid evaporation rate of the fresh MGO that render the scenario of treatment with dispersant while still unweathered unrealistic and the results unreliable. In Tables 5.9–5.11, 1<sup>st</sup> and 2<sup>nd</sup> (and 3<sup>rd</sup> for unweathered IFO-180) refer to duplicate experiments, which were then averaged in the next column. The "minus control" column indicates the average dispersed by the dispersant minus the average dispersed control, and the relative standard deviation (RSD) was calculated from the formula:

$$RSD = \frac{\sigma}{\mu} \tag{5.5}$$

where  $\sigma$  is the standard deviation between the efficiency measurements and  $\mu$  is the mean value of the same measurements.

Tested sample	MGO	MGO weathered to 16% mass loss												
Temperature	0°C	;				5°C	;							
	Efficie	ency %	dispersed	minus		Efficiency %dispersed minus								
Test No	1st	2nd	Average	control	RSD%	1st	2nd	Average	control	RSD%				
Control	3	3 4	4		6.0	5	5 5	5 5		4.1				
Ardrox 6120	81	77	79	75	3.2	77	77	77	72	0.2				
Slickgone EW	75	5 78	3 <b>76</b>	73	2.6	80	) 79	79	75	0.9				
Slickgone LTSW	70	) 73	3 <b>72</b>	68	3.0	79	) 79	79	74	0.6				
Slickgone NS	75	5 78	3 <b>77</b>	73	2.6	82	85	5 <b>83</b>	78	2.4				
Finasol OSR-52	80	) 79	79	76	1.1	78	3 79	79	74	0.9				
Corexit T9500	84	87	<sup>7</sup> 85	82	2.9	76	5 81	79	74	4.4				

Table 5.9. Efficiency of six dispersants on the weathered MGO at 0°C and 5°C. The applied DOR was equal to 1:25.

As can be seen in Table 5.9, the MGO fuel can be successfully dispersed by all the dispersants at polar and sub-polar temperatures. A crucial factor for the successful dispersion is the viscosity of the fuel at the specific temperature. The MGO is a light marine diesel and the viscosity of the weathered fuel remains low and equal to 8.0 cP and 9.6 cP at 0°C and 5°C respectively. This low viscosity permits the penetration of the dispersant into the fuel and the creation of easily dispersed droplets. Comparison of the six different dispersants show that there is no clear advantage for any of the six dispersants, with their efficiencies being close together and within the repeatability limits of the method.

Tested sample	IFO-180 unweathered														
Temperature	0°C	)					5°C								
	Ef	ficiency	/ (% dis	spersed)	minus		Efficiency (% dispersed) minus								
Test No	1st	2nd	3rd	Average	control	RSD%	1st 2	nd Av	erage	control	RSD%				
Control	2	1	2	2		24.7	3	3	3		7.7				
Ardrox 6120	14	14	11	13	12	13.9	26	18	22	20	24.5				
Slickgone EW	20	21	17	19	18	10.3	34	38	36	34	7.8				
Slickgone LTSW	14	17	11	14	12	21.4	32	23	28	25	23.9				
Slickgone NS	22	18	19	20	18	10.4	33	29	31	28	9.0				
Finasol OSR-52	17	23	20	20	18	14.7	44	33	38	36	20.5				
Corexit T9500	18	18	17	18	16	3.0	27	37	32	30	22.2				

Table 5.10. Efficiency comparison on the dispersion of unweathered IFO-180. The viscous IFO-180 fuel cannot be dispersed effectively at polar temperatures (0°C). At the sub-polar temperature of 5°C there is potential for partial dispersion. The applied DOR was equal to 1:25.

The results in Table 5.10 for the unweathered IFO-180 show poor performance for all the dispersants, with  $\leq$ 20% dispersed at 0°C. The efficiency of the dispersants increases significantly in just a few degrees centigrade rise to 5°C, although a dispersal efficiency <40% can only be characterised as partial dispersion. The results at 5°C appear to be in good agreement with the previously published BFT results (Srinivasan et al., 2007) where the efficiency of Corexit 9500 was found to be 35.6% at 5°C (32% in this study). The performance comparison between the dispersants indicates a small advantage for Finasol OSR-52 and Slickgone EW over the other dispersants, with the worst performers being the Slickgone LTSW and Ardrox 6120. Corexit T9500 and Slickgone NS fall in the middle of the range of dispersal efficiency for unweathered IFO-180, but we have to point out that the differences are small and close to the repeatability limit of the method. The IFO-180 is a heavy and viscous fuel with viscosity equal to 7,266 cP and 12,930 cP at 5°C and 0°C respectively. Since the chemical composition of the fuel remains the same, this 100% increase of the viscosity in just 5 degrees appears to explain the drop of the performance of all the dispersants to one half from 36% to below 18%.

Tested semals		100.000	othorod to C	0/ 2000	1000									
rested sample	pr-0-1	IFU-100 weathered to 0% mass loss												
		_					_							
Temperature	0°C	2				5°C	2							
	Effici	iency %	dispersed	minus		Effici	ency %	dispersed	minus					
Test No	1st	2nd	Average	control	RSD%	1st	2nd	Average	control	RSD%				
Control	1	2	2		25.0	2	2	2		12.4				
		_	-		2010		-	-						
Ardrox 6120	6	5	5	2	127	6	7	6	4	1/1				
	0	5	5	3	12.7		1	0	4	14.1				
	_	-	•		~~~~		4.0	40	4.0	045				
Slickgone Evv	5	1	6	4	22.6	17	10	13	12	34.5				
Slickgone LTSW	6	6	6	4	2.4	5	7	6	4	18.5				
Slickgone NS	10	13	11	10	20.1	15	14	14	13	3.4				
Ŭ														
Finasol OSR-52	7	q	8	6	10.0	8	8	8	6	4 0				
	'	5	0	0	10.0		0	0	0	4.0				
		~	-	-	04.0	1	0	•	-	0.0				
Corexit 19500	8	6		5	21.9	10	8	9	1	9.6				

Table 5.11. Efficiency of the dispersants on the weathered IFO-180 at 0°C and 5°C water temperature. The dispersants are unable to achieve even partial dispersion of the weathered fuel. The applied DOR was equal to 1:25.

The viscosity of the weathered IFO-180 reaches 40,639 cP at 5°C and 80,674 cP at 0°C and it becomes extremely difficult for the dispersants to penetrate the body of the fuel and break it into droplets even at the sub-polar temperature of 5°C (Table 5.11). These results demonstrate the importance of treating the spilled fuel as soon as possible after an accidental release into the environment, since the weathering processes will continuously increase the viscosity of the fuel.

To summarise the results, the viscous IFO-180 can only be partially dispersed while still fresh and only at sub-polar temperatures of 5°C or above. The best dispersants for this task from the suite of the tested dispersants in this study are Finasol OSR-52 and the Slickgone EW.

It needs to be noted that the composition and the physical properties of the IFO-180 fuel can vary depending on the origin of the fuel and the process that it has undergone in the refining stage. IFO 180 is the designation for any intermediate fuel oil having a viscosity of 180 cSt or lower at 50°C, but there is no further restriction on the viscosity at lower temperatures. Depending on the source of the fuel its rheological behaviour at lower temperatures can vary, resulting in different dispersion efficiencies. IFO-380 is a similar fuel also consisting mainly of a heavy residual fuel (Bunker C), with a small addition of 2-3% light distillate. This wide variation in the properties and dispersant efficiency of IFO-380 was demonstrated in a study conducted for the New Zealand Maritime Authorities (Stevens and Roberts, 2003) (Table 5.12). The results presented here are only valid for the specific IFO-180 sourced from the Whinstanes Terminal, Brisbane in October 2009, and can only serve as an indication that IFO-180 type fuel is expected to be a challenging fuel to treat with dispersants at polar and sub-polar temperatures.

IFO-380 Source	Viscosity (cP)	Efficiency (%)						
	Temperature 15°C							
Antwerp	90,325	39						
Cristobel	8,000	59						
Kee Lung, Taiwan	2,908	66						
Marsden Point, NZ	7,000	35						
Nagoya	12,086	58						
Rotterdam/Flushing	15,200	51						
Santos, Brazil	6,294	76						
Singapore	13,268	62						
Токуо	9,155	66						

Table 5.12. The variation of viscosity and dispersant efficiency for IFO-380 fuels originating from different sources (Stevens and Roberts, 2003). The effectiveness presented is for the dispersant Corexit 9500 applied with a DOR of 1:25 at 15°C, following the Warren Spring Laboratory LR 448 protocol.

In order to further investigate the effect of the viscosity and temperature on the performance of the six dispersants we extended the testing programme to include a full range of temperatures from 0°C up to 22°C and selected the IFO-180 for this testing as it exhibits a wide range of viscosity values over this temperature range. In Table 5.13 we present the results for all the dispersants for the remaining temperatures up to 22°C. The results for the complete range of temperatures can be easier observed on the bar graph (Figure 5.10).

Tested sample	IFO-180 u	nweath	ered										
Temperature	10°C				15°C				22°C				
	Efficiency	(% disp	ersed)		Efficiency	(% disp	ersed)		Efficiency	′ (% dis	persed)		
Test No	1st 2n	nd Av	verage R	RSD%	1st 2ı	nd A	verage R	RSD%	1st 2	nd A	verage F	RSD%	
Ardrox 6120	43	52	47	13.8	69	58	63	13.0	71	64	67	7.4	
Slickgone EW	57	57	57	0.0	62	68	65	6.2	77	79	78	1.8	
Slickgone LTSW	55	43	49	16.2	56	51	54	7.0	66	58	62	9.2	
Slickgone NS	51	52	52	0.8	65	70	67	5.6	68	76	72	7.7	
Finasol OSR-52	49	61	55	15.4	69	66	68	3.5	84	83	84	0.7	
Corexit T9500	55	46	51	12.1	63	69	66	6.4	75	81	78	5.5	

Table 5.13. The performance of six dispersants on unweathered IFO-180 for the temperature range 10°C to 22°C. The applied DOR was equal to 1:25.



Figure 5.10. Comparison of dispersal efficiency for six dispersants on the unweathered IFO-180 for the complete range of water temperatures from 0°C to 22°C. Where Ardrox, EW, LTSW, NS, OSR52 and T9500 in caption refer to Ardrox 6120, Slickgone EW, Slickgone LTSW, Slickgone NS, Finasol OSR-52 and Corexit T9500 respectively. The applied DOR was equal to 1:25.

