FATE, TRANSPORT AND RISK OF POTENTIAL ACCIDENTAL RELEASE OF HYDROCARBONS DURING ARCTIC SHIPPING

By

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This thesis is dedicated to God Almighty, and my Mum, Mama Lizzy.

Abstract

Arctic shipping may present risks to the Arctic marine ecosystem. One of the potential sources of risk is accidental oil spills which require mitigation. In order to reduce this risk, there is a need to respond to oil spills in a timely manner. This requires models to evaluate the fate, transport and risk of oil spills in ice-covered waters. Modeling the fate and transport of oil spills is difficult, and the presence of ice makes it complicated. The focus of this study is the application of the models to potential oil spills during Arctic shipping. This study is carried out through a scenario based analysis of potential accidental releases during Arctic shipping accidents. The main application of the work in this thesis is for contingency planning and providing guidance to policies for Arctic shipping operations. This thesis presents a series of studies that review oil weathering and transport models for open and ice-covered waters, update current open water weathering and transport algorithms to make them ice-covered water capable, develop a fugacity based partition model, integrate aforementioned models as well as source models in an ecological risk assessment framework, and develop an accident forecasting methodology. The review shows that current oil spill models are inadequate for predicting the behaviour of oil in ice-covered waters. It also highlights missing algorithms for encapsulation and de-encapsulation processes which are very critical for oil behaviour in ice-covered waters. A refined weathering and transport model is applied to a hypothetical case study involving a potential Arctic shipping accident. The outcome shows that the predictions of the refined models agree reasonably well with oil in ice data from the area under study. The partition model presented is also applied to a hypothetical case study of a shipping vessel passing through the North-West passage. The results predict the level of contamination of the different compartments. The compartments include air, water, ice and sediments. The ecological risk assessment framework developed is applied to a case study in the Kara Sea. The Kara Sea was chosen mainly to draw attention to a potential site for Arctic shipping accidents. The results show acceptable level of risk in the water column since the Risk Quotient (Ratio of predicted concentration and predicted no effect concentration from ecotoxicological studies) is less than 1. An accident forecasting methodology based on the Bayesian approach is presented. This is illustrated with a ship-ice-berg collision scenario. The fate and transport models are used for assessing the consequences of a potential oil spill, while the Arctic shipping forecasting methodology is used for the probability of occurrence. The methodology may also be useful for choosing potential scenarios for the application of the fate and transport models developed. A sensitivity analysis is performed to identify the most critical parameters of the occurrence of the scenario. This information is useful for prioritization of resources during mitigation.

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List of abbreviations

ADIOS: Automated Data Inquiry for Oil Spills

AMOP: Arctic Marine Oil Spill Program

AMAP: Arctic Monitoring and Assessment Program

API: American Petroleum Institute

ASTM: American Society for Testing and Materials

BN: Bayesian Network

BP: British Petroleum

CDF: Cumulative Density Function

CFAC: Contributing Factors in Accident Causation

CPT: Conditional Probability Table

COSIM: Chemical/Oil Spill Impact Model

DAG: Direct Acyclic Graph

ERA: Ecological Risk Assessment

ERM: Environmental Resource Management

EU: European Union

FRAM: Functional Resonance Accident Model

HBM: Hydrocarbon Block Method

HMWH: High Molecular Weight Hydrocarbons

HOF: Human and Organizational Factor

IMO: International Maritime Organization

IOSC: International Oil Spill Conference

ITOPF: International Tanker Owners Pollution Federation Limited

JIP: Joint Industrial Projects

JPD: Joint Probability Distribution

L/MMWH: Low and Medium Molecular Weight Hydrocarbons.

LC: Langmuir cells

LC: Lethal Concentration

LD: Lethal Dose

MCS: Monte Carlo Simulation

MMBMs: Multimedia Mass Balance Models

MMS: Minerals Management Service

MORT: Management Oversight and Risk Tree

MPMA: Multi- Processes Modeling Approach

NOAA/HAZMAT: National Oceanic and Atmospheric Administration Hazardous Material Response Division

NOAA: National Oceanic and Atmospheric Administration

NSR: Northern Sea Route

NWP: North-West Passage

OSCAR: The Oil Spill Contingency and Response

OWM: Oil Weathering Model

PEC: Predicted Exposure Concentration

PNEC: Predicted No Effect Concentration

QWASI: Quantitative Water Air Sediment Interaction

RQ: Risk Quotient

SHEL: Software-Hardware-Environment-Livewire

SINTEF: *Stiftelsen for industriell og teknisk forskning* "The Foundation for Scientific and Industrial Research"

SPMA: Singular Process Modeling Approach

SPM: Suspended Particulate Matter

SSD: Species Sensitivity Distribution

TAP: Trajectory Analysis Planner

UV: Ultraviolet

List of symbols used in equations

Symbol	Meaning
F	spreading force
σ_w	surface tension of water
σ_o	surface tension of oil
σ_{ow}	oil-water interfacial tension
A	area of slick
V_m	volume of spilled oil

K	constant with default value 150^{-1}
t	time
r	radius
g	acceleration due to gravity
v	kinematic viscosity of water
Δ	density difference between air and water.
ρ	density of sea water
ρ_o	density of oil
W	wind speed
μ_o	dynamic viscosity of oil.
V_r	radial velocity
V_θ	velocity in the θ direction
V_z	velocity in the z direction
B	constant accounting for hydraulic roughness of ice cover (0.467)
Q	discharge rate
$\forall$	constant volume
σ_n	net interfacial tension force per unit length
X	spreading rate of the slick at the water surface near the top of the ice cover
r_1	top slick radius
B_1, B_2	constants based on the hydraulic roughness of ice.
h_∞	final slick thickness
D	molecular diffusivity
$A_{\mu I}$	corrected area for spreading in pack ice
f_I	fraction of ice cover,
μ	viscosity of water
T_h	thickness of a the wind-herded slick
h_o	original thickness of oil
γ	kinematic viscosity of oil
$\vec{V}$	advection velocity
$\overrightarrow{V_m}$	mean velocity
$\overrightarrow{V_t}$	accounts for local turbulent diffusion
$\overrightarrow{V_w}$	wind velocity at 10m above water surface
$\overrightarrow{V_C}$	depth-averaged current velocity
α_w	wind drift coefficient with default value of 0.03
α_C	current drift coefficient with default value of 1.15.
Δt	time step
R_n	normally distributed random number of mean value 0 and standard deviation 1
θ	uniformly distributed random angle between 0 and π
D_e	dispersion coefficient due to mechanical spreading
D_T	diffusion coefficient

$Q(d_o)$	entrained mass of oil droplets
D_{bw}	dissipating breaking wave energy per unit surface area
C_o	constant that is oil type dependent
d_o	droplet size
Δd	range of droplet size interval
D	rate of entrainment
D_a	fraction of sea surface dispersed per hour
D_b	fraction of dispersed oil not returning to a slick
H	water depth
ε	rate of energy dissipation
$\frac{dA_d}{dt}$	rate of oil loss due to the oil-sediment adherence process
S_L	sediment load
S_a	salinity
F_V	volume fraction of hydrocarbons evaporated
T	ambient temperature
T_G	slope of the modified ASTM distillation curve
T_0	initial boiling point of the modified distillation curve
θ	evaporative coefficient
A_S	spill area
k	mass transfer coefficient
x	slick thickness
K_W	air-side mass transfer coefficient
K_O	oil internal mass transfer coefficient
H	henry's law constant
D_s	diffusivity of oil in snow
L	depth of oil below the snow's surface
Z	constant and takes values between
Y	fraction of water in oil
Y_{max}	final fraction of water content and is dependent on oil type
A_c	percentage of asphaltene
C_4	constant with value 10
J	dissolution mass transfer coefficient (0.01 mh^{-1})
f_s	surface fraction covered by oil
S	solubility in water
S_O	solubility of fresh oil
α	constant that takes the value 0.1
m	concentration of hopane in sediments
k	first-order rate
N	concentration of hydrocarbon
p	growth rate of biomass
Y_X	biomass yield coefficient for growth on hydrocarbon

Ú	sun's radiation angle to the slick surface
C_A	coefficient that varies with slick thickness
Ÿ	constant with a value of 0.467
S_e	sensitivity
f_a	Fugacity of pollutant in air
f_i	Fugacity of pollutant in ice
f_w	Fugacity of pollutant in water
f_s	Fugacity of pollutant in sand
*	See tables 13, 14,16,17,18,19 for the symbols used in the fugacity model
$P(A\|E)$	Posterior probability
$P(E\|A)$	likelihood which represents how likely the evidence is true
$P(A)$	probability of A
$P(E)$	normalization factor

Chapter 0: Introduction

Accidental oil releases from shipping, oil and gas exploration, transport and production of oil in the Arctic are likely to increase commensurate with the forecasted Arctic shipping activities (Mattson, 2006; Lee et al., 2015; Olsen et al., 2011; Chang et al., 2014; Papanikolaou, 2016). Releases may present negative consequences to Arctic marine species (Lee et al., 2015; Lee et al., 2011; Drozdowski et al., 2011). Potential consequences include altering the reproductive cycle of Arctic marine species, destruction of coastal zones and reduction in tourist activities, as well as other economic ventures (Brussard et al., 2016; Olsen et al., 2011; Chang et al., 2014; Papanikolaou, 2016). These consequences require mitigative measures. Decisions regarding the implementation of these measures are informed by environmental risk assessment (Lee et al., 2015). Environmental risk assessment consists of different steps, but the most critical is the analysis step. This step requires the use of models to predict the consequence of a pollutant (Olsen et al., 2011; Chang et al., 2014; Papanikolaou, 2016). This thesis is focused on developing such models with a goal of integrating them in a risk assessment framework for decision making.

Developing such models and the risk assessment framework requires envisaging a potential accident, understanding the behavior of oil in ice covered waters, and build models to predict the fate and transport of an oil spill in ice-covered waters. The fate and transport of oil is a complex process and difficult to model; the presence of ice makes it more complicated (Lee et al., 2015; Lee et al., 2011; Drozdowski et al., 2011). The fate and transport of an oil spill in ice-covered waters is characterised by spreading, evaporation, emulsification, dispersion, advection, photo-oxidation, biodegradation, dissolution, and encapsulation, which occur simultaneously after an oil spill and are dependent on each other (Reed et al., 1999; Sebastiao and Soares, 1995; Yang et al., 2015; Spaulding et al., 1988; Bobra and Fingas, 1986). Oil in ice is influenced by the location of the spill, seasonal variations, and type of release (Elise et al., 2006).

While in-depth knowledge exists for some of the processes that occur after an oil spill in open water, there is little known about those in ice-covered waters (Brandvik et al., 2006; Reed et al., 1999), which presents a challenge for developing a risk assessment framework specifically for oil spills in these contexts (Lee et al., 2015; Afenyo et al., 2015; Lee et al., 2015; Johansson et al., 2013). While some level of risk assessment has been conducted over the years, there is need to update techniques and data to reflect new challenges in the Arctic region (Lee et al., 2015; Anon., 2010). Some factors unique to the Arctic include seasonal variations and extremely low temperatures (Lee et al., 2015).

The objectives of this research are:

i) To present a state-of-the art review of oil spill modelling in open and ice-covered waters.

ii) To develop a model to predict the physio-chemical properties of spilled oil in ice-covered waters. This is an improvement of current models.

iii) To develop a partition model capable of predicting the concentration of hydrocarbons in air, ice, water, and sediments after an oil spill in ice-covered waters. This is also an improvement on current models mainly for application in ice-covered waters.

iv) To integrate models into an ecological risk assessment framework for decision making purposes.

v) To develop an accident scenario forecasting methodology from past accident data for decision making purposes.

Each of these objectives is addressed and forms the core of the papers used for this thesis.

Some previous studies have been conducted with regards to oil spills in the Arctic. Most of these are Joint Industrial Projects (JIP), which have focused mostly on the recovery of oil and weathering processes. There is currently a lot of work on-going in this regard. Even though research by SINTEF involved experimental study of some of the weathering processes, e.g. emulsification, evaporation, and dispersion (Brandvik et al., 2006), these have not captured the dependency of the processes on each other and have adopted a different approach to estimating risk. None of these studies have focused on releases from potential Arctic shipping accidental releases. Further, the Arctic oil spill response JIP, which comprises 6 oil companies, has focused on efficiency of dispersants use in ice-covered waters, activities of micro-organisms in oil recovery, in situ burning, and the detection of oil in ice (Buist et al., 2013).

Table 1 contains the contribution to knowledge and professional development that have emerged during my doctoral studies by way of journal publications, conference proceeding publications, conference presentations, and seminar presentations. Figure 1 is the flow chart showing the framework for the study and how the contents of Table 1 are linked.

Table 1: Journal papers, conference and seminal contributions during the doctoral program

Paper	Details- Journal papers
1	Afenyo, M., Veitch, B., Khan, F. 2016. A state-of-the-art review of fate and transport of oil spills in open and ice-covered water. Ocean Engineering.119:233-248.
Link:	http://www.sciencedirect.com/science/article/pii/S002980181500551X
2	Afenyo, M., Khan, F. Veitch, B., Yang, M. 2016. Modeling oil weathering and transport in sea ice. Marine Pollution Bulletin. 107(1):206-215.
Link:	http://www.sciencedirect.com/science/article/pii/S0025326X16301904
3	Afenyo, M., Khan, F. Veitch, B., Yang, M. 2016. Dynamic fugacity model for accidental oil release during Arctic shipping. Marine Pollution Bulletin 111(1-2):347-353.
Link:	http://www.sciencedirect.com/science/article/pii/S0025326X16304921
4	Afenyo, M., Khan, F. Veitch, B., and Yang, M. 2017. Arctic shipping accident scenario analysis using Bayesian Network approach. Ocean Engineering. 133:224-230.
Link	http://www.sciencedirect.com/science/article/pii/S0029801817300525
5	Afenyo, M., Khan, F., Veitch, B., and Yang, M. 2017. A probabilistic ecological risk model for Arctic marine oil spills. Journal of Environmental Chemical Engineering. 5:1494-1503.
Link	http://www.sciencedirect.com/science/article/pii/S2213343717300726
	Seminars and conferences
6	Afenyo, M., Khan, F., Veitch, B., Yang, M. (October 24-26, 2016). An exploratory review of weathering and transport modeling of accidental oil releases in Arctic waters. Arctic Technology Conference, St. John's.
Link:	https://www.onepetro.org/conference-paper/OTC-27436-MS
7	Afenyo, M. (April 27-28, 2015). Dispersion and fate modelling of oil Spills in Ice-Covered Waters, Newfoundland and Labrador's Environmental Industry Association's Oil and Environment symposium (NOTES 2015), St. John's-Canada.
8	Afenyo, M. (March 11, 2015). Fate and transport modelling of oil Spills in Ice-Covered Waters: a review NSERC CREATE Offshore Technology Research seminar, St. John's.

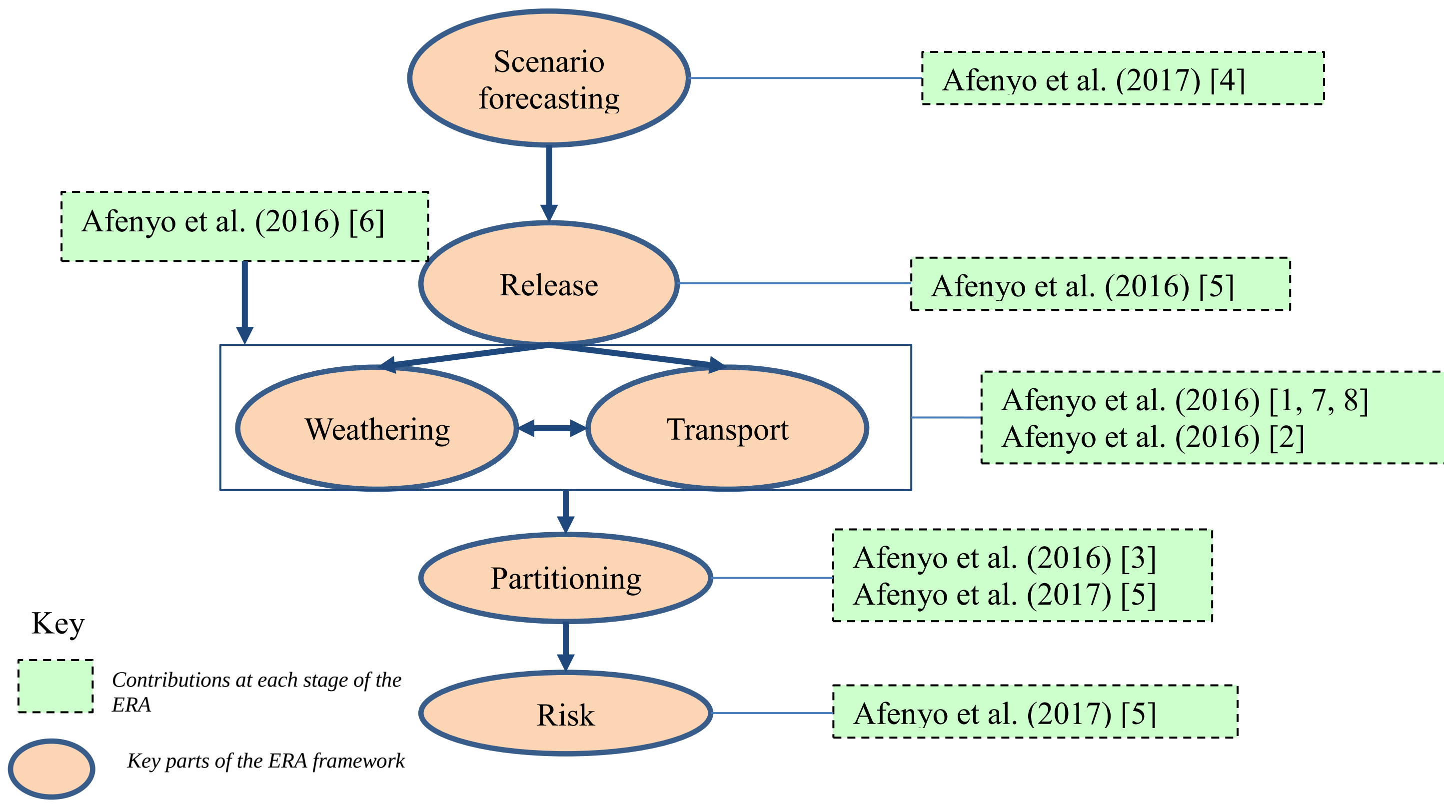

Figure 1: A flow chart showing the proposed framework for Ecological Risk Assessment (ERA) for Arctic marine environments and the contribution of the thesis for critical stages

Co-authorship statement

My role in each of the manuscripts for each journal paper, and in essence the thesis, is the same and includes the following: that, I Mawuli Afenyo i) took the lead in the identification of the problem, and design of the research proposal and Drs. Khan, Veitch and Yang offered guidance and advice, ii) performed data analysis and implemented the research with guidance from Drs. Khan, Veitch and Yang except in chapter 1 (Afenyo, M., Khan, F., Veitch, B. 2016. A state-of-the-art review of fate and transport of oil spills in open and ice-covered water. Ocean Engineering.119:233-248), which did not involve data analysis, and iii) prepared the manuscripts with critical reviews from Drs. Khan, Veitch and Yang before submission to journals for publication.

The same support was received for all manuscripts except for the first chapter, which Dr. Ming Yang was not involved with. Details of publications are shown in Table 1.

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Chapter 1: A state-of-the-art review of fate and transport of oil spills in open and ice-covered water*

1. Background

Accidental releases like the grounding of the Exxon Valdez oil spill that released 37,000 tonnes of Alaska North Slope crude (Rice et al., 1996; Wells et al., 1995; Galt et al., 1991; Loughlin, 1994) has negative consequences on the marine ecosystem. During the three months of the BP oil spill in the Gulf of Mexico, approximately 486,000 tonnes of crude oil was released at a water depth of 1,520 m (McNutt et al., 2011) and resulted in the pollution of 9900 km^2 of water surface (Wei et al., 2014). BP spent over $30 billion to manage the spill (Vesser, 2011).

Traffic in the arctic has increased recently (Arrigo, 2013). Increased traffic may increase the probability of an oil spill in arctic waters (Johansson et al., 2013). To better prepare for emergency response and mitigation of such spills, there is a need to predict the fate and transport of different oil types (Brandvik et al., 2006).

Fate and transport of spilled oil is a complex process and the presence of ice makes it more complicated. It is governed by spreading, evaporation, emulsification, dispersion, advection, photo-oxidation, biodegradation, dissolution, encapsulation and sedimentation, which take place simultaneously after an oil spill (Bobra and Fingas, 1986; Spaulding, 1988; Sebastiao and Soares, 1995; Reed et al. 1999; Yang et al., 2015).

This chapter is taken from the author's paper: Afenyo, M., Veitch, B., Khan, F. 2015. A state-of-the-art review of fate and transport of oil spills in open and ice-covered water. Ocean Engineering.119:233-248. I led the identification of the problem, conducted the review and wrote the first manuscript with guidance from my supervisors: Profs. Khan and Veitch

Understanding the processes involved in the fate and transport of oil spills is key to good modeling, particularly in developing emergency spill response models (Anon., 2003). These composite models are used to predict where the spill will go, and how it will weather. This information is important to determine response priorities (Anon., 2003), help make better predictions of the possible impact of petroleum related developments, and prepare contingency and mitigating measures (Mackay and McAuliffe, 1988; Fingas, 2015).

Compared to the knowledge that exists for fate and transport of oil spills in open water, knowledge regarding oil spills in ice-covered waters is more limited and at an ad hoc level (Brandvik et al, 2006; Reed et al., 1999). The goal of this chapter is to present a state-of- the art review of fate and transport modeling of oil spills in ice-covered waters. This chapter builds upon earlier works by Spaulding (1988), Reed et al. (1999), and Fingas and Hollebone, (2003). The current work identifies knowledge gaps, and proposes potential ways of addressing some of these gaps. It also presents the latest and most used models. The study further reports recent advancement and attempts to study oil in ice behaviour.

1.1 Oil Characteristics

Fate and transport of spilled oil and refined petroleum are influenced by their chemical and physical properties (Buist et al., 2013). Oil here refers to crude oil. Its composition depends on a number of factors and includes the geology of the area and the reservoir. The basic composition of oil is hydrocarbons which are combined with smaller quantities of volatile and non-volatile components. The compounds making up crude oil number approximately 17500 and new ones are still being discovered. Each oil type have special characteristics hence their behaviour when spilled (Speight, 2014; Fingas, 2015). Table 2 is a typical crude oil composition The composition of crude oil can broadly be presented as organic which includes aliphatic, alkenes, alkynes, naphthenoaromatic compounds, resins, asphaltenes, aromatics and the inorganic compounds made up of Sulfur, Nitrogen and some metals (Speight, 2014; Fingas, 2015). Each of these compounds has unique characteristics (Lehr, 2001). Percentage of light and volatile components of crude is dependent on the type of crude. For example sweet crude has a high percentage of light and volatile components, therefore it evaporates quickly once exposed (Buist et al., 2013; Fingas, 2011). Heavy oils on the other hand have a low percentage of volatiles (Fan and Buckley, 2002; Speight, 2014; Fingas, 2015).In ice covered waters, percentage of volatiles will decreases precipitously. A more comprehensive data base on different oil compositions for the types of oil can be referred to in Fingas (2015).

Table 2: Crude composition by percentage (adapted from Fingas, 2015).

Group	Class	Gasoline	Diesel	Light crude	Heavy crude
Saturates		50-60	65-95	55-90	25-80
	Alkanes	45-55	35-45	40-85	20-60
	Cycloalkanes	5	25-50	5-35	0-10
Olefins		0-10			
Aromatics		25-40	5-25	10-35	15-40
	BTEX	15-25	0.5-2	0.1-2.5	0.01-2
	PAHs		0-5	10-35	15-40
Polar compounds			0-2	1-15	5-40
	Resins		0-2	0-10	2-25
	Asphaltenes			0-10	0-20
Sulfur		0.02	0.1-0.5	0-2	0-5
Metals (ppm)				30-250	100-500

Properties critical to describing the fate and transport of spilled oil are the following density, viscosity, specific gravity, interfacial tension, flash point, and pour point (Fingas, 2015).

Viscosity describes the resistance to flow. It is influenced by the fractions of saturates, aromatics, resins and asphaltenes. Higher percentage of saturates and aromatics, and lower values of resins and asphaltenes, produces a less viscous oil. As evaporation rate of oil increases, so is its viscosity. In cold environments like the Arctic, the viscosity of the oil increases at a high rate. High oil viscosity hampers clean up and reduces the rate of transport on the sea (Speight, 2014; Fingas, 2015).

Density on the other hand is the mass per unit volume of a substance. It indicates how heavy an oil sample is. Most oils are lighter than water and will float on its surface. However at very low temperature, heavy crude and residuals may contract and sink as the density becomes higher than that of water. Further as weathering of the oil proceeds and light components of the oil escape through evaporation, the oil may eventually sink. This shows how weathering has a tremendous effect on the physical property of oil. Density of an oil is differentiated from specific gravity, in that the latter is a comparison of the density of oil to that of water. This parameter is often used to evaluate the quality of oil (Speight, 2014; Fingas, 2015).

Surface tension is the force per unit length and determines the eventual size of the slick. It is partly responsible for the spreading of oil. Lower interfacial tension between oil and water means a large area of spread and a thinner slick thickness (Lee et al., 2015; Fingas, 2015).

For recovery of oil spill, the flash point is very critical. The flash point is the temperature at which the vapor at the surface of the oil is likely to ignite. The more weathering a spill undergoes the higher the likelihood of ignition. It is therefore very important to take this into consideration during cleanup for safety purposes (Lee et al., 2015; Fingas, 2015).

The pour point on the other hand is the temperature at which the oil will appear to pour very slowly. That is it becomes semi-solid (Lee et al., 2015; Fingas, 2015).

The influence of chemical properties is attributed to the composition of crude oil, as it is made up of hundreds of different organic compounds (Lehr, 2001).

From a spill perspective, volatility, insolubility, spreadability, and the tendency of oil to form emulsions are the most important physical properties for consideration (Buist et al., 2013).

Studies have shown that crude oil is generally insoluble in water except for alkanes and aromatics, which are slightly soluble in water (Buist et al., 2013; Reed et al., 1999). Apart from highly viscous oils and oils with a pour point above ambient temperature, oil will generally spread because of its unique surface tension. The presence of natural surfactants (asphaltenes and resins) in the right proportions creates the condition for emulsion formation (Buist et al., 2013; Reed et al., 1999). These physical and chemical properties are important inputs for oil spill models (Reed et al., 1999). Table 3 and 4 shows the solubility of different oil types at different temperatures and different aromatic components at different temperatures. This shows that solubility varies with different oil types, composition, temperature and salinity.

Table 3: Solubility of different oil types at different temperatures and (adapted from (Anon., 2002).

Oil type	Solubility ($\frac{mg}{L}$)	Temperature	Salinity (%)
Prudhoe Bay	29	22	Distilled
Lago Media	24	22	Distilled
Lago Media	16.5	22	33
Diesel fuel	3	20	Distilled
Diesel fuel	2.5	25	33

Table 4: Solubility of some aromatic components of oil (adapted from (Anon., 2002).

Compound	Solubility ($\frac{mg}{L}$)
Benzene	1700
Toluene	530
Ethylbenzene	170
1-Methyl naphthalene	28
1,3,6-Trimethyl naphthalene	2

1.2 Oil Spill Models

The goal of oil spill modeling is to predict where oil is likely to go after a spill. This is accomplished through the use of data on ocean currents, winds, waves and other environmental factors (Drozdowski et al., 2011). There are three major components of an oil spill model: (i) the input (ii) weathering and transport algorithms to quantify the processes involved, and (iii) the output, which produces the required results in an appropriate way (Sebastiao and Soares, 1995; Yang et al., 2015; Spaulding, 1988). Figure 2 attempts to capture different steps and processes involved in oil spill modeling.

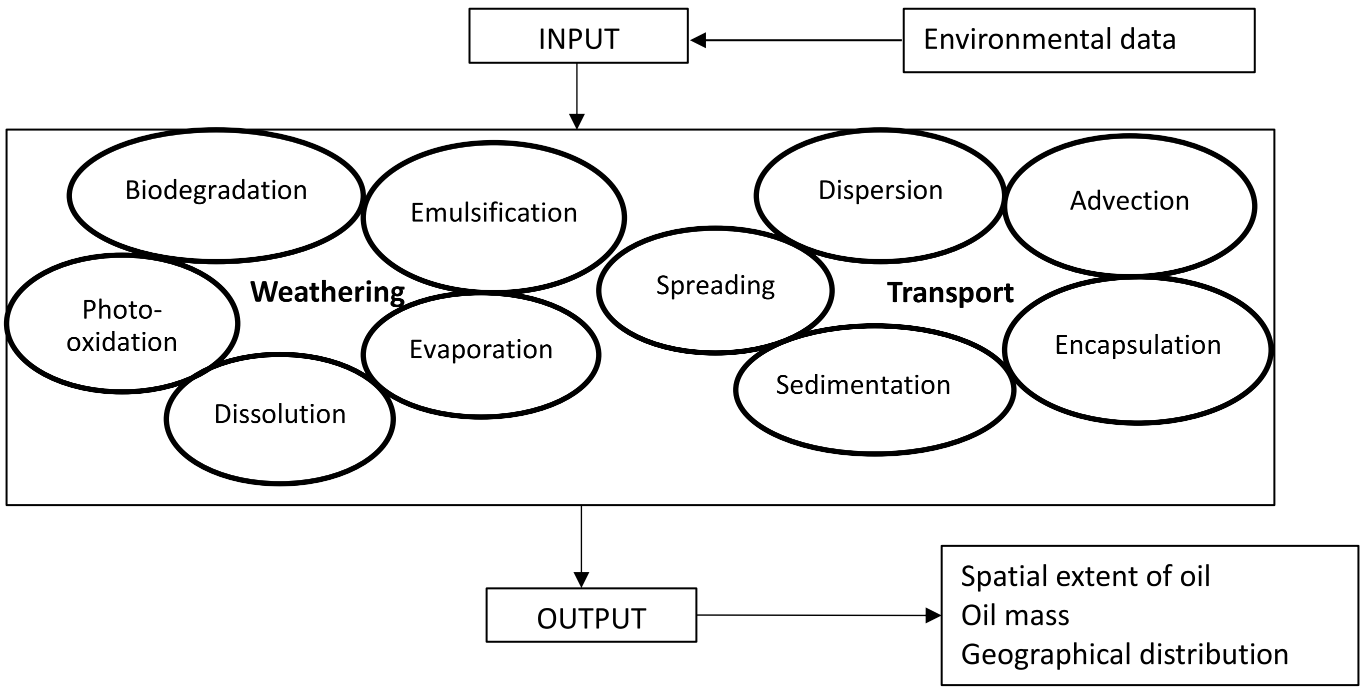

Figure 2: General structure of an oil spill model (after Reed et al., 1999)

Environmental data include wind, current, temperature, and ice in space and time. Oil type, physical and chemical properties of oil, release rates and location make up the oil data (Reed et al., 1999). The output is a representation of the spatial extent of the spill and oil mass balance by environmental compartments, geographical distribution and properties as a function of time (Spaulding, 1988). Weathering and transport algorithms link the output and the input models (Spaulding, 1988; Reed et al., 1999). Individual processes act together to bring about weathering (Sebastiao and Soares, 1995). The processes are dependent on each other as illustrated in Figure 3. Linkages and dependencies among the weathering and transport processes are not limited to Figure 3 as illustrated.