When observing the results for the complete temperature range we can conclude that Finasol OSR-52 and Slickgone EW are the best performing dispersants on IFO-180 at all the temperatures, including 10°C to 22°C. They are closely followed by the dispersant Corexit 9500 which achieves the third best efficiency. Slickgone NS and Ardrox 6120 are in the middle of the performance range, with Slickgone LTSW appearing to be the least efficient dispersant with IFO-180.



Figure 5.11. Dispersant efficiency versus fluid viscosity for the complete range of temperatures from 0°C to 22°C for the three best performing dispersants. A logarithmic trend emerges for the efficiency of the dispersants against the viscosity. The applied DOR was equal to 1:25.

Figure 5.11 shows the dispersion efficiency results against the corresponding viscosity of the IFO-180 for the complete temperature range for the three best performing dispersants. All three dispersants exhibit the same logarithmic trend of dispersion efficiency versus viscosity. This logarithmic trend was observed earlier in the previously presented study (Stevens and Roberts, 2003) by the heavy fuel IFO-380 (Figure 5.7). This trend indicates that viscosity could explain why the dispersion of IFO-180 is almost complete in temperate waters, while at polar and sub-polar temperatures the dispersion is unsuccessful. Between 22 and 10°C, the IFO-180 viscosity is in the range of 1465 to 4461 cSt (or 1387 to 4265 cP) and the efficiency of dispersion is over 50%. Between 5 and 0°C the viscosity increases to 7571 and 13423 cSt (or 7266 and 12930 cP) and the dispersion efficiency drops to between 35% and 20%. It seems that for the IFO-180 there is a critical viscosity range in the order of 4000-5000 cP where dispersion becomes only partial or poor. These viscosity values seem to be in agreement with the observations of other investigations (Daling and Strøm, 1999; Trudel et al., 2005), which also showed a sudden drop in the dispersion efficiency for viscosity values over 4000 cP (Figures 5.2-5.3). This information is important for emergency response authorities in order to assist when making decisions on the feasibility of the use of dispersants and the available time window of opportunity when the viscosity of the weathered fuel permits the use of dispersants.

All the results presented so far refer to marine fuels. We now present the effects of polar conditions on the dispersibility of a crude oil and we compare this with the effects on the fuels. The Kuwait crude oil is frequently used by the Australian Maritime Safety Authorities for the assessment of dispersant performance and it is considered a reference oil for comparisons. We tested this oil in polar and sub-polar temperatures as well as at the reference temperature of 15°C for comparison reasons. The Kuwait crude oil contains a significant amount of light hydrocarbons that evaporate rapidly, so the efficiency tests were performed on the artificially weathered Kuwait crude oil where 22% of mass that contains the volatile

220

hydrocarbons had been removed. Table 5.14 shows the efficiency of the six dispersants at these three temperatures.

Tested sample	Kuwait Crude Oil weathered to 22% mass loss															
Temperature	0°C					5°	С				1	5°C				
-	Efficien	cy %	dispersed	minus		Effic	iency %	disperse	d minus		E	fficien	cy %o	dispersed	minus	
Test No	1st 2	nd	Average	control	RSD%	1st	2nd	Average	contro	I RSD%	1	st 2	nd	Average	control	RSD%
Control	1	2	1		16.0		2	2	2	7.2		3	2	2		4.8
Ardrox 6120	24	23	24	22	2.6	4	1 3	1 3	6 34	20.1		49	45	47	45	5.8
Slickgone EW	27	26	26	25	4.1	3	9 3	6 3	7 35	4.4		43	48	45	43	7.9
Slickgone LTSW	22	18	20	19	15.7	2	9 3	2 3	0 28	7.0		30	30	30	27	0.0
Slickgone NS	28	27	27	26	2.5	а (	8 3	5 3	7 35	5.8		40	39	40	37	1.8
Finasol OSR-52	28	27	27	26	2.3	3	8 3	7 3	8 35	0.9		44	41	43	40	5.2
Corexit T9500	31	22	27	25	23.7	3	1 3	73	4 32	11.1		40	39	39	37	2.2

Table 5.14. Performance comparison of the six dispersants on the weathered Kuwait crude oil. The oil has been tested at polar and sub-polar water temperatures of 0°C and 5°C respectively, and at a reference temperature of 15°C. The applied DOR was equal to 1:25.

The relative performances of the different dispersants on weathered Kuwait crude oil are easier to be compared on a bar graph (Figure 5.12). It can be seen that the temperature drop affects each dispersant to a different degree. While Ardrox 6120 and Slickgone EW are the best performers at 15°C, their performance drop rapidly at lower temperatures and these dispersant are among the worst performers at 0°C. In contrast, although Finasol OSR-52, Slickgone NS and Corexit T9500 achieve relatively lower performance at 15°C, their effectiveness is maintained to a greater degree at 5°C and 0°C. Lastly, Slickgone LTSW appear to be the least compatible with this specific crude oil, and achieves the lowest performance at all temperatures.



Figure 5.12. Comparison of the relative performances of the six dispersants at 15°C, 5°C and 0°C on weathered Kuwait crude oil. Temperature drop affects to a different degree each dispersant. See Figure 5.10 for dispersant abbreviations. The applied DOR was equal to 1:25.

Again, this performance drop can be associated with the viscosity increase at lower temperatures. It appears that at this low viscosity range, a linear relationship with the performance better describes the drop rate of dispersant performance (Figure 5.13).



Figure 5.13. Relationship of dispersal efficiency for weathered Kuwait crude oil versus viscosity, for the three best performing dispersants. The rate of performance drop appears to exhibit a linear relationship with increase of viscosity in this low viscosity range. Although Ardrox 6120 achieves the highest performance at low viscosity values, it exhibits the worst performance at higher viscosity values for the same oil. The applied DOR was equal to 1:25.

#### 5.6 Conclusions

This study has produced missing information on the feasibility of using dispersants for the treatment of the fuels used in the Australian Antarctic Territory at seawater temperatures as low as 0°C.

The results of this study indicate that MGO can be successfully treated with dispersants in both sub-Antarctic and Antarctic marine conditions at seawater temperatures of 5°C and 0°C, respectively. Due to the MGO's slower weathering rate in polar conditions than in temperate regions, it is expected to persist in the marine environment for months if not treated. The treatment with dispersant appears to be one of the alternative viable solutions. All dispersants tested on MGO were efficient and the differences were small and within the method repeatability limits. Corexit 9500, Finasol OSR-52 and Slickgone EW exhibited a small advantage in effectiveness at 0°C, while Slickgone NS had a small advantage over the rest at 5°C.

The unweathered IFO-180 was non-dispersable at 0°C, but has indicated potential for partial dispersion at 5°C. For this application the best performing dispersants appear to be Finasol OSR-52 and Slickgone EW. The artificially weathered IFO-180 proved to be non-dispersable at both 0°C and 5°C, with efficiency below 15% for all the dispersants. This result emphasises the need for a rapid response if there is an IFO-180 spill within the window of opportunity for the dispersion to be successful.

An important finding of this study is that the temperature drop affects the efficiency of each dispersant to a different degree. This result indicates that the order of efficiency for a suite of dispersants can change significantly between two temperatures. As shown in Figure 5.12, Ardrox 6120 exhibits the best efficiency for treating the Kuwait crude oil at 15°C, but in contrast at 0°C this dispersant is one of the worst performers on the same crude oil. This highlights the need to test the dispersants at each temperature of interest in order to identify the most efficient dispersant for the specific fuel or oil. This need is even greater at polar temperatures where we do not have enough information from previous studies. When comparing results between dispersants under identical conditions, including the same mixing energy, temperature, method of application and type of fuel, which translates to same viscosity and composition, then the differences can be attributed to the formulation of the dispersant. The two main factors that depend on the formulation and are crucial for the effectiveness of the dispersant are: a) the mixture of solvent that gives the dispersant the necessary rheological characteristics to effectively be delivered and distributed to the oil surface, and b), the ability of the active chemicals (surfactants) to lower the interfacial tension between the oil and water that lowers the required energy for the oil to enter the water. Ultimately, when all the other parameters are identical the lowering of the interfacial tension is the factor that controls the efficiency of each dispersant.

Lastly, a logarithmic trend has been identified to exist between the efficiency of a dispersant and the viscosity which is due to the temperature change in viscous fuels such as IFO-180 and IFO-380. This could provide a useful insight for modellers to develop more accurate efficiency correlations in the future.

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#### Summary and conclusions

### 6.1. Fuel characteristics and environmental conditions.

Petroleum fuels are very complex mixtures that consist of hundreds, sometimes thousands of components. Each type of fuel, including the three types used in the Australian Antarctic Territory, have unique chemical composition and physical properties (Section 2.3.1), resulting in different weathering behaviour. The physical properties and the detailed molecular composition of the three fuels as well as the corresponding water accommodated fractions (WAFs) were determined using advanced techniques such as spectral deconvolution and two dimensional GC interfaced to time of flight MS. Furthermore, the Antarctic environmental conditions are very different to those of temperate marine environments, and are characterised by low temperatures, ice coverage and limited light for most of the year. These conditions affect each weathering process to a different degree, and so there are different compound partition ratios for the fuel, water and gas phases. Application of correlations and models based on experimental data originating from temperate conditions would lead to erroneous assessment of the phase distribution of a fuel spill in Antarctic waters.

#### 6.2. The evaporation process

Evaporation is an important weathering process because it is responsible for the greatest mass loss during the initial stages of the weathering. This process is greatly affected by the low Antarctic temperatures. Compared to a similar fuel spill under temperate conditions (20°C) the initial evaporation rates are 4.1,

3.5 and 3.5 times slower at 0°C for Special Antarctic Blend (SAB), Marine Gas Oil (MGO) and Intermediate Fuel Oil 180 (IFO-180) respectively. This evaporation rate decrease is solely due to the lower temperature and it does not include the effect of ice coverage. Ice floes can operate as natural barriers and restrict the spreading of the fuel spill to a smaller area than in open sea conditions. The evaporation rate of the whole spill is proportional to the total area of the fuel-atmosphere interface. The evaporation rate calculation in Section 2.2.3 is given per unit of area (moles s<sup>-1</sup> m<sup>-2</sup>), and the rate is multiplied by the total spill area to give the evaporation rate of the whole spill. The floating ice operates as a natural barrier and restricts the spreading of the spill and reduces the evaporation rate of the whole spill. A simplistic evaluation of the reduction the ice causes on the evaporation rate of the same spill in ice-free waters. This approximation ignores other effects caused by the presence of ice, such as the reduction of the wind velocity over the spill caused by the damping effect the ice has on the wind.