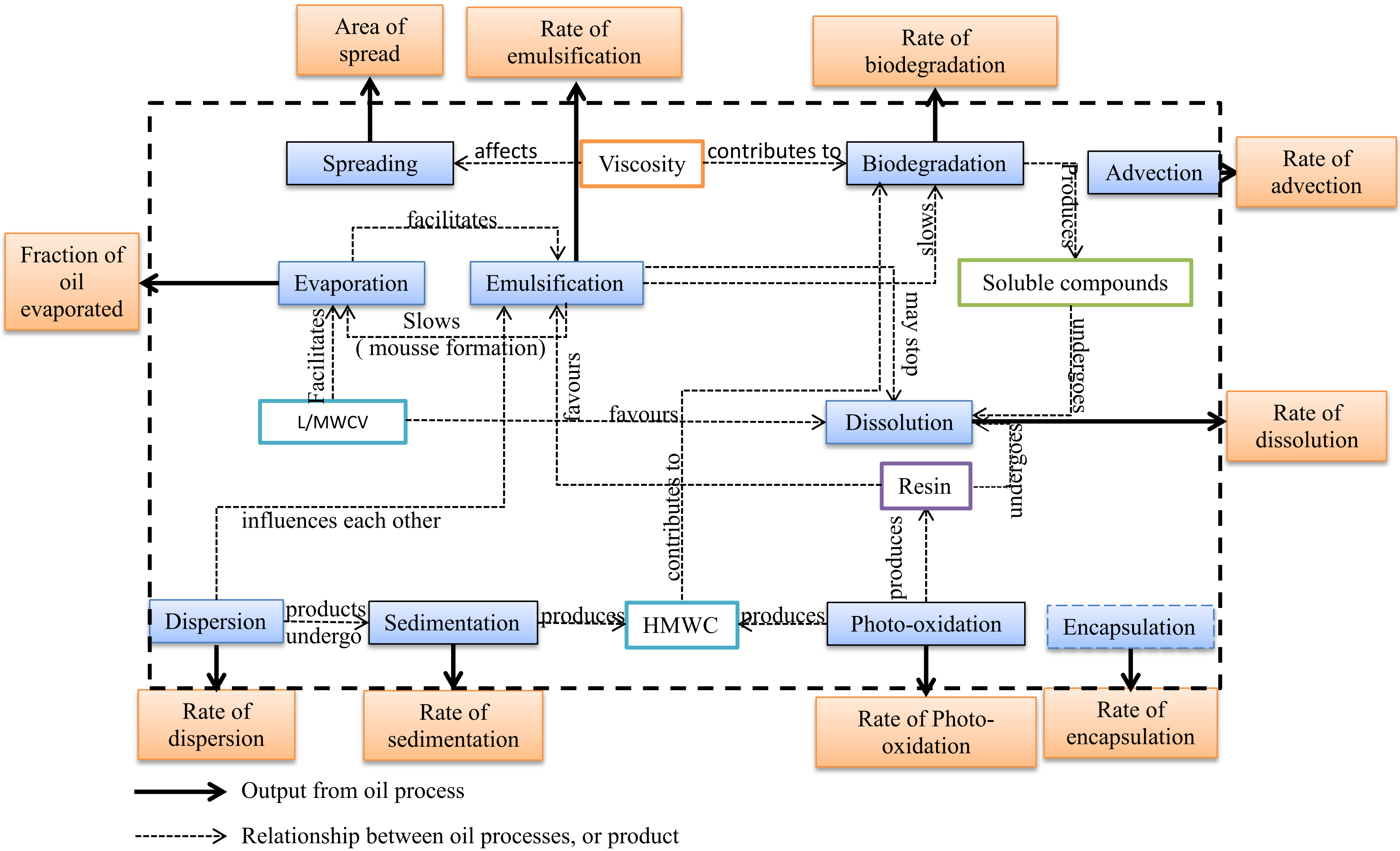

Figure 3: Diagram illustrating the linkages among the weathering processes (after Xie et al., 2007). L/MMWH means low and medium molecular weight hydrocarbons. HMWH means high molecular weight hydrocarbons. Encapsulation occurs only in ice-covered waters.

For instance, evaporation facilitates emulsification through the formation of mousse; lighter components of some oil types evaporate to yield the level of resin and asphaltenes required to stabilize emulsions (Buist et al., 2013; Reed et al., 1999). Resins here refers to a large group of polar constituents in oil that serves as a solvation agent for asphaltenes during emulsification. Emulsification and dispersion influence each other. For example emulsification makes the oil slick resistant to dispersion. Both processes are controlled by hydrodynamic factors and oil properties. The hydrodynamic factors include frequency of breaking waves, mixing intensity and depth of mixing. Density, viscosity and interfacial tension are the important oil properties for emulsification and dispersion (Sjöblom, 2006; Daling et al., 2003; Fingas, 2015). Resins produced from photo-oxidation may cause the formation of water-in-oil emulsions (Fingas, 2015). Interdependencies of weathering processes imply that the algorithm describing the weathering processes may have common inputs and sometimes the output of one algorithm may be the input of another. The implementation of the model is important. Two models containing the same algorithm and receiving the same inputs may produce different results because of the difference in the implementation (Reed et al., 1999).

1.2.1 Oil Spill Models for Open Waters

Abascal et al. (2010) presented a study on the development of a statistical oil spill model and its validation. The validation was carried out using the oil slick observation during the Prestige accident. The model has been applied to the Bay of Biscay (Spain) to support spill response planning along the Cantabrian coast (Hānninen and Sassi, 2010; Abascal et al., 2010). The National Oceanic and Atmospheric Administration (NOAA) developed the Trajectory Analysis Planner (TAP) to statistically analyse the output from an oil spill trajectory model (Hānninen and Sassi, 2010). Automated Data Inquiry for Oil Spills (ADIOS) was developed by the National Oceanic and Atmospheric Administration Hazardous Material Response Division (NOAA/HAZMAT) to aid responders during oil spill clean-up. It predicts the weathering of oil after a spill. A revised version of ADIOS named ADIOS 2 is now available (Lehr et al. 2002). GNOME, OILMAP, SIMAP are the most used oil spill trajectory and fate models in the industry (Zelenke et al., 2012; Word, 2014; Lee et al., 2015). OILMAP 7 the latest oil map version is suitable for contingency planning, evaluating the impact of an oil spill and making response decisions (Word, 2014).

Ovsienko et al. (1999) developed a model to forecast the behavior and spreading of oil at sea (Ovsienko et al., 1999; Hānninen and Sassi, 2010) using the particles-in-cell technique on a quasi-Eurelian adaptive grid. This model has been developed further by the Russian State Oceanographic Institute to a model and software called SPillMod (Ovsienko, 2002; Jolma et al., 2011; Lehikoinen et al., 2012). The Oil Spill Contingency and Response (OSCAR) program developed by SINTEF is a state-of-the art modeling tool for predicting the fate and transport of spilled oil during accidental release. It uses weathering and transport algorithms for modeling and validate the results using laboratory and field experiments (Daling and Strøm, 1999). The Chemical/Oil Spill Impact Model (COSIM) by Environmental Resource Management (ERM) is another model for oil and chemical spills (Anon., 1994; Camp et al., 2010)

1.2.2 Oil Spill Models for Ice-Covered Waters

Oil spill models for ice covered waters rely on those from open water with some modifications, by updating input parameters using oil in ice experiments. At the moment, few oil spill models for ice-covered waters exist (Yang et al., 2015). For instance, the SINTEF Oil Weathering Model (OWM), which is part of the Oil Spill Contingency and Response (OSCAR) model system, was updated with experimental and field results from ice conditions (Brandvik and Faksness, 2009; Faksness et al., 2011). Selected findings from the meso-scale experiments at the SINTEF ice lab were verified on a larger scale with field trials on the Barents sea ice (Brandvik and Faksness, 2009; Faksness et al., 2011). Data obtained from the experiments were used to calibrate the SINTEF Oil Weathering Model (OWM) to predict the weathering of oil spills in ice-covered waters (Brandvik and Faksness, 2009; Faksness et al., 2011). The model developed by Ovsienko et al. (1999) predicts spreading of oil in between fixed ice floes.

1.3 Fate and Transport of Spilled Oil in Ice-Covered Waters

When oil is spilled, it is subjected to transport and weathering. It is transported by advection, spreading, sedimentation and dispersion. In the presence of ice, encapsulation becomes an additional process (Spaulding, 1988; Drozdowski et al., 2011). The weathering processes include evaporation, emulsification, photo-oxidation, biodegradation and dissolution. These processes start and end at different times as illustrated in Figure 5 (Anon., 2014). Some start immediately after the spill, while others occur weeks later (Sebastiao and Soares, 1995). Figures 2, 3 and 4 illustrate weathering and transport processes. In open water, oceanographic forces are the main driving forces for weathering; in ice-covered waters, it is the nature of ice and seasonal variations such as temperature that determine the weathering processes to a large extent (Sørstrøm et al., 2010; Drozdowski et al., 2011). Table 2 shows the relevant factors that affect oil spilled in ice covered waters (Elise et al., 2006).

Table 5: Factors influencing the movement of oil in ice conditions (after Elise et al., 2006 and Brandvik et al., 2006)

Category	**Relevant factors**
Nature of ice	Type of ice (land fast, pack ice, brash ice, first year, multi-year), and presence of structural anomalies (leads, polynyas, brine channels).
Properties of the spilled oil	Viscosity, boiling point, dispersability, emulsification, volatility, asphaltenes and resins content.
Location of the spilled oil	On ice, on snow, under ice, on water in presence of ice, in leads, under first year ice, under multiyear ice, under packed ice, absorbed by snow.
Distribution of the spilled oil	Thickness of oil, whether it is pooled or sprayed, whether it has landed on ice and become integrated in the ice due to freeze-thaw cycle and snowfall.
Weather condition	Wind, currents, temperature

The fate and transport of oil in ice-covered waters is not totally different from that in open water. The main difference is the presence of ice (Bobra and Fingas, 1986; Brandvik et al., 2006). Figure 4 illustrates the processes that take place after an oil spill. Figure 5 illustrates when the weathering and transport processes start and end. Figure 6 shows the complexity involved in ice-covered waters (Bobra and Fingas, 1986; Dickins, 2011). Apart from the processes that are common to those in open water, more complexity is observed when oil moves into leads, spills in snow, spills on and under different ice types, and when oil is engulfed in ice (Bobra and Fingas, 1986; Brandvik et al., 2006). The fate of oil trapped under ice is influenced by the roughness of the ice bottom, size of the ice cover, ice concentration, droplet size distribution, freezing and melting (Beegle-Krause et al., 2013; Brandvik et al., 2006). Ice is driven by the wind, which in turn drives the water. Water currents may also drive the ice. In both scenarios, the under-ice roughness and the relative velocity between the water and the ice determines the turbulence profile and hence the oil droplet trajectories. Wind and waves may also contribute to this process (Beegle-Krause et al., 2013). Oil drifts with ice, except under ice in currents exceeding 15 to 20 $\frac{cm}{s}$ (Buist et al., 2013). Under the bottom of smooth ice, oil moves freely and drifts rapidly compared to oil in rough or ridged pack ice. A highly consolidated ice pack reduces energy due to the damping of waves (Beegle-Krause et al., 2013).

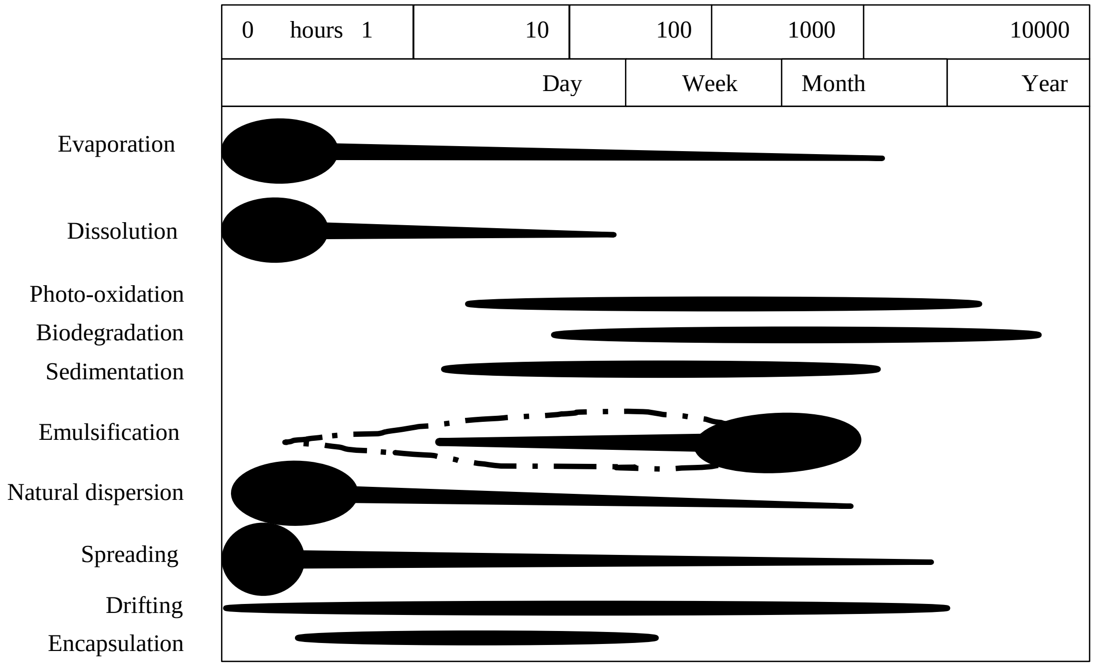

Figure 4: Evolution of weathering process with time (after Anon., 2014)

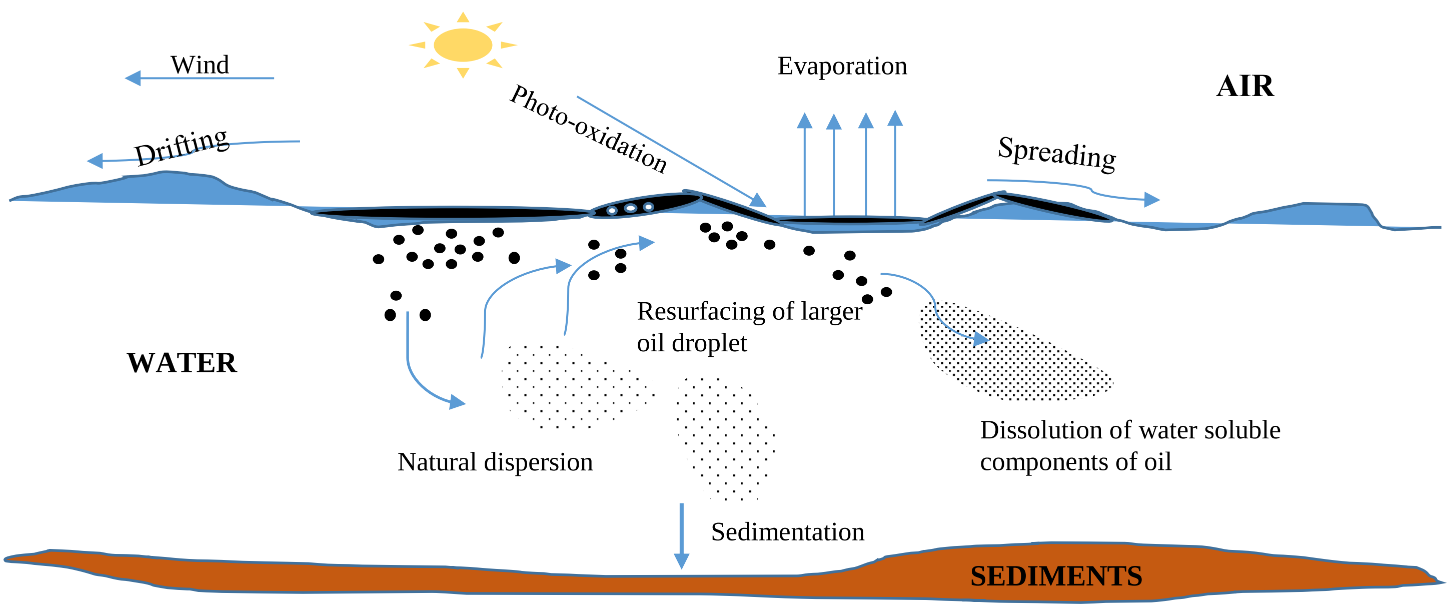

Figure 5: Typical weathering processes that take place as a result of oil spill at sea (after Xie et al., 2007).

Table 6: Approximate period of dominance after the spill

Process	Period of dominance (Hours)
Evaporation	0-1
Spreading	0-1
Dissolution	0-1
Natural dispersion	0-5
Emulsification	0.3-900
Drifting	0-1000
Encapsulation	1-100
Photo-oxidation	1-7000
Sedimentation	0.5 to 7000
Biodegradation	10- 9000

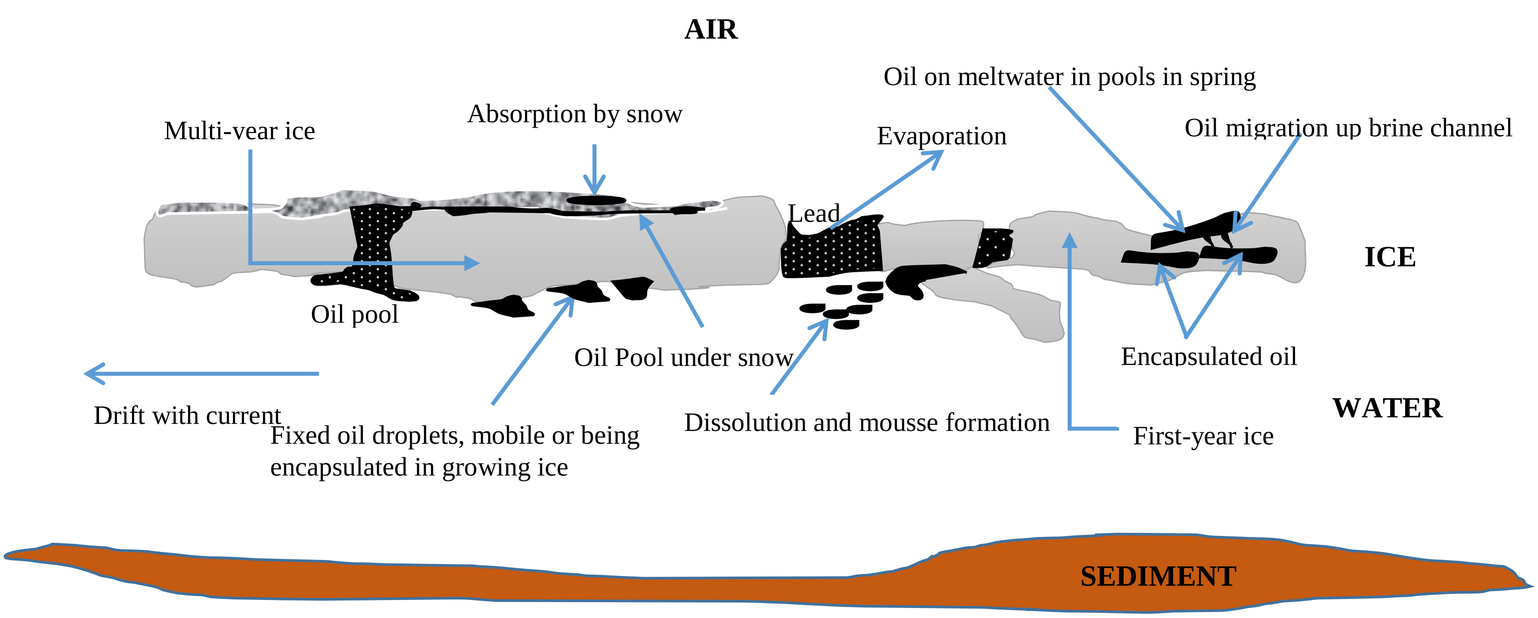

Figure 6: Dynamics and characteristics of sea ice and oil interaction at the sea surface (after Elise et al., 2006).

From Table 6 and Figure 5, the early dominant processes are evaporation, dissolution, natural dispersion, and emulsification while the later stage is dominated by photooxidation, sedimentation and biodegradation. Drifting is relevant through the lifetime of the spill as long as the waves, wind and current are present.

The seasons of the year also affect the fate and transport of oil in ice-covered waters (Beegle-Krause et al., 2013). Studies conducted along the Alaskan North slope, (Kovacs, 1977, Barnes et al., 1979, Kovacs et al., 1981, Comfort, 1986, Goodman et al., 1987), showed that under ice storage capacities in late winter (April) were high, with an estimation of 60,000m^3 per km^2.

The level of salinity has an effect on the biodegradation of the oil. This is highly dependent on the microbial community. Different oil degrading microbes have optimum salinity ranges at which they operate. A decrease in salinity may result in an increase in dissolution. Salinity also has an effect on the Oil Aggregate Mineral (OMA) formation (Lee et al., 2015).

1.4 Modeling of Oil Spill Spilled Weathering and Transportation

Spilled oil is transported by spreading, advection, encapsulation and sedimentation in ice-covered waters.

1.4.1 Spreading

Spreading is the phenomenon where spilled oil, under the influence of viscous, gravitational, buoyancy and surface tension forces causes a thin slick to cover a large area (Drozdowski et al., 2011). There are two dimensions to spreading: thickness of the oil while it spreads and the areal extent of the oil contaminated zone (Vankatesh et al., 1990). The former is significant in ice-covered waters (Vankatesh et al., 1990).

The tendency for oil to spread is governed by Equation 1 (James, 2004).

$$\boldsymbol{F = \sigma_w - \sigma_o - \sigma_{ow}} \quad (1)$$

where F is the spreading force, σ_w is the surface tension of water, σ_o is the surface tension of oil and σ_{ow} is the oil-water interfacial tension. Most oils produce positive spreading forces. They continue to spread as long as the surface and interfacial tension is unchanged (James, 2004). Fay (1969) identified three regimes following a spill. Initially, oil motion is due to gravity and viscosity. This is followed by a gravity-inertia regime. When the slick becomes thin, the effect of gravity diminishes and the dominant forces in the final regime are surface tension and viscosity. This concept is the basis for most spreading models (Cuesta and Francesc, 1990).

The Langmuir effect contributes to spreading but its influence is minimal (Lehr, 2001). The Langmuir effect refers to a pattern of repeating Langmuir cells (LC) below the surface of the sea that creates a system of ridges and troughs on the surface (Anon., 2003). The result is lines of oil that may spread over a large geographical area (Lehr, 2001).

1.4.1.1. Spreading in Open Water

In open water, oil begins to spread immediately after a spill. Sometimes in the presence of waves and currents, the importance of the oil properties becomes less relevant in spreading. Under such conditions, spreading in open water is dominated by oceanographic forces (Anon., 2011). The rate of change of area of spreading oil is given by Equation 2. It was developed by Mackay et al. (1980). This has been used by Reed (1989) and Spaulding et al. (1992), and is based on the gravity-viscous formulation of Fay (1969) and Hoult (1972).

$$\frac{dA}{dt} = KA^{\frac{1}{3}}\left[\frac{V_m}{A}\right]^{\frac{4}{3}} \tag{2}$$

where A is the area of slick (m^2), V_m is the volume of spilled oil (m^3), K is a constant with default value 150^{-1}, and t is the time (s).

1.4.1.2 Spreading in Ice-Covered Waters

In the presence of ice, spreading is dependent on ice type and ice coverage. Increasing ice coverage is accompanied by increasing oil thickness (Brandvik et al., 2006). The location of spilled oil (that is on ice, under ice, under broken ice, under first year ice, under multi-year ice, in pack ice, on cold water, in leads, on snow and absorbed into snow) is a determinant of spreading in ice-covered waters (Fingas and Hollebone, 2003). Some of this is illustrated in Figure 5. Compared to open water, the presence of ice reduces the spread of spilled oil (Fingas and Hollebone, 2003). The presence of ice floes or irregularities on and under the ice surface further retards the spreading of spilled oil because the ice can create natural barriers to oil movement (Evers et al., 2004). Spilled oil may move several kilometers from the original point of the spill if it is trapped under ice or gets encapsulated in ice (Wilson and Mackay, 1987; Buist et al., 2013; Fingas, 2015).

1.4.1.2.1 Spreading on Ice

Equations for modeling spreading of oil on ice are based on Fay (1969, 1971) and Hoult (1972).The equations are based on gravity-inertia, gravity-viscous, surface tension regime for one dimensional and radially symmetric spreading. Equation 3 shows the gravity-viscous regime for radially symmetric spreading. For details of the other equations, the reader is referred to Fay (1969) and Hoult (1972).

$$r(t) = 1.45\left(\Delta g {V_m}^2 t^{\frac{3}{2}} v^{\frac{-1}{2}}\right)^{\frac{1}{6}} \tag{3-1}$$

where r is the radius (m), t the time $(s), V_m$ is the volume of spill (m^3), g is the acceleration due to gravity (9.8 $\frac{m}{s^2}$), v is the kinematic viscosity of water ($m^2 s^{-1}$), $\Delta = \rho - \rho_o$, ρ is the density of sea water $\left(\frac{kg}{m^3}\right)$ and ρ_o is the density of oil $\left(\frac{kg}{m^3}\right)$.

Some of the limitations of the initial model include the following:

- The equations do not account for the reduced spreading rate of viscous oil(s).
- Break-up of oil slicks into small patches is not considered.
- The formation of elongated slicks with a thin film trailing behind the slick is not addressed.
- The dependency of the spreading rate on the discharge conditions (instantaneous versus continuous release and surface versus subsurface) has not been taken into account (Fingas and Hollebone, 2003).

Lehr et al. (1984) proposed Equation 4 to address the shortcomings of the Fay (1969) and Hoult (1972) equations. The formula calculates the total slick area on the premise that spreading is separated into two major regimes: a thick 'black oil' regime and thin 'sheen' regime. They noted that most spreading algorithms assume instantaneous release of oil in open water, but that in reality, not all spills follow this trend.

$$A = 2270\left[\frac{\Delta\rho}{\rho_o}\right]^{\frac{2}{3}} {V_m}^{\frac{2}{3}}\, t^{\frac{2}{3}} + 40\left[\frac{\Delta\rho}{\rho_o}\right]^{\frac{1}{3}} {V_m}^{\frac{1}{3}}\, W^{\frac{4}{3}}\, t \tag{4}$$

where A is the area of slick (m^2), W is the wind speed (knots), V_m is the volume of spill (barrels), t is time (minutes), ρ_o is the oil density, and $\Delta\rho$ is the density difference between air and water.

As oil leaks continuously, the oil moves farther from the source with winds and currents. In such conditions, at some point, lateral spreading forces will be dominant while forces along the axis of the slick reduce (Reed et al., 1999).

Glaeser and Vance (1971), Chen (1972), McMinn (1972), Chen (1974) and Kawamura et al. (1986) developed equations for spreading of oil on ice, through laboratory experiments. None of the relations describing spreading of oil on ice developed by these researchers produce the same results. They also fail to predict field results accurately, according to Fingas and Hollebone, (2003). The relation developed by Chen et al. (1974) which is time dependent is shown in Equation 5.

$$\frac{r}{V_m^{\frac{1}{3}}} = 0.24\left[\frac{t\rho g V_m^{\frac{1}{3}}}{\mu}\right]^{\frac{1}{5}} + 0.35 \tag{5}$$

where r is the slick radius as a function of time, V_m is the volume of oil spilled , t is the time after spillage, ρ is the oil density, g is the acceleration due to gravity, and μ_o is the viscosity of oil.

1.4.1.2.2 Spreading Under Ice

Oil spreads under ice, filling the nearest available under-ice depressions first before moving to the next depression. Volumetric analysis is considered the best method for evaluating spreading of oil under ice. Volumetric models developed so far have adopted an empirical approach. Lack of field data is a challenge to this approach (Fingas and Hollebone, 2003).

Yapa and Chowdhury (1989) derived Equations 7 and 8 for an oil spill under solid ice in constant discharge mode and constant volume mode respectively. The formulation was based on a simplified form of the Navier-Stokes equation. The Navier – Stoke equation is shown as Equation 6.

$$\frac{\partial V_r}{\partial t} + V_r \frac{\partial V_r}{\partial r} + \frac{V_\theta}{r}\frac{\partial V_r}{\partial \theta} - \frac{{V_\theta}^2}{r} + V_z \frac{\partial V_r}{\partial z} = g_r - \frac{1}{\rho_o}\frac{\partial p}{\partial r} + \frac{\mu_o}{\rho_o}\left\{\frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}(rV_r)\right] + \frac{1}{r^2}\frac{\partial^2 V_r}{\partial \theta^2} + \frac{\partial^2 V_r}{\partial z^2} + \frac{2}{r^2}\frac{\partial V_\theta}{\partial \theta}\right\} \tag{6}$$

Where z is the vertical direction, ρ_o is the oil density ($\frac{Kg}{m^3}$), μ_o is the oil viscosity ($\frac{Kg}{ms}$), V_r is the radial velocity ($\frac{m}{s}$), V_θ is the velocity in the θ direction ($\frac{m}{s}$), V_z is the velocity in the z direction,($\frac{m}{s}$) r is the radius to a point in the slick, (m) and $\frac{\partial p}{\partial r}$ is the pressure gradient in the radial direction.

They conducted experiments to test Equations 7 and 8.The experiments involved the use of a plexiglass tank of dimensions 122 ×122×61cm. A mirror was hinged to the frame below the tank and a video camera recorded the reflected image. The researchers used artificial ice covers, smooth real ice covers, and rough real ice covers, and varied viscosity, flowrates, ice roughness height, and volume of oil during the experiment. The results show close agreement between the output of the theoretical formulation and the experimental results. The authors recommended that the results should be verified with field data when they become available.

$$r = B\left[\frac{\Delta\rho g Q^3}{\mu_o}\right]^{\frac{1}{8}} t^{\frac{1}{2}} \quad \text{(Constant flow rate)} \tag{7}$$

where r is the slick radius, B is a constant accounting for hydraulic roughness of ice cover (0.467), $\Delta\rho$ is the density difference between water and oil, g is the acceleration due to gravity, Q is the discharge rate, μ_o is the dynamic viscosity of oil, t is the time after the spill started.

$$r = B\left[\frac{\Delta\rho g V^3}{\mu_o}\right]^{\frac{1}{8}} t^{\frac{1}{8}} \quad \text{(Constant volume)} \tag{8}$$

Studies related to spreading of spilled oil under ice are not limited to those described here. For more information, refer to Fingas and Hollebone (2003) and Fingas (2015).

According to Fingas and Hollebone (2003), numerical models for spreading of spilled oil under ice have been less successful. This is because the models may not consider factors like the under- ice roughness.

1.4.1.2.3 Spreading Under Broken Ice

Yapa and Weerasriya (1997) carried out a study of an oil spill under broken ice. They developed relations for axis-symmetrical spreading and unidirectional spreading under broken ice. They argued that, for broken ice, there are three regimes involved. Under permissible conditions, the oil seeps through the broken ice cover. With time, some of the oil gets to the water surface near the top side of the ice. They developed relations for spreading under ice and the water surface near the top of ice. Relations for bottom slick length during unidirectional spreading, top slick length for unidirectional spreading, and top slick length for axis-symmetrical spreading (constant discharge and constant volume) were developed. Equations 9 and 10 were derived to calculate top slick length for axis symmetrical spreading under constant discharge and constant volume conditions respectively.

$$r_1 = K_1 \left[\frac{Q\ \sigma_n}{\mu_o}\right]^{\frac{1}{4}} t^{\frac{1}{2}} \qquad \text{(Constant flowrate)} \tag{9}$$

$$r_1 = K_2 \left[\frac{(\forall\ \sigma_n}{\mu_o}\right]^{\frac{1}{4}} t^{\frac{1}{4}} \qquad \text{(Constant volume)} \tag{10}$$

where ∀ is constant volume, σ_n is the net interfacial tension force per unit length, X is the spreading rate of the slick at the water surface near the top of the ice cover r_1 is the top slick radius, μ_o is the dynamic viscosity of oil, B_1, B_2 are constants based on the hydraulic roughness of ice.

1.4.1.2.4 Spreading Under First Year Ice

Few field spills under first year ice have been reported (Buist et al., 2013). Studies conducted in laboratory and test tanks suggest that within the first few hours after a spill, ice forms a lip around the edge of the oil and encapsulates it. In the encapsulated state, the properties of oil remain unchanged (Buist et al., 2013). The oil remains there until maximum thickness of oil is reached. Vertical migration of oil is initiated, as ice warms. Vertical migration is a function of the degree of brine drainage within the ice (a function of internal temperature), trapped oil pool thickness, and oil viscosity (Buist et al., 2013).

From freezing time to mid-winter, when the thickness of ice grows fastest, migration of oil is slowest. This is because the ice develops few brine channels. With an increase in temperature, brine trapped within the crystal structure of the ice drains down, creating vertical channels for migration of the oil to the surface (Buist et al., 2013; Anon., 1975).

An experiment conducted in the Beaufort Sea under the Baleana Bay Project by Dome Petroleum in 1979 to 1980 indicated that oil spilled in early winter remained in the form of a discrete lens until temperatures increased from -20℃ to -12 ℃ in February. A brine channel network became more connected during March and April, facilitating the movement of oil to the surface (Buist et al., 2013). A SINTEF and University Centre in Svalbard's experimental spill conducted at Svalbard in March 2006 had the same rate of oil surfacing as that of the Dome Petroleum experiment in the Canadian Beaufort Sea from 1979 to1980. Spilled oil rose through the full ice thickness (60 to 70 cm) to reach total exposure of spilled oil in 40 days (Dickins et al., 2008).

1.4.1.2.5 Spreading Under Multi-Year Ice

Similar to first year ice, spilled oil under multi-year ice is retained by under-ice roughness features. Under-ice storage capacity may be greater in multi-year ice. Compared to smooth first year ice, individual pools of oil are thicker. This is because hollows underneath multi-year ice tend to be larger so can store more oil (Comfort and Purves, 1982; Kovacs, 1977). Ice grows downward and encapsulates the oil in winter. Weathering of oil is slower than in first year ice, while in the state of encapsulation in the multi-year ice. Migration through brine channels to the surface during the melt season still takes place despite the low salinity of multi-year ice (Buist et al., 2013). The oil appears on the surface in the melt pools but takes a longer time to do so compared to the first year ice because of the thickness of multi-year ice (Milne et al., 1977).

Comfort and Purves (1982) conducted a field experiment using three pools of crude oil placed under old ice 2.5 to 2.9 m thick in the Canadian High Arctic on June 1, 1978. 90 to 99% of the oil, originally under the old ice, surfaced by September 1979 (Buist et al., 2013).

Trapped oil under multi-year ice could persist in the marine environment for years (Anon., 1998) and get released only when it moves to the surface. Some researchers estimate oil could be trapped under multi-year ice for up to ten years (Anon., 2003).

1.4.1.2.6 Spreading on Cold Water

Glaeser and Vance (1971), Fazal and Milgram (1979), Tebeau et al. (1984), Anon. (1986), Anon. (1987), Anon. (1988) and Sayed and Løset (1993) have studied the behaviour of oil on cold water. Anon. (1987) and Anon. (1988) suggested the substitution of oil viscosity for water viscosity in the Fay spreading equations. Buist et al. (2008) also conducted a series of one dimensional and two dimensional spreading tests with Alaskan crude oils of different physical properties. The results indicated that, except for oils at temperatures below their pour point, the data support the theory of Fay (1969) and Fay and Hoult (1971). Equation 11 was used to estimate the maximum thickness of the oil slick.

$$h_\infty = \left(\frac{\rho^2 v D^3 {V_m}^2}{\sigma^2}\right)^{\frac{1}{8}} \tag{11}$$

where h_∞ is the final slick thickness (cm), v is the kinematic viscosity $\left(\frac{cm^2}{s}\right)$, V_m is the volume of oil (mL), and D is the molecular diffusivity $\left(\frac{cm^2}{s}\right)$ of value approximately 1×10^{-4}.

1.4.1.2.7 Spreading of oil in Pack Ice

Spilled oil spreads less in pack ice compared to open water. Spreading of oil in pack ice-covered waters is a function of ice concentration. For pack ice concentration above $\frac{7}{10}$, the ice floes touch and provide a high degree of natural containment. This limits the spread of oil. Spreading of oil returns to open water status at an ice concentration below $\frac{3}{10}$ (Buist et al., 2013).

Free et al. (1982), Tebeau et al. (1984), Sayed and Ng (1993), Weerasuriya and Yapa (1993), Yapa and Belaskas (1993) and Anon. (1987) studied the spreading of spilled oil in pack ice. The conclusion from their studies was that the presence of pack ice significantly slowed down the spread of oil. Another conclusion from studies by Anon. (1987) is that in open drift ice, oil and ice moved together at 3% of wind speed. The study by Anon. (1987) compared results from an adjusted Fay model and Kawamura's adjusted empirical model. The Kawamura model is described in Fingas and Hollebone (2003). The adjusted Fay model predicted the spreading in pack ice better than that of Kawamura (Fingas and Hollebone, 2003). The adjusted Fay models are given by Equations 12 to 14 for the different regimes. Fingas and Hollebone, (2003) recommend the use of Equation 15 instead, which calculates a corrected area of spread in pack ice.

Gravity-inertia $A = 4.1(\Delta g V t^2)^{\frac{1}{2}}$ (12)

Gravity-Viscous $A = 6.6 \frac{\left[\Delta g V^2 t^{\frac{3}{2}} \rho^{\frac{1}{2}}\right]^{\frac{1}{3}}}{\mu^{\frac{1}{2}}}$ (13)

Surface tension-Viscous $A = 16.6 \left(\frac{\sigma^2 t^3}{\rho \mu}\right)^{\frac{1}{2}}$ (14)

$$A_{\mu I} = \left[\frac{\mu_O}{\mu}\right]^{-0.15}(1 - f_I)A \tag{15}$$

where A is the area, $A_{\mu I}$ is the corrected area for spreading in pack ice, f_I is the fraction of ice cover, μ_O is the viscosity of oil, and μ the viscosity of water.

SINTEF's Oil Weathering Model (OWM), part of the OSCAR package has been updated to have the capability to model weathering processes of an oil spill in pack ice (Brandvik, 2009).

1.4.1.2.8 Spreading in Leads and Polynyas

In leads and polynyas, spreading is more rapid compared to spreading on the surface of ice-covered waters (Wilson and Mackay, 1987). The mechanism of spreading of oil in leads and polynyas is not well known. Anon. (1990) suggests that oil released in a polynya moves to the downwind edge. The oil may freeze or collect behind floating ice segments. Buist et al. (1987) studied the fate and transport of oil in leads using the sink tank test. They developed Equation 16-1 to calculate the thickness of wind-herded slick.

$$T_h = 1.01h_o + 0.72W \tag{16}$$

where T_h is the thickness of a the wind-herded slick, h_o is the original thickness(mm), and W is the wind speed $\left(\frac{\mathrm{m}}{\mathrm{s}}\right)$.

"Lead pumping" is a dominant oil transport mechanism in the early hours of a spill according to some researchers (Fingas and Hollebone, 2003). It is the movement of oil to the surface of the ice, as a result of the pumping action of rapid lead closure. MacNeill and Goodman (1987) and Cammaert (1980) studied the behaviour of oil in leads. MacNeill and Goodman (1987) found that deeper leads required higher currents to remove oil. Cammaert (1980) concluded that a low lead closure rate forces oil under ice, while a high closure rate forces the oil on top of the ice. The study also suggested that a closure rate of 12 $\frac{cm}{s}$ or more is required to force oil to the top of ice.

Field analysis in the Beautfort Sea and Lancaster Sound shows that lead closure rates may not be sufficient in moving oil onto the ice surface under normal conditions. This can only happen in a scenario where ice is closing behind a ship (Puestow et al., 2013).

1.4.1.2.9 Spreading on Snow and Absorption to Snow

Spreading of oil in snow has not been studied extensively, and is poorly understood. In substantial quantities, spilled oil in snow flows down to the layer of ice, and spread slowly outwards (Buist et al., 2013).

Studies conducted by Glaeser and Vance (1971), McMinn (1972), Chen et al. (1974), Anon. (1975), Mackay et al. (1975), and Kawamura et al. (1986) suggested that the presence of snow reduces the spread of oil (Anon., 1988; Bech and Sveum, 1991). According to Buist et al. (2013) the type of release affects the area of a spill in snow (Buist et al., 2013).

Anon. (1988) developed equations for different scenarios for oil spills in snow. These include continuous and instantaneous release of oil in snow, horizontal spreading of oil on an impermeable surface beneath a snowpack, and oil infiltration into a snowpack. They also developed equations for the linear rate of oil penetration.

Equations 17 and 18 were developed to calculate the radius of the spread of spilled oil in snow, from a continuous and instantaneous release respectively.

$$r = \left(\frac{gQ^2}{\pi\gamma^{\frac{1}{2}}}\right)^{\frac{1}{6}} t^{\frac{1}{2}} \tag{17}$$

$$r = \left(\frac{gV^2}{\pi\gamma^{\frac{1}{2}}}\right)^{\frac{1}{6}} t^{\frac{1}{4}} \tag{18}$$

where g is the gravitational acceleration, Q is the oil flow rate $\left(\frac{\mathrm{m}^3}{\mathrm{s}}\right)$, V_m is the oil volume (m^3), t is the time (s), r is the radius (m), ρ is the density of oil $\left(\frac{\mathrm{Kg}}{\mathrm{m}^3}\right)$, and γ is the kinematic viscosity of oil $\left(\frac{\mathrm{m}^2}{\mathrm{s}}\right)$.

1.4.1.3 Advection

Anon. (1985) defined Advection is the movement of oil due to the influence of overlying winds and underlying currents. Limited studies have taken place on the subsurface advection of oil (Spaulding, 1995). Observations from these studies suggest that oil moves as the bulk water moves (Spaulding, 1995; Fallah and Stark, 1976; Reed, 1992). Methods to estimate advection include 1) the random walk process (Reed and Spaulding, 1979), 2) the Markov Chain process (Smith et al., 1982) and 3) meteorological models (Hess and Kerr, 1979) and a combinations of any of the three (Spaulding, 1988). The use of a drift current of 3% to 4% of the wind speed has been adopted by most models (Reed et al., 1998; Reed et al., 1994a). The use of hydrodynamic models in oil spill modeling to simulate advection currents is becoming common (Reed et al., 1999). This approach has been used in operational oil spill response systems (Elliot et al., 1992; Morita et al., 1997; Martinsen et al., 1994).

Langmuir Circulation (LC) influences advection but little research has been conducted to understand the phenomenon (Anon., 2003). This is however changing rapidly following the BP oil spill in 2010. A growing literature of oil spill modeling and experimental work is in circulation. One of this is a database developed by the Arctic Oil

Spill Response technology program (Word, 2014). This has a database of all work related to Arctic oil spills over the years.

Advection velocity is made up of two components. One accounts for the mean wind speed and currents while the other accounts for local turbulent diffusion (Davidson et al., 2006). Equation 19 shows how advection is calculated.

$$\vec{V} = \overrightarrow{V_m} + \overrightarrow{V_t} \tag{19}$$

where $\overrightarrow{V_m}$ is the mean velocity, and $\overrightarrow{V_t}$ accounts for local turbulent diffusion.

The two components can be calculated using works by Hoult (1979) and Fisher et al. (1979) respectively in Equations 20 and 21.

$$\overrightarrow{V_m} = \alpha_w \overrightarrow{V_w} + \alpha_C \overrightarrow{V_C} \tag{20}$$

where $\overrightarrow{V_w}$ is the wind velocity at 10m above water surface, $\overrightarrow{V_C}$ is the depth-averaged current velocity, α_w is the wind drift coefficient with default value of 0.03, α_C is the current drift coefficient with default value of 1.15.

$$\overrightarrow{V_t} = R_n e^{-i\theta} \sqrt{\frac{4(D_e + D_T)}{\Delta t}} \tag{21}$$

where Δt is the time step, R_n is the normally distributed random number of mean value 0 and standard deviation 1, θ is the uniformly distributed random angle between 0 and π, D_e is the dispersion coefficient due to mechanical spreading, and D_T is the diffusion coefficient.

In open water, wind elongates the slick in the direction of prevailing wind (Nazir et al., 2008). Spills occurring on and under ice move with the ice except under ice currents above 15 to 20 $\frac{cm}{s}$ (0.3 to 0.4 knots). Uzuner et al. (1979) and Cox and Schultz

(1980) presented a series of flume experiments to measure the stripping velocity and subsequent advection of oil slicks in the presence of large, under-ice roughness features. According to Buist et al. (2013) studies conducted by Cammaert (1980) and Puskas et al. (1987) established that in under-developed first-year sea ice, a minimum threshold current of 20 $\frac{cm}{s}$ is required to initiate and sustain movement of an oil lens under the ice surface.

In high ice concentration, the ice moves with the oil while at lower ice concentration ($\frac{3}{10}$) the oil and ice move at different rates (Buist et al., 2013).

1.4.1.4 Encapsulation

Oil encapsulation in ice is often refer to as “oil-ice sandwich” (Evers et al. (2004); Izumiyama et al. (2004); Anon. (2003), encapsulation occurs only in ice. It is a fluid mechanics and thermodynamically driven process. When there is a release under growing sea ice, oil will freeze and remain there as it cannot evaporate (Fingas and Hollebone 2003; Lee et al., 2011). A review of field tests and laboratory experiments by Fingas and Hollebone (2003) suggests that oil may be partially encapsulated within four hours and be fully encapsulated as quickly as 24 hours after contact with the ice. Encapsulation is temperature dependent, which in turn is influenced by the seasons. For example, in subarctic areas, encapsulation may not take place before melting because of insufficient ice growth. The processes of encapsulation are i) formation of an ice lip around the oil (and or gas) and ii) ice growth from the lip to the center of the pool of oil. The result is new ice growth under the oil, after total encapsulation by the ice sheet (Buist et al., 2013). The downward growing of ice sheet, as a means of incorporating oil in ice has been observed for all experiments carried out so far to study encapsulation (Fingas, 2015; Buist et al., 2013; Lee et al., 2011).

1.4.1.5 Dispersion

Dispersion of an oil slick is the process by which breaking waves force oil droplets into the water column; the smallest droplets do not resurface and remain in the water column (Buist et al., 2013; Lehr, 2001). Dispersion of oil is poorly understood (Fingas, 2015; Mackay and McAuliffe, 1988). It occurs in both the vertical and horizontal directions (Anon., 2003). Waves and turbulence break slicks into droplets of different sizes. These mix into the upper water column. Smaller droplets remain in suspension while the larger ones return to the surface, coalescing with other water droplets. On reaching the surface, the droplets reform into a slick or spread out in a thin film. This results in a reduction of the oil concentration in the sea and enhances processes like biodegradation, dissolution and sedimentation (Anon., 2003; Anon., 2011). Modeling of natural dispersion is essential for assessing the lifetime of an oil spill (Lee et al., 2011, Reed et al., 1998). In ice covered waters, dispersion reduces with an increase in ice coverage (Word, 2014).

1.4.1.5.1 Horizontal Dispersion

In oil spill modeling, horizontal dispersion is often combined with spreading, but they are essentially different, characterized by varying time scales (Anon., 2003). Both begin immediately after an oil spill occurs but stop at different times in the life of the oil slick (Anon., 2003).

1.4.1.5.2 Vertical Dispersion

Vertical dispersion is accounted for in most oil spill models. Vertical dispersion is the movement of sizes of less than 100 μm into the water column. Blaikely et al. (1977), Mackay et al. (1980) and Aravamudan et al. (1979) have developed models for dispersion of oil. The model proposed by Delvigne and Sweeney (1988) has been used in the ADIOS model, (Anon. (1994)), OSCAR (Reed et al. (1995); Aaomo et al. (1997)), and OILMAP (Reed et al., 1999). The relation is shown in Equation 22.

$$Q(d_o) = C_o {D_{bw}}^{0.57} d^{0.7} \Delta d d_o \tag{22}$$

where $Q(d_o)$ is the entrained mass of oil droplets $\left(\frac{kg}{m^2 s}\right)$, D_{bw} is the dissipating breaking wave energy per unit surface area $\left(\frac{J}{m^2}\right)$, C_o is a constant that is oil type dependent, d_o is the droplet size, and Δd is the range of droplet size interval (m). For example, light oil takes values of 1000 to 1800, medium oil 500 to 1000, and less than 500 for heavier oil (Fingas, 2015). $Q(d_o)$ falls in an interval of Δd (m) around d_o. According to Delvigne and Sweeney (1988), d_o between $-\frac{1}{2}\Delta d$ and $+\frac{1}{2}\Delta d$ per unit surface area and per unit breaking event are the most appropriate for Equation 20 (Lehr, 2001; Delvigne and Sweeney, 1988). NOAA came up with a simplified relation based on Equation 22. The use of a specific threshold diameter undermines the authenticity of Equation 22 and subsequently that developed by NOAA. This is because large vertical turbulent motions and high droplet velocities support permanent entrainment of dispersed oil (Reed et al., 1999). This means permanent entrainment is controlled by droplet rise velocities and sea state instead of droplet size. This argument is further supported by the elongation of the oil slick. Dispersed oil lags behind the surface slick due to wind-induced current shear in the upper part of the water column. This has been incorporated into some oil drift models based on the particle concept (Johansen, 1987; Elliot, 1991; Reed et al. 1994a; Reed et al., 1999).

Measuring the numerous factors that control dispersion is a challenge. A small number of tests have been performed at sea. Tests conducted so far suggest that the mixing depth is approximately 1.5 times the wave height (Lehr, 2001; Reed et al., 1999). Mackay et al. (1980) developed Equation 23 to calculate the rate of permanent entrainment. This was used by Reed et al. (1989).

$$D = D_a D_b = [0.11(W+1)^2]\left[\left(1 + 50\mu^{\frac{1}{2}} h \sigma_{ow}\right)^{-1}\right] \tag{23}$$

where D is the rate of entrainment $\left(\frac{\mathrm{m}^3}{\mathrm{m}^2\mathrm{s}}\right)$, D_a is the fraction of sea surface dispersed per hour, D_b is the fraction of dispersed oil not returning to a slick, W is the wind speed $\left(\frac{\mathrm{m}}{\mathrm{s}}\right)$, μ is the viscosity (cP), h is the slick thickness (m),and σ_{ow} the oil-water interfacial tension $\left(\frac{\mathrm{dyne}}{\mathrm{m}}\right)$.

In ice-covered waters, dispersion is not dominant and unlikely except near an ice field's open water edge (Anon., 1987; Singsaas et al., 1994; Sørstrøm et al., 2010). The presence of ice damps the action of waves hence reducing the rate of dispersion. The motions of ice floes may momentarily cause some local dispersion, but droplets so formed will be too large to remain in the water column. They will rise up and re-coalesce with surface oil or accumulate beneath the floes (Buist et al., 2013).

Experiments conducted by Martin et al. (1976), Metge and Telford, (1979), Anon. (1980) and Anon. (1987) of an oil spill in ice established that natural dispersion was negligible in ice-covered waters. The main fate of spilled oil in pack ice is evaporation until ice melts in spring when dispersion starts (Hirvi et al., 1992). Other studies by Stochmal and Gurgul, (1992) and Singsaas et al. (1994) suggest that the presence of ice significantly reduces the rate of dispersion, or suppresses it altogether (Buist et al, 2013).

Lehr and Simecek-Beatty (2001) studied the effect of Langmuir Cell (LC) on dispersion. The study suggested that LC could be an important factor for natural dispersion of oil in the water column. Theory suggests that wave breaking will drive oil droplets approximately one wave height into the water column, whereas LC could drive smaller near-neutrally buoyant droplets as far as the bottom of the mixed layer of the water column. LC is not accounted for in oil spill models because there is no suitable validated algorithm (Anon., 2003). Development of a simple algorithm of Langmuir Cell hydrodynamics will improve the accuracy of oil spill models (Anon., 2003). The oil spill models have improved since the BP oil spill and a lot of work has been done after the review by the authors.

1.4.1.6 Sedimentation

Sedimentation and sinking are often confused. Sedimentation is the adhesion of oil to suspended sediments that ultimately move out of the water column and settle on the seafloor (Anon., 2003; Lehr, 2001). Sinking is a mechanism by which oil masses denser than water are transported to the bottom of the sea (Anon., 2003). The actual physical process of sedimentation is complicated and research in this area has been fragmented (Anon., 2003; Lehr, 2001). Research has focused on the interactions between fine particles (clay) and oil stranded on the shoreline. During the Exxon Valdez oil spill, it was observed that oil attached to fine particles is more available for biodegradation (Bragg and Owens, 1995; Anon., 2003).

A mixing test in the laboratory has been used to measure sedimentation but factors controlling the rate at which oil gets attached to sediments have not been identified (McCourt and Shier, 2001). Lack of data makes sedimentation a difficult process to study (Fingas, 2015). The percentage of clay in the Suspended Particulate Matter (SPM) population is proposed as the main factor influencing sedimentation (Meyers and Quinn, 1973; Bassin and Ichiye, 1977; Meyers and Oas, 1978; Xuercher and Thuer, 1978; Kirstein et al., 1985; Spaulding, 1988). Though some studies have taken place, few models exist for predicting the dynamic processes of sedimentation (Lehr, 2001). Studies by Payne et al. (1987) proposed Equations 24 and 25 to calculate total sedimentation rate per unit area of slick and the mass lost per unit water volume per unit time, respectively (Lehr, 2001).

$$Q_{sed} = \int_0^{1.5H} q_{sed}\, dz \tag{24}$$

where H is the water depth

$$q_{sed} = K_S \sqrt{\frac{\varepsilon}{V_w}}\, C_{oil} C_{sed} \tag{25}$$

where ε is the rate of energy dissipation, K_S depends on the type and size of suspended material (Lehr, 2001).

Based on experimental results, the rate of oil loss due to the oil-sediment adherence process is given by Equation 26 (Korotenko et al., 2000).

$$\frac{dA_d}{dt} = 1.4 \times 10^{-12} S_L (1 - 0.023 S_a) \tag{26}$$

where $\frac{dA_d}{dt}$ is the rate of oil loss due to the oil-sediment adherence process $\left(\frac{\mathrm{m}^3}{\mathrm{s}}\right)$, S_L is the sediment load, and S_a is the salinity (Korotenko et al., 2000). Few studies have taken place on the processes of sinking and sedimentation in ice-covered waters and these are not well understood. In terms of oil clean up, sedimentation poses a challenge because of the slow rate of anaerobic biodegradation of the attached oil to the sediments. (Lee et al., 2011).

1.4.2 Weathering

Weathering is the change of physical and chemical composition of oil with time after a spill (Reed et al., 1999). It involves evaporation, emulsification, biodegradation, dissolution, and photo-oxidation (Reed et al., 1999; Buist et al., 2013).

1.4.2.1 Evaporation

Among the weathering processes, evaporation is the most important both in open water and ice-covered waters. Evaporation may be the only transformative process included in some oil spill models (Fingas, 1995; Fingas 2015). Evaporation in open water typically accounts for 20% to 40% of spilled oil mass balance. The basic physics and chemistry of oil spill evaporation are not well understood (Fingas, 1995). The challenge with respect to evaporation is its combined dynamics of oil spill in an evolving environment like the ocean where other mechanisms also occur simultaneously. Understanding the physics and chemistry of evaporation of spilled oil is a challenge because oil is made up of a mixture of hundreds of compounds (Fingas, 1995; Fingas, 2015).

The rate of evaporation differs from winter to summer in the Arctic, where there are periods of 24 hours of darkness and 24 hours of sunlight respectively (Buist et al., 2013).

Studies conducted by Glaeser and Vance, (1971), Chen et al.(1972), McMinn, (1972), Tebeau et al. (1982), and Anon. (1987) concluded that in ice-covered waters, the presence of ice greatly reduces the rate of evaporation. This is because the temperature is low and the oil slicks are thicker (Buist et al, 2014).

The analytical method and pseudo-component methods are the most common methods for modeling evaporation. The pseudo-component method is a complex method but more accurate. The pseudo-component approach involves the computation of a fraction of oil evaporated as a function of time and temperature (Fingas, 1997; 1999). This approach has been used in the SINTEF's oil weathering model (Daling et al., 1997). Due to the large data requirements and computational complexity of the pseudo-component method, a simpler analytical method developed by Stiver and Mackay (1984) has become popular. It is often referred to as the standard equation of modeling evaporation for an oil spill. It was used in the ADIOS oil spill model developed by Lehr et al. (1992). Anon. (1988) also applied it to model an oil spill under snow (Buist, 2013). It is given by equation 27.

$$F_V = \left\{\frac{T}{BT_G}\right\} In\left[1 + B\left(\frac{T_G}{T}\right)\theta exp\left(A - \frac{BT_0}{T}\right)\right] \text{ and } \theta = \frac{kA_St}{V} = \frac{kt}{x} \tag{27}$$

where F_V is the volume fraction of hydrocarbons evaporated $(\%)$, T is the ambient temperature (K), T_G is the slope of the modified ASTM distillation curve (K), T_0 is the initial boiling point of the modified distillation curve (K), θ is the evaporative coefficient, A_S is the spill area (m^2), k is the mass transfer coefficient $\left(\frac{\mathrm{m}}{\mathrm{s}^{-1}}\right)$, t is the time (s), x is the slick thickness (m). The value of T_G varies for different oil types. A and B are dimensionless and varies for different oils.

The challenge with the Stiver and Mackay (1984) equation is that it does not predict evaporation for light crude well beyond the first 8 hours. It mostly over-predicts the percentage evaporated. It also mis-predict evaporation at the initial stages (Fingas, 1995). The difference could be 10% evaporative loss at the 24 hour mark. This may be due to the fact that oil is a mixture of different hydrocarbons and so a constant value of the physical and chemical properties is not possible. A major assumption of this equation is that the relationship between the boiling point of the liquid phase and fraction lost by evaporation is linear (Reed et al, 1999). This a simplification of the process. Curves exist which represent the boiling rate. These curves could be used and may be a way of addressing this flaw.

The approaches discussed so far are based on the assumption that evaporation rate is a function of spill area, wind speed, vapour pressure, slick thickness and temperature (Fingas, 1995; Fingas, 2013).

Fingas (1995) stressed the need for further research, to develop equations that are simple and more accurate for modeling evaporation of oil spills. Fingas (2013) proposed a new way of thinking, hence new equations to model evaporation. He argued that evaporation equations proposed earlier, which he referred to as adopting air-boundary concepts, show differences in the fraction of hydrocarbon evaporated for different oil types under the same conditions. The relations could not explain and predict evaporation accurately in the long term (Fingas, 2008, 2011). He conducted experiments to develop new models known as diffusion-regulated models. The results of the experiments established that wind and the surface area are not major factors affecting evaporation. The new study concluded that evaporation is dependent on temperature, time and the percentage (by weight) of oil distilled at 180℃. His study produced Equations 28 and 29. Equation 28 describes the diffusion regulated evaporation for most oils except for diesels, kerosene and jet fuel. Equation 29 has been developed for such fuels (diesel, kerosene and jet fuel). (Fingas, 2008; 2011; 2015).

$$Percent\ evaporated = [0.165(\%D) + 0.45(T - 15)]In(t) \tag{28}$$

$$Percent\ evaporated = [0.0254(\%D) + 0.01(T - 15)]\sqrt{t} \tag{29}$$

where $\% D$ is the percentage (by weight) distilled at 180℃, T is the temperature (℃), and t the time (minutes).

It should be noted however that most oil spill models continue to use Stiver and Mackay (1984) models in modified forms. Each model has its limitations and depending on the available data for input parameters, some modelers may opt for one model over another.

1.4.2.1.1 Evaporation in Pack Ice

Deslaurier et al. (1977), Anon. (1987b), Wilson and Mackay (1987) and Singsaas et al. (1994) performed tests to measure evaporation of spilled oil in pack ice. The results of these tests established that evaporation in pack ice is slower compared to that in open water. SINTEF conducted similar studies to update their Oil Weathering Model (OWM), which was originally developed for open water (Brandvik and Faksness, 2009), and made the same observation for the rate of evaporation in pack ice compared to that open water.

A series of spill experiments using diesel and gasoline in the Russian Arctic suggested that evaporation of light distilled fuels is faster on the surface of ice floes in spring and summer (Serova, 1992; Ivanov et al, 2005).

1.4.2.1.2 Evaporation in snow

Research into evaporation of oil in snow has received little attention. Current models are inadequate to estimate the evaporation rate in snow (Buist, 2000; Owens et al., 2005). McMinn (1972), Anon. (1988), and Bech and Sveum (1991) conducted experiments to measure evaporation of oil in snow-covered sea ice. The conclusion from these experiments suggests that the presence of snow reduced the rate of evaporation of oil. Anon. (1988) proposed Equation 30 for modeling evaporation of oil beneath a snow pack. The approach is referred to as the evaporative exposure approach.

$$\frac{1}{K} = \frac{1}{K_W} + \frac{H}{K_O} + \frac{L}{D_s} \tag{30}$$

where K_W is the air-side mass transfer coefficient $\left(\frac{\mathrm{m}}{\mathrm{s}}\right)$, K_O is the oil internal mass transfer coefficient $\left(\frac{\mathrm{m}}{\mathrm{s}}\right)$, H is Henry's law constant, D_s is the diffusivity of oil in snow $\left(\frac{m^2}{\mathrm{s}}\right)$, and L is the depth of oil below the snow's surface (m).

1.4.2.1.3 Evaporation in melt pools

In the spring, encapsulated oil gets exposed on the surface in an almost fresh state. Evaporation will occur as the oil floats on melt pool water (Anon., 1975; Dickins et al., 2008). Oil on melt pools tends to be herded by wind against the edge of the pool. Evaporation of a melt pool slick is slow compared to that in open water (Buist et al., 2013).

1.4.2.2 Emulsification

Emulsification is the process by which dispersed water droplets in oil form a 'mousse' of increased viscosity and volume (Spaulding, 1988; Berridge et al., 1968). The physics and chemistry of emulsification is not well understood (Spaulding, 1988; Bobra, 1990 and 1991; Walker et al., 1993; Fingas and Fieldhouse, 2011). Mclean et al. (1998) suggest that the two important factors for emulsification of spilled oil are viscosity of oil and the presence of surface-active agents.

Fingas (2015) believes asphaltenes and resins form a "skin" around the smaller oil droplets preventing the coalescing of smaller droplets to form bigger ones. The process is as follows: 1) water droplets are introduced into oil by turbulence or wave action, 2) resins stabilise droplets of water partially in minutes, 3) asphaletenes then displace resins from the water surface and form more stable water droplets, 4) asphaltenes continue to move to the surface and further stabilise the water droplets (Fingas, 2015). Studies conducted by Sjöblem et al. (1999) and Mclean et al. (1998) established that asphaltenes form barriers of greater strength compared to those of resins. The role of resins is that of a solvation media for asphaltenes. Four types of emulsions have been identified. These include stable emulsions, meso-stable emulsions, unstable emulsions and entrained water. They are distinguished by their colour and their ability to stabilize an oil slick to form emulsions. Stable and meso-stable emulsions are reddish-brown in appearance. Entrained water-in-oil types are black and viscous in appearance. Unstable emulsions are those that decompose into water and oil after mixing within a few hours and therefore do not form any of the aforementioned three (Anon., 2003; Fingas, 2015). Stability is the main criterion for classing emulsions; hence, unstable emulsions and entrained water are not considered emulsions in terms of oil spills (Fingas et al., 2000; Anon., 2003). Recently, Fingas (2015) developed a method to predict the stability of emulsions based on the starting viscosity of the oil, elastic modulus and the complex modulus on the first day. The reader is referred to Fingas (2015) for details of this method. Formation of emulsions presents a challenge for clean-up operations because of the increase in viscosity of spilled oil (Fingas, 2015).

Oil spill emulsification is one of the most difficult processes to model or predict on a spill-specific basis (Xie et al., 2007). The strategy adopted has been the use of a laboratory test called the Rotating Flask Test, which measures the tendency of oil to form an emulsion and the stability of the emulsion once formed. This test does not predict the rate of spill emulsification in the field (Anon., 2003; Reed et al., 1999).

Mackay et al. (1980a, b) developed Equation 31, to model emulsification. It is the most used equation for modeling emulsification. It has been used in ADIOS by NOAA and in a slightly modified form in the SINTEF OWM. Yang et al. (2015) and Nazir et al. (2008) have also used it for oil spill modeling purposes.

$$\frac{dY}{dt} = ZW^2\left[1 - \left(\frac{Y}{Y_{max}}\right)\right] \tag{31}$$

where Z is a constant and takes values between 1 and 2 $\left(\frac{\mathrm{ms}}{\mathrm{m}^2}\right)$, Y is the fraction of water in oil, Y_{max} is the final fraction of water content and is dependent on oil type. For instance a value of 0.7 is used for crude oil and heavy fuel. W is the wind speed $\left(\frac{m}{s}\right)$, and t is the time(s).

Two important parameters control this equation. They are the maximum water content and water uptake rate. Both are derived from laboratory experiments (Lehr, 2001). Studies established that these parameters vary for different oil types and weathered condition of the oil (Daling and Brandvik, 1988). Owing to these differences, Daling et al. (1990) suggested that laboratory experiments should be used to determine the parameters of emulsification. Fingas et al.'s (1997, 1990) review of emulsification related models suggested that empirical data should be the basis for further development of emulsification models. The studies also proposed that the models should take into account the stability of emulsions formed by different oil types (Aamo et al., 1993; Daling et al., 1997). The SINTEF oil weathering model has adopted this approach (Khelifa, 2011, Brandvik, 2012).

Mousse formation causes an increase in viscosity and is calculated using Equation 32 (Yang et al., 2015).

$$\mu = \mu_o exp\left[\frac{2.5Y}{1-C_3Y}\right] \ , \quad \mu_o = 224A_C^{\frac{1}{2}} \tag{32}$$

where μ_o is the viscosity of parent oil (cP), and A_c is the percentage of asphaltene. Evaporation also causes viscosity change and this is represented by Equation 33 (Sebastiao and Soares, 1995).

$$\mu = \mu_o exp\ (C_4F_E) \tag{33}$$

C_4 is taken as 10 and F_E is the fraction of hydrocarbons evaporated.

Metge and Telford (1979) observed emulsification of crude oil during a study of the behaviour of crude oil in frazil ice. Payne et al. (1987) conducted a series of experiments and established that there was a steady increase in the water content of the oil slick to 50% in open water over 6 days, a rapid increase to 64% in an hour then maintaining the same water content for 6 days in first year ice break-up and a slow increase to 28% in multi-year ice at break up.