Furthermore, as the weathering progresses, the physical properties and molecular compositions of the spill change, which affects the evaporation rate of the spill. In particular, the viscosity of medium and heavy fuels can increase by a few orders of magnitude in the icy cold Antarctic waters. In such a case a compositional gradient can develop between the surface of the spill and its inner body. The evaporation rate is significantly reduced due to this gradient and a complex controlling mechanism is then established involving diffusing forces in the body of the fuel and a boundary layer on its surface.

### 6.3. Modelling the evaporation process.

In order to provide accurate predictions of the progression of the evaporation process over long periods of time, a novel evaporation model was developed (Chapter 3) which is the first that takes into account the interplay between the evaporation through a boundary layer and the diffusion forces in the inner body of the fuel. The model was able to predict the experimental evaporation data with high accuracy (Section 3.4.2), and it can be used in a wide range of environmental conditions and regions, since it takes into account the wind velocity, the barometric pressure, and the seawater temperature. Additional to the prediction of the amount of evaporation loss, the developed model also gives predictions on the progression of a range of oil properties during evaporation, including molecular composition, density, viscosity, average boiling temperature, and average molecular mass.

#### 6.4. Predicting the viscosity of weathered fuel.

The fuel viscosity is a key property for the calculation of the diffusion coefficients and diffusion velocities in the fuel body. A new correlation was developed during this project that predicts fuel viscosity under various physical conditions, and exhibits 2 to 4 times greater accuracy compared to previously published empirical correlations (Chapter 4). The higher accuracy of the new fuel viscosity correlation can be attributed to the usage of an extensive suite of 137 crude oils from multiple locations around the world and to the novel utilisation of their properties. The new correlation requires only the specific gravity at 15°C and the average boiling point of the oil as inputs.

#### 6.5. Evaporation rates and prediction accuracy for the three fuels.

Long term evaporation experiments have shown that for SAB evaporation remains the main weathering process until it is completely evaporated, even at polar conditions, since it is a narrow distillate with a large majority of its components  $<C_{15}$ . Specifically, the light SAB fuel needs approximately 3 days at 15°C and 10 days at 0°C to lose 95% of its mass. The prediction of the new model closely matches this experimental data, with correlation coefficients (R<sup>2</sup>) of 0.996 and 0.998 at 0 and 15°C, respectively. MGO fuel is also a pure distillate but it has a much wider distribution of components, with some components

 $>C_{25}$ . Evaporation remains the dominant process during the first couple of months of weathering of this fuel. Specifically, evaporation progresses fast during the first 10 days, with approximately 30% and 45% of MGO mass lost at 0°C and 15°C, respectively. Evaporation then progressively slows down until it practically stops after 3 months, leaving a 50% and 35% residue at 0°C and 15°C respectively. The model gives an accurate prediction for this fuel, with R<sup>2</sup> = 0.990 and 0.993 at 0°C and 15°C, respectively (Section 3.4.2). Other slower processes are expected to continue the weathering of MGO, such as oxidation, photolysis and biodegradation (Fingas, 2010), but further investigation is required in order to determine the rates of these processes under polar conditions.

Although IFO-180 from different origins can vary considerably in composition and physical properties, they are all heavy, viscous fuels consisting mainly of distillation residue. Generally, 90% of the IFO-180 mass is distillation residue (Bunker C), with the rest (8-10%) being a distillate such as MGO (Section 2.2.1) (ETC, 2015). The initial viscosity of the specific IFO-180 under investigation was 12,926 mPa s at 0°C, which can increase rapidly by a few orders of magnitude with the loss of the light end of the fuel. The high viscosity combined with low diffusion coefficients creates a steep compositional gradient between the surface and the inner body of the fuel as evaporation progresses, which reduces the evaporation rate greatly. It is a challenging fuel to predict evaporation rate for, and for a theoretical model to succeed it is required to take its heterogeneity into account. A long term evaporation experiment has shown that only 4% of IFO-180 mass is lost during the first 10 days at polar conditions (0°C). Evaporation then continues at a slower rate, with about 8-10% of its mass being lost after three months. At this time the viscosity of IFO-180 has reached 188,063 mPa s, and evaporation practically stops. The results from the long term experiment at 15°C have shown 10% mass loss after 10 days, and 19% mass loss after three months. The model predictions for evaporation of the viscous IFO-180 were close to the experimental results at both Antarctic (0°C) and temperate conditions (15°C), with  $R^2 = 0.976$  and 0.993 at 0 and 15°C, respectively (Section 3.4.2). Further investigation is needed of IFO-180, in order to determine the rate of weathering

232

caused by other processes such as oxidation, biodegradation and photolysis, as the processes examined in this study indicate that a spill of IFO-180 can persist in the Antarctic marine environment for years.

#### 6.6. The dissolution process

The dissolution process under Antarctic conditions was investigated for the three fuels used in the AAT. The aromatic fraction of the fuel is the main contributor of dissolved compounds due to their high solubility induced by the monopolar aromatic ring (Section 2.3.4). The amount of dissolved fuel compounds in the seawater is determined by the solubility of these compounds in water and their dissolution rate. Solubility is affected by environmental conditions such as water temperature and water salinity, and also by the molecular composition of the fuel, since this is responsible for co-solution effects in the water phase (Eganhouse and Calder, 1976) and supercooled liquid effects in the fuel phase (Vadas et al., 1991) (Section 2.3.4). The dissolution rate of a fuel compound is affected by its molar fraction in the fuel, its solubility, the water current velocity under the spill, and the spill length down-current (Section 2.2.5). Therefore, the solubility and dissolution rate of the compounds found in the WAFs produced by each type of fuel were experimentally measured at Antarctic conditions. Furthermore, the dissolution constants Q of the compounds found in the WAFs were determined in order to be used in any spill scenario under Antarctic conditions, since they are independent of the changeable water current velocity, spill dimensions and molar fraction of the compound. The produced data can be used to predict the initial dissolution rate of any of the three fuels investigated, or their components under Antarctic conditions.

#### 6.7. Modelling the dissolution process.

As with the evaporation process, the long term prediction of the dissolution process requires a model that takes into account the interplay between dissolution through a boundary layer on the fuel-water interface, and the diffusion forces in the inner body of the fuel. This model also needs to accommodate the changes in the conditions that affect the solubility and dissolution rate, such as the water temperature, salinity, water current velocity, changing fuel composition and spill dimensions. This model is in the final stages of development, and is going to complement the newly developed evaporation model in an effort to accurately predict the weathering of viscous oils under a wide range of environmental conditions. However, it is not yet ready to be incorporated into this PhD thesis.

#### 6.8. Partitioning among the fuel, seawater and atmosphere

Using the above (Section 6.6) data it was calculated that the dissolution of fuel compounds into the water phase accounts for a minor fraction of the mass loss due to weathering of the fuel, which at 0°C is equal to 1.96‰, 0.734‰ and 0.685‰ of that attributed to evaporation for the SAB, MGO and IFO fuel, respectively. The dissolution rate at 0°C is roughly half of that at 20°C for all three fuels. Despite this, the absolute amount of hydrocarbons that are dissolved in the water column at 0°C is 105.8%, 79.9% and 63.2% higher than that at 20°C for SAB, MGO and IFO-180, respectively, because the evaporation rate drop is roughly double that of dissolution (Section 2.3.5). This is an important observation since the dissolved hydrocarbons together with the dispersed ones are responsible for the bioavailability of the fuel spill to the organisms living in the water column. This observation, combined with the slower metabolic rate of the Antarctic marine organisms compared to those in temperate regions (Gillooly et al., 2001; Peck, 2005), highlights the necessity for measurements of the toxicity of the WAFs produced by the three fuels to the Antarctic organisms.

#### 6.9. Natural dispersion and depletion of dissolved compounds

Other weathering processes that may affect Antarctic fuel spills were also examined, including natural dispersion and the depletion of hydrocarbons from the water column. It was found experimentally using the baffled flask test that natural dispersion under polar conditions can only account for a minor loss of fuel spills, in the range of 4% mass loss for the MGO, and 2% for the IFO-180 (Section 5.5). Results from the hydrocarbon depletion test indicate that evaporation from the water surface is an important depletion process and its rate depends on the water surface-to-volume ratio (Section 2.3.7). In other words, the evaporation rate increases when we move from deep to shallow waters. Other processes also participate in the depletion of hydrocarbons, with photo- and bio-oxidation probably being the next most effective processes. Further investigation is needed in order to determine the rate of depletion caused by other processes.

#### 6.10. Applicability of chemical dispersion under Antarctic conditions.

The applicability and efficiency of a suite of six dispersants was examined for the chemical dispersion of the three fuel used in the AAT. The baffled flask test was used for this study, and although its results cannot accurately represent the results under real field conditions, it is one of the best lab tests for comparative studies presently available because it recreates the turbulent flow regime found when there are breaking waves at sea (Kaku et al., 2006).

There is no necessity to use chemical dispersion on the light SAB diesel because it is going to evaporate completely from the sea surface in a matter of a few days, even under Antarctic conditions. In contrast, due to MGO's slower weathering rate in polar conditions it is expected to persist in the marine environment for months if not treated. The results of this study indicate that MGO can be successfully treated with dispersants in both sub-Antarctic and Antarctic marine conditions at seawater temperatures of 5°C and 0°C, respectively. Treatment with dispersant appears to be one of the alternative viable

solutions for dealing with a MGO spill. All dispersants tested on MGO were efficient and the differences were small and within the method repeatability limits. The unweathered IFO-180 was non-dispersible at 0°C, but has indicated potential for partial dispersion at 5°C. For this application the best performing dispersants appear to be Finasol OSR-52 and Slickgone EW. The artificially weathered IFO-180 proved to be non-dispersible at both 0°C and 5°C, with efficiency below 15% for all the dispersants. This result emphasises the need for a rapid response if there is an IFO-180 spill within the window of opportunity for the dispersion to be successful (Section 5.5).

An important finding of this study is that the temperature drop affects the efficiency of each dispersant to a different degree. This result indicates that the order of efficiency for a suite of dispersants can change significantly between two temperatures. This finding highlights the need to test the dispersants at each temperature of interest in order to identify the most efficient dispersant for the specific fuel or oil.

Finally, a logarithmic trend has been identified to exist between the efficiency of a dispersant and the viscosity, which is due to the temperature change in viscous fuels such as IFO-180 and IFO-380. This could provide a useful insight for modellers to develop more accurate efficiency correlations in the future.