Experiments conducted by Hirvi et al. (1992) and Singsaas et al. (1994) suggested that waves and ice coverage have an effect on emulsification. A series of experiments conducted with Stratjford crude in pack ice (0%, 30% and 90% coverage) (Brandvik and Faskness, (2009), suggested that oil emulsified much more slowly in dense pack ice than in open water (Brandvik et al., 2010a). Emulsification of oil on melt pools is expected to be negligible (Buist et al., 2013).

Yang et al. (2015) proposed Equation 34 for an ice cover of 90% based on Equation 31.

$$\frac{dY}{dt} = 6.8 \times 10^{-7}(1 + W)^2 \left[1 - \left(\frac{Y}{Y_{max}}\right)\right] \quad (34)$$

where W is the wind speed and the other symbols remain as in Equation 29-1. Emulsification decreases with an increase in ice coverage (Word, 2014).

1.4.2.3 Dissolution

Dissolution is the process by which the soluble fraction of oil breaks into small particles, mixing with water and forming a homogeneous mixture (Anon., 2003). It is active in open water immediately after an oil spill (Spaulding, 1988; Fingas, 2015). Due to the presence of relatively small quantities of soluble hydrocarbons, it is suspected that only small percentage of hydrocarbons may dissolve (Lehr, 2011). The equilibrium solubility of hydrocarbons is a function of temperature and salinity most predominantly. Studies have however shown that the percentage may be higher than earlier studies discovered (NRC, 2002).

The rate of dissolution was estimated by Cohen et al. (1980) by using Equation 35 (Janeiro et al., 2008).

$$\frac{dDiss}{dt} = Jf_s A_s S \text{ and } S = S_O e^{\alpha t} \tag{35}$$

where J is the dissolution mass transfer coefficient (0.01 mh^{-1}), f_s is the surface fraction covered by oil, A_s is the oil slick area (m^2), S is the solubility in water, S_O is the solubility of fresh oil (30 gm^3), α is a constant and takes the value 0.1, and t is time after spill (hrs).

In ice-covered waters, dissolution of water soluble components will occur, according to Payne et al. (1984). Experiments conducted in Svalbard to study the dissolution of different oil types from February to June concluded that water-soluble components would diffuse down through the ice-sheet to the bottom (110-cm thick), but the concentrations at the bottom would be low (Buist et al., 2013).

1.4.2.4 Biodegradation

Biodegradation is regarded as the ultimate fate of weathered oil in the marine environment. The process takes place over a relatively long period of time (Lee et al., 2011). Degradation rates are difficult to predict because of high hydrocarbon dilution and variability (Lehr, 2001). Saturates degrade faster, compared to aromatics and asphaltenes (Fingas, 2015). Biodegradation is normally described by multi-substrate monod model (Vilcāez and Hussbard, 2013). Geng et al. (2012) and Geng et al. (2014) have developed analytical models to predict the biodegradation of low solubility hydrocarbons and residual hydrocarbon in a variably-saturated sand column respectively. The model developed by Geng et al. (2014) is the BIOB (BIO Batch).The model was developed on the premise that biodegradation is proportional to the biomass growth. This model was applied to a beach environment. They utilized Equation 36.

$$\frac{dN}{dt} = -\frac{p}{Y_X}X + \frac{N}{m}\frac{dm}{dt}\ ,\frac{dm}{dt} = -km \tag{36}$$

where m is the concentration of hopane in sediments ($\frac{mg}{kg}$), k is first-order rate (day^{-1}), N is the concentration of hydrocarbon ($\frac{mg}{Kg}\ sand$), p is the growth rate of biomass (day^{-1}) and Y_X is the biomass yield coefficient for growth on hydrocarbon ($\frac{mg\ X}{mg\ S}$). This model is very simplified and does not account for temperature, salinity and ice concentration. It can be further developed to account for some of these factors.

For details of the application of the model, the reader is referred to Geng et al. (2014). Vilcāez et al. (2013) have also developed a model to assess the biodegradation rate of dispersed oil droplets with different constituents. Their model has been applied to the Deepwater Horizon oil spill in the Gulf of Mexico (Vilcāez et al., 2013). Biodegradation in ice-covered waters has received much attention lately because of the Deepwater Horizon oil spill (Anon., 1998). Genomics has been an essential tool in recent times for estimating the possibility of communities of micro-organisms to biodegrade oil spills in freezing environments (Lee et al., 2011). Brooijmans et al. (2009) has presented a review of the importance of genomics in relation to biodegradation of oil. For detail information on the subject, readers are referred to the article. In ice-covered waters, degradation is slower compared to temperate regions. This is because of the high viscosity of the oil slick and the slow rate of evaporation, making oil slicks less accessible to microorganisms (Anon., 1998). McFarlin et al. (2014) carried out a study on the biodegradation of dispersed oil in ice-covered waters at $-1°C$. The studies shows that indigenous microorganisms have the capability to biodegrade dispersed oil effectively. The study was conducted using Alaska North Slope Crude. A recent study which forms part of the Artic oil spill response JIP shows that biodegradation is very important. There are microbes that are specifically adapted to breaking down oil slick in cold environments (Word, 2014). It is also known that biodegradation affects and is also affected by some of the weathering processes. For example an emulsified oil is difficult to biodegrade compared to that which has not undergone emulsification (Word, 2014).

1.4.2.5 Photo-oxidation

Photo-oxidation is the process by which oil exposed to solar radiation undergoes oxidation, resulting in the generation of polar water soluble, oxygenated products (Fingas, 2015). This process is not important during a spill until after a week. Photo-oxidation is the least studied and less understood process among the weathering and transport processes occurring after an oil spill (Garrett et al., 1998). The effect of photo-oxidation increases dissolution, dispersion and emulsification while affecting spreading as well (Fingas, 2015, Lee et al., 2011). Most weathering models do not include photo-oxidation except for a model reported by Huang (1983).

Studies conducted by Overton (1980) exposing crude to sunlight observed the effect of photo-oxidation. Photo-oxidation was also observed during the Mega Borg oil spill in the Gulf of Mexico in the form of crusts on floating tar mats and tar balls (Far, 1997; Lehr, 2001).

Garrett et al. (1998) conducted a study using gas chromatography, x-ray absorption spectroscopy and thin-layer chromatography. They irradiated the oil with UV to identify which components of crude oil are most susceptible to photo-oxidation. They used three oil types which were representative of recent oil spills, the Alaska North Slope (Exxon Valdez), Gullfaks (Braer) and Forties (Sea Empress). The studies established that saturated compounds are resistant to photo-oxidation but aromatics are not. Increased alkyl substitution increases the sensitivity of aromatic hydrocarbons to photo-oxidation according to the study.

In ice-covered waters, an oil slick on the surface will interact in various ways with snow and surface ice and also undergo direct photo-oxidation. A series of experiments of spills using diesel and petrol in the Russian Arctic suggested that photo-oxidation is a more significant process in the first 24 hours of day light than in temperate climates (Serova, 1992; Ivanov et al., 2005). Cochran and Scott (1971) proposed Equation 37 for calculating the rate of photo-oxidation (Korotenko et al., 2000).

$$\frac{\partial P}{\partial t} = \left(\frac{\text{Ú}}{70}\right)(1 - C)C_A \tag{37}$$

where Ú is the sun's radiation angle to the slick surface (°), C is the fractional cloud cover, and C_A is a coefficient that varies with slick thickness. This model is simplified. It has been scarcely used in oil spill modeling.

Albedo plays a major role in the interaction of sunlight and ice. Reflectivity (albedo) of snow and ice causes the oiled regions to melt quickly compared to the un-oiled regions (Sydnes, 1991). According to Fingas and Hollebone (2003), studies by Anon. (1975) measured the effect of albedo on oil in ice, and established that the presence of oil in ice accelerated ice melt by 1 to 3 weeks. The area of oil in ice had an albedo as low as half the surrounding area.

1.5 Summary

In this chapter, the state-of- the- art of fate and transport modeling of spilled oil in ice-covered waters has been presented. An assessment has been made of the state of understanding of the transport and weathering processes after a spill in ice-covered waters. The review shows that oil spill science in ice-covered waters is at an adhoc level. The survey also suggests that the presence of ice reduces the rate of weathering and transport processes. For response and contingency planning of an oil spill in ice-covered waters: 1) evaporation, 2) emulsification, 3) dissolution, 4) photo-oxidation, and 5) biodegradation is the order of importance of weathering processes. For the transport processes, they are as follows: 1) spreading, 2) encapsulation 3) advection 4) dispersion, and 5) sedimentation. Algorithms for evaporation follow air-regulated and diffusion regulated mechanisms. The latter produces better results. Evaporation of oil in ice-covered waters may be partially air- regulated and not fully diffusion regulated. The latest approach to modeling emulsification is based on the presence of resin and asphaltenes. Stability of the oil slick is therefore the main criteria for emulsification. Dissolution is important when considering the toxicity of hydrocarbons in the water column. Photo-oxidation is the least studied but an important process in ice-covered waters. Biodegradation has received a lot of attention lately; mathematical algorithms and genomic models have been developed to predict the process. Ice-specific algorithms for spreading have been developed through laboratory experiments. The survey shows that encapsulation is the only process specific to ice covered waters. Advection and dispersion have been studied extensively but dispersion may not be dominant in ice-covered waters because of the dumping effects of waves. Sedimentation is a difficult process to study because of the scarcity of data, according to the review.

1.5.1 Knowledge gaps

Knowledge gap ranking for weathering processes, from least understood to the most understood process is as follows: 1) photo-oxidation 2) biodegradation 3) dissolution 4) evaporation 5) emulsification. Emulsification and evaporation have received much attention and therefore better understanding, though they are not fully understood. For the transport processes the order is: 1) sedimentation, 2) encapsulation, 3) dispersion, 4) advection, 5) spreading. Except for spreading, there are no ice-covered waters specific algorithms for the weathering and transport processes. Spreading algorithms produced different results for the same oil and environmental data. The difference between the results was large. Evaporation in ice may not follow the air-regulated mechanism totally; therefore current diffusion regulated models may not predict evaporation in ice-covered waters accurately. Current emulsification models are based on the stability of the oil slick. The models have the capability to predict the potential for emulsion to form but not when, or the quantity, of emulsions that will be formed with time. The old model which has this capability does not consider asphaltenes and resins. Dissolution does not have a good continuous algorithm at the moment. Sedimentation of spilled oil has not been studied much because of the lack of data and therefore not well understood. Photo-oxidation seems to be an important process in ice covered waters but is not well understood hence no ice-specific algorithms exist. Availability of data to validate current fate and transport models in ice-covered waters is a challenge. There is currently no comprehensive data base for spilled oil in ice-covered waters. This is however changing with the output from the Arctic oil spill response JIP, which has produced a comprehensive data base of all works related to Arctic oil spill. More however needs to be done in this regard. Data is available for only a limited range of oil, ice types and release scenarios. At the moment, models such as GNOME/ADIOS 2, OSCAR and OILMAP has the capability to simulate the weathering and trajectory model of an oil spill but with limitations. Work is ongoing in this respect. This thesis is an attempt to address part of this gap. The thesis also uses a scenario based approach for addressing potential risk of an oil spill during Arctic shipping. This approach has been taken mainly due to the lack of data on oil spill accidents in the Arctic This is done by examining different potential scenarios and applying developed models to estimated weathering processes of oil (Chapter 2), concentration of oil in air, ice, water and sediments (Chapter 3) and subsequently estimate the level of risk in the Arctic marine eco-system from a potential oil spill (Chapter 4).

1.5.2 Way forward

More studies (experimental and field) to understand transport and weathering processes in ice-covered waters is ongoing but more effort is required in this regard. There is a need to develop ice-specific algorithms for the weathering and transport processes in ice-covered waters. In terms of priorities the order is as follows: 1) evaporation 2) emulsification 3) spreading 4) encapsulation 5) photo-oxidation 6) dispersion. There is a lot of current research on evaporation and emulsification but not specifically in ice covered waters. A new model based on the premise that evaporation of spilled oil in ice-covered waters will be partially air-boundary regulated is required. A hybrid of the old and new models of emulsification is required to better predict emulsification for response and contingency planning purposes.

It may be important to do a critical study of encapsulation, which is the only process specific to ice-covered waters. This will contribute to understanding the relationship between encapsulation and other weathering and transport processes and hence improving modeling in ice-covered waters. Photo-oxidation has been identified as an important process in ice-covered waters, therefore there is a need to intensify research to study photo-oxidation of oil spills in ice-covered waters to better understand how it contributes to the overall mass balance. Research is on-going in Alaska to evaluate the effectiveness of dispersant use in ice-covered waters. More research in this area is needed to understand the mechanism of dispersion in ice-covered waters. This is because, dispersion is dependent on waves, and ice-covered waters tend to damp the effects of waves. To improve response and contingency planning, development of quantitative models specific to ice-covered waters is required for advection, sedimentation, dissolution and biodegradation as well. There is a need to develop a comprehensive model to predict the fate and transport of oil spilled in ice-covered waters .To better prepare for spilled oil in the arctic, there is a need for field trials to test existing models and those to be developed. There is also a need for a comprehensive data base for oil spills in ice-covered waters. Such a database would facilitate progress in this research area and aid validation of current and future models.

Environmental regulations and implications of field trials present important constraints and therefore only few controlled trials have taken place. Controlled trials have been performed mostly in Norway, out of the Arctic countries and currently Alaska as well. More field trials are required to build the capacity of stakeholders adequately for oil spills in the Arctic especially in areas such as Canada. Table 3 is a summary of the weathering and transport processes in ice covered waters, their importance in ice-covered waters and recommendations for future work.

Table 7:State of knowledge of weathering and transport processes in ice-covered waters, importance and recommendations

Process	Current state	Importance to ice-covered waters	Recommendation
Evaporation	Ice-specific algorithm is non-existent. Understanding of the process in ice-covered waters is underdeveloped.	Most important process on the surface of the water.	Develop new algorithm based on partial air-regulated evaporation phenomena.
Emulsification	Ice specific algorithm is non-existent. The presence of resins and asphaltenes in oil is the most important factor.	Occurs in ice-covered waters but rate is reduced.	Develop ice-specific algorithms based on the presence of resins and asphaltenes as the main factors for consideration.
Encapsulation	No model is available at the moment. The process is dependent on thermodynamic principles.	The most critical process to modeling oil-ice interaction.	Experimental study of the process and development of a model is required.

Natural Dispersion	Ice-specific models are not available. Understanding is underdeveloped in ice-covered waters.	The shielding effect of waves by ice may lower the importance of dispersion in ice-covered waters.	Development of ice-specific model for dispersion is needed. A study to better understand dispersion in ice-covered waters is also required.
Dissolution	Models are not available for ice-covered waters. The contribution to the amount of oil slick in water column is insignificant.	Process is not important. It may be ignored in models except when toxicity is a priority.	More research is required to develop ice-specific algorithms.
Sedimentation	No continuous algorithms exist. Ice-specific algorithms do not exist.	Process is more important for modeling long term fate of oil slick.	Development of ice-specific algorithms is necessary.
Biodegradation	Models exist for modeling.	Process is more important to a long term fate of oil slick.	Continuous research is required to improve upon current models.
Photo-oxidation	No ice-specific algorithms exist. Process has received limited attention.	It is believed to be an important process in ice-covered waters.	More studies required to better understand the contribution of the process to the entire

			weathering phenomenon in ice-covered waters.
Spreading	Ice-specific algorithms exist but inconsistent in predictions.	The most important transport phenomena.	An effective generalised model for ice-covered waters is required.
Advection	Models exist but they are complex.	Important phenomena especially when oil is encapsulated	A simple model is required.

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Chapter 2: Modeling Oil Weathering and Transport in Sea Ice†

2. Background

Oil spill preparedness and response in the Arctic has become a main focus for potential oil exploration and production and Arctic shipping activities (Walker et al., 2014; Dickins, 2011). It is projected that these activities will increase and therefore so will the possibility of an oil spill in the Arctic (Dickins, 2011; Yapa and Chowdhury, 1990). Accidental oil spills in open water represent 5% of total oil pollution, but the impact on the environment is high (Janeiro et al., 2008). An oil spill in the Arctic presents higher risks. This is because such an ecosystem is sensitive and presents challenges for the response and mitigation of the spilled oil. The harsh nature of the environment, limited response capacity, remoteness, complex nature of oil-ice interaction, and the lack of daylight are some of the factors responsible for these challenges (Dickins, 2011; Lissauer and Murphy, 1978).

The capacity to predict weathering and transport processes is key to aiding contingency planning, clean up, and the assessment and risk evaluation of environmental impact of accidental releases of oil and gas in sea ice (Daling and Strøm, 1999; Yapa and Chowdhury, 1990).

Different accidental release scenarios result in different behavior of spilled oil. A blowout beneath the ice cover may result in the spread of the oil beneath the ice. The

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I led the identification of the problem, performed the modeling and wrote the first manuscript with guidance from my supervisors: Profs. Khan, Veitch and Yang

blowout may force the plume of oil and gas through the ice cover, creating a broken ice-oil interaction (Gjøsteen and Løset, 2004). In the event of an oil spill from a ship or a rig in open water, a possible outcome is an oil slick on the surface of the water. An accidental release from a ship in the Arctic could result in the spilled oil moving between the floes. The oil may move below the floes as well. The oil may also become encapsulated by ice due to the nature of the ice cover (Drozdowski et al., 2011; Gjøsteen and Løset, 2004). This interaction and movement of oil is illustrated in Figure 7. In the presence of snow and leads, the oil-ice interaction becomes even more complex (Afenyo et al., 2016).

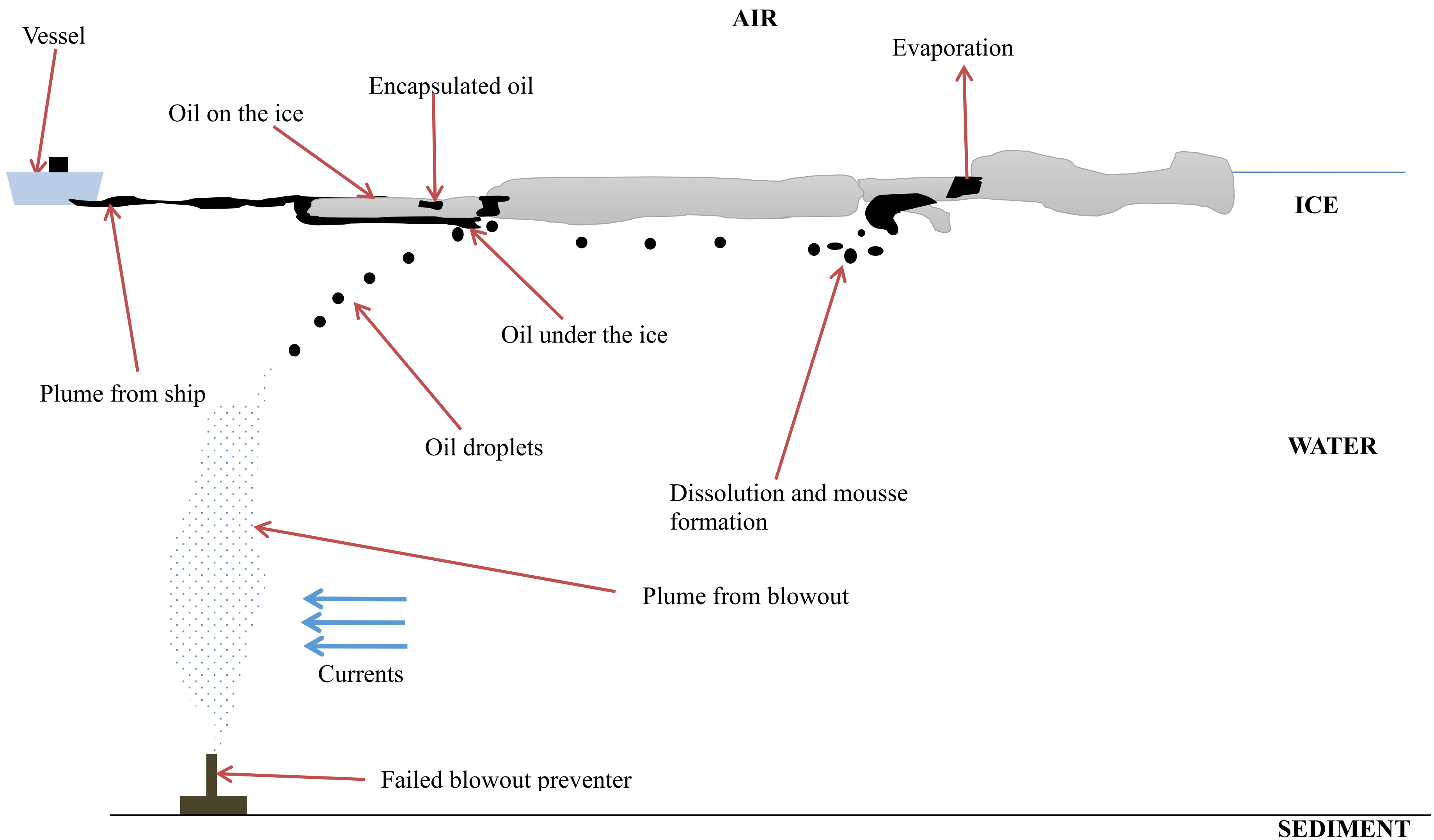

Figure 7: Oil- ice interaction during Arctic shipping and an offshore blowout scenario (after Afenyo et al., 2016; Drozdowski et al., 2011).

Weathering and transport processes of an oil spill in ice-covered waters are studied through experiments and oil spill models (Sebastião and Soares, 1995; Gjøsteen and Løset, 2004). Laboratory experiments may be appropriate for studying a single or limited number of factors and their effects, but modeling provides more flexibility for studying multiple factors and their effects concurrently (Gjøsteen and Løset, 2004). Oil spill modeling makes use of both weathering and transport algorithms. Both processes influence each other. The complex, interactive nature of the processes makes numerical models a good tool for solving the interactions at varying time scales (Janeiro et al., 2008). The weathering processes include evaporation, emulsification, photo-oxidation, biodegradation, and dissolution. The transport processes are spreading, dispersion, sedimentation, advection and encapsulation. These processes are functions of the environment in which the spill occurs and the oil characteristics (Reed et al., 1999; Fingas, 2015). Figure 8 shows the structure of a typical oil spill model, which is made up of an input section, calculation section, and an output section (Afenyo et al., 2016; Reed et al., 1999).

Spill models are used to predict the physical and chemical properties of weathered oil, the location of spilled oil at a particular time, and the oil mass balance (Fingas, 2015; Reed et al., 1999). In the past, models based on "mixing rules" have been used and were found to be inadequate and less successful for predicting most oil properties. "Mixing rules" refer to the use of physical properties of oil, based on the transformation of the composition of oil, as a consequence of evaporation of the lighter fraction of the oil. Such models were only successful for predicting the density of spilled oil and not properties like pour point and viscosity (Daling and Strøm, 1999). Most oil spill modeling efforts have focused on modeling the processes singularly. In reality, the processes occur simultaneously and are dependent on each other (Sebastião and Soares, 1995).

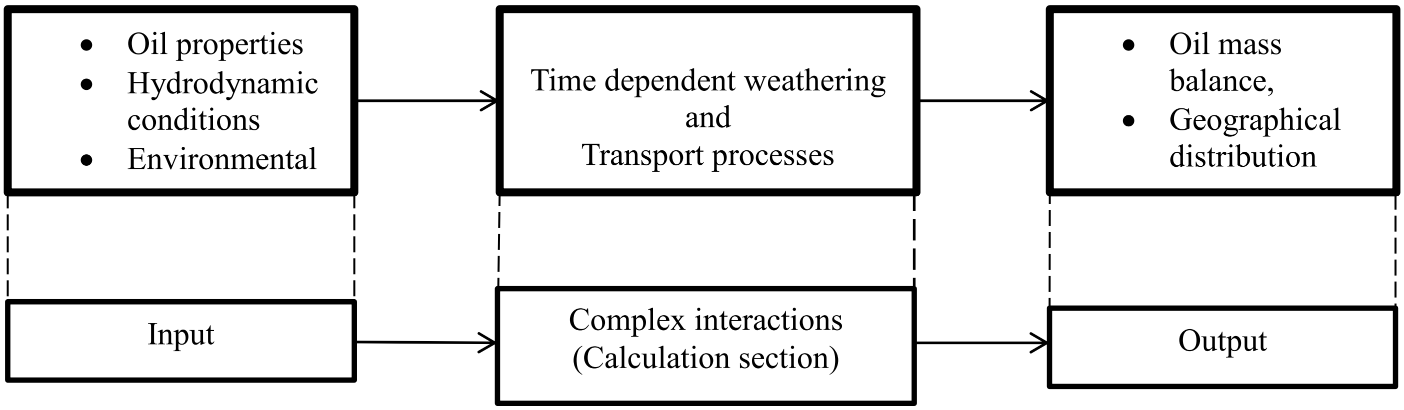

Figure 8: Structure of an oil spill model (after Afenyo et al., 2016; Reed et al., 1999).

Modeling weathering and transport of an oil spill in sea ice is complicated. The uncertainties and unknowns about oil-ice interaction make it more challenging. This is because of the scarcity of data and limited studies on the subject, compared to open water conditions. Predicting the weathering and transport processes singularly in ice has been a challenge. Individual processes are still not understood properly (Afenyo et al., 2016; Lee et al., 2015). Modeling these processes simultaneously presents more complexity (Afenyo et al., 2016).

This chapter focuses on the simultaneous occurrence and time dependency of weathering and transport process after an oil spill in sea ice. The chapter presents the approach adopted for model formulation and its application. A calibration exercise is carried out to match the model output with large scale field experimental data conducted by SINTEF. This has not been done in previous studies because of the scarcity of data on releases of oil spills in ice-covered waters.

2.1 Weathering and transport modeling of oil spill

Two approaches are used for modeling the weathering and transport of spilled oil. These are referred to in this chapter as the Singular Process Modeling Approach (SPMA) and the Multi- Processes Modeling Approach (MPMA). The SPMA refers to a modeling approach in which the interdependencies and linkages effects of processes after an oil spill are not considered; modeling is performed for a single process. This is illustrated in Gjøsteen (2004) where the data from Sayed and Løset (1993) is used to model oil spreading in cold waters. This model does not consider the effect of other weathering and transport processes. The MPMA considers the effects of linkages and the interdependences of relevant processes to a particular oil spill scenario. The success of both approaches is dependent on the availability of algorithms describing the processes of interest (Sebastião and Soares, 1995; Yang et al., 2015). SPMA is useful when the goal of the study is to evaluate the effect of individual parameters involved in the description of a particular weathering or transport process (Gjøsteen and Løset, 2004). If this is the case, SPMA presents a more focused approach. From an oil spill contingency planning perspective, the interdependencies among the weathering processes are important. This is because the interactions affect the overall mass balance of the spilled oil, which is important information for the team involved in planning, response, and recovery of the oil spill (Afenyo et al., 2016). MPMA offers a better option for this purpose. Sections 2.1 and 2.2 describe some of the works that have adopted the two approaches.

2.1.1 Singular Process Modeling Approach-SPMA

Researchers have developed models for individual transport and weathering processes for ice-covered waters. Fingas and Hollebone (2003) and Afenyo et al. (2016)

have presented reviews of models for freezing environments. The algorithms developed for these processes through laboratory experiments have focused on studying individual processes (Fingas and Hollebone, 2003; Gjøsteen and Løset, 2004). The preparation of oil samples for the experiments to support the development of the Oil Spill Contingency and Response Model (OSCAR) was done in such a way as to avoid the effect of other processes, so the processes under investigation could be studied individually (Daling et al., 1997; Fingas, 2015).

2.1.2 Multiple Processes Modeling Approach-MPMA

Sebastião and Soares (1995) and Mishra and Kumar (2015) have adopted an MPMA for modeling spilled oil in open water. Part of this concept will be used in the methodology of this chapter. This approach considers the effect of linkages and dependencies between weathering and transport processes. The algorithms adopted for the current work are based on studies conducted by Sebastião and Soares (1995), Mishra and Kumar (2015), Janeiro et al. (2008) and Yang et al. (2015).

2.2 Methodology

Figure 9 illustrates the methodology proposed for modeling the weathering and transport of spilled oil in sea ice. The steps are described in detail from sections 3.1 to 3.7. The steps are as follows:: (i) identify spill properties, (ii) define the scope of the model, (iii) choose appropriate processes to describe the oil spill, (iv) choose appropriate time dependent algorithms for the processes chosen and adapt them to Arctic conditions, (v) obtain the differential forms of these equations, vi) solve the system of differential equations simultaneously, and vii) calibrate the results. How closely experimental data and model predictions need to match is subjective, and depends on the modeler's criteria for matching model output to experimental data. The success of this methodology is dependent on the availability of data for spilled oil in sea ice and ice specific algorithms to describe the possible processes involved.

The assumptions underlining this work include the following: i) the spread of oil is assumed to be in a circular pattern, ii) oil is assumed to be a continuous slick in the dispersion algorithm, iii) oil is assumed to evaporate as water, therefore becoming air-boundary regulated rather than diffusion regulated. It is known that oil in ice may follow a partial-diffusion evaporation process. Also a linear relationship between the boiling point of the liquid phase and fraction lost by evaporation is assumed. iv) Emulsification is assumed to be largely dependent on wind speed (however, emulsion formation is highly dependent on the presence of resin and asphaltenes; this is not accounted for in the emulsification algorithm used in the methodology), and v) it is assumed that there is no roughness beneath the ice surface. The ice surface is assumed to be flat.

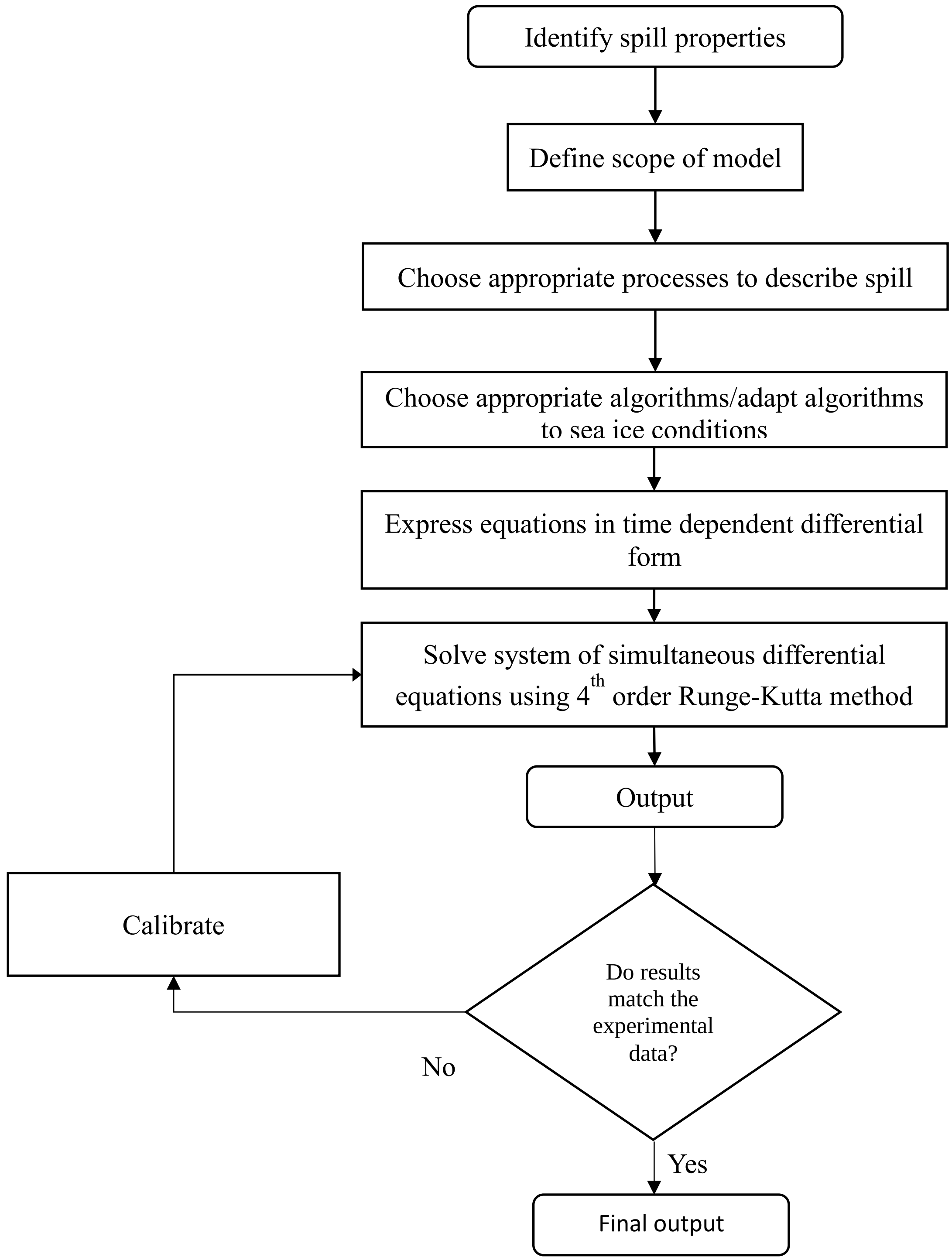

Figure 9: Methodology for modelling weathering and transport of spilled oil in ice-covered waters.

2.2.1 Identify spill properties

Spill properties here refer to the nature of the spill, for example, whether the oil is coming from a blowout or from a shipping accident. It also includes whether the oil spill is continuous or instantaneous. A shipping accident will produce an oil slick in the upper water column, so the processes of concern may be different from a blowout. The blowout will have the plume move upwards from beneath the ice. The example used in this chapter focusses on an instantaneous release during a controlled experiment in the Arctic. This is likely to result in the distribution of an oil slick in the upper water column, a scenario relevant to a release from an Arctic shipping accident.

2.2.2 Define scope of model and evaluate environmental conditions

This step entails the duration and the conditions of the scenario under investigation. This is important because some processes start immediately after the spill whilst others start weeks or months after the spill. For example, spreading, dissolution and evaporation start immediately after the spill, while biodegradation, photo-oxidation and sedimentation may start a week later. This stage also involves the evaluation of the release environment, which includes, for example, the ice type and coverage.

2.2.3 Choose appropriate processes to describe spill

Based on step 3.2, the appropriate processes are chosen. The selection of appropriate processes is the decision of the modeler according to the overall objectives. The various steps are illustrated in the analysis section of the numerical example for clarity. These processes are evaluated and the most relevant ones chosen. It should be noted that not all of the processes identified need be included in the analysis. For example, generally, dissolution contributes negligible percentage to the total oil mass in the water column, but it is the single most important process contributing to toxicity. It could be ignored if the modeler is not interested in this information.

2.2.4 Choose appropriate algorithms or adapt algorithms to arctic conditions

Algorithms corresponding to the selected processes are chosen next. For the purpose of this study, the algorithms considered are time dependent. This is necessary because the processes are changing with respect to time. A challenge is that some of these processes do not have ice-specific algorithms. Where this is the case, open water models are adapted to ice conditions using available data regarding oil in ice.

2.2.5 Express corresponding equations in differential form

The algorithms for the selected processes are expressed in differential form with respect to time. The expression of the weathering and transport relations in differential form highlights the evolution of these processes with time. In some cases, differential equations already exist in the literature. Where this is the case these equations are used. The challenge here is that most of these algorithms were adapted to ice conditions without validation. This is one of the reasons calibration is required at the end of the modeling process.

It should be noted that the relevance of the processes evolves with time. For example, dissolution and evaporation processes are very relevant during the first week after oil spills. Dissolution diminishes while evaporation remains dominant. Models such as those for photo-oxidation and biodegradation are not important in the first 24 hours, but rather in the long term. Since the methodology is not focused on the long-term fate of the spilled oil, these two processes are not considered in the proposed model.

2.2.6 Solve system of differential equations

The system of differential equations is solved simultaneously. This step is necessary to fulfill the simultaneous occurrence of the processes. Although the processes start and end at different times, they take place concurrently. In order to solve such a system of differential equations, the 4th order Runge-Kutta method is used.

2.2.7 Refine model boundary conditions

The solution of the differential equations yields results that include the area of spread on ice, area of spread under ice, fraction of hydrocarbon evaporated, amount of water content in weathered oil, viscosity of weathered oil, vertical dispersion of oil in water column, and dissolution of the soluble component of oil with respect to time, depending on the processes under consideration. Following the solution, the results are calibrated using oil in ice data. This is done by changing the transformation factors in the model. Transformation factors here refer to the values that differentiate the open water equations of a particular process from those of ice-covered waters. After this alteration, the simulation is run. This cycle continues until a desired fit to available data is achieved. This step is to fit model results to experimental data as much as possible to avoid too much deviation from the available experimental data since the original algorithms may not be specific to ice-covered water. In the next section an illustration is presented using the numerical example. For example, for evaporation, 0.55 is the transformation factor. This value is altered several times, and each time the entire model is run. As stated earlier, the guide for this exercise in our case will be the experimental data and model matching as closely as possible. The availability of results from experimental studies of the various processes is key to producing a reasonably accurate model. In the present study, relevant experimental results are available only for evaporation, emulsification and the change of viscosity of weathered oil.

2.3 Numerical example

In order to illustrate the use of this methodology, a case is presented and evaluated using the steps 2.2.1 to 2.2.7. A sensitivity analysis is conducted and model outputs are compared with results of experimental work presented in Brandvik et al. (2010).

SINTEF conducted a field experiment in the Barents Sea, northeast of Hopen Island. This was conducted specifically in the marginal ice zone, from May 9 to 25, 2009. As part of the oil in ice Joint Industrial Program (JIP), this study aimed to inform an understanding of the fate and behaviour of oil spilled in ice-covered waters. To accomplish this, $7m^3$ of Troll crude were released from a single point from a stationary vessel. The characteristics of Troll crude are presented in Table 4. Troll crude is a naphtanic crude with a low pour point. This means that solidification of the oil in ice is not likely. The initial release produced a circular oil slick. Ice concentration was approximately 70% to 90%. According to the forecast, the researchers expected the ice field to open up the week after the release, but this did not happen. A higher ice concentration than planned was experienced. Prevailing conditions during the period of experimental activities were that the seawater temperature was $-1.8℃$ and the air temperature fluctuated between $-2℃$ and $-10℃$. There were twenty-four hours of sunlight in May. Visibility was good during this period and the area experienced light showers of snow for three to four hours every day. The wind speed was generally between 5 and 10 $\frac{m}{s}$ and peaked at 15 to 20 $\frac{m}{s}$ on the 17th of May and 18th of May. For the purpose analysis, an initial temperature of $-10℃$ is used. Movement of ice floes was limited. Ice thickness was 2 to 10 cm. The evaporative loss, water uptake of emulsified oil and the change in viscosity of the weathered crude oil are some of the processes measured (Brandvik et al., 2010).

Table 8: Physical properties of troll crude (after Fingas, 2015)

Property	**Value**
Density ($\frac{Kg}{m^3}$) $15℃$	885.2
Viscosity ($\frac{Kg}{ms}$) at $15℃$	0.0235
Surface tension ($\frac{Kg}{S^2}$) at $15℃$	28.8
Interfacial tension of sea water ($\frac{Kg}{S^2}$)	22.6
Interfacial tension of fresh water ($\frac{Kg}{S^2}$)	24.6
API gravity	28.3

2.3.1 Analysis of numerical example using proposed methodology

As the specific gravity of the oil under investigation is less than sea water, it will end up on the upper layer of the water column. Therefore, evaporation, spreading and entrainment (dispersion) best describes the weathering and transport of spilled oil on the water surface (Reed, 1989). Fractions of the spilled oil will be found in the column as well. This is appropriately described by emulsification, dispersion and dissolution. The processes under consideration will also be those that start mostly within the first hour after the spill. Therefore sedimentation, photo-oxidation and biodegradation are not considered in this analysis. Dissolution is also ignored for this particular analysis. These processes may be added, should the modeler find it necessary.

The processes to be considered for this analysis are spreading on ice, spreading under ice, evaporation, water uptake of emulsified oil (emulsification), dispersion, and dissolution. The corresponding algorithms are discussed in the next section. The algorithms to be discussed may have limitations and users may use their own algorithms to suit the scenario under study. An oil slick thickness of 0.01m is used, the same order of magnitude as used in Andreassen and Sørheim (2013). Andreassen and Sørheim (2013) used an initial oil slick thickness of 0.02m for the OSCAR model.

2.3.1.1 Spreading on ice

Spreading occurs as a result of the influence of gravitational, viscous, buoyancy and surface tension forces causing a thin slick of oil to cover a large area (Fingas, 2015). Studies conducted by Fay (1969) identified three regimes of spreading: gravity-viscosity, gravity-inertia and surface tension-viscosity. In ice-covered waters, the interfacial tension-viscous phase is negligible (Chen et al., 1967). Equation 38 is a quasi-empirical relation developed by Chen et al. (1974) for the spreading of oil on ice. This equation will be used as the spreading algorithm for modeling oil spilled on ice. It is suitable because it is time dependent. Equation 38 is transformed into Equation 39 on the assumption that oil spreads in a thick continuous layer with a circular pattern (Yang et al., 2015; Sebastião and Soares, 1995).

$$\frac{r}{V^{\frac{1}{3}}} = 0.24\left[\frac{100\rho t g V_m}{\mu}\right]^{\frac{1}{5}} + 0.35 \tag{38}$$

where r is the slick radius as a function of time (m), V is the volume of oil spilled (m^3), t is the time after spillage (s), ρ is the oil density ($\frac{Kg}{m^3}$), g is the acceleration due to gravity with a value of 9.81 ($\frac{m}{s^2}$), and μ is the viscosity of oil ($\frac{Kg}{ms}$).

$$A = \pi \left[0.24 \left(\frac{t \rho V^{\frac{1}{3}}}{\mu} \right) + 0.35 \right]^{\frac{1}{5}} \tag{39}$$

where A is the area of spread on ice (m^2). The rest of the parameters remain the same as in Equation 38. Yang et al. (2015), used the differential form of Equation 39 in a multimedia fate model, as shown in Equation 40.

$$\frac{dA}{dt} = \frac{0.37V\left[0.29\left(tV^{(0.33)}\right)^{0.2} + 0.35\right]}{(tV^{0.33})^{0.8}} \tag{40}$$

2.3.1.2 Spreading under ice

Under ice, the force responsible for spreading is buoyancy. The surface tension-viscous phase is negligible under ice (Yapa and Chowdhury, 1990). Yapa and Chowdhury (1990) derived Equation 41 to model the spread of oil under ice from the initiation of an oil spill to termination, for constant volumetric flow rate. This was expanded to Equation 42 by Yang et al. (2015).

$$r = 0.01K \left[\frac{10^{-5} Q^3 \Delta \rho g}{\mu_o} \right]^{\frac{1}{8}} t^{\frac{1}{2}} \tag{41}$$

where r is the radius (m), t is the time (s), Q is the discharge rate ($\frac{m^3}{s}$), μ_o is the viscosity ($\frac{Kg}{ms}$), $\Delta\rho$ is the density difference between water and oil, g is the acceleration due to gravity, Ÿ is a constant with a value of 0.467.

$$A_u = 0.01\pi \ddot{Y}^2 \left[\frac{10^{-5} Q^3 \Delta \rho g}{\mu_o} \right]^{\frac{1}{4}} t \tag{42}$$

where A is the radius (m^2). The differential form of Equation 42 as used by Yang et al. (2015) is given as Equation 43.

$$\frac{dA}{dt} = 2.9 \times 10^{-3}(V_m)^{0.75} \tag{43}$$

2.3.1.3 Evaporation

In oil spill modelling, evaporation is the most significant weathering process. It accounts for a large percentage of mass loss. For instance, light, medium, and heavy petroleum lose approximately 75%, 40%, and 10% respectively of mass through evaporation (Betancourt et al., 2005). For this reason, it is the only process represented in some oil weathering models (Fingas, 2015). Equation 44, referred to as the evaporative exposure method, is used for modeling evaporation. It was developed by Stiver and Mackay (1984).

$$F_V = \left\{\frac{T}{DT_w}\right\} In\left[1 + D\left(\frac{T_w}{T}\right)\frac{K\,A_S t}{V} exp\left(C - \frac{DT_u}{T}\right)\right] \tag{44}$$

where F_V is the fraction of hydrocarbons evaporated (%), T is the ambient temperature (K), T_w is the slope of the modified ASTM distillation curve (K), A_S is the oil slick area (m^2), T_u is the initial boiling point of the modified distillation curve (K), t is the time (s), and V is the initial oil volume (m^3). C and D are constants with magnitudes of 6.3 and 10.3, respectively, as used in the Automated Data Inquiry for Oil Spills (ADIOS) model (Lehr et al., 2002), Janeiro et al. (2008) and Yang et al. (2015).

$$A_s = \frac{V}{h} \tag{45}$$

where h is the thickness of the slick. In this model a uniform slick thickness is assumed

$$T_u = 532.98 - 3.1295 \times API \tag{46}$$

$$T_w = 985.62 - 13.597 \times API \tag{47}$$

API is the API gravity of the oil.

K is the mass transfer coefficient and is given by Equation 48

$$K = 2.5 \times 10^{-3} W^{0.78} \tag{48}$$

where W is the wind speed.

Ice specific algorithms do not exist for evaporation at the moment. Equation 44 is adapted for 90% ice cover and the differential form is shown as Equation 49 (Yang et al., 2015).

$$\frac{\boldsymbol{dF_V}}{\boldsymbol{dt}} = 0.55K \frac{A_S}{V} exp\left(C - \frac{D}{T}(T_u + T_w F_V\right) \tag{49}$$

The parameters are the same as in Equation 44 to Equation 48.

It should be noted that since the original equations were developed for open water, the application of the model to an ice-covered scenario limits its capability. This is a weakness of the model.

2.3.1.4 Emulsification (Water uptake)

Emulsification, referred to as water uptake in the analysis, involves the entrainment of water droplets in oil. It has a significant effect on the viscosity of the slick and to some extent its volume and density. Recent studies have shown that the presence of resins and asphaltenes are necessary for emulsification (Fingas, 2015). Currently, algorithms do not exist to predict this process satisfactorily because of the lack of understanding of the mechanism of the process and how to quantify energy levels at sea (Buist et al., 2009). The algorithm most used by modelers was developed by Mackay et al. (1980) and is shown as Equation 50 (Yang et al., 2015). This has been used in OSCAR and ADIOS oil spill models (Gkonis et al., 2008).

$$Y = C_f \left[1 - exp\left(\frac{-2\times10^{-6}}{C_f}(1+w^2)t\right)\right] \tag{50}$$

where C_f is the final water fraction, W is the wind speed $(\frac{m}{s})$, and t is the time (s).

Like the algorithms for evaporation, ice specific relations do not exist to model emulsification. Yang et al. (2015) modified Equation 50 for a 90% ice cover and obtained the differential form as Equation 51.

$$\frac{dY}{dt} = 6.8 \times 10^{-7}(W+1)^2(1-\frac{Y}{C_f}) \tag{51}$$

2.3.1.5 Viscosity Changes

Evaporation and emulsification result in the viscosity change of the spilled oil in ice. Emulsification causes the formation of mousse while evaporation also causes an increase in viscosity. This phenomena is modeled using Equations 52 and 53 for emulsification and evaporation respectively. A combined equation is presented by Yang et al. (2015) for a 90% ice cover. Sebastião and Soares (1995) have a similar equation for open water. Recent studies have shown that evaporation could eventually result in the sinking of oil (Stevens et al., 2015). This is not considered in this analysis.

$$\mu = \mu_o exp\left[\frac{2.5Y}{1-C_3Y}\right] \;,\quad \mu_o = 2.24A_C^{\frac{1}{2}} \tag{52}$$

where μ_o is the viscosity of parent oil $\left(\frac{Kg}{ms}\right)$, and A_c is the percentage of asphaltene.

Evaporation of the oil causes viscosity change and this is represented by Equation 53 (Sebastião and Soares, 1995).

$$\mu = \mu_o exp\,(C_4F_V) \tag{53}$$

where C_4 is taken as 10 and F_V is the fraction of hydrocarbons evaporated.

Equation 54 is the equation of the combined effect of emulsification and evaporation resulting in the change of viscosity. This equation is applicable to 90% ice-covered water (Yang et al., 2015).

$$\frac{d\mu}{dt} = C_4 \frac{dF_V}{dt} + \frac{0.07\mu}{(1-C_f Y)^2} \frac{dY}{dt} \tag{54}$$

2.3.1.6 Natural dispersion

Natural dispersion is a wave dependent process that involves the incorporation of small oil droplets (less than 0.1mm) in the water column. The product of natural dispersion, unstable and larger oil droplets (greater than 0.1mm) may coalesce and move to the surface (Nazir et al. 2008). Dispersion speeds up dissolution. Though not fully understood, dispersion is modelled using an equation produced by Mackay et al. (1980).

The equation estimates the fraction of spilled oil not returning to the surface. The assumption underlining this formulation is that residual oil will eventually be driven into the water column. This is shown as Equation 55.

$$\frac{dm}{dt} = \frac{0.11m(1+W)^2}{1+1.5811\times10^{-4}\sigma\mu^{0.5}h} \tag{55}$$

where μ is the dynamic viscosity ($\frac{kg}{ms}$), h is the slick thickness (m), σ is the oil-water interfacial tension ($\frac{kg}{S^2}$), W is the wind speed ($\frac{m}{s}$), and m is the mass of oil that remains at the surface.

In a scenario where hazardous substances form a surface slick, a correction factor D_Q is applied to equation 55. D_Q is given by Equation 56.

$$D_Q = K_b \left(\frac{S}{M}\right)^{0.2} \tag{56}$$

where S is the solubility $\left(\frac{kg}{m^3}\right)$, M is the molecular weight $\left(\frac{kg}{mol}\right)$ and K_b is a constant with a value of 10 (Shen et al., 1993).

2.3.2 Solution to series of differential equations

The differential Equations 40, 43, 49, 51, 54, and 55 with the appropriate support equations where needed, as presented in earlier sections are solved simultaneously using the fourth order Runge-Kutta method for solving series of differential equations. The results are shown in Figure 10 to Figure 15

2.3.3 Results

The results of the simulation which gives the physio-chemical processes change of the bulk phase of the spilled oil as a function of weathering time are shown in Figure 10 to 16. This model predicts the trend of the weathering and transport processes as shown in similar studies conducted by Yang et al. (2015), Sebastião and Soares (1995), Janiero et al. (2008), Aghajanloo and Pirooz, (2011) and Betancourt et al. (2005).The trend is also the same for the experimental results available for evaporative loss, water uptake and viscosity change of the scenario modelled. These three processes will form the basis for the refinement exercise in the next section.

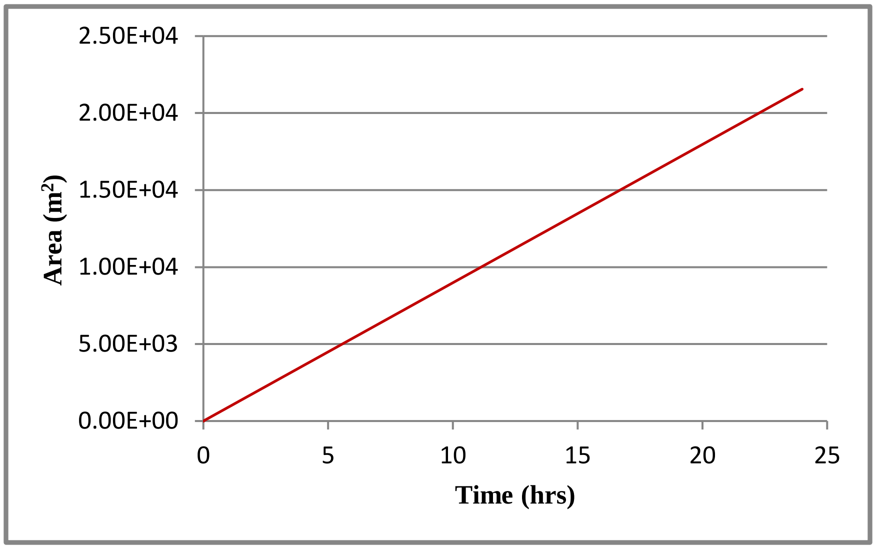

Figure 10: Area of spread in ice

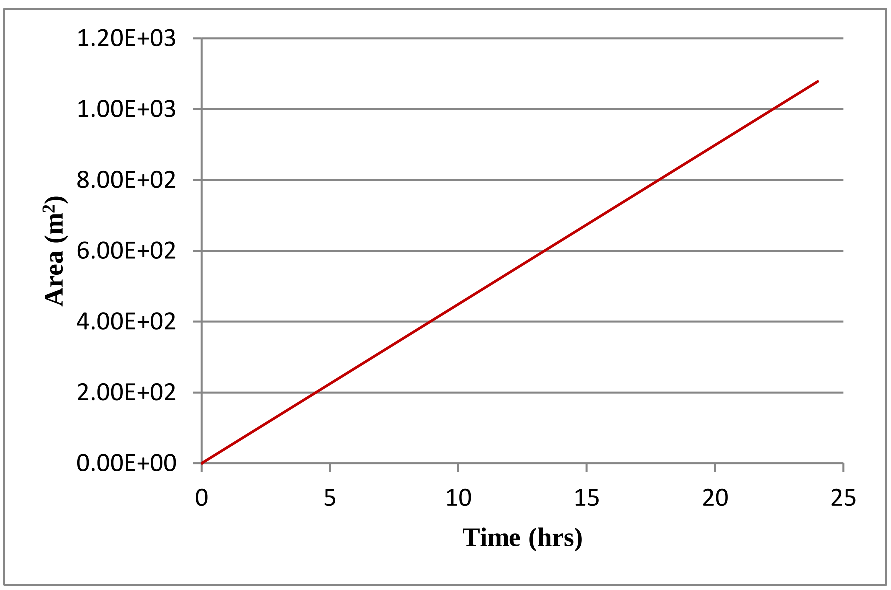

Figure 11: Area of spread under ice

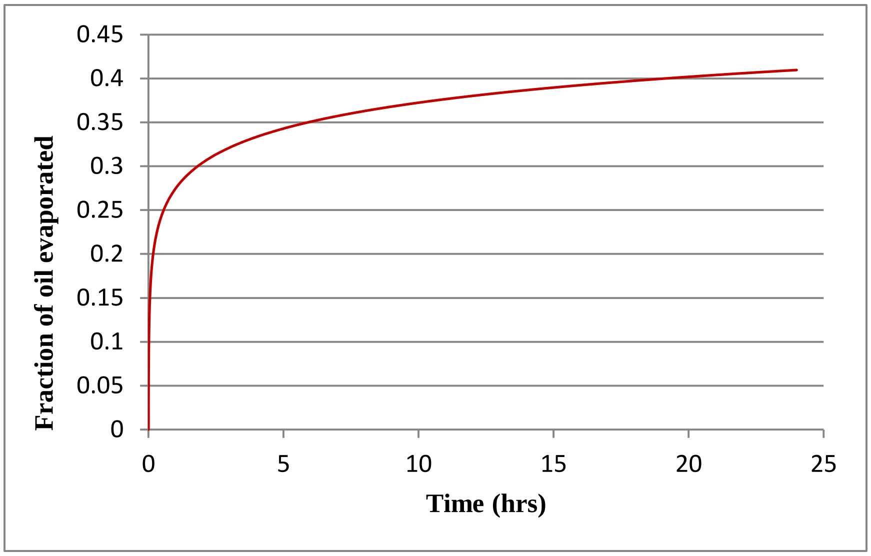

Figure 12: Evaporation of spilled oil

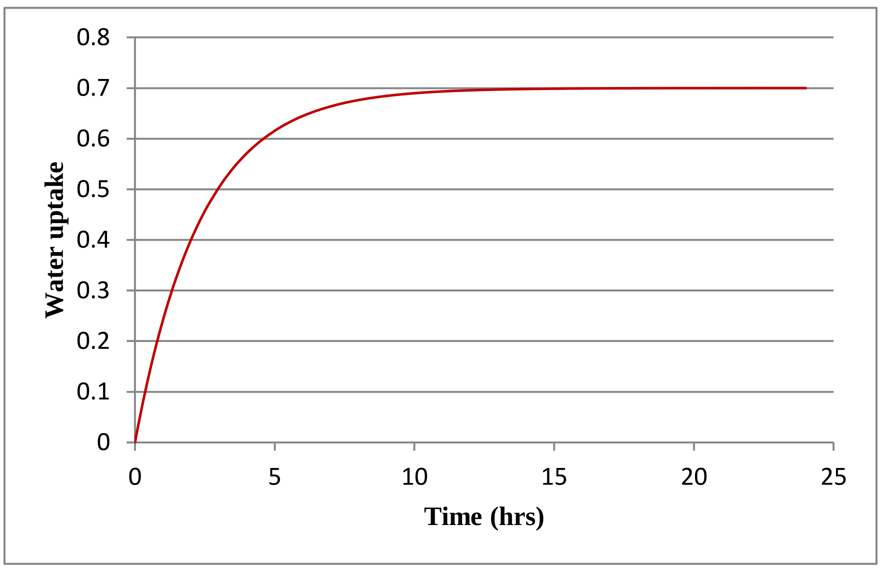

Figure 13: Water uptake of spilled oil

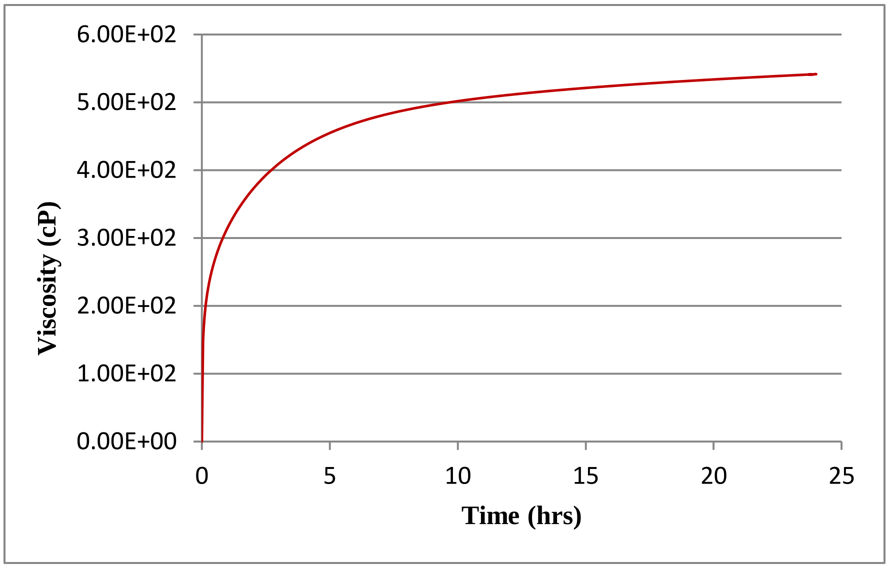

Figure 14: Viscosity change of spilled oil

$*cP = \frac{kg}{100ms}$

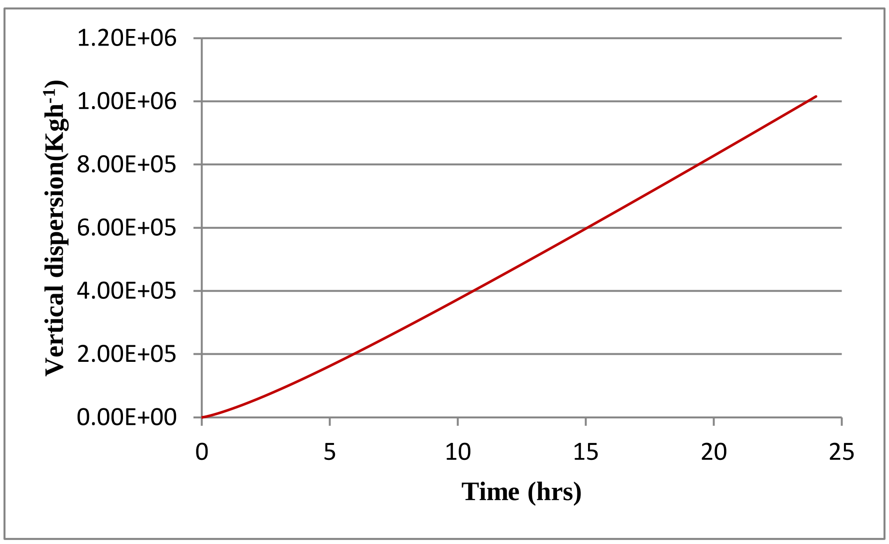

Figure 15: Dispersion in the water column

2.3.4 Model refinement

The comparison of the model prediction and the experimental data is shown in Figures 16 to 18. The deviation between the model's predictions and the experimental data is large. This may be due to the fact that the algorithms were not validated with oil in sea ice data. It may also be largely due to the fact that the algorithms, which were developed originally for open water, may not follow a simple linear transformation to ice-covered waters. An adjustment of the transformation factors was made to obtain the best fit for the large-scale experimental data. Transformation factors here refer to the factors differentiating the oil in ice algorithms from those of open water. In this exercise, the transformation factors for evaporation (5.5×10^{-1}), water uptake (6.8×10^{-7}), and viscosity change (7×10^{-2}), were 1×10^{-3}, 2×10^{-8}, and 9.0×10^{-1} respectively, after carrying out the refining exercise described in section 3.7. This exercise is conducted for only evaporation, emulsification and viscosity change because only these processes had data available for the scenario simulated. Data for the first 24 hours is used for the exercise. The comparison of model predictions, refined model predictions and the experimental data (see Figure 16 to 18) shows that adapted open water algorithms may not be adequate to predict the physio-chemical properties of oil spilled in ice-covered waters without proper validation with experimental data. The post-refining exercise results, as shown by the comparison in Figure 16 to 18 show that the refined model result accurately matched the experimental data. It is very likely relations can be obtained specifically for ice-covered waters, which are similar in form to relations in open water. This, however, requires extensive investigation and proper validation with experimental work. The open water algorithms offer a first step to exploring this possibility.

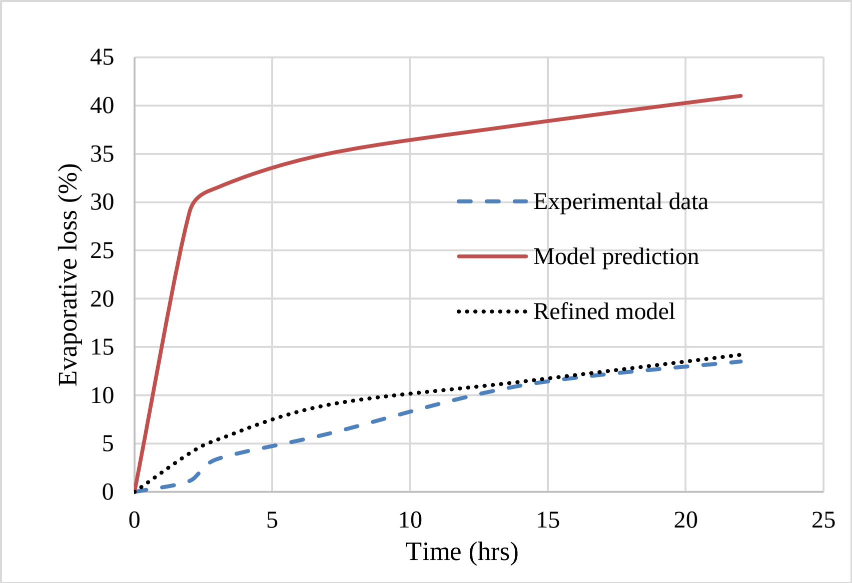

Figure 16: Comparison of model and experimental results for evaporation

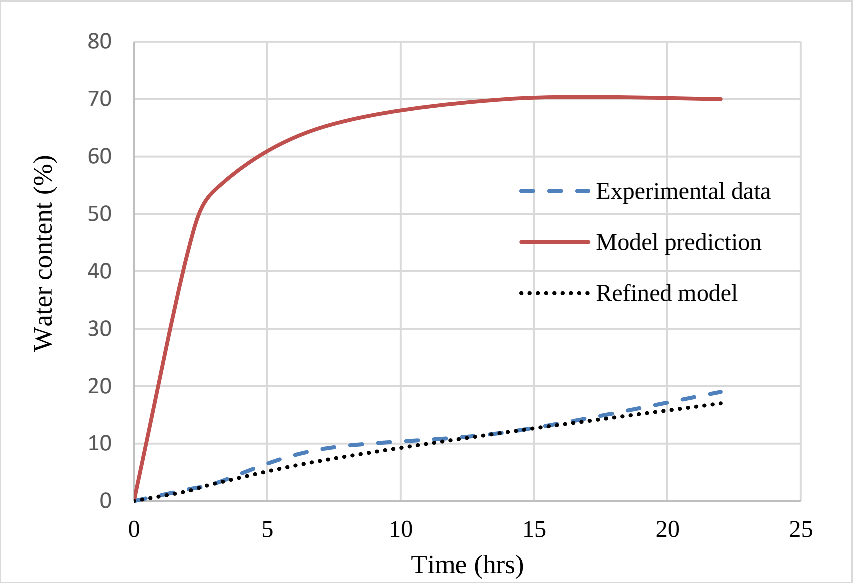

Figure 17:Comparison of model and experimental results for emulsification.