In conclusion, the experimental results and correlations produced in this work have provided the missing data on the weathering behaviour of the fuels used in the Australian Antarctic Territory. This work provides the necessary tools for the prediction of the weathering rates of the two most important processes that determine the fate and the bioavailability of fuels in the Antarctic marine environment. Additionally, this work has assessed the applicability of dispersants for the treatment of fuel spills in polar and sub-polar temperatures. The dispersant efficiency data produced give the emergency response authorities a clear picture on the potential of dispersants as an additional counter-measure for the response planning against fuel spills in polar marine environments.

236

#### 6.11. Further investigation.

There is need for investigating other processes that contribute to the weathering of the fuel spills under Antarctic conditions, especially for heavier fuels, such as the IFO-180, that persist in the marine environment for long periods of time. Evaporation and dissolution act on the fuel mainly at the initial stages of weathering, and other processes such as biodegradation and photo-oxidation continue to weather the spill for long periods of time. The rates of these processes under Antarctic conditions are currently unknown for the fuels used in the AAT. Additionally, modelling these processes for extended periods of time, especially for heavy and viscous fuels such as the IFO-180, could provide important insights for emergency response planning.

Although a first attempt was made to measure the depletion rate of dissolved fuel compounds in seawater, there is need for further investigation to measure the rates of the individual processes such as evaporation, biodegradation and photo-oxidation. This investigation will contribute to the better understanding of the fate of the dissolved fuel compounds and the exposure of the marine biota to these pollutants.

Only recently have the first models on evaporation and dissolution of oil and fuel spills that take into account the diffusion limited transfer rates been published, and these have had only limited testing on oil and fuel spills in controlled environments (Arey et al., 2007; Lemkau, 2012). More testing is required under controlled conditions, such as medium and large wave tanks, for the evaporation model presented here, as well as the previously mentioned models.

237

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# Assessing fuel spill risks in polar waters: Temporal dynamics and behaviour of hydrocarbons from Antarctic diesel, marine gas oil and residual fuel oil

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#### Statement of authors' contribution

This Appendix is a published article in Marine Pollution Bulletin. Kathryn E. Brown is the main author of the article and it will be included in her final thesis. She designed and performed the ecotoxicology experiments. She wrote and designed the structure of the paper. I developed the chemical analysis methods. I performed the analyses of the samples from the aforementioned experiments on the gas chromatograph coupled with flame ionisation detector and mass spectrometer detector. I processed all the data derived from the chemical analyses (contribution 25%). All co-authors carefully reviewed and provided feedback and valuable refinements on the final version of the manuscript, and approved it for submission and publication. Neither this manuscript nor one with similar content under our authorship has been published or is being considered for publication elsewhere, except as described above. ELSEVIER

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# Assessing fuel spill risks in polar waters: Temporal dynamics and behaviour of hydrocarbons from Antarctic diesel, marine gas oil and residual fuel oil



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#### ABSTRACT

As part of risk assessment of fuel oil spills in Antarctic and subantarctic waters, this study describes partitioning of hydrocarbons from three fuels (Special Antarctic Blend diesel, SAB; marine gas oil, MGO; and intermediate grade fuel oil, IFO 180) into seawater at 0 and 5 °C and subsequent depletion over 7 days. Initial total hydrocarbon content (THC) of water accommodated fraction (WAF) in seawater was highest for SAB. Rates of THC loss and proportions in equivalent carbon number fractions differed between fuels and over time. THC was most persistent in IFO 180 WAFs and most rapidly depleted in MGO WAF, with depletion for SAB WAF strongly affected by temperature. Concentration and composition remained proportionate in dilution series over time. This study significantly enhances our understanding of fuel behaviour in Antarctic and subantarctic waters, enabling improved predictions for estimates of sensitivities of marine organisms to toxic contaminants from fuels in the region.

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#### 1. Introduction

The seas surrounding the Antarctic continent are some of the most remote and unpolluted marine environments on earth (Halpern et al., 2008). A key concern for the Southern Ocean and for Antarctic marine waters is the accidental release of large volumes of petroleum fuel (Poland et al., 2003; Ruoppolo et al., 2013). The risk of such contamination is rising with increasing vessel traffic from an expanding tourism industry, fishing, and research and supply vessels operating in the area. Ship-to-shore fuel transfer and storage of fuel at Antarctic research stations poses a controlled but additional risk (Snape et al., 2006; Aronson et al., 2011). Polar environmental factors such as extreme weather, ice and isolation increase the risk of accidents and contamination and are also likely to impede or restrict responses to fuel pollution incidents.

The Antarctic near-shore environment is ice-covered for much of the year which reduces wave action resulting in low energy sea conditions. This creates the potential for spills to be enclosed or encapsulated in ice and thus persist in the environment for extended periods. Low temperatures and presence of ice can significantly reduce oil spreading, increase viscosity and reduce the evaporation rate of the volatile components of oils in polar waters (Payne et al., 1991; Fingas and Hollebone, 2003; Faksness and Brandvik, 2008b; Brandvik and Faksness, 2009). In addition, biodegradation rates are much slower than might be expected in temperate areas

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(Siron et al., 1995; Delille et al., 1998; Garrett et al., 2003; McFarlin et al., 2014). These factors may result in prolonged exposure of marine organisms to hydrocarbons in Antarctic waters (Stark et al., 2003).

In the event of a spill, only a certain proportion of the petroleum compounds within a fuel are water-soluble, and will dissolve into seawater producing a water accommodated fraction (WAF) (Singer et al., 2000). The hydrocarbon concentration of a WAF is dependent on fuel composition and the solubility of the various compounds within it, and is influenced by environmental conditions, particularly temperature. Hydrocarbon solubility decreases at low temperatures, however, aromatics become enhanced in seawater due to reduced evaporation (Payne et al., 1991). The components in a WAF are considered to be a major contributor to ecological impacts of an oil spill as soluble compounds are bioavailable to marine organisms in the water column and therefore have the potential to cause toxic effects (Neff, 2002; Faksness and Brandvik, 2008a).

An important consideration in the assessment of the impact of fuel spills in Antarctic and subantarctic waters is the toxicity of these watersoluble hydrocarbons to marine organisms. However, there is a paucity of such toxicity data in general for polar species and particularly for Southern Ocean organisms (Chapman and Riddle, 2005; Olsen et al., 2013; Bejarano et al., 2014). Studies of the effects of petroleum spills in cold and ice-covered waters have largely tested effects of crude oils on Arctic and boreal species (e.g. Barron et al., 2003; Perkins et al., 2003; Hansen et al., 2011; Gardiner et al., 2013). However, under the terms of the current Protocol on Environmental Protection to the Antarctic Treaty (Madrid Protocol), oil exploration is not undertaken and crude oil is not

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carried in bulk in Antarctic waters. The carriage of heavy residual fuel oil is also regulated (International Maritime Organisation, 2010) and the heaviest fuel oil now allowed in Antarctic Treaty waters is an intermediate grade (IFO 180). Light diesel and gas oils, and intermediate residual fuel oils are commonly carried as bunker fuels in Antarctic and subantarctic marine areas (ATCM, 2005) and are transferred from ship to shore to supply the energy needs of research stations. Although there have been some studies with the types of fuel oils used and carried in the Southern Ocean (e.g. McDonald et al., 1995; Smith and Simpson, 1995, Stark et al., 2003, Lane and Riddle, 2004; Payne et al., 2014) current understanding of fuel toxicity to subantarctic and Antarctic species is very limited.

Toxicity tests with polar ectotherms generally need to be conducted over extended exposure durations to account for the slower response of organisms at low temperatures (King and Riddle, 2001; Chapman and Riddle, 2005). One challenge in conducting such tests with petroleum fuel contaminants is that the concentration of volatile components in WAFs of petroleum fuels change through time, which result in changing concentrations and compositions of treatments during static tests (Redman and Parkerton, 2015). The initial measured concentration at the start of a toxicity test is commonly used in determining point estimates. For fuels however, this initial concentration does not adequately represent the actual exposure concentration throughout the test duration as there is likely to be considerable loss of hydrocarbons from test solutions over time. Its use is therefore likely to underestimate toxicity. A more accurate estimation of the overall exposure concentrations can be gained by measuring hydrocarbons during the course of exposure in toxicity testing and modelling total hydrocarbon content (THC) of WAFs through time to determine exposure concentrations, which are then used to derive point estimates (Tsvetnenko and Evans, 2002; Landrum et al., 2012).

Measuring the THC in a petroleum contaminated water sample quantifies the contributions of all hydrocarbons in the dissolved and accommodated fraction. This metric is often used to estimate the sensitivities of organisms to petroleum products. It is also utilised for risk assessments in a spill situation, including the development of species sensitivity distributions (Barron et al., 2013; Bejarano et al., 2014) and setting remediation targets and water quality guidelines for hydrocarbon contamination (Tsvetnenko, 1998; Tong et al., 1999). However, individual hydrocarbon compounds within the THC are usually not identified and the detailed chemical composition is often unknown, which limits our understanding of these complex mixtures. An increased understanding can be gained from data obtained using methods such as high performance gas chromatography-flame ionisation detection (GC-FID), which allows separation of THC into equivalent carbon number (ECN) ranges defined by approximate carbon numbers and boiling point in the GC column (Tong and Karasek, 1984; TPHCWG, 1997). ECNs can be expressed as groups (e.g. F1-3), which allows the complex hydrocarbon content within a fuel to be grouped into fractions based on individual compound mass. The relative contribution of each carbon number group to the total WAF content can be measured and temporal patterns in proportions in each fraction described. Fractions defined by ECN provide a useful metric for use in toxicity testing (Erlacher et al., 2013).

The aim of this study was to investigate hydrocarbon concentration and composition in WAFs generated at Antarctic and subantarctic marine temperatures (0 and 5 °C) from Special Antarctic Blend diesel (SAB), marine gas oil (MGO), and an intermediate grade of residual fuel oil (IFO 180). The patterns of subsequent hydrocarbon losses from these WAFs are compared in time series exposures over seven days at 0 and 5 °C, including the relative proportions in ECN groups.

# 2. Methods

# 2.1. Test fuels description and source

Two diesel fuels (SAB and MGO) and a residual fuel oil (IFO 180) were selected for this study based on their common use within the Antarctic and subantarctic region. Table 1 shows physical properties of the three fuels. SAB is a middle distillate produced by a straight run refinery process and contains *n*-alkanes in the range  $n-C_{9-14}$ , with the highest peak around  $n-C_{12}$ , along with other branched and cyclic alkanes and aromatic hydrocarbons (Snape et al., 2005). MGO is a marine distillate composed mainly of *n*-alkanes, cycloalkanes and aromatic hydrocarbons, predominantly in the  $n-C_{9-25}$  range (Shell, 2010). IFO 180 is produced by straight run and catalytic cracking processes and is a combination of mainly residual oil blended with around 6 to 7% of middle distillate components of *n*-alkanes, branched and cyclic alkanes and aromatic hydrocarbons. Composition of an IFO 180 can vary according to source oil, refinery process and percentage of distillate added (Uhler et al., 2007). This complex mixture can have a carbon range from C<sub>6</sub> to >  $n-C_{40}$  and may contain polycyclic aromatic hydrocarbon compounds from cracked components (BP, 2006).