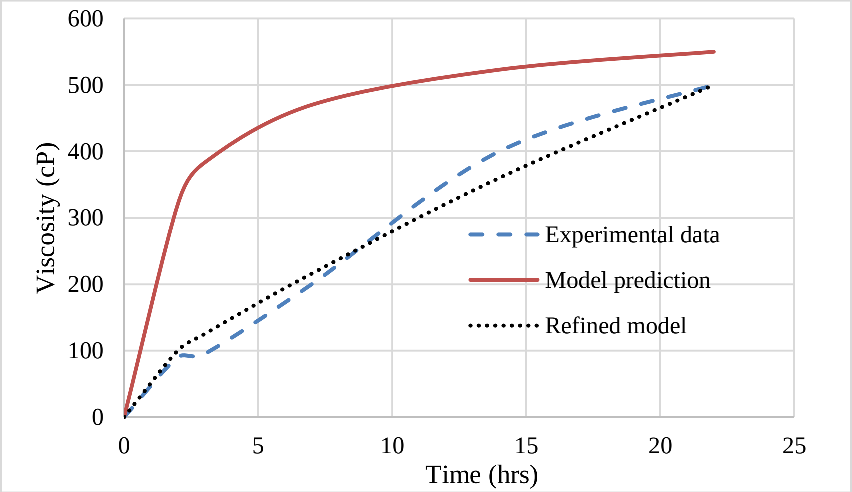

Figure 18: Comparison of model and experimental results for the viscosity change of weathered oil.

2.3.5 Sensitivity Analysis

In order to test the robustness of the model developed, a sensitivity analysis is conducted. This analysis is also done to determine the most sensitive parameters for which data is necessary. The volume of spill, ambient temperature, wind speed, initial viscosity of spilled oil, and oil interfacial tension were altered to see the effect on the output of the model. The sensitivity is calculated using Equation 56. This is a semi-quantitative method. In simple terms, the properties for example temperature is increased by 100% and percentage change calculated. Values obtained would vary from point to point and from model to model. The response of the model to the change in individual processes is shown in Figures 19 to 24. The individual process analysis shows that the area of spreading under ice and on ice responded the most to volume change of spilled oil. Evaporation and viscosity change showed significant variations as well. Wind speed change affected dispersion, water uptake (emulsification), viscosity change of weathered oil, and evaporation (in order of most influenced to least). In the same way, oil viscosity changes in the model input affected dispersion and viscosity change due to weathering. A temperature change in the model affected evaporation and viscosity change of oil.

$$S_e = \left[\frac{Change\ in\ output}{Output} \times \frac{Input}{Change\ in\ input}\right] \times 100 \tag{57}$$

where S_e is the sensitivity (%).

The results in Figure 19 show that wind speed and temperature are the two most sensitive (variable) factors in the entire model. The most sensitive factor is therefore the environment. The environment is beyond our control. Figure 19 also shows that volume of spill, viscosity and interfacial tension are relatively less sensitive in the model compared to the environment. This exercise also identifies which variables to focus on when running an uncertainty analysis. An uncertainty analysis of this model is beyond the scope of this chapter.

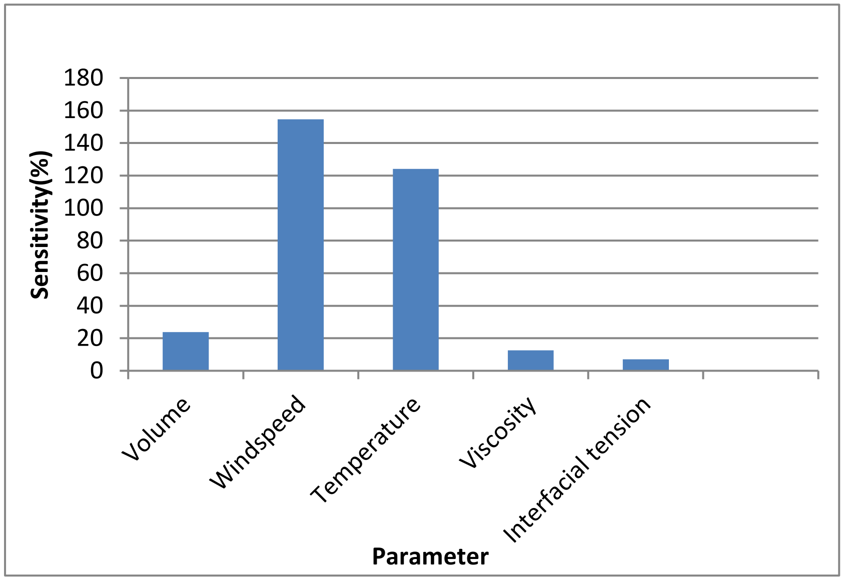

Figure 19: Sensitivity of different parameters in the model

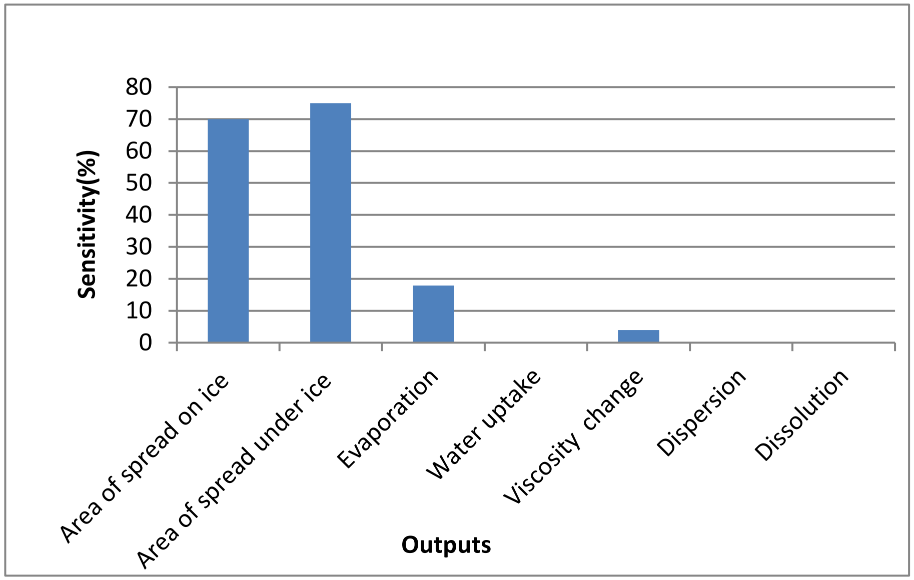

Figure 20: Model response to volume change

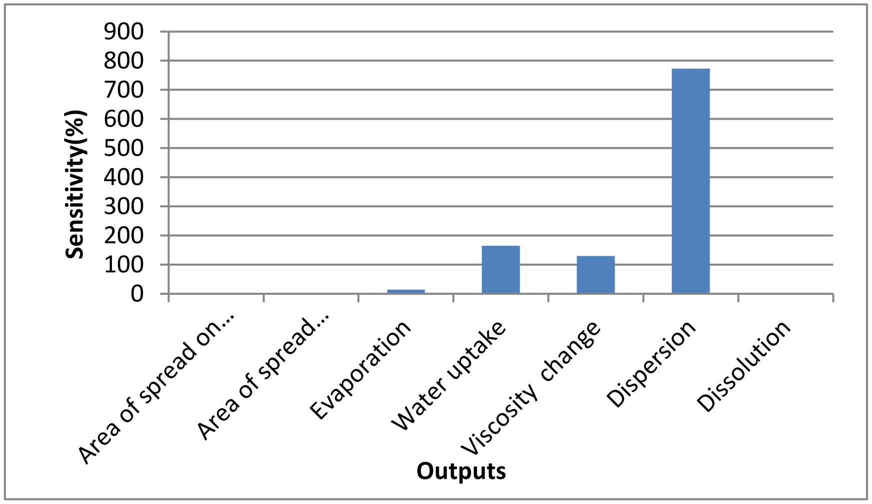

Figure 21: Model response to wind speed change

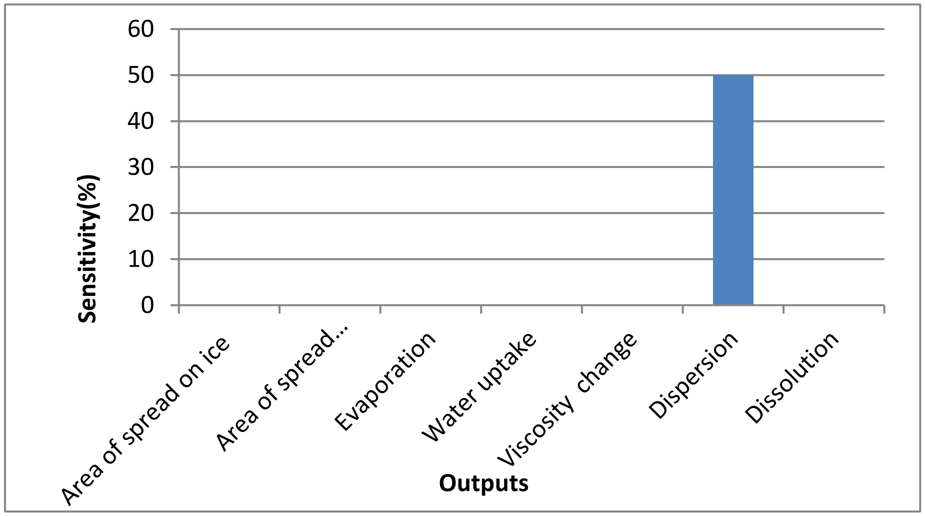

Figure 22: Model response to interfacial tension change

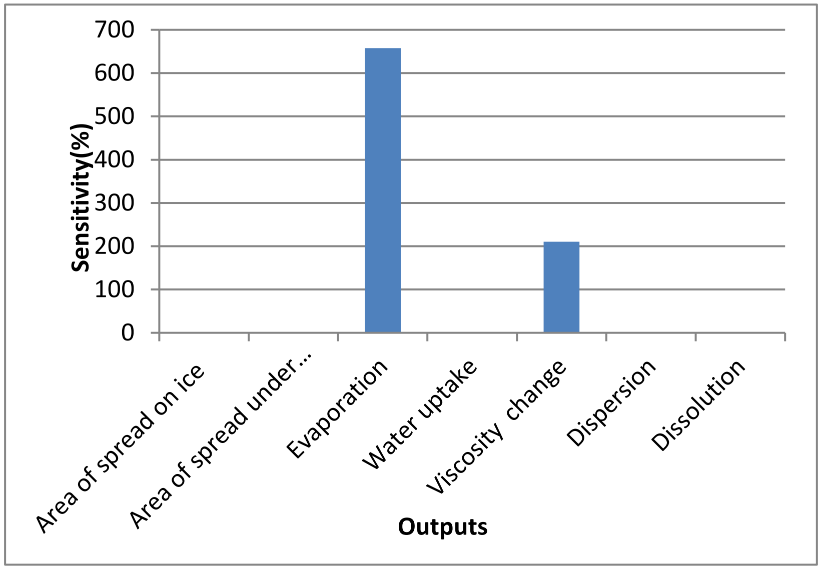

Figure 23: Model response to temperature Change

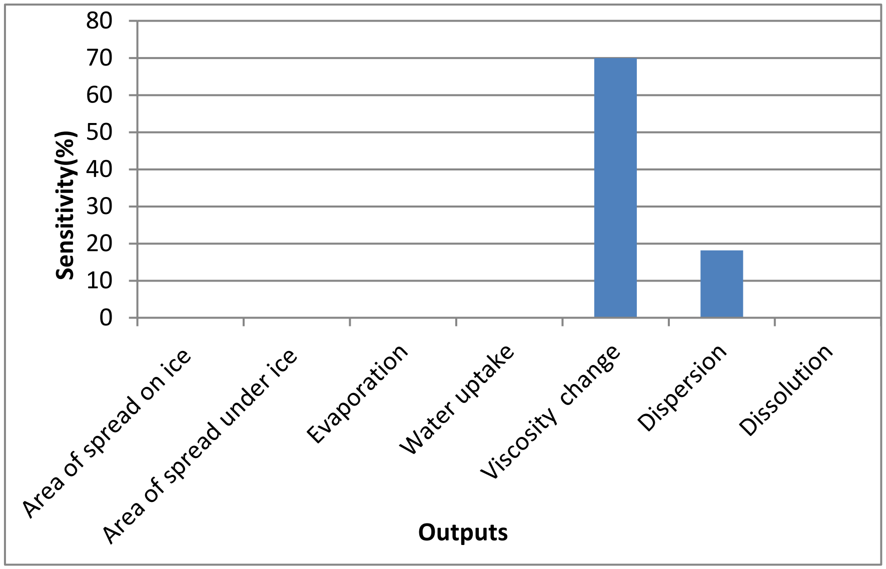

Figure 24: Model response to viscosity change

It should be noted that viscosity here refers to the physical property of the oil while "viscosity change" is the process of change of viscosity of the oil as a result of weathering.

5. Discussion

Figures 10 to 15 show the variation of the physio-chemical properties of the bulk phase of spilled oil in sea ice as a function of weathering time. Figure 16 to 18 show a comparison of the model results, refined model outputs and the experimental data, which shows a close match between the latter two. Figure 16 is the plot for the comparison of evaporation and shows that the evaporative loss graph of the refined model agrees well with experimental data. The difference between unrefined model prediction and the experimental data is high. This same observation applies to Figures 17 and 18, which are the graphs for the comparison of water uptake of weathered oil and viscosity of weathered oil respectively. The difference between the unrefined model results and the experimental results shows the inadequacy of the adapted algorithms to modeling oil spills in ice-covered waters. It should be noted that the difference may also be due to data quality, missing information, improper calibration and equation choice. The fact that most of these algorithms were developed for open water may limit their performance in ice-covered waters.

Further, the original equations used in the proposed model were developed for open water thus temperature above freezing point. The application of the model to an ice-covered scenario limits its capability. This a weakness of the model. The oil properties values used were not extensively corrected for temperature and salinity. This may account for some of the trends in the prediction. Future works should look at this carefully to improve the model. Further most of the algorithms used assume static temperature and not varying. In reality this is not the case. This is a further simplification and challenge of the model presented. Future work should therefore use inputs that would enable this to be captured, interms of the temperature data. Also most of the processes are temperature dependent but the corresponding algorithms don't account for it. This needs to be addressed in future work.

Figure 19 is the graph of sensitivity analysis of the entire model. The results show that the environment is the most sensitive factor in the model while factors including volume, viscosity and the oil interfacial tension are relatively less sensitive.

Figures 20 to 24 are the analysis of model response to changes in volume, wind speed, oil interfacial tension, temperature and oil viscosity respectively. The fraction of hydrocarbon evaporated increased with an increase in temperature. Increase in evaporation also means an increase in the viscosity of spilled oil. The area also increased with an increase in volume and time. The longer the time, the more space the oil finds and spreads. The water incorporated into oil and dispersion increased with an increase in wind speed. An increase in wind speed means the water gets absorbed into the oil and more oil droplets in the water column.

Model prediction has uncertainties that may affect the final output of each process investigated. The use of single values for environmental inputs in the model could be the reason for the difference. There were no data available to compare the area of spread on ice and under ice, dispersion and dissolution. Lack of data remains a challenge to modeling weathering and transport processes in ice-covered waters.

The method utilized incorporated the dependency of weathering and transport processes after an oil spill in ice-covered waters in the model. The simulation is more representative of the oil spill scenario in a real environment, compared to modeling it on an individual process basis.

The refining exercise shows that open water algorithms provide a first step to developing specific algorithms for oil spills in ice-covered water, in spite of their inadequacies in predicting weathering and transport processes in ice-covered waters. The current method provides a cheap and flexible way of studying the physio-chemical processes for an oil spill in ice covered water. More study is required to develop standard relations that will be applicable to all sites without going through the refining exercise.

2.4. Summary

A methodology was presented to model the main processes describing the weathering and transport processes of an oil spill in ice covered waters. The method accounts for the coupling effect of these processes. The method was illustrated through the formulation of a model, the results of which were compared with other works in the literature. The fraction of oil evaporated, emulsification and the change of viscosity of weathered oil due to evaporation and emulsification were compared with results of experiments conducted by SINTEF. The inadequacy of current algorithms to predict the main weathering and transport processes in ice-covered waters was evident from the comparison. A refining exercise was performed to match the experimental data with the predictions of the model. The results are satisfactory. More experimental work is required to further explore the possibility of tuning current open water algorithms to make them ice-covered waters capable.

A sensitivity analysis of the model developed shows that wind speed and temperature are the two most sensitive parameters in the model.

The methodology offers a better way of modeling the oil-ice interactions, which is absent in current oil spill models. The model presented here is only a first step for the prediction of the physio-chemical processes' changes of the bulk phase of the spilled oil in sea ice as a function of weathering time. This model could be coupled with a level IV fugacity model for estimating the concentration and persistence of hydrocarbons in air, water, ice and sediments and subsequently performing a risk assessment.

The model could be improved with the availability of ice-specific algorithms. Data for oil spills in ice-covered waters are scarce, which makes it difficult to validate the behavior of all the processes under study. Proper validation of models like this is important for stakeholders' acceptance. It is important that particular effort is dedicated to obtaining data by performing more field experiments in ice-covered waters. This will significantly improve such models, risk analysis and response to oil spills in ice-covered waters.

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Chapter 3: Dynamic fugacity model for accidental oil release during Arctic shipping[‡]

3. Background

The Northern Sea Route (NSR) and the North-West Passage (NWP) are already [§]navigable. The number of vessels going through the Arctic shipping routes has increased over the past decade (Østreng et al., 2013**;** Marchenko, 2012). It is estimated that using the NWP will save more time and money compared to using the Panama Canal (Østreng et al., 2013). This presents opportunities for transportation and tourism. These opportunities also come with risks, such as the potential accidental release caused by sinking, collision and grounding of shipping vessels. For instance the oil spill incident involving the Odyssey off the coast of Nova Scotia, Canada, resulted in the release of approximately 43 million gallons of oil (Black, 2012). An area of 16 km by 5km of water was polluted. Some of the oil also started drifting towards England. The 27 people on board were not found and there was significant impact on the flora and fauna in that area. The harsh conditions on the sea means that the Canadian coast guard could not respond in a timely manner (Hooke, 1997).

At the moment, shipping traffic volume is low in the Arctic but an oil spill during Arctic shipping and operations has potential high consequences on the marine ecosystem

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[‡] *This chapter is taken from the author's paper: Afenyo, M., Khan, F. Veitch, B., Yang, M. 2016. Dynamic fugacity model for accidental oil release during Arctic shipping. Marine Pollution Bulletin 111(1-2):347-353.I led the identification of the problem, performed the modeling and wrote the first manuscript with guidance from my supervisors: Profs. Khan, Veitch and Yang.*

(Afenyo et al., 2016; Østreng et al., 2013). These include the distortion of the reproduction cycle of Arctic species, chemical toxicity of the released oil, ecological changes, smothering, elimination of valuable ecological species, and air pollution. These effects depend on the quantity of spilled oil, type of spilled oil, ambient environment and seasonal variation. The aforementioned effects could be short term or long term (Lee et al., 2015). These potential impacts on the Arctic ecosystem require an Ecological Risk Assessment (ERA).

Ecological risk is defined as the likely impact of the exposure of a stressor (e.g. oil) to an environment. The steps required for an ERA are shown in Figure 25. The three main phases of ERA include: 1) the problem formulation phase, 2) the exposure analysis and effects phase and 3) the risk characterization phase. Before the main phase of problem formulation, risk managers and other stakeholders plan the risk assessment (Anon., 1998; Burgman, 2005; Nazir et al., 2008). The key to conducting an ERA for an accidental release of oil in ice-covered waters is the exposure analysis, which seeks to achieve the following:

i) to determine the extent of contamination in all media, ii) to identify organisms exposed and exposure pathways, iii) to identify the routes and path of exposure. The potential exposure paths include: ingestion of contaminated food and water, inhalation, and dermal absorption of hydrocarbons and iv) to identify how organisms respond to the exposure of a stressor over time (Burgman, 2005). The focus of this chapter is to accomplish the first objective. The other objectives are focussed on different outcome and are not relevant for the study presented in this chapter. This requires the estimation of the concentration of the stressor in different media of contact (Nazir et al., 2008; Anon., 1998). In order to achieve this, a partition model is used. An important approach to performing partition modeling is the use of the fugacity concept. The outcome of the exposure analysis is subsequently used for risk characterisation.

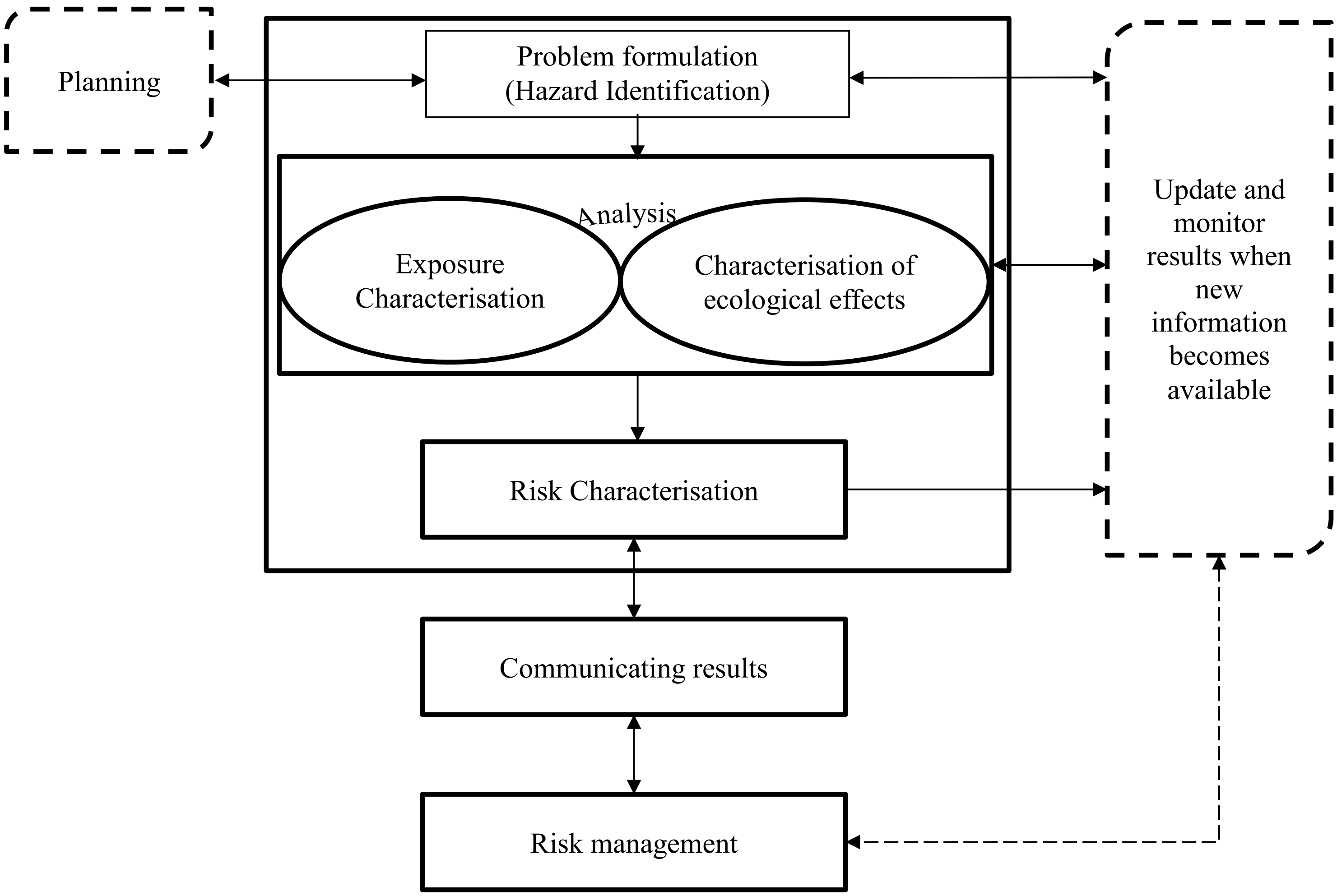

Figure 25: An Ecological Risk Assessment Framework (after Burgman, 2005; Nazir et al., 2008).

The fugacity concept has been used by researchers Clark et al. (1990), Mackay (1991), Sadiq (2001), Golding et al. (2008), Nazir et al. (2008) and Bock et al. (2010) to address different ecological problems. This chapter uses the fugacity approach to estimate the concentration of oil (surrogate: naphtalene) in air, ice, water and sediments which are the likely media of contact for an accidental release during Arctic shipping. The Level IV approach has been used to analyse different environmental problems (e.g. Wania et al., 2006; Wania and Mackay, 1995). The application of the Level IV fugacity model to an accident scenario of an instantaneous oil release during Arctic shipping is new. This fugacity model simplifies the modeling and analysis of contaminant transfer between phases in Arctic environments because fugacity is continuous between phase interfaces while concentration is not. The QWASI (Quantitative Water Air Sediment Interaction) model in Mackay (1991) forms the basis for this work, as well as works by Yang et al. (2015), Nazir et al. (2008), Sweetman et al. (2002) and Sadiq et al. (2001). The uniqueness of this work is the development of a Level IV fugacity based model with the capability to predict the concentration of oil in an ecosystem involving ice.

3.1 Multimedia partition modelling

An essential detail of exposure analysis is the estimation of the concentration and persistence of the stressor in the media of contact. In order to achieve this, Multimedia Mass Balance Models (MMBMs) are utilized. Important uses of MMBMs include: identification of fate processes, estimation of long range transport, estimation of residence time of a pollutant, bioaccumulation of chemicals in organisms, identifying the potential for persistence and the tendency for intermedia transport, and the evaluation of ecological concentration (MacKay and MacLeod, 2002; Gouin et al., 2001). Similar to other models, MMBMs may not be an exact representation of the real problem, likewise the corresponding solution but provides a tool to simplify and analyze a complex problem (MaCleod et al., 2010).

As a decision supporting tool, MMBMs are useful for documenting the origins and nature of pollutants and potential recovery strategies, performing risk assessment, as well as assessing impacts of alternative actions (Macleod et al., 2010). In MMBMs, compartments are represented by boxes and the chemical released is assumed to be homogeneous throughout the boxes. Predicted MMBMs results could vary by a factor of 2 from the actual data (Mackay et al., 2001). The most used MMBM is that which uses the fugacity concept.

3.1.1 Fugacity approach

The fugacity concept is used as a substitute for chemical potential as a thermodynamic equilibrium to describe the fate of a chemical. Fugacity describes the escaping tendency of a particular chemical and is analogous to partial pressure. In the mass balance equations, fugacity is used as a surrogate for chemical potential (Mackay et al., 2001). Mathematically, it is described by Equation 58, which shows fugacity, f, and concentration, C, are related by a term referred to as the fugacity capacity, Z; that is the tendency of a medium to absorb a chemical. A medium with a higher fugacity capacity has a high tendency to absorb more chemicals, hence will have higher concentration, assuming two media have the same fugacity (Mackay, 1991; Yang et al., 2015). It is important to note that Z depends on the type of compartment and the partition coefficient. Z partly describes the solubility of the pollutant in the media. Therefore dissociation for example causes an increase in Z-value. The more a substance can take or allow dissociation in it, the higher the Z value and the higher the concentration of the media (Mackay, 1991).

$$C = Z \times f \tag{58}$$

where C is the concentration $(\frac{mol}{m^3})$, f is the fugacity (Pa) and Z is the fugacity capacity $(\frac{mol}{m^3 Pa})$

It should be noted that the approach presented here is an approximation of fugacity. A more complete way to do it would be using non-ideal solution (activities) for liquids and fugacities for gases. This has its own challenges. Different disciplines view fugacity in different ways. Chemist define it different from chemical engineers. The definition used here is more related to that of chemical engineers.

There are four levels of complexity of fugacity models: Level I, Level II, Level III and Level IV. The Level I involves a fixed quantity of pollutant in a closed environment; that is, it involves the partitioning of a non-reacting chemical in equilibrium in a closed steady state system. Level II provides a solution for a steady state scenario of a chemical in equilibrium. It builds upon Level I by introducing exit pathways and the processes of reaction and advection. The same fugacity applies. Level III accounts for intermedia mass transport between well mixed media. It applies to compartments in non-equilibrium, where each medium has its own fugacity. Level IV is an unsteady state version of the level III (MacKay and MacLeod, 2002).

In the steady state models, the situation is that, the pollutant emissions and environmental related parameters are static with respect to time. In the Arctic marine ecosystem, the temporal variability of the fate and exposure of the pollutant is important.

The seasonal and temperature variations effect of a pollutant in the Arctic marine environment means that steady state models are not suitable and so the Level IV is best (Webster et al., 2005). The Level IV fugacity model is dynamic in nature. It is able to compute time dependent fugacity and thus capture the variation of concentrations of pollutants over a period of time. In simple terms it is an unsteady state non-equilibrium fugacity model applied for an open system (Mackay, 1991).

Gouin et al. (2001) presented a review of fugacity models, highlighting their applications, strengths and weaknesses. The review shows that the use of the Level IV fugacity model has received little attention. One of the few works related to the use of a Level IV fugacity model is the work by Sweetman et al. (2002) where the fate of polychlorinated biphenyls in the United Kingdom over a 60 year period was estimated using the fugacity approach. Yang et al. (2015) have also explored the possibility of combining the Level IV fugacity model and some oil weathering models to predict the concentrations of oil in different media.

An essential advantage of the fugacity approach is that it offers a simplification of analysing the path of a chemical in different media, and managing large amount of data. The application of the same fugacity to a medium with different sub-elements makes the use of this approach convenient. For example, in a lake made up of suspended solids and biota in equilibrium, the fugacity of water applies (Mackay et al., 2001). A limitation of using the fugacity models is that it is not effective for evaluating the partition of high concentration chemicals, as the concept was developed for chemicals with low concentration (Yang et al., 2015; Mackay, 1991).

For a scenario of accidental release of oil during Arctic shipping, four media will be involved: air, ice, water and sediments. The system under investigation is in unsteady state with the four media in non-equilibrium. This makes the Level IV fugacity model the best choice to address this problem. The next section describes the methodology to be adopted, based on the Level IV fugacity model. The type of decay considered in this work is mainly chemical decay.

3.2 Methodology

The methodology adopted to estimate the concentration for an accidental release of oil during Arctic shipping is shown in Figure 26. The first step is to produce a conceptual model of the scenario to be evaluated and to identify the most relevant processes. In this case, it is a vessel involved in an accident in Arctic waters, which results in the release of oil into ice-covered water. The second step is to identify the potential media that could be affected. Here, air, ice, water and sediments are the media considered. For the purpose of modeling, the dimensions of these media are estimated. These may include the volume, depth and the area of the media under evaluation. The third step is to obtain the physical and chemical properties of the pollutant. In this chapter, the stressor under consideration is crude oil. Crude oil composition is heterogeneous, therefore a surrogate is used in the model. Naphthalene is selected for this purpose. The physical and chemical properties of naphthalene are shown in Table 11. The fourth step is the formulation of the mass balance equations using the information from the conceptual model. Some of the unknowns in the mass balance equation are the advection and the reaction rates of naphthalene in the media under evaluation. These are obtained from literature. The *Z*-values are calculated as the fifth step using relations in Table 12. The Z value relations are not the same for each media and also vary for the bulk media as well. This is also shown in Table 12.The transport parameters referred to as *D*-values are calculated in step six. D (transport parameter) values are the product of the flowrate and the Z value. Given that the concentration of the pollutant is the product of Z value and fugacity, the product of the D value and fugacity gives the transport rate of the pollutant, analogous to the rate constants in chemical reactions. A slow process therefore has a small D value. An important use of the D value is to determine the dominant transport processes in an environmental system (Mackay, 1991). The formulas used are shown in Table 13. With the unknown parameters obtained, the mass balance equations for each medium is re-written and solved to obtain the fugacities, which are then multiplied by the fugacity capacity to obtain the concentration in the different media of contact. Should there be an omission or new information after the simulation, the new information is incorporated into the mass balance equation, and the cycle is repeated as before.