SAB was obtained from a storage tank at Davis Station, East Antarctica in January 2010. The MGO sample was drawn from the bunker of the Australian research and supply vessel *Aurora Australis*, after refuelling in Hobart in December 2009. IFO 180 was supplied by BP Australia from the Whinstanes Terminal, Brisbane in October 2009.

# 2.2. Production of the water accommodated fraction

Replicate experiments were conducted to determine the THC and ECN ranges in WAFs from SAB, MGO and IFO 180 fuels in seawater at Antarctic (0 °C; n = 7) and subantarctic (5 °C; n = 1) temperatures. The methods for preparing WAFs were based on standard protocol (Singer et al., 2001) with some recommended modifications (Barron and Ka'aihue, 2003). These experiments were run in conjunction with toxicity tests with Antarctic and subantarctic marine invertebrates (Harrison et al., 2013; Brown et al., 2015a).

Natural seawater was filtered ( $0.5 \mu m$ ) to produce filtered seawater (FSW) and chilled to test temperature. Average salinity of FSW was 34.9%, pH 8.10, and dissolved oxygen 10.98 mg/L.

Water accommodated fractions of each fuel made at 0 °C had a fuel to seawater loading of 1:25 (n = 4) or 1:40 (n = 3). The WAFs made at 5 °C (n = 1) had a fuel to seawater loading of 1:40. Chilled 10 L glass aspirator bottles were filled with FSW at the required temperature leaving 20% headspace. Fuel was carefully added to the FSW at the volume specific to the loading ratio for each experiment. The bottles were sealed and set on magnetic stirrers in unlit temperature-controlled cabinets at either  $0 \pm 1$  or  $5 \pm 1$  °C. The magnetic bar rotation speed was ~200 rpm, which created a minimal vortex of <1 cm depth. The 1:40 WAFs (at 0 and 5 °C) were stirred for ~26 h and drawn off after a 10 min settling period (after Singer et al., 2000). The 1:25 WAFs (at 0 °C only) were stirred for 18 h and WAFs were drawn off after a 6 h settling period. These WAF generating methods replicated methods used in companion toxicity tests. The difference in stirring times reflected a change in methodology between two series of toxicity tests when a WAF settlement period was incorporated.

WAFs were drawn off into chilled glass bottles and samples were either, extracted immediately for measurement of initial THC and ECN fractions (WAF initial concentration), or placed into climate controlled cabinets in time series tests. See Fig. 1 and Table 2 for test design.

#### 2.3. Measurement of initial concentrations in water accommodated fractions

Samples were extracted immediately after WAFs were decanted for measurement of the initial THC and ECN fractions in WAFs (Time 0).

# Table 1

Physical	properties	of t	he 1	three	test	fuels.
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Test fuel		Vapour pressure (kPa)	Viscosity (cSt)	Density (g/cm3 at 15 °C)
Special Antarctic Blend diesel	SAB	<0.1	<7 at 40 °C	0.81
Marine gas oil	MGO	<0.1	3.0 at 40 °C	0.85
Intermediate residual fuel oil	IFO 180	<0.1	180 at 50 °C	0.99



Fig. 1. Illustration of test setup to measure the total hydrocarbon content (THC) in water accommodated fractions (WAF) of fuels at 0 and 5 °C. Abbreviations are; filtered seawater (FSW), dichloromethane (DCM) and gas chromatography-flame ionisation detection (GC-FID).

Volumetric dilutions were made of the freshly decanted WAF stocks of SAB, MGO and IFO 180 with FSW (Table 2). Replicate samples were extracted immediately after dilutions were made. Samples (~480 mL) of the 100% WAF stock and of each dilution were dispensed into 500 mL beakers, and then poured into 500 mL amber glass bottles for extractions. These decanting methods were used so as to be identical to the conditions in the time series tests. The initial THC and ECN ranges were calculated for each fuel from Time 0 concentrations of one 1:40 WAF at 5 °C, and mean concentrations of 1:40 WAFs (n = 3) and 1:25 WAFs (n = 4) at 0 °C. Further testing of loss of hydrocarbons from WAFs was performed in time series tests.

# 2.4. Time series tests

Time series tests were conducted to measure the loss of hydrocarbons from decanted WAF over 7 days at Antarctic (0 °C) and subantarctic (5 °C) seawater temperatures (Table 2). Replicate samples of dilutions and 100% WAFs of SAB, MGO and IFO 180 made at 5 °C, and two of the 1:25 loading 0 °C WAFs, were dispensed into beakers for sampling at multiple time points from 6 to 168 h. These beakers were placed into temperature-controlled cabinets at 0  $\pm$  1 °C or 5  $\pm$  1 °C which were lit by three fluorescent tubes.

Time series tests were performed under conditions which conformed to protocols used in companion toxicity tests conducted on Antarctic and subantarctic marine invertebrates (Harrison et al., 2013; Brown et al., 2015a), and to simulate evaporation of hydrocarbons from open water in polar conditions. Each individual dissolved hydrocarbon compound is expected to evaporate into the air following an exponential concentration curve calculated with the air to water partition coefficient of that hydrocarbon (Mackay et al., 1979). Salinity adjustments were made in the 0 ° C time series tests every two days to replicate conditions in toxicity tests, in which purified and deionized water (Milli-Q) was added to open beakers to limit increases in salinity due to water evaporation. The meniscus was marked with a line after beakers were filled with treatments, and on the second day, and each consecutive two days, water that had evaporated from any remaining beakers was replenished to the line with drops of Milli-Q water at the test temperature. To compare loss of hydrocarbons under open and sealed conditions, 1 L sealed glass bottles of 100% WAF were also kept in the temperature-controlled cabinets to be sampled at 24 and 168 h (Table 2).

# 2.5. Analysis of total hydrocarbon content

Samples were extracted immediately after dilutions were made in initial concentration tests, or immediately after removing beakers from the temperature-controlled cabinets at the appropriate time point in time series tests. For measurement of THC of sealed WAFs, a sample was dispensed from the bottle into a 500 mL beaker at the required time point.

The contents of the beakers were poured into 500 mL amber glass bottles and  $100 \,\mu$ L of an internal standard (cyclooctane, bromoeicosane, *p*-terphenyl, tetracosane-d50, 1,4-dichlorobenzene diluted in

#### Table 2

Design of tests to measure total hydrocarbon content (THC) from 0 to 168 h in dilutions and 100% stock solutions of water accommodated fractions (WAF) of Special Antarctic Blend diesel (SAB), marine gas oil (MGO) and intermediate fuel oil (IFO 180) in open and sealed containers at 0 and 5 °C. Loading ratios indicate fuel: seawater volumes. 1:25 WAFs were stirred for 18 h with a 6 h settling period and 1:40 WAFs were stirred for ~26 h.

Fuel:	Temperature	Sampling	Dilutions (% WAF)			
seawater loading	(°C)	times (h)	SAB	MGO	IFO 180	
1:25	$0\pm 1$	0 ( $n = 4$ ), 6, 12, 18 <sup>c</sup> , 24, 48, 72 <sup>d</sup> , 96, 168 ( $n = 2$ ) 24 sealed ( $n = 2$ )	1ª, 10, 25 <sup>b</sup> , 50, 100 100	1ª, 10, 50, 100 100	1ª, 10, 50, 100 100	
1:40	$0 \pm 1$	0 (n = 3) 168 sealed (n = 2)	1, 10, 50, 100 10 <sup>e</sup> , 50 <sup>e</sup> , 100	1, 10, 50, 100 10 <sup>e</sup> , 50 <sup>e</sup> , 100	1, 10, 50, 100 10 <sup>e</sup> , 50 <sup>e</sup> , 100	
1:40	5 ± 1	0 ( <i>n</i> = 1) 6, 24, 48, 72, 168 ( <i>n</i> = 1) 168 sealed ( <i>n</i> = 1)	10, 50, 100 100 100	10, 50, 100 100 100	10, 50, 100 100 100	

<sup>a</sup> THC in 1% WAFs was analysed in 0 and 6 h samples only.

<sup>b</sup> THC in 25% SAB WAF was analysed from 0 h samples only.

<sup>c</sup> THC at the 18 h time point was analysed from 100% WAFs only.

<sup>d</sup> THC at the 72 h time point was analysed from 50 and 100% WAFs only.

<sup>e</sup> THC in 10 and 50% dilutions measured in one test only.

dichloromethane) was added. The samples were extracted with 10 mL of dichloromethane and aliquots were transferred to 2 mL vials and refrigerated until analysis. Samples of seawater blanks and SAB spiked seawater blanks were included.

The extracts were analysed for THC with an Agilent 6890N GC-FID with a split/splitless injector and Agilent 7683 ALS auto-sampler. Four microlitres of extract was injected (5:1 pulsed split) with helium carrier gas at 30 psi, 310 °C and velocity of 10.1 mL/min at injector. Column flow was 1.3 mL/min held for 17 min and then increased to 3.0 mL/min for 7 min. The initial oven temperature was 36 °C for 3 min, and then increased at 18 °C/min until reaching final temperature of 320 °C, which was held for 7 min. The detector temperature was 330 °C.

The response of all aromatic compounds dissolved in the WAF were considered equal as the WAFs consist almost exclusively of monoaromatic and diaromatic hydrocarbons, and response factors of individual hydrocarbons on GC-FID are practically identical within the same class of hydrocarbons (Tong and Karasek, 1984). The relative response factors (RRFs) of the compounds in the internal standard mixture were determined separately since some are not pure hydrocarbons but contain heteroatoms (e.g. 1,4-dichlorobenzene), rendering their response on GC-FID considerably different. A synthetic mix of alkanes from undecane to hexatriacontane (n-C<sub>11</sub> to n-C<sub>36</sub>) and the internal standard compounds, all in known quantities, was used to determine the relative response factor (RRF) of each internal standard against the alkanes. These RRFs were used to quantify the WAF THC by converting the total

GC-FID integrated area to mass of dissolved hydrocarbons extracted from a known volume of seawater. Total hydrocarbon content was reported as mass per litre of seawater (µg/L).

The proportion of total hydrocarbon content in equivalent carbon number (ECN) fractions was calculated as:

- F1- $\Sigma$  hydrocarbons with equivalent carbon numbers  $< n-C_9$ ;
- F2- $\Sigma$  hydrocarbons within the range *n*-C<sub>9</sub> to *n*-C<sub>18</sub>;
- F3– $\Sigma$  hydrocarbons within the range *n*-C<sub>19</sub> to *n*-C<sub>28</sub>.

The partitioning of compounds with a carbon number above  $n-C_{28}$  is minimal in seawater and any hydrocarbons in the fraction  $>n-C_{28}$  are likely to be from micro droplets of fuel in suspension in the seawater (Redman et al., 2012). The methods used to generate WAFs were designed to only have the soluble fractions in solution (Singer et al., 2000), and minimal presence of micro droplets was expected. Micro droplets in WAF are likely to be mainly composed of alkanes which have low toxicity compared to aromatic hydrocarbons (Anderson et al., 1974; Adams et al., 2014). Aromatic hydrocarbons are highly soluble in seawater (Eganhouse and Calder, 1976) and exert toxicity by disrupting the biological membrane function of marine organisms (Sikkema et al., 1994), whereas suspended particles are not dissolved and are less bioavailable. Including the heaviest fraction  $>n-C_{28}$  in the calculation of THC would skew toxicity by assigning the same toxicological effect to the undissolved micro droplets as to



Fig. 2. Chromatograms from GC-FID analysis of fresh fuels (left) and 100% water accommodated fractions (WAF) at 0 °C (right) of (a) Special Antarctic Blend diesel (SAB) (b) marine gas oil (MGO) and (c) intermediate fuel oil (IFO 180).

the dissolved fraction (Neff et al., 2013). This would overestimate the concentration of toxic hydrocarbons present in WAFs and so lead to an underestimation of the toxicity of the mixture to organisms in ecotoxicological investigations. Therefore compounds  $>n-C_{28}$  are not included in THC of WAFs.

Preliminary chemical analyses showed an acceptably low level of variability between replicate samples in initial concentrations of all tests (mean SD = 4.8%) and therefore the hydrocarbon content in one replicate from each time point was used in the analysis of results. A sample of each of the fresh fuels was analysed by GC-FID, under the same conditions as above, to compare chromatograms of fuels with those of WAFs (Fig. 2).

# 2.6. Data analysis

For each fuel, the relative (%) loss of THC from 100% WAFs in the time series tests was calculated as the percentage of the mean initial THC remaining at 6 to 168 h (Fig. 3). The hydrocarbons ( $\mu$ g/L) in fractions F1–3 were calculated as percentages to illustrate changes in ECN proportions in WAFs over time (Figs. 4 and 5). To compare agreement between measured and nominal values of THC over the duration of time series tests, a Pearson product correlation regression was used to test for a linear relationship between WAF dilution (%) and measured THC ( $\mu$ g/L) in the 0 °C time series test at time points from 0 to 168 h (Fig. 5).

#### 3. Results

# 3.1. Composition of water accommodated fractions

The WAFs showed a reduced range of hydrocarbons compared with the fresh fuels (Fig. 2). The chromatograms of the fresh fuels display the homologous series of *n*-alkanes characteristic of crude oil-derived fuels, although the highly refined SAB has a narrower range than MGO and IFO 180. These *n*-alkanes and the insoluble higher molecular weight compounds are at trace concentrations in WAF chromatograms, which indicates that the WAFs did, as intended, contain the water-soluble components of the fuel.

The WAFs of each fuel contained mostly monoaromatic and diaromatic hydrocarbons. The dominant compounds in the SAB WAF were 1,2,4-trimethylbenzene, naphthalene and 2-methylnaphthalene (Fig. 2a). The most abundant compounds in the MGO WAF were benzene, toluene, *m*-xylene and 1,2,4-trimethylbenzene (Fig. 2b), while the IFO 180 WAF was dominated by benzene, toluene, *m*-xylene, 1,2,4-trimethylbenzene, naphthalene and 2-methylnaphthalene (Fig. 2c).

The three WAFs showed different distributions of hydrocarbons in the defined ECN fractions, due to the different chemical compositions of the fuels. Hydrocarbons in the SAB WAFs were in the ranges  $< n-C_9$ and  $n-C_9-C_{18}$ , therefore THC in SAB WAFs was calculated as the sum of the weight of compounds in these two ECN ranges (F1 and F2). Compounds were present over a greater carbon range in MGO and IFO 180 and THC was calculated as the sum of  $< n-C_9$ ,  $n-C_9-C_{18}$  and  $n-C_{19}-C_{28}$ , (F1, F2 and F3). Compounds heavier than  $n-C_{28}$  were not included in the calculation of WAF THC as they were likely to be mainly derived from micro droplets of fuel (see Methods) and only minor traces were present (mostly < 1% in freshly made 100% WAFs).

# 3.2. Initial concentrations of hydrocarbons in water accommodated fractions

Total hydrocarbon content in the freshly made WAFs differed between the three fuels. Overall, SAB was the most water-soluble fuel, having the highest THC in WAFs, followed by MGO, with much lower THC in IFO 180 WAFs (Table 3). Measured hydrocarbon concentrations were generally consistent between replicate WAF mixes at 0 °C (standard errors ranged from 2.65 to 3.64% in 1:25 loading, and from 2.81 to 9.39% in 1:40 loading WAFs). The distribution of hydrocarbons in ECN fractions F1, F2 and F3 showed a consistent pattern for each fuel across the freshly decanted WAFs, although for IFO 180 proportions were lower in F2 and higher in F3 at 1:25 loading than in the 1:40 loading WAFs (Table 3). The 1:40 SAB and MGO WAFs at 0 °C had higher THCs than those with the same fuel loading made at 5 °C. This difference was not apparent in the IFO 180 WAFs, which had similar initial concentrations at both 0 and 5 °C.

# 3.3. Hydrocarbon content in WAF time series tests

The THC through time in 100% WAFs of the three fuels is shown in Table 4, with the mean ( $\mu$ g/L  $\pm$  % SD) of two time series tests at 0 °C, and the results of one test at 5 °C. Total hydrocarbon loss rates were different between the fuels, with MGO depleting faster than SAB and IFO 180 (Table 4, Fig. 3). Initial THC in WAFs was in the order SAB > MGO > IFO 180. From 72 h this order changed to SAB > IFO 180 > MGO.

When standard deviations at 0 °C were calculated as relative standard deviations (% RSD), over time variability was lowest in IFO 180 WAFs (mean 3.3%), and test variability was somewhat greater in MGO and SAB WAFs (mean 10.0 and 9.6% respectively). The generally low between-test variations in THC over time indicate relatively high reproducibility of the temporal exposure tests.

The relative loss of THC for each fuel WAF is shown in Fig. 3 as the percentage of the initial concentration of 100% WAFs from 0 to 168 h. The relative THC in each fuel WAF differed over time due to their respective hydrocarbon depletion rates (Fig. 3). The MGO WAF exhibits the fastest depletion rate with a curve closest to exponential. MGO WAF has the greatest percentage of the light F1 with the remainder predom-



**Fig. 3.** Relative loss of total hydrocarbon content (THC) from 100% water accommodated fractions of Special Antarctic Blend diesel (SAB), marine gas oil (MGO) and intermediate fuel oil (IFO 180) exposed at 0 °C and 5 °C in time series experiments from 0 to 168 h. Inset shows detail of 0–24 h region.

inantly in the medium fraction F2 (Table 3) and there is a small contribution from the heavier F3 at longer depletion times. The SAB WAF exhibits a depletion curve which is in between exponential and square root shape because of the existence of dissolved hydrocarbons with smaller partition coefficients contributing more to the curve at longer depletion times. The IFO 180 WAF has the widest range of dissolved hydrocarbons with large variation in partition coefficient, which results in a composite depletion rate that most closely approaches the square root shaped curve. The initial depletion rate is fast due to the presence of the F1 compounds but drops significantly as heavier components dominate the WAF composition. Depletion of SAB continued throughout the test duration, in contrast to the other two fuels which plateaued around 72–96 h.

# 3.3.1. Effect of temperature on THC depletion

Differences in the behaviour of the 0 and 5 °C WAFs were observed, with the effect of temperature most pronounced in SAB. For this fuel depletion rates were similar at both temperatures up to 24 h, but thereafter THC depletion was faster at 5 °C than at 0 °C (Fig. 3). SAB showed similar depletion characteristics to IFO 180 at 0 °C, but at 5 °C followed a similar exponential trend to the MGO WAF. At 5 °C SAB was almost 75% depleted after 48 h, however it took nearly 168 h at 0 °C to deplete to the same proportion. This pattern resulted in SAB and IFO 180 WAFs at the subantarctic temperature having almost the same THC after





7 days exposure (Table 4) despite initial SAB WAF concentrations being over three times greater.

# 3.3.2. Proportions of THC and ECN fractions through time

The initial composition and patterns of depletion of the three ECN fractions (F1 < n-C<sub>9</sub>; F2 n-C<sub>9</sub>-C<sub>18</sub>; F3 n-C<sub>19</sub>-C<sub>28</sub>) for MGO and IFO 180 WAFs are illustrated in Fig. 4. SAB is not included in Fig. 4 as 99% of hydrocarbons were in the F2 range (Table 3). This is an expected match with the main carbon range of the neat fuel (n-C<sub>9</sub>-C<sub>14</sub>). The 1% of F1 hydrocarbons present in SAB WAFs at 0 h had dissipated entirely by 96 h.

The volatile lower molecular weight compounds in the F1 hydrocarbon fraction ( $<n-C_9$ ) were initially most abundant in the MGO WAFs at both 0 and 5 °C (26 and 28% of THC respectively) (Fig. 4a and b) while the freshly decanted IFO 180 WAFs had 14% of compounds in F1 at both temperatures (Fig. 4c and d). As the THC in the MGO WAF was reduced over time, the loss was proportionally greater in F1, which had mostly evaporated at around 96 h, when 92% of THC had been lost. The F1 in the IFO 180 WAF was similarly depleted by 96 h, although 71% of THC had been lost by that





**Fig. 4.** Proportions of total hydrocarbons in F1 (<*n*-C<sub>9</sub>), F2 (*n*-C<sub>9</sub>-C<sub>18</sub>) and F3 (*n*-C<sub>19</sub>-C<sub>28</sub>) during time series exposures of 100% water accommodated fractions of marine gas oil (MGO) at a) 0 °C and b) 5 °C and intermediate fuel oil (IFO 180) at c) 0 °C and d) 5 °C. Dots show the percentages of total hydrocarbon content (THC) remaining at each time point. Error bars in 0 °C tests show standard deviation from mean. Data are for open conditions except for far right columns which were sealed.

time. After F1 was depleted, the levels of THC in the WAFs remained steady to 168 h.