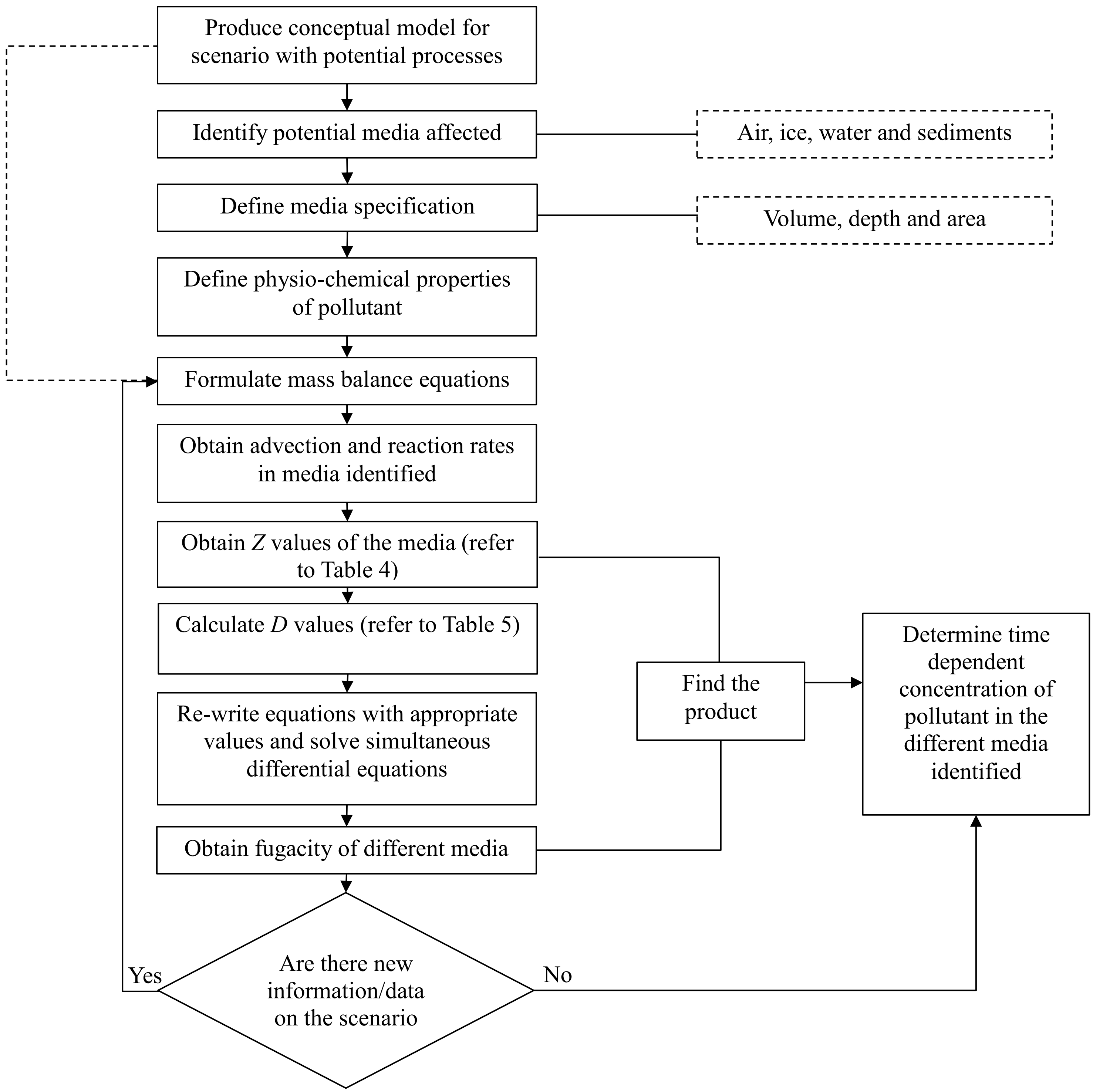

Figure 26: The proposed methodology based on a level IV fugacity concept

3.2.1. Numeric example

To illustrate the methodology developed, an oil tanker going through the North West Passage is assumed to be involved in a minor collision with an ice floe releasing approximately $7\mathrm{m}^3$ of oil. An ambient temperature of $-20^\circ\mathrm{C}$ is assumed. This purely based on a hypothetical oil spill scenario case and not related to the one in the previous chapter. The proposed methodology is used to estimate the concentration of oil (surrogate: naphthalene) released during this hypothetical accident. The next section presents an analysis of the hypothetical scenario using the proposed procedure. In this example, the following are assumed i) the release is instantaneous, ii) the oil is released in the water and then, it partitions into the ice and air media as well as the sediment compartment, iii) the concentration of the oil is also assumed to be low after undergoing dispersion, iv) weathering processes like encapsulation, emulsification, photo-oxidation are not accounted for v) The use of a surrogate for crude oil is a simplification of the scenario.

3.2.1.1 Analysis

Following the steps outlined in Figure 26, the conceptual model, with processes to be considered for analysis, is presented in Figure 27. The Figure shows relevant processes for analysis and these include absorption, evaporation, melting, ice growth, diffusion, sediment burial, advection and reaction, sediment deposition, sediment resuspension. While these may not be all the processes that may be involved in the scenario, they are chosen for the purpose of illustrating the application of the proposed methodology. The area of the compartments, dimensions, physiochemical characteristics of naphthalene, relations for the calculation of Z values, intermedia transfer, D, and other parameters to be used for illustration of the proposed model are shown in Tables 9, 10, 11, 12 , 13, and 14 respectively. Equations 61, 62, 63 and 64 are the mass balance equations for air, ice, water and sediment compartments.

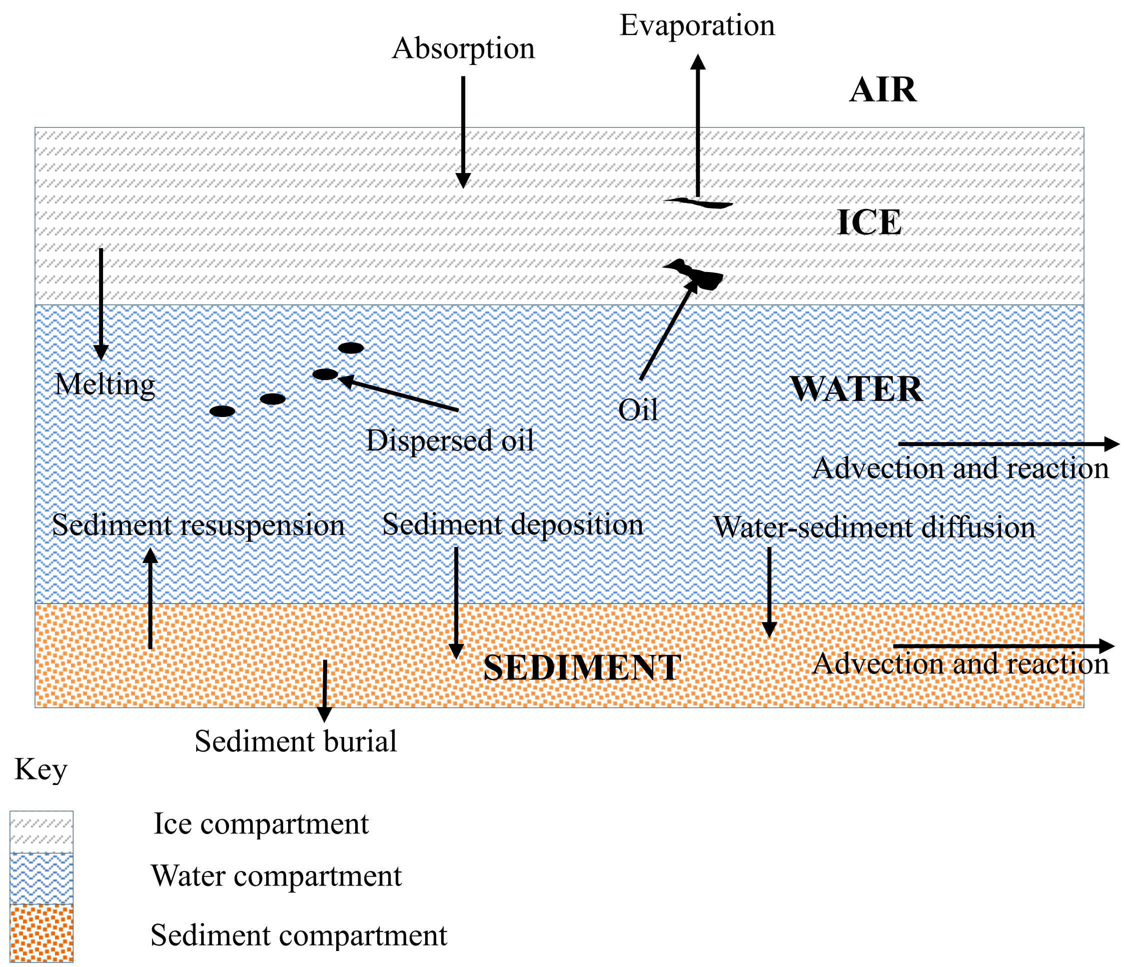

Figure 27: Compartments and processes involved in the scenario

Generally, the mass balance for a compartment x and y takes the form of Equation 59 (Mackay, 1991).

$$V_x Z_y \frac{df_x}{dt} = I_x + \sum\left(D_{yx} f_y\right) - D_{Tx} f_x \qquad (59)$$

Where V is the volume of the compartment, Z is the bulk fugacity capacity, I is the input rate and may be a function of time, $D_{yx}f_y$ is intermedia input transfer, $D_{Tx}f_x$ is the total output. All other symbols are the same as described earlier. The characteristic response time could be evaluated using Equation 60 (Mackay, 1991).

$$\frac{V_x Z_y}{D_{Tx} f_x} \quad (60)$$

This information may be useful for estimating the time required for a contaminated system to be restored.

$$\frac{df_{(a)}}{dt} = \frac{I_{(a)}+D_{(i-a)}f_{(i)}-f_{(a)}(D_{(a-i)})}{V_{(a)}Z_{(a)}} \quad (61)$$

$$\frac{df_{(i)}}{dt} = \frac{I_{(i)}+D_{(a-i)}f_{(a)}+D_{(ic.)}f_{(w)}-(D_{(i-a)}+D_{(adv)}+D_{(rct)})f_{(i)}}{V_{(i)}Z_{(i)}} \quad (62)$$

$$\frac{df_{(w)}}{dt} = \frac{I_{(w)}+(D_{(mel.)}f_{(i)}+D_{(s-w)}f_{(s)}-(D_{(w-i)}+D_{(w-s)}+D_{(vol)}+D_{(adv)}+D_{(rct)})f_{(w)}}{V_{(w)}Z_{(w)}} \quad (63)$$

$$\frac{df_{(s)}}{dt} = \frac{I_{(s)}+D_{(si)}f_{(w)}-(D_{(diff.)}+D_{(res)}D_{(bur)}+D_{(rct)}+D_{(adv)})f_{(i)}}{V_{(s)}Z_{(s)}} \quad (64)$$

a denotes air, w denotes water, i denotes ice and s sediment compartments. The corresponding intermedia transfer values (D-values) $\left(\frac{mol}{Pa\ h}\right)$ are defined in Table 13. $V_{(a)}, V_{(i)}, V_{(w)}, V_{(s)}$ are the volumes of the air, ice, water and sediment compartments (m^3), $Z_{(a)}, Z_{(i)}, Z_{(w)}, Z_{(s)}$ are the bulk fugacity capacities of the air, ice, water and sediment compartments $(\frac{mol}{m^3 Pa})$. $f_{(a)}, f_{(i)}, f_{(w)}, f_s$ are the fugacities of the pollutant in the air, ice, water and sediment compartments (Pa), $I_{(a)}, I_{(i)}, I_{(w)}, I_{(s)}$ are the emissions in the air, ice, water and sediment compartments $\left(\frac{mol}{h}\right)$.

In order to calculate the amount of oil dispersed in the water column, Equation 65 is used.

$$I(t) = Q \times C_i \tag{65}$$

where Q ($\frac{m^3}{s}$) is the volumetric flow rate of the oil and is obtained from the dispersion formulation by Mackay et al. (1980) and shown as Equation 66. C_i is the initial molar concentration of the pollutant.

$$\frac{dD_{(disp)}}{dt} = \frac{(1+W)^2}{\left(1+50\mu^{\frac{1}{2}}\delta\sigma_{ow}\right)} \tag{66}$$

$\frac{dD_{(disp)}}{dt}$ is the dispersion rate ($\frac{kg}{h}$), W is the wind speed ($\frac{m}{s}$), μ is visocity of spilled oil ($10^{-3} Pa\ s$) and δ is the slick thickness (m), σ_{ow} is the oil-water interfacial tension ($\frac{10^{-3}N}{m}$).

The parameters are incorporated in the mass balance equations and solved simultaneously to obtain the fugacities in the compartments under consideration. This is achieved by using the fourth order Runge-Kutta method. The $f_{(a)}, f_{(i)}, f_{(w)}, f_s$ are obtained once the solution is obtained for the simmulation. The fugacities obtained are a function of time. This is multiplied by the fugacity capacities of the various media to obtain the corresponding concentrations according to Equation 58.

3.3 Results and Discussions

The results of the simulation are shown as Figures 28 to 31. Generally, the concentrations in all the media are high initially and decrease rapidly with time. The concentrations of the surrogate reduced until very small values (almost zero) at 2000 hours for the air compartment, 500 hours for the ice compartment, 1500 hours for the water compartment and 1500 hours for the sediment compartment. The results also show that the concentration for sediment is highest followed by water, air and then ice. The lack of consideration of some of the processes that occur after an oil spill indicates that, there is a possibility of overestimation in the concentration profile of water. The high concentration at the beginning and subsequent reduction is consistent with what would be observed, where the concentration is greatest at the beginning but reduces with time. Concentration is highest in the sediment compartment because of the adsorption property of the pollutant. The pollutant may undergo biodegradation after a period of time. This is reflected by the almost negligible concentration in the water column hence the other compartments after some time.

The fugacity capacities calculated for the four media are consistent with the model predictions. That is, the higher the fugacity capacity of a medium the higher the concentration of the pollutant in that medium. Similar trend was observed by Yang et al. (2015) and Nazir et al. (2008). The results may not be exact but are useful as a first estimate of the extent of contamination of the different media should there be an accidental release of oil in the Arctic, during shipping. This information is important for long term planning of the consequence of a potential oil spill during Arctic shipping and operations

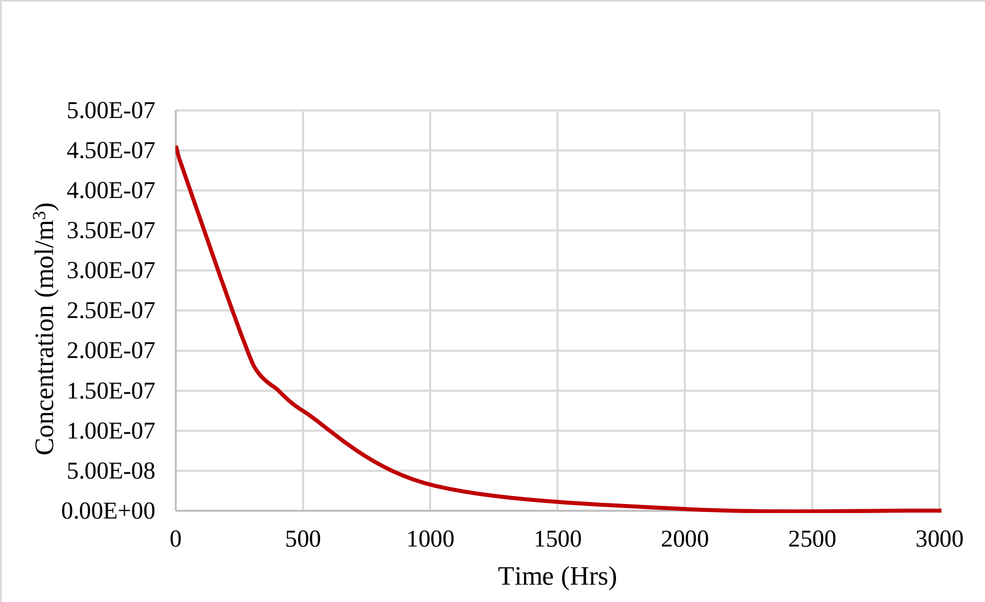

Figure 28: Concentration profile of surrogate in air compartment

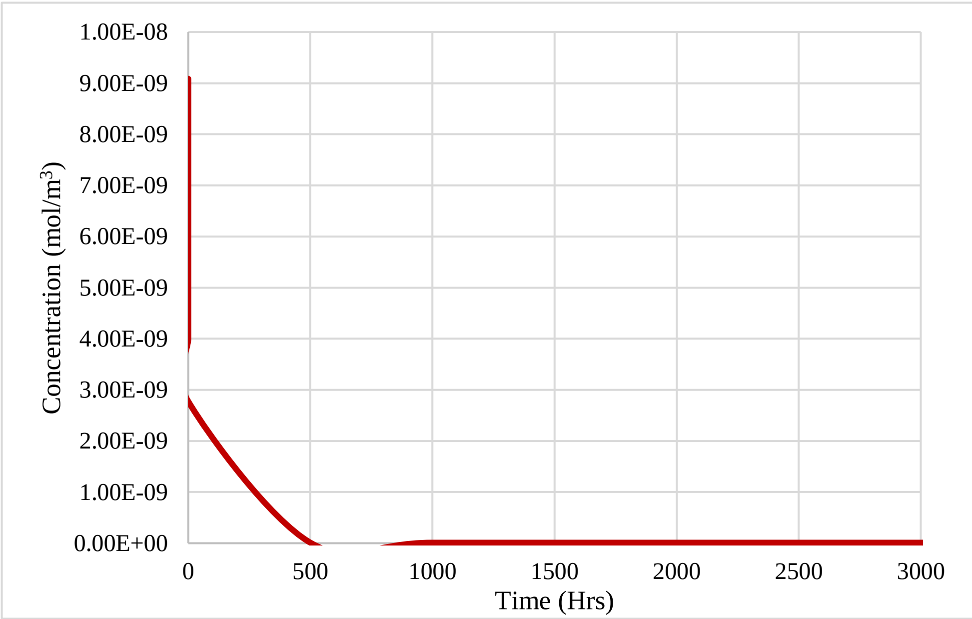

Figure 29: Concentration profile of surrogate in ice compartment

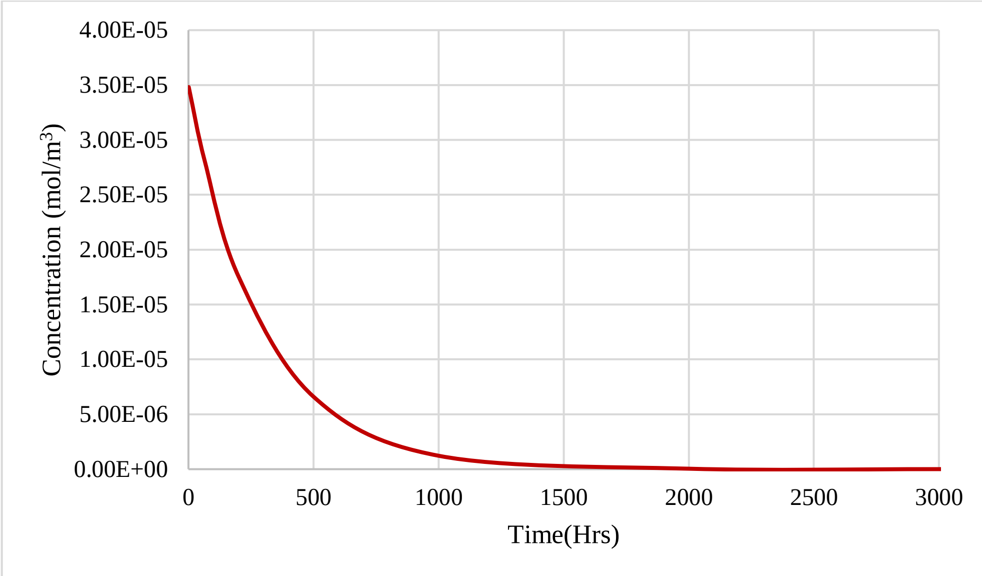

Figure 30: Concentration profile of surrogate in water compartment

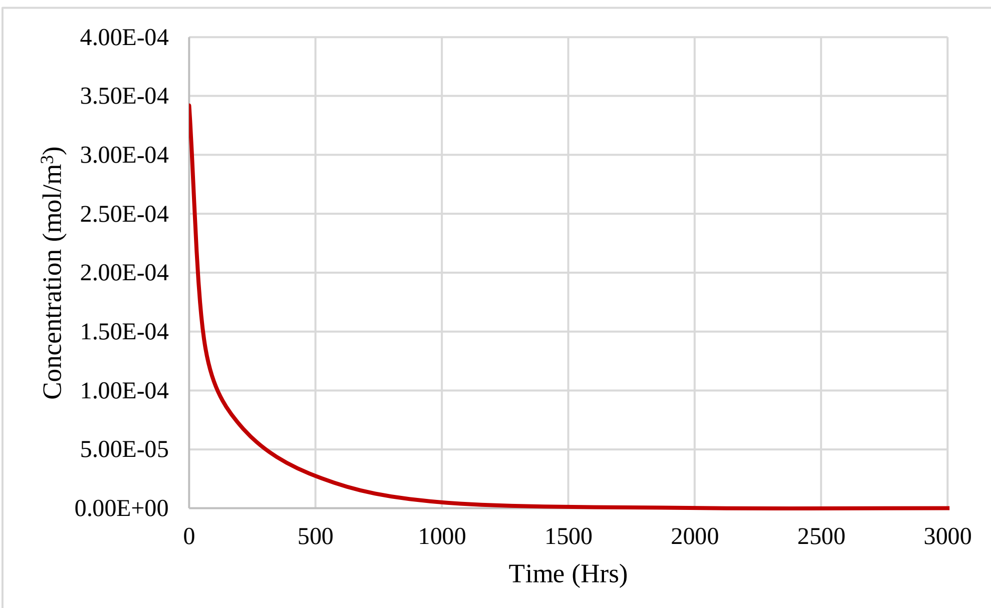

Figure 31: Concentration profile of surrogate in sediment compartment

The Arctic is temperature sensitive and therefore, the concentration profile for summer is likely to be different from that of winter. In summer, the water level is likely to rise thus rendering the ocean surface ice free. This will in turn reduce the concentration through a dilution effect. This has not been addressed in the current model. A comparison of two models for the different seasons would illustrate this. The use of the surrogate also means that predictions may be an underestimation or overestimation.

The fugacity approach was developed for low concentration chemicals. This is not the case for spilled crude. This is a limitation of the proposed approach. Further it the extensive non-correction of the temperature also limits the capability of the model proposed. The fugacity concept used here is an approximation of the actual fugacity (activity) which highly dependent on temperature. Fugacity is understood from different perspectives and that should be noted when using the concept presented here.

Uncertainties in the proposed model exist and are rooted in the following sources i) variation in the input parameters, ii) assumption and simplifications made in the model. The use of a single value for the input parameters and not for example distributions is a source of uncertainty. For a dynamic model such as the one presented in this chapter, uncertainty and sensitivity analysis are very complex, due to the changing nature of the system. While traditional uncertainty analysis can only identify uncertainties of the model at a static point as in the case of Levels I, II and III, the effect of the uncertainties becomes small in a dynamic model such as this. A Morris classification screening method may be used for the sensitivity analysis. In this method a selected variable is changed to fixed step size while the other parameters are held constant. The Monte Carlo simulation may be used to study the uncertainty of the model results.

3.4 Summary

The chapter developed and applied a level IV fugacity model. This was applied using the scenario of Arctic shipping accidental release of oil. A surrogate was used (naphthalene) in the simulation. The results show that the medium with the highest fugacity capacity has the highest concentration of the pollutant and is the most likely to be the most contaminated. The model may not predict the exact value of concentrations in the media, but offers a good tool for decision making in terms of the risk a potential accidental release will pose to the Arctic environment in the long term.

This methodology and subsequently the model formulated compromises on details mainly based on data availability, understanding of how the system works, and the particulars of a scenario. The following were not accounted for in the developed model: i) the incorporation of other pollutants apart from oil in the water into ice, ii) sediment particles in ice through suspension freezing iii) encapsulated oil in ice. It is a challenge estimating how much of spilled oil gets encapsulated, partly because of the unavailability of a model to predict the percentage of spilled oil that will be engulfed by ice. There is still limited data on some of the processes in ice. Since this approach has not been extensively applied to ice conditions, there are still many unknowns about the reaction rate of different chemicals in ice. The fugacity approach was developed for chemicals with low concentrations. The fugacity model is employed to model the low-concentration of naturally dispersed oil. The fate and transport of high concentration weathered oil is modeled using weathering and transport algorithms, which is not the subject of this chapter. The method is therefore not applied to high concentration chemicals. Released oil may be highly concentrated even in the dispersed form, and so may become a challenge using this model. The use of a surrogate also simplifies the real scenarios, oil may behave relatively different compared to naphthalene. Uncertainties in the model have not been addressed. Point estimates (Single numbers) have been used for the input parameters, this may compromise the accuracy of the predictions. Validation of the fugacity model is mostly challenging and therefore is best used as a first point estimate of the potential partitioning of the spilled oil. Plans for future work includes the following i) developing a fugacity based model capable of predicting concentrations in space and time. This model should also address in detail the oil-ice-interaction particularly the processes of encapsulation and de-encapsulation ii) developing a Level IV fugacity model that addresses uncertainties in the input estimates using a Monte Carlo simmulation or other probabilistic approaches iii) developing a method that uses substitute mixtures of oil instead of naphthalene. The development of pseudo-component mixture may serve this purpose.

An essential use of the output of this model is its use in exposure model for Arctic species in the event of an oil spill during shipping and operations. The exposure model is key to estimating the ecological risk posed by the released oil.

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Appendix

Table 9: Area of the compartments under consideration

Compartments	Area (m^2)
Air-ice	300000
Air-water	700000
Water-sediment	700000
Water-ice	700000

Table 10: Dimensions of the compartments under considerations

Compartment	Depth (m)	Volume (m^3)
Air	6000	6000000000
Ice	0.15	45000
Water	10	7000000
Sediment	0.03	21000

Table 11: Physiochemical characteristics of naphthalene (after Nazir et al., 2008; Yang et al., 2015).

Parameter	Value	Units
Molecular weight	128.2	$\frac{g}{mol}$
Vapour pressure at 25℃	10.4	Pa
Solubility at 25℃	31.7	$\frac{g}{m^3}$

Log K_{ow}	3.35	n/a

A concentration of 0.1 $\frac{mol}{m^3}$ (ppm) is used in the model.

Table 12: Relations for the calculation of Z values (Nazir et al., 2008; Yang et al., 2015).

Z value calculation:	Relations
Bulk compartment(Z)	
Air	$Z_{(a)} = Z_{11} + \gamma_{aw} Z_{13}$
Ice	$Z_{(i)} = \gamma_{wa} Z_{21} + \gamma_{wi} Z_{22} + \gamma_{ww} Z_{23} + (\frac{A_{2a}}{V_2}) A_{2a}$
Water	$Z_{(w)} = \gamma_{ww} Z_{32} + \gamma_{ssw} Z_{33} + \gamma_{bw} Z_{34}$
Sediment	$Z_{(s)} = \gamma_{sss} Z_{42} + \gamma_{pws} Z_{43}$
Sub compartments	
Air ($\boldsymbol{Z_{i1}}$)	$\frac{1}{RT}$ where R is the universal gas constant =8.314 $\frac{Pam^3}{mol\ K}$ and T is the absolute temperature (K)
Water ($\boldsymbol{Z_{i2}}$)	$\frac{1}{H}$ where H is the Henry's law constant =8.314 $\frac{Pam^3}{mol}$
Solids ($\boldsymbol{Z_{i3}}$)	$\frac{X_{ij} K_{OC} \rho_s}{H}$ where X_{ij} is the organic carbon fraction, ρ_s is the density of solids $(\frac{Kg}{L})$, K_{OC} is the organic carbon partition coefficient=$0.41 K_{ow}$
Aerosols ($\boldsymbol{Z_{13}}$)	$\frac{6\times10^6}{P_L^s RT}$ where P_L^s is the liquid vapour pressure (Pa),
Biota ($\boldsymbol{Z_{34}}$)	$\frac{0.048 \rho_b K_{ow}}{H}$ where ρ_b is the density of the biota $\approx 1000 \frac{Kg}{m^3}$
Ice-air interface ($\boldsymbol{Z_{ia}}$)	$\frac{K_{ia}}{RT}$ where K_{ia} is the ice surface-air partition coefficient (m)

Organic carbon in ice-cover (Z_{23})	$In\ K_{ia}$ (12.5℃) $= 0.68\ InK_{ow} - 19.63 + InK_{wa}$ where is the water-air partition coefficient $\frac{0.41K_{ow}}{H}$

Table 13: Intermedia transfer D, values and their multiplying fugacities (Mackay, 1991; Nazir et al., 2008; Yang et al., 2015).

Process	D values	Formulas for individual D values	Multiplying fugacity	Total D
Air to ice diffusion	D_{dif}	$\frac{1}{\left(\frac{1}{\varkappa_{va}A_{a-i}Z_a + \varkappa_{vi}A_{a-i}Z_i}\right)}$	f_a	$D_{a-i} = D_{dif} + D_{si} + D_{abs}$
Ice to water diffusion	D_{dif}	$\frac{1}{\left(\frac{1}{\varkappa_{va}A_{a-i}Z_a + \varkappa_{vi}A_{a-i}Z_i}\right)}$	f_i	
Deposition from air to ice and water	D_{si}	$A_{a-i}U_{di.}\gamma_{ssw}Z_w$	f_a	$D_{i-a} = D_{dif}$
Absorption	D_{abs}	G_aZ_a	f_a	
Volatilization	D_{vol}	G_vZ_w	f_w	$D_{w-a} = D_{vol}$
Sediment deposition	D_{sed}	$A_{w-s}U_{sd.}Z_{w-s}$	f_w	$D_{w-s} = D_{dif} + D_{sed}$

Sediment burial	D_{bur}	$A_{w-s}U_{bur}Z_s$	f_s	
Sediment resuspension	D_{res}	$A_{w-s}U_{res}Z_{w-s}$	f_s	$D_{s-w} = D_{bur} + D_{res} + D_{dif}$
Sediment to water diffusion	D_{dif}	$\dfrac{1}{\left(\dfrac{1}{\varkappa_{pw}A_{w-s}Z_w + \Delta l B_{dif} A_{w-s}Z_w}\right)}$	f_s	
Water to sediment diffusion	D_{dif}	$\dfrac{1}{\left(\dfrac{1}{\varkappa_{pw}A_{w-s}Z_w + \Delta l B_{dif} A_{w-s}Z_w}\right)}$	f_w	
Reaction in sediment	D_{rct}	$\varkappa_i V_i Z_i$ where I refers to any medium	f_s	
Advection sediment	D_{adv}	Generally G_iZ_i: $Z_{sed}d_sKA_S^{\frac{1}{3}}\left[\frac{V_s}{A_s}\right]^{\frac{4}{3}}$ K is a constant with default value 150^{-1}, V_s is the volume of spilled oil (m^3), A_s is the area of slick (m^2)	f_s	
Ice growth	D_{ic}	$A_{w-i}U_{ic.}Z_w$	f_w	$D_{w-i} = D_{ic}$
Melting	$D_{mel.}$	$A_{w-i}U_{mel.}Z_i$	f_i	$D_{i-w} = D_{mel.}$

Table 14: Parameters used in the level IV fugacity model.