WAFs with temperature, with little change in proportions of the F2 fraction after 7 days at 5  $^{\circ}$ C (1% increase) compared to a 10% decrease over the same time period at 0  $^{\circ}$ C.

Although temperature did not greatly affect the pattern of total hydrocarbon depletion in MGO and IFO 180, there were temporal differences in the proportions of ECN fractions between 0 and 5 °C in these fuels. As the proportions of lighter F1 hydrocarbons in MGO WAFs were reduced, there was a corresponding increase in the proportion of heavier F3 hydrocarbons, while the F2 percentage remained relatively unchanged over time at 0 °C. This was not observed in the 5 °C experiment, with only minimal increase in the F3 proportions. There was a different pattern in the F2 of the IFO 180

The results showed loss of hydrocarbons from the WAFs was minimal in sealed conditions after 24 h at 0 °C and after 168 h at 5 °C, with concentrations close to those in open samples exposed for 6 h (Fig. 4). The relative composition of the sealed samples also showed little change over time. The three fractions were at the same proportions at 24 h at 0 °C as they were at the start and there was a slight reduction in the proportion of F1 hydrocarbons after 168 h at 5 °C.



**Fig. 5.** Relationship between dilution and total hydrocarbon content ( $\mu$ g/L) at time points from 0 to 168 h at 0 °C. Trend lines and R<sup>2</sup> values are for dilutions of a) Special Antarctic Blend diesel (SAB), b) marine gas oil (MGO) and c) intermediate fuel oil (IFO 180) WAFs. Error bars show standard deviation from mean and are sometimes smaller than the symbols. Column graphs show the proportions of total hydrocarbons (% µg/L  $\pm$  SD) in equivalent carbon number groups F1 < *n*-C<sub>9</sub>, F2 *n*-C<sub>9</sub>-C<sub>18</sub> and F3 *n*-C<sub>19</sub>-C<sub>28</sub> in dilutions of 10, 50 and 100% WAFs at time points from 0 to 168 h.

#### Table 3

Mean initial total hydrocarbon content (THC)  $\mu$ g/L ( $\pm$  standard deviation) measured by GC-FID in undiluted (100%) WAFs of Special Antarctic Blend (SAB), marine gas oil (MGO) and intermediate fuel oil (IFO 180) prepared at 0 and 5 °C for 1:25 and 1:40 fuel to seawater loadings. The percentage of THC in each fraction based on equivalent carbon number ranges is shown for F1 (<n-C<sub>9</sub>), F2 (n-C<sub>9</sub>-C<sub>18</sub>) and F3 (n-C<sub>19</sub>-C<sub>28</sub>).

	1:25 loading at 0 °C ( $n = 4$ )			1:40 loading at 0 °	1:40 loading at 5 °C ( $n = 1$ )				
THC	SAB	MGO	IFO 180	SAB	MGO	IFO 180	SAB	MGO	IFO 180
$\mu g/L \pm SD$	$2912 \pm 178.5$	$1515 \pm 110.2$	$567 \pm 40.3$	$2825\pm 649.9$	$1920\pm107.7$	$746 \pm 135.8$	2394	1439	737
(%) F1 F2 F3	1 99	26 72 2	14 71 15	1 99	27 72 1	15 75 10	1 99	28 71 1	14 77 9

#### Table 4

Total hydrocarbon content (mean  $\mu$ g/L  $\pm$  % standard deviation) in time series tests measured by GC-FID for undiluted (100%) WAFs of Special Antarctic Blend diesel (SAB), marine gas oil (MGO) and intermediate fuel oil (IFO 180) with exposure durations of 0 to 168 h at Antarctic (0 °C, n = 2) and subantarctic (5 °C, n = 1) marine temperatures.

WAF	Time (h)								
	0	6	12	18	24	48	72	96	168
0 °C SAB MGO IFO 180	$2769 \pm 3.28$ $1589 \pm 7.26$ $599 \pm 1.03$	$\begin{array}{c} 2413 \pm 4.47 \\ 1230 \pm 1.64 \\ 497 \pm 4.80 \end{array}$	$\begin{array}{c} 2124 \pm 5.64 \\ 973 \pm 1.28 \\ 436 \pm 0.74 \end{array}$	$\begin{array}{c} 1808 \pm 5.78 \\ 798 \pm 1.01 \\ 385 \pm 0.19 \end{array}$	$\begin{array}{c} 1494 \pm 14.90 \\ 587 \pm 4.37 \\ 325 \pm 1.10 \end{array}$	$1047 \pm 12.71$ 298 ± 19.46 254 ± 1.17	$872 \pm 11.84$ $169 \pm 11.17$ $194 \pm 2.84$	$\begin{array}{c} 789 \pm 14.93 \\ 133 \pm 17.62 \\ 172 \pm 11.72 \end{array}$	$685 \pm 12.77$ $112 \pm 26.09$ $172 \pm 6.56$
5 °C SAB MGO IFO 180	2394 1439 737	2176 1061 641			1261 543 462	648 227 297	426 108 269		266 106 258

# 3.3.3. Dilution concentration relationship through time

We found good agreement between measured and nominal values in WAF dilutions for all three fuels at the start of the 0 °C time series test, with significant correlations between percent dilution and mean THC ( $\mu$ g/L) (SAB  $\alpha$  = 0.001, R<sup>2</sup> = 0.9993; MGO  $\alpha$  = 0.01, R<sup>2</sup> = 0.9994; IFO 180  $\alpha$  = 0.001, R<sup>2</sup> = 0.9991, Fig. 5). The relationships were also strong through time, indicating that the loss rate was similar in each WAF dilution. SAB WAFs maintained the strongest correlations over time (R<sup>2</sup> > 0.9973) which were significant at each time point up to 168 h. As total hydrocarbons in the WAF test solutions were depleting, the dilution/concentration relationships in IFO 180 and MGO were slightly lower than for SAB, although R<sup>2</sup> values remained high for the duration of the test (168 h R<sup>2</sup> = 0.9925 and 0.9572 for MGO and IFO 180, respectively) and dilution/concentration were significantly correlated at 24 h in IFO 180 and at 48 h in MGO.

The relative proportions in F1, F2 and F3 were very similar in 100% and 50% WAFs and these proportions remained closely matched through time at 0 °C (column graphs in Fig. 5). Differences between the proportions in the ECN fractions across all dilutions were less apparent at the start of tests, however, over time the 10% dilutions showed some variation in the proportions in carbon ranges when compared to the full strength and 50% WAFs. This variation was most apparent in the F3 fraction in the 10% MGO WAF, and became greater as the lighter range hydrocarbons dissipated from solution over time and the THC remaining dropped to very low levels.

#### 4. Discussion

#### 4.1. Chemical composition of cold seawater WAFs

The WAFs of SAB, MGO and IFO 180 made at Antarctic and subantarctic seawater temperature show patterns of solution and depletion of hydrocarbons influenced by the effects of temperature. The WAF initial compositions are different from those of the neat fuels and consist mainly of aromatic hydrocarbons. Monoaromatic hydrocarbons exhibit higher solubility in cold than in temperate seawater, contrary to diaromatic hydrocarbons which show lower solubility at 0-5 °C compared to 15–20 °C (Bohon and Claussen, 1951; Economou et al., 1997). However, temperature has a significant effect on the partial vapour pressures of the fuel hydrocarbons. Low Antarctic temperatures increase the viscosity of a fuel, and as a consequence decrease the molecular diffusion velocity of the hydrocarbons in the fuel body. This greatly decreases the rate of evaporation of the fuel components, increasing the contact time with the seawater and increasing the ratio of dissolved to evaporated hydrocarbons. Increased proportions of volatile and semi-volatile organic analytes and aromatic hydrocarbons, particularly those with one and two aromatic rings, have previously been found in cold seawater WAFs compared to those produced with warmer seawater (Anderson et al., 1974; Camus et al., 2015; Faksness et al., 2008; Perkins et al., 2003, 2005). The higher aromatic hydrocarbon content in diesels means they may be more toxic than other oils (Anderson et al., 1974; Neff et al., 2000) with the potential for acute toxicity to aquatic organisms by general and polar narcosis (Rowland et al., 2001). High aromatic content of these two cold water WAFs may enhance their toxicity in relation to comparitive distillate WAFs made at higher temperatures.

The chemical composition of WAFs of these three fuels which are carried in Antarctic and subantarctic waters differed in initial THCs and proportions in ECN fractions due to their chemical and physical properties. The two distillate fuels tested here (SAB and MGO) have similar density and viscosity but differed in the hydrocarbon content in WAFs. Initial THC was substantially higher in SAB, up to twice as much as in MGO. Special Antarctic Blend is a highly refined diesel developed for use in polar conditions and 99% of hydrocarbons which dissolve into WAFs are in the F2 fraction ( $n-C_9-C_{18}$ ), with peaks of the monoaromatic 1,2,4-trimethylbenzene, and the diaromatics

naphthalene and 2-methylnaphthalene. The IFO 180 had a much lower THC in WAF compared to the distillate fuels due to its higher viscosity.

The proportion of THC in the ECN F1 fraction  $(< n-C_9)$  was substantial in freshly decanted MGO WAFs (26-28%) and was also a notable percentage in IFO 180 (14%) (Fig. 4, Table 3). The monoaromatics in F1, benzene, toluene, ethylbenzene and xylene (BTEX) are sometimes considered to be an insignificant proportion of residual fuel oils such as IFO 180 (Anderson et al., 1974; Bellas et al., 2013) and are therefore often not considered in risk assessment of these fuels in other regions. However, the increased monoaromatic solubility at cold temperatures may have contributed to the proportion of F1 in IFO 180 WAF observed here. The chemical composition and physical properties of residual fuel oils can also vary widely worldwide according to the source of feed stock and the refinery processes, with varying quantities of light diesel blended with residuum to bring the fuel to the required density (Uhler et al., 2007). This causes concurrent differences in toxic effects from residual fuels of the same grade (Hatlen et al., 2010) therefore the results with the batch of IFO 180 used in the present study may differ from other IFO 180 s made under the same conditions.

This study shows that the light F1 fraction can persist in solution in seawater at polar temperatures for up to 96 h before depletion. These results support the recommendation that the contribution of the more volatile organic compounds should be considered in risk assessment of fuel spills at low temperatures (AMAP, 2010) due to the relatively high concentration and much slower evaporation of aromatics than is seen in warmer climates. Lighter fractions containing BTEX are acutely toxic but are generally assumed to pose a toxicity risk for only a matter of hours in warmer regions due to their volatility (Neff et al., 2000; Wang and Fingas, 1997; Camilli et al., 2010). However, the results from this study indicate that this period of risk is protracted in polar seawater.

The higher molecular weight F3 fraction  $(n-C_{19}-C_{28})$  contributed a greater percentage to the cold water IFO 180 WAF, which is characterised by a wider range of hydrocarbons than the other fuels tested. Both the IFO 180 and MGO WAFs were composed of all three fractions for up to 96 h, with F3 becoming proportionally greater as F1 was depleted. This heavier fraction persisted over time to become a substantial fraction of the IFO 180 WAF (Fig. 4) and is likely to be of greater risk to marine organisms due to the toxicity of higher molecular weight PAHs (Adams et al., 2014).

The fuel loadings used in these experiments may be considered a worst case scenario (Singer et al., 2000), however the possibility of greater fuel thicknesses are more likely in low temperatures and ice-covered environments which can enclose spills, reduce spreading, increase viscosity and reduce evaporative loss (Payne et al., 1991; Brandvik and Faksness, 2009; Fingas and Hollebone, 2003). These factors, combined with extreme isolation and limited cleanup capabilities in polar environments (Ruoppolo et al., 2013), are likely to contribute to greater persistence of oil (Tsonopoulos, 2001). This persistence, along with enhanced concentrations of aromatics in solution in seawater at cold temperatures, slower evaporation of volatiles and slow degradation rates (Siron et al., 1995; Delille et al., 1998) could result in marine organisms being exposed to toxic compounds for extended periods and potentially increases the risks from fuel spills to Antarctic and subantarctic marine biota in the water column.

# 4.2. Temporal WAF depletion patterns and influence of temperature

Evaporation out of solution (diffusion through water-air interface) is assumed to be the main process of depletion observed in this study after the WAF is separated from the fuel, with the total depletion rate being the sum of all the individual hydrocarbon rates. As the more volatile hydrocarbons deplete faster, the resulting composite THC curve is influenced more by the lighter hydrocarbons earlier in time, and later by the heavier dissolved hydrocarbons (or the hydrocarbons with smaller  $K_{iaw}$ ). This gradual shift gives a shape to the composite THC curve that is intermediate between the exponential and square root shape curve depending on the composition and the range of partition coefficients of the dissolved hydrocarbons (see Fig. 3).

Exponential loss of THC at polar temperatures was most notable in MGO in this study with this loss occurring over 72 h. This is in contrast to patterns of depletion of THC from WAFs at higher temperatures that have been characterised by an exponential loss in the first 12 h. The THC percentages remaining in the WAFs after 24 h at Antarctic and subantarctic temperatures are considerably higher than those measured in similar experiments at tropical temperatures by Tsvetnenko and Evans (2002), who found only 5 to 37% of total hydrocarbons remained of the water-soluble fraction of volatile crude oils after 24 h. The curve of SAB depletion at 0 °C is similar to that modelled for diesel fuel evaporation (Fingas, 1997) at a rate consistent with a square root with time equation. The depletion curves for SAB were different at Antarctic compared to subantarctic temperatures with a slower decline at 0 °C, potentially due to greater enhancement of the aromatic hydrocarbon content in the F2 hydrocarbons in that fuel at 0 °C. Greater persistence of components of the highly refined SAB fuel is observed at Antarctic temperatures (mean 685 µg/L after 7 days), with the recalcitrant compounds in WAFs present for more than three times longer at 0 °C than at 5 °C. Defining smaller ECN ranges would give more insight into the composition of SAB using this method to enable further understanding of this difference. Contrasting patterns at 5 °C than 0 °C were observed in IFO 180 with slower depletion at 5 °C, however THC was initially higher in the 5 °C WAFs, possibly due to the longer stirring time.

#### 4.3. Implications for toxicity testing of Antarctic organisms

The sensitivities of marine organisms determined from laboratory toxicity tests of WAFs are utilised in decision-making in spill situations, risk assessments and in establishing acceptable water quality guidelines. As THC is a commonly used metric in these assessments, the enhanced understanding of the behaviour of hydrocarbons and THC in cold seawater WAFs from fuels provided by this study, which are carried at high volumes in Antarctic and subantarctic waters, is relevant for management of petroleum use in these regions. These findings will be used in studies of the toxicity of these three fuels to Antarctic and subantarctic marine invertebrates. They illustrate the complexity of fuel dynamics in cold seawater and therefore the importance of measuring the hydrocarbon content in toxicity test treatments for estimation of the sensitivity of marine organisms to petroleum contaminants, rather than reporting concentrations based on loading rate of oil or percent WAF dilution (Bejarano et al., 2014; Coelho et al., 2013; Redman and Parkerton, 2015; Singer et al., 2001).

It is particularly important to show the changes in exposure concentrations during toxicity testing in open static exposures, which are characterised by declining total concentration, time-varying rates of loss and changing composition of test solutions (Landrum et al., 2013; Redman and Parkerton, 2015). This study showed variable loss rates from open WAFs, with higher rates in the first 24 h (between 37 and 63% loss) compared to 12 to 26% loss in the following 24 h period. These measured hydrocarbon concentrations in WAFs of the three fuels in test solutions provide an accurate estimate of the THC to which organisms are exposed for the duration of tests. Using only the initial concentration at the start of a test, or the mean of an initial and final (end of test) concentration to determine point estimates gives a higher value for the THC exposure concentration and consequently underestimates the toxicity of the mixture. The time weighted mean THC can be calculated using more frequent measurements over time, to derive exposure concentrations which enable more realistic sensitivity estimates (Landrum et al., 2013; Tsvetnenko and Evans, 2002).

Polar ectotherms exhibit slow responses to contaminants, which requires toxicity tests to be conducted over longer exposure periods to generate sensitivity data (Chapman and Riddle, 2005; King and Riddle, 2001; Marcus-Zamora et al., 2015; Sfiligoj et al., 2015). In long exposures an integrated concentration that takes into account the THC can be calculated from measurements weighted to time, with more frequent measurements needed during the early exposure period when declines from WAFs are greatest. Exposure concentrations for each endpoint can be derived that account for depletion of hydrocarbons and any renewal of treatments in tests of extended duration. Depletion of hydrocarbons also results from uptake into test organisms and it is possible to measure THC in the organisms compared to nominal and measured water concentrations in order to determine internal body burden. Uptake of hydrocarbons is particularly relevant in polar species that depend on stored lipids to provide energy through the polar winter (Clarke and Peck, 1991), and hence have relatively high lipid content compared to temperate species, increasing their potential to accumulate lipophilic hydrocarbons (Goerke et al., 2004).

For assessment of the concentration-response relationship in ecotoxicological experiments, it is essential that the concentration of a toxicant is proportional in tested dilutions, and that this dilution series remains constant over time (Landrum et al., 2013; Neff et al., 2013). The relationship between concentration and dilution in the freshly decanted WAFs of each fuel in this study shows very strong correlation ( $R^2 = 0.980-0.999$ ). This relationship remains strongest over time in samples of SAB WAF exposed for up to 168 h at 0 °C. The  $R^2$  was >0.92 at each time point for the other two fuels, indicating that the proportions of THC in dilutions of 10% to 100% WAFs remained approximately constant over time.

Organisms in static renewal toxicity tests conducted at low temperatures would be exposed to all three fractions of these fuels during the course of a 96 h test, albeit at substantially reduced proportions of the lightest fraction after 48 h. The relative fractions of hydrocarbons in toxicity test treatments need to be proportionate in all dilutions, and to remain so for the duration of exposure of an organism to the toxicant. With complex mixtures of hydrocarbons that have different volatilities this is unknown unless measurements are taken over time. A constant relative concentration of the three fractions appears to be maintained at acceptable levels for 168 h down to 10% dilutions, and in the 1% dilutions up to 6 h. There was little variability between tests in the temporal pattern of proportions in each fraction, indicating dilution of full strength WAFs of these fuels can produce test treatments with compositions that are proportionately similar, and that these proportions are maintained during static exposures with declining total concentrations. These findings support recommendations of dilution of WAF stock solutions instead of variable loading for making test treatments in toxicity tests (Barron and Ka'aihue, 2003, Neff et al., 2000), as the relationship between increased oil to water loading ratio and hydrocarbon concentration and composition of the resulting WAFs is often not well correlated, particularly in cold water WAFs (Perkins et al., 2003; Swigert et al., 2014).

Experiments with both open and sealed WAF showed changes in composition and concentration after 24 h and 7 days in samples in sealed vessels comparable to those at 6 h in open vessels. Testing sealed WAF is relevant to experimental procedures involving exposure of organisms to WAFs in sealed containers or conditions in static renewal toxicity tests, when stored WAFs are used for renewal of test solutions. The results of these sealed WAF experiments may also be compared to behaviour in ice covered waters, where contaminated seawater is not exposed to the air and evaporation is inhibited. There is little loss of volatile components from oil encapsulated in ice (Faksness and Brandvik, 2008b; Payne et al., 1991) and the water-soluble components can then leak through brine channels into the water column (Faksness and Brandvik, 2008a). The presence of ice over contaminated Antarctic marine waters may reduce the loss of volatile components, resulting in long exposure times for marine organisms to toxic components,

particularly benthic and planktonic organisms in shallow waters (Payne et al., 1991, 2014; Brown et al., 2015b), with under-ice (epontic) organisms being particularly vulnerable (Chapman and Riddle, 2005).

# 5. Conclusion

This study has provided greater understanding of the behaviour and potential toxicity of SAB, MGO and IFO 180 WAFs in cold seawater. In polar conditions, these fuels generate WAFs of high aromatic content that exhibit reduced evaporation over time, with proportions of these toxic contaminants persisting in WAFs for over 7 days. This study shows the partitioning and depletion of hydrocarbons in these three fuels is affected by temperature, with differences in patterns at Antarctic and subantarctic sea temperatures. The use of equivalent carbon number fractions allows some characterisation of these fuels and greater understanding of their potential toxicity in Antarctic/subantarctic conditions. A constant relative concentration of hydrocarbons in three equivalent carbon number fractions appears to be maintained in dilutions of cold seawater fuel WAFs at acceptable levels for up to 7 days. This understanding provides more confidence that the concentration response relationship is maintained through time, which may allow future studies to analyse a reduced number of samples from test treatments, thus reducing experimental costs. The measured changing concentrations of THC over time can be used in determining exposure concentrations in toxicity tests of Antarctic and subantarctic marine invertebrates and assessing ecological risks associated with fuel use in polar waters.

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