Parameter	Symbol	Value	Units
Volume fraction of pore water	γ_{pw}	0.63	
Volume fraction of suspended solids in air	γ_{ssa}	2×10^{-11a}	
Volume fraction of suspended solids in ice	γ_{ssi}	5×10^{-11a}	
Volume fraction of suspended solids in water	γ_{ssw}	5×10^{-11b}	
Volume fraction of suspended solids in sediments	γ_{sss}	0.37^{c}	
Volume fraction of air in water	γ_{aw}	0	

Volume fraction of water in ice	γ_{wi}	0	
Volume fraction of water in water	γ_{ww}	1	
Volume fraction of biota in water	γ_{bw}	1×10^{-6a}	
Organic carbon fraction in suspended solids	φ_{ss}	0.2^{b}	
Organic carbon fraction biota	φ_{biot}	0.05^{c}	
Organic carbon fraction in ice	φ_{ice}	0.2^{a}	
Organic carbon fraction in sediment	φ_{sed}	0.04^{b}	
Density of suspended solids	ρ_{ss}	1500^{b}	$\frac{g}{m^3}$
Advection rate in water	U_{adv}	0.018^{d}	$\frac{m}{s}$
Deposition rate of suspended solids	$U_{ssd.}$	5×10^{-7b}	$\frac{m}{h}$
Deposition rate of solids	$U_{sd.}$	4.6×10^{-8e}	

Diffusion path length in sediment	$\Delta l = 0.5d$ d is the depth of sediment	calculated	m
Density of sediments	ρ_s	2400	$\frac{kg}{m^3}$
Re-suspension rate of sediment	$U_{res.}$	1.1×10^{-8e}	$\frac{m}{h}$
Burial rate of sediment	$U_{bur.}$	$3.4 \times 10^{-8c,d}$	$\frac{m}{h}$
Air-side Mass Transfer Coefficient (MTC) over ice cover	$\varkappa_{va}$	2^e	$\frac{m}{h}$
Ice-side MTC	$\varkappa_{vi}$	0.01^e	$\frac{m}{h}$
Water-side MTC over sediment	$\varkappa_{pw}$	0.01^e	$\frac{m}{h}$
Aeorosol deposition velocity	$U_{di.}$	10.8^e	$\frac{m}{h}$
Melting rate	$U_{mel.}$	3.9×10^{-5e}	$\frac{m}{h}$
Ice growth rate	$U_{ic.}$	2.3×10^{-5e}	$\frac{m}{h}$
Sediment-water phase effective diffusivity	B_{dif}	4×10^{-6e}	$\frac{m^2}{h}$
Absorption	A	0.040	

Reaction rate constant in water	$\varkappa_w$	2.89×10^{-3f}	$\frac{1}{h}$
Reaction rate constant in sediment	$\varkappa_s$	1.93×10^{-4f}	$\frac{1}{h}$
Equivalent flow for volatilization	G_v	500	$\frac{m^3}{h}$
Equivalent flow for absorption	G_a	1.6	$\frac{m^3}{h}$
a Sweetman et al.(2002)			
b Mackay et al. (1992)			
c Mackay (1991)			
d Sadiq (2001)			
e Yang et al. (2015)			
f Nazir et al. (2008)			

Chapter 4: A probabilistic ecological risk model for Arctic marine oil spills[**]

4. Background

Increased potential for oil and gas exploration, as well as shipping through the Arctic (Olsen et al., 2011) has prompted governments of Arctic countries, the International Maritime Organization (IMO), and other stakeholders to review existing regulations aimed at addressing marine pollution (Chang et al., 2014; Mattson, 2006; Papanikolaou, 2016). This review is necessary to incorporate the potential risk posed by oil spills in the Arctic (Afenyo et al., 2016) into policies and regulations. The risks from a potential oil spill in the Arctic range from social to environmental (Chang et al., 2014; Pimlott et al., 1976).

While the expected frequency of occurrence of oil spills is low, the potential environmental consequences to the marine Arctic ecosystem could be high (Anon., 2014; Atlas and Hazen, 2011; Lee et al., 2015). Evaluating the corresponding risk requires estimating the probability of occurrence of a particular scenario as well as its consequences. The product of these two parameters describes the risk (Anon., 2014; Burgman, 2005).

[**] *This chapter is taken from the author's paper: Afenyo, M., Khan, F., Veitch, B., and Yang, M. 2017. A probabilistic ecological risk model for Arctic marine oil spills. Journal of Environmental Chemical Engineering. 5:1494-1503.I led the identification of the problem, performed the modeling and wrote the first manuscript with guidance from my supervisors: Profs. Khan, Veitch and Yang.*

Progress has been made in Environmental Risk Assessment (ERA), but a framework for Arctic oil spills that incorporates the various elements of an ERA specifically for the Arctic eco-system is nonexistent (Afenyo et al., 2016b; Afenyo et al., 2016c; Lee et al., 2015). This is made more difficult by our lack of knowledge about the Arctic, and the overall lack of data (Lee et al., 2015). The goal of this article is to present a framework for conducting an ERA for Arctic oil spills, and to illustrate its application through a case study. The proposed model presents a novel approach of integrating a fugacity model in a probabilistic framework with the aim of applying it to Arctic conditions. This chapter focuses on ecological risk as opposed to human risk.

While some studies with similar goals have been presented in the past, none adopts the current approach and the focus has been slightly different. This is because the current methodology adopts a combination of dispersion, multimedia partition (fugacity based), and Monte-Carlo Simmulation to assess potential risk of oil spill during shipping in the Arctic. A study by Navaleinan et al. (2016), presented qualitative food web based risk assessment framework for the Arctic while Blaken et al. (2017) used a worse-case scenario evaluation strategy to calculate the risk for a well blowout in the Arctic Ocean. In Jolma et al. (2014), the authors used a series of softwares to simulate the potential of saving the ecological biota from a shipping accident in the Gulf of Finland. French-MacCay (2011)'s review of her models shows the use of a combination of trajectory and biological effect models to address risk in marine environments. Willemse (2011), on the other hand developed an accident modeling based methodology to evaluate the deep-water horizon oil spill. The study utilized a combination of a fault tree and event tree for this purpose.

4.1 Ecological Risk Assessment

The procedure for conducting an Ecological Risk Assessment (ERA) as described by the United States' EPA involves the following: i) problem identification phase, ii) analysis phase, iii) risk characterization phase, iv) risk management and communication phase (Burgman, 2005; Lehr, 2001). The problem formulation phase involves identifying hazards, assessing end points, and planning for exposure assessment. The analysis phase encompasses the assessment of exposure and effects on a particular ecosystem. The risk characterization phase uses the information from the problem formulation phase and the analysis phase to predict the risk profile of the pollutant in an ecosystem. This phase is followed by the development of mitigation strategies and communicating these to the stakeholders (Nazir et al., 2008) Out of these, the analysis phase is the most critical and is the focus of the methodology presented in this chapter.

In ERA, the end point is the risk posed to the ecosystem. The starting point for an ERA is the assumption that the event has already occurred (e.g an oil spill). This means that the probability of such an occurrence is 1. The focus therefore shifts to the consequence associated with such event. Evaluating the consequence of an oil spill to the Arctic eco-system requires information upon which to base a decision (Gustavan et al., 2016; Smith et al., 2005). Deriving such a quantity requires the estimation of concentration of pollutants in different media and a comparison of the value in each medium with a standard value.

In this study, a quantity referred to as the Risk Quotient (RQ), described by Equation 67, is adopted for this purpose. If the $RQ \leq 1$, the risk quotient is acceptable; otherwise mitigative measures need to be put in place to reduce it.

$$RQ = \frac{PEC}{PNEC} \tag{67}$$

The Predicted Exposure Concentration (PEC) is evaluated using a fugacity model. The Predicted No Effect Concentration ($PNEC$), which represents the ecosystem response, is obtained from ecotoxicological studies. The PNEC is taken from a publication by Anon. (2007) for the purpose of this study.

The complex nature of petroleum presents difficulties when estimating the concentration of pollutants in the media of contact and subsequently when performing an ERA. This is made more difficult when an ice medium is involved because oil-ice interaction is difficult to predict (Buist et al., 2013) and data is scarce (Afenyo et al., 2016; Buist et al., 2013).

Some authors e.g. Redman et al. (2014), have adopted the Hydrocarbon Block Method (HBM) to address this complexity. In their approach, blocks of chemicals with similar properties are used. A different approach is adopted in this chapter. Here, a surrogate is used (naphthalene/NAP) to represent crude oil. This simplifies the process and does not compromise the end goal. The properties of naphthalene make it a good substitute for crude oil. This is because it is persistent, a key component of petroleum, toxic and dissolves in water (Anon., 2003). It should be noted that even though NAP could well represent crude oil, BTEX could also be used. The use of NAP is for illustration purposes. When released into water, concentrations are high in the immediate vicinity, but reduce with distance from the release site (Anon., 2003).

Exposure concentration may not be enough to evaluate the effect of an oil spill on the ecosystem. We also need to know the concentration in the body of a species exposed to oil. This concentration is responsible for the death and the disruption of the reproductive cycle of the species under study (Baas et al., 2010; Rozman and Doul 2000).

The main objective of ecotoxicological modeling in the context of ERA is to provide a basis on which to make decisions for addressing potential damage (Burgman, 2005; Sánchez-Bayo, F., 2008). This information is key to conducting an ERA (Olsen et al., 2013). Different measures exist for achieving this. Among them are, median lethal concentration (LC_{50}), median lethal dose (LD_{50}), median effective concentration (EC_{50}), and No Effect Concentration (NEC). The discussion here will focus on the LC_{50} and the NEC. These parameters are a description of the tolerance of species when exposed to pollutants (Burgman, 2005; Olsen et al., 2011). They also describe the accumulation of pollutant with time (Baas et al., 2010; Rozman and Doul, 2000). Standard tests are normally carried out in laboratory settings by exposing species to different pollutant concentrations. These standard tests are collectively known as the 96 hour toxicity tests. The LC_{50} and the NEC are derived from these.

In their study, Olsen et al. (2011) exposed 17 species, 11 of which are Arctic, and 6 of which are from temperate environments, to 2-methyl naphthalene. The LC_{50} (96h) and NEC were deduced to a 95% confidence level. They compared PNEC values of temperate and Arctic species. The authors concluded that there is insignificant difference between the PNEC values for species in temperate environments and those in Arctic environments. It is therefore proposed here to use the temperate PNEC values of a particular medium as a stand-in for Arctic species. Derivation of PNEC values for Arctic species for different chemicals is only beginning to receive attention (Olsen et al., 2011). Some researchers have questioned the need to conduct studies specifically for Arctic species (Olsen et al., 2011; S$\acute{a}$nchez-Bayo, 2008). Models could be developed using the data from the temperate species to make some of these predictions. This is an area of research that is evolving (S$\acute{a}$nchez-Bayo 2008) and is not the focus of this chapter.

It should be noted that even though data obtained are from laboratory experiments, a fitting exercise is carried out to produce a generic graph. This is used to estimate LC_{50} or NEC values for different concentrations at different times for a particular chemical under investigation (S$\acute{a}$nchez-Bayo 2008).

In Anon. (2003) and Anon. (2007), different methods have been used to perform ecotoxicological modeling, which eventually leads to deriving PNEC values for different compartments. To obtain the PNEC value for marine water, the following steps are adhered to: the first step involves the compilation of data on LC_{50} or NEC from the scientific literature. These are screened using a set of criteria developed by the EU working group on the risk assessment of naphthalene. Normalization factors are applied to the selected data where there is abnormality in the screened data. Some of these anomalies may be due to the duration of the test conducted to obtain LC_{50} or NEC. Care is also taken to avoid repetition of the same data.

Values of LC_{50} or NEC are plotted and fitted to log-normal or log-logistic relations to obtain a Species Sensitivity Distribution (SSD) (Burgman, 2005; Smith et al., 2005). NEC values are scarce compared to those of LC_{50}, which describe the concentration at 50% mortality. This is mainly because of the nature of the experiments required for deriving the NEC (Nazir et al., 2008). Most researchers therefore use LC_{50}.

The uncertainties associated with the input parameters of the exposure model necessitate the use of distributions instead of single values. The result is a probabilistic profile of the pollutant. The US Environmental Protection Agency (EPA) recommends the use of percentiles between 90-99 (Citra, 2004). The 95th percentile is used in this chapter. The probabilistic based fugacity model is used to estimate the $PEC_{95\%}$. The $PEC_{95\%}$ is the 95th percentile of the predicted exposure concentration. This is compared with the $PNEC_{5\%}$, which is the 5th percentile of the concentration from the ecotoxicological models (Smith et al., 2005).

4.2 Methodology

The proposed methodology encompasses the use of a dispersion model, a fugacity based partition model, and the linking of a toxicological model with the aforementioned to describe the risk posed by an accidental oil release. Figure 32 represents the proposed methodology.

The logic behind the methodology is that when there is a shipping accident (e.g. collision, grounding, fire, and explosion) involving an oil tanker, crude oil is released into the Arctic marine ecosystem. This is what the release model attempts to capture. The released oil will be dispersed, transported and partitioned into different compartments (e.g. air, ice, water, and sediments). This produces a concentration which describes the extent of pollutant intensity in each compartment. A risk assessment is conducted by comparing this value to the outcome of an ecotoxicological model. Because of the uncertainties in the quantities, a probabilistic approach is adopted for the partition model. This involves the use of Monte-Carlo Simmulation. After the comparison of the outcome of the fate and transport model and the outcome of the ecotoxicological model, a decision can be made. If the risk quotient ratio is less than 1, the concentration is considered acceptable. Otherwise, interventions would have to be carried out to reduce it. These interventions are categorized under design measures, control measures, response measure and operation measures.

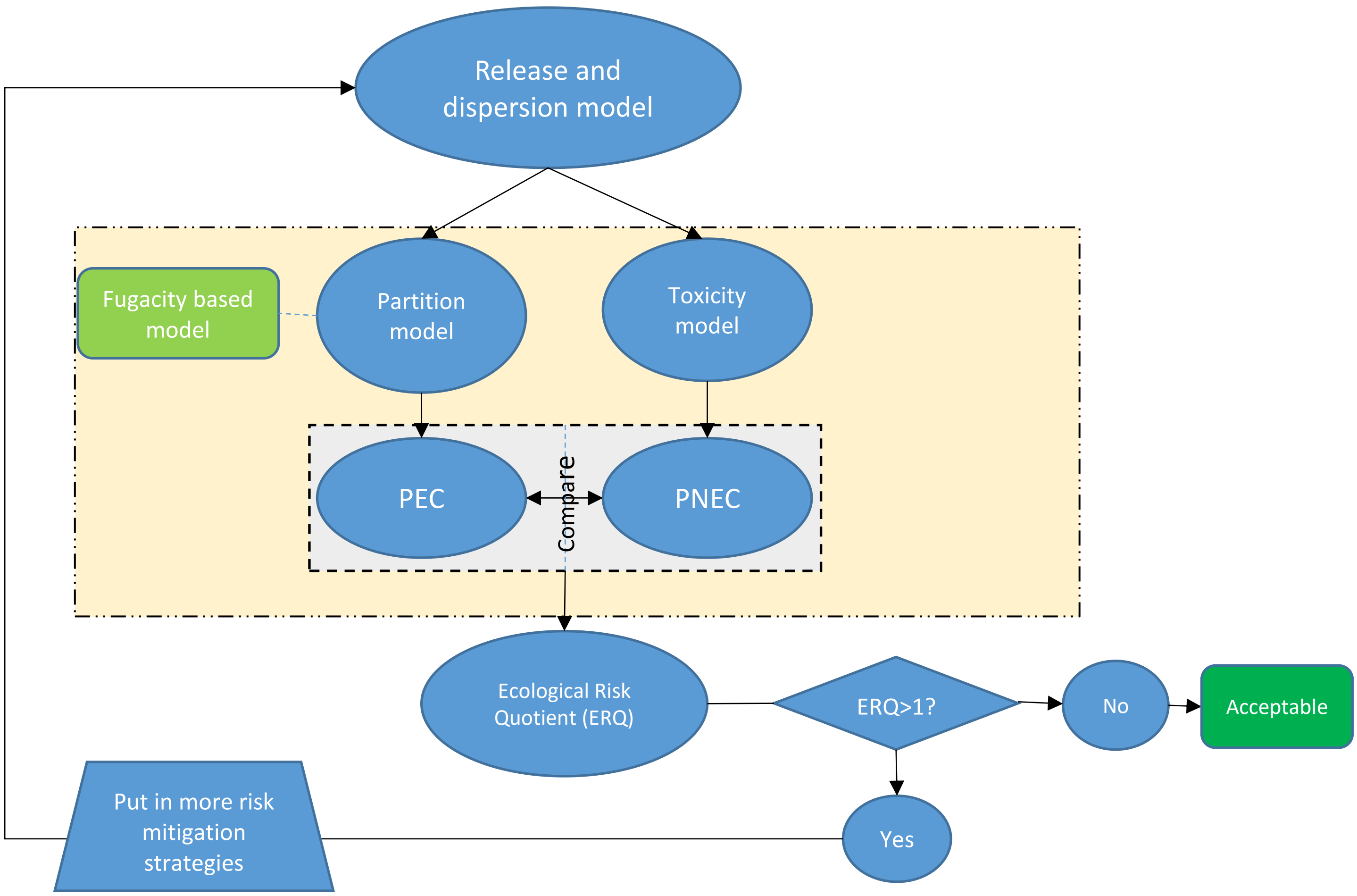

Figure 32: The proposed methodology for assessing the ecological risk after an accidental release during shipping in the Arctic

The details of each component and steps of the proposed methodology are described from sections 2.1 to 2.3.

4.2.1 Fate and transport

In this chapter, the fate and transport model is represented by a dispersion model and a probabilistic based fugacity model. The focus of the fugacity model is to predict the concentration of the pollutant (oil) in different media. The models that critically examine the prediction of the physiochemical properties of the pollutants are discussed elsewhere in Afenyo et al. (2016b), Afenyo et al. (2016c), Korotenko et al. (2013), Lehr, (2001), Nazir et al. (2008), Yang et al. (2015).

Mathematically, fugacity has a relationship with concentration (Mackay, 2001), which is described in Equation 58.

In Afenyo et al. (2016b), the processes and the different media involved when an accidental oil release occurs in the Arctic are presented. Readers may consult the publication. Together, these are used in the formulation of mass balance equations for each media. The equation for each media is solved simultaneously for fugacities. These fugacities are then converted into concentrations by applying Equation 58.

In order to convert the concentration obtained by Equation 58 to a Predicted Exposure concentration, Equation 68 is used.

$$PEC = P_r \times C \times BAF \tag{68}$$

Where P_r is the exposure probability, calculated using Equation 69, C is the concentration obtained from Equation 58, and BAF is the bioavailable fraction, which is dependent on the log K_{ow} of the pollutant under investigation.

$$P_r = \frac{Impact\ area}{Total\ area\ under\ study} \tag{69}$$

With the exposure concentration calculated in the probabilistic form, the 95th percentile exposure concentrations are taken as the values that are representative of the various compartments.

4.2.2 Dispersion model

The causes of an accidental release of oil range from a rupture of a marine riser to a hole in a ship's hull. Relations exist for modeling the release and are referred to as source models. They are not the focus of this chapter. They are described briefly here to show how they can be linked to the dispersion model in the proposed methodology. The likely amount of oil spilled can be obtained from the release model if the necessary parameters are known (Crowl, and Louvar, 2011). Most often, responders and contingency planners only have the information on the amount of oil released (Korotenko et al., 2013).

Results obtained from these models are estimates. This is because the physical properties may not be characterized fully and sometimes it may be that these processes are not adequately understood. Crowl and Louvar (2011) describe the different types of release models. These models are used in estimating the mass flow rate, which can be used to calculate the mass of oil released given the appropriate parameters, such as the dimensions of the hole and the vessel carrying the fluid, pressure on the surface of the fluid, the height of the crude oil above the hole where the release is taking place, the duration of the spill, and the density of the fluid. The flowrate becomes an input to the dispersion model.

A vessel going through the Arctic may be involved in an accident, which may result in an instantaneous or continuous release of oil into the water column (Afenyo et al., 2016a; Afenyo et al., 2016b; Afenyo et al., 2016c). This chapter focuses on an instantaneous release. Readers may consult Hemond and Fechner (2015) and Logan (2012) for analysis of continuous release. The released plume is regulated by dispersion-advection phenomena as illustrated by Figure 33. Dispersion models describe the movement of oil plumes some distance away from the release point in time and space (Logan, 2012). This follows the dispersion-advection equation which can be referred to in Hemond and Fechner (2015) and Logan (2012). In Equation 70, a simplified version which ignores boundary effect is presented.

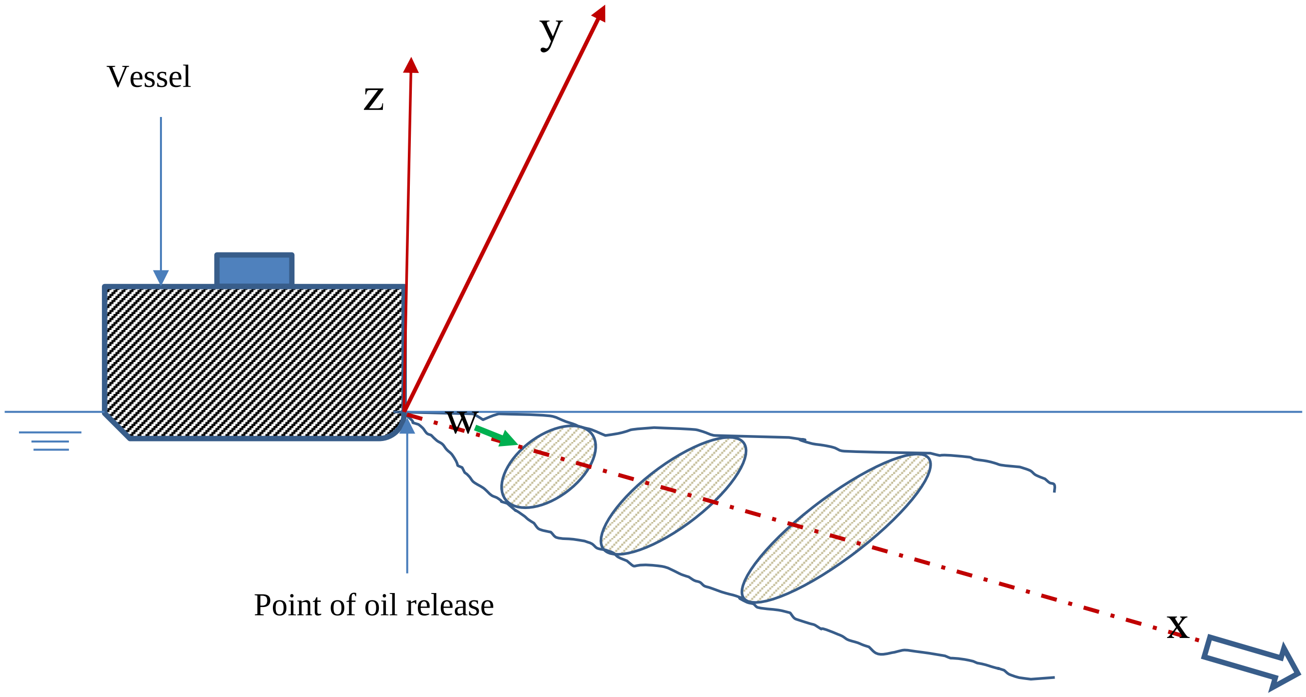

Figure 33: Dispersion-advection transport of oil after a leakage from a ship

$$C(r,t,x,y,z)=K\,\frac{exp\left[\frac{-(x-wt)^2}{4D_xt}\right]}{\sqrt{4\pi D_xt}}\,\frac{exp\left[\frac{-(y)^2}{4D_yt}\right]}{\sqrt{4\pi D_yt}}\,\frac{exp\left[\frac{-(z)^2}{4D_zt}\right]}{\sqrt{4\pi D_zt}} \qquad (70)$$

where K is the amount released per area, and w is the wind speed.

For an accidental release of oil, assuming that the released oil is uniformly distributed in the water column and no degradation occurs, Equation 70 is converted into Equation 71 for transport along the x-axis (Fjeld et al., 2007;Hemond and Fechner 2015; Logan 2012).

$$C(r,t,x)=K\,\frac{exp\left[\frac{-(x-wt)^2}{4D_xt}\right]}{A\sqrt{4\pi D_xt}} \qquad (71)$$

Equations 70 and 71 show a decrease in concentration from the point of release. They are used for predicting the concentration of the pollutant (oil) at different points and times (Hemond and Fechner 2015).

4.2.3 Uncertainty analysis

Uncertainty analysis is essential for describing the lack of knowledge inherent in a model and its parameters (Coleman and Steele, 2009; Uusitalo et al., 2015). Different forms of uncertainties exist and include the following: parameter uncertainty, model uncertainty, dependency uncertainty (Burgman, 2005). It should be noted that different authors classify uncertainties in different ways but the literature generally agree on two main forms. These are the aleatory and the epistemic uncertainty. Aleatory uncertainty refers to uncertainties that result from the random occurrence of a scenario, while epistemic uncertainty refers to the uncertainty about the lack of knowledge about the process (Coleman and Steele, 2009). The main uncertainty addressed in this chapter through the methodology is data uncertainty, an important form of epistemic uncertainty. Model uncertainty, which seeks to address deficiency in the model's structure (Uusitalo et al., 2015), is not addressed in this chapter. Figure 34 shows the schematic of the approach for addressing the uncertainties in the fugacity model input parameters. The approach adopted for addressing uncertainties is the Monte Carlo Simulation (MCS). MCS is chosen because it is flexible, easy to use and does not suffer from multidimensionality and non-linearity (Zio and Pedroni, 2013).

The exposure model has an output that is a function of $Q = f(X_1, X_{2,} X_3 \ldots . X_j \ldots . . X_k)$ of *k* variables with uncertainties, where $X_j, j \in \{1,2 \ldots \ldots . k\}$.

This condition allows for the use of MCS. The process involves sampling randomly, $X_j, j = 1,2,3, \ldots\ldots k$ and subsequently calculating the function $Q = f\left(X_1, X_{2,} X_3 \ldots . X_j \ldots \ldots X_k\right)$ for each value of the sampled variables. The final output is a cumulative distribution of the concentration in different media of contact.

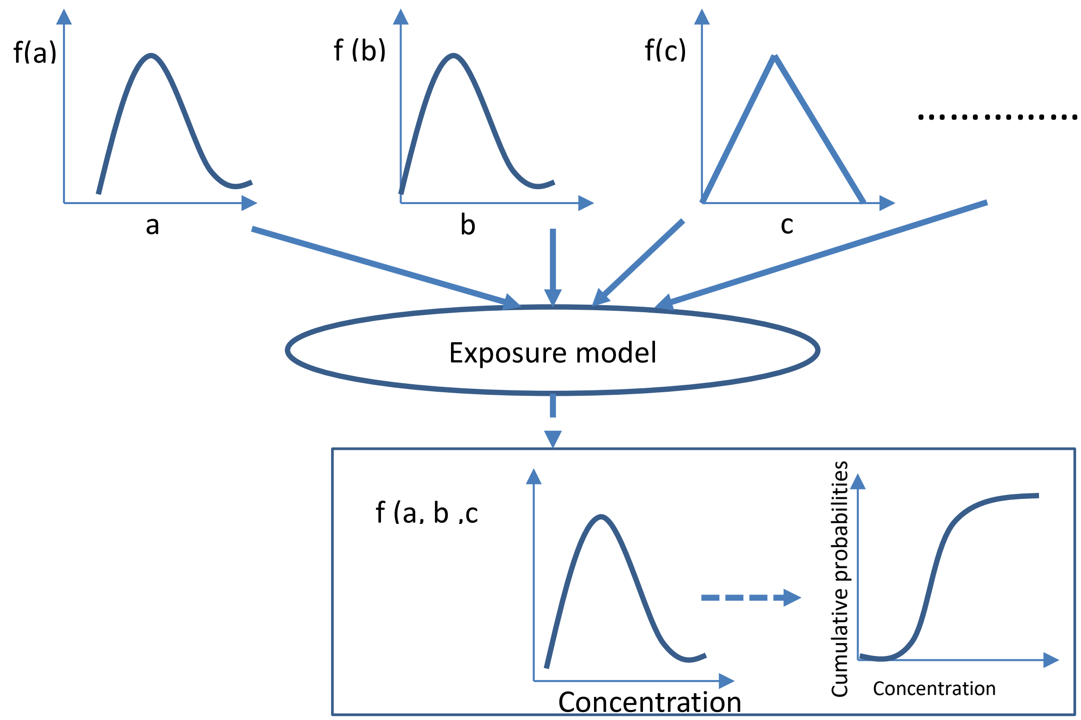

Figure 34: The schematic of how the uncertainties are addressed in the exposure model.

4.3 Application of the methodology

In order to analyze a potential scenario, a surrogate is used for oil (naphthalene) which has its physiochemical properties shown in Table 16. The bioavailability is also taken to be 1, since naphthalene has a log K_{ow} less than 5.

Dispersion modeling is implemented using the Equation 71 and the fugacity model is used to estimate the exposure concentration. The Tables 17 to 19 show input parameters and their corresponding distributions, and relations for the calculation of Z and D values. Equations 72, 73, 74, and 75 are the mass balance equations for air, ice, water and sediment compartments respectively.

$$I_a + D_{(b-a)}f_b - (D_{(a-b)} + D_{(a-advection)} + D_{(a-reaction)})f_a = 0 \quad (72)$$

$$I_b + D_{(a-b)}f_a - D_{(c-b)}f_c - (D_{(b-a)} + D_{(b-advection)} + D_{(b-reaction)}f_b = 0 \quad (73)$$

$$I_c + D_{(b-c)}f_b - D_{(d-c)}f_d - (D_{(c-b)} + D_{(c-d)} + D_{(c-advection)} + D_{(c-reaction)}f_c = 0$$
(74)

$$I_d + D_{(c-d)}f_c - (D_{(d-c)} + D_{(d-c)resp)} + D_{d-bur} + D_{(d-reaction)}f_d = 0 \quad (75)$$

where $a, b, c,$ and d are the compartments of air, ice, water, and sediments respectively. I_a, I_b, I_c, I_d are the emissions in air, ice, water and sediments respectively, and $f_a,\ f_b, f_c, f_d$ are the fugacities of air, ice, water and sediment compartments respectively. D represents the transfer parameters for different processes involved during an accidental release in the Arctic marine waters.

Equations 72 to 74 are solved simultaneously to obtain the individual fugacities of each compartment. Equation 58 is applied to the fugacities to obtain the concentrations. With the concentrations known, they are transformed through Equations 68 and 69 for use as the predicted exposure concentration. This simulation is done in a probabilistic mode using the Monte Carlo Simulation as described earlier. The results are represented in the cumulative distribution format. An advantage of using probabilistic distributions is to provide flexibility in representing exposure concentration as well as the RQ. For the purpose of this chapter, the focus will be on the concentration in the water column, which is subsequently compared with a PNEC of marine water. The $PEC_{95\%}$ is obtained from cumulative distribution graph generated and compared with the Predicted No Effect

Concentration $(PNEC_{5\%})$, which is taken from a study conducted by Anon. (2007). The $(PNEC_{5\%})$ for naphthalene in marine water as reported by Anon. (2007) is 0.002 ppm. Equation 76 is used to calculate the Risk Quotient (RQ).

$$RQ = \frac{PEC_{95\%}}{PNEC_{5\%}} \tag{76}$$

The RQ is also represented in a cumulative distribution form and the 5th percentile of risk quotient is selected with the goal of protecting 95 percent of the Arctic marine species in the potential area under study. The next section describes a case study to illustrate the model.

4.3.1 Case study

In this section, a case study is presented with the aim of illustrating the proposed methodology. The setting of the case is taken from Miquel (2001) in his study on the Kara Sea. The Figure 35 is the map showing the Kara Sea and where the scenario is set. The coordinates of the Kara Sea are 75.1043° N, and 73.1950° E. This site has been chosen to draw readers' attention to a potential area of an oil spill. The quantities used are for the purpose of illustrating the methodology.

Figure 35: Setting of the scenario for analysis. Picture courtesy google map

An oil tanker going through the Arctic Ocean, north of the west Siberial lowlands, is involved in an accident. The vessel collides with another vessel due to poor visibility. This results in the release of approximately 11500 kg of oil. The area involved has an average depth of approximately 200m. The body of water is approximately $300 \times 10000\ m^2$ while the area affected by the oil spill is $1000m^2$. This part of the sea collects water from seven different rivers. This affects the temperature change, especially in the summer during ice melt. The surface of that part of the water body is covered with ice during significant periods of the year. Average water temperature during the summer is between 0 to 9 °C while in the winter it is -1.8 to -1.2°C. The average wind speed of the area is $7\,\frac{m}{s}$ and the water body has longitudinal diffusion coefficient of $5400000\,\frac{m^2}{s}$. The proposed methodology is used to analyse this case as a typical scenario in winter.

The steps described in the previous section on application of methodology is followed in this analysis. @risk 7 software, academic version from Palisade Corporation, is used to complete this work.

4.4 Results and Discussions

Figure 36 shows the results of dispersion modelling. Figures 37 and 38 show the profile of the exposure concentrations in water and sediment compartments. These have been chosen mainly for the purpose of illustration. The values of the $PEC_{95\%}$ are shown in Table 21. The RQ profile for the water compartment is shown in Figure 39.

Figure 36 shows that the highest concentrations of the pollutants are between $0.02ppm$ and $0.03ppm$. This level is comparable with results obtain from Anon. (2002), where a value of 0.07 ppm and 0.13 ppm were reported for the Argo merchant and Amoco Cadiz accidents. It should be noted that the concentrations are site specific dependent and results may vary based on different depths and environmental conditions. The highest range of concentration is localized near the point of release. Such an observation means that in the case of an accidental release, the most damage is likely to occur immediately, at the point of release up to short distances away from this point. This is important information for responders, because, the faster the response, the less negative impact the pollutant may have on the eco-system. Species around this area are likely to be affected negatively. The level of concentration that is tolerable for species varies. Some species may still face risks to a certain distance from the point of origin depending on their tolerance level. This conclusion is made based on the assumption that the species are evenly distributed all across the region used for the study. In reality this might not be the case. The white portion in the plume is not for lack of release but as a result of the initial values chosen for the simmulation. The effect of the plume starts from the red region.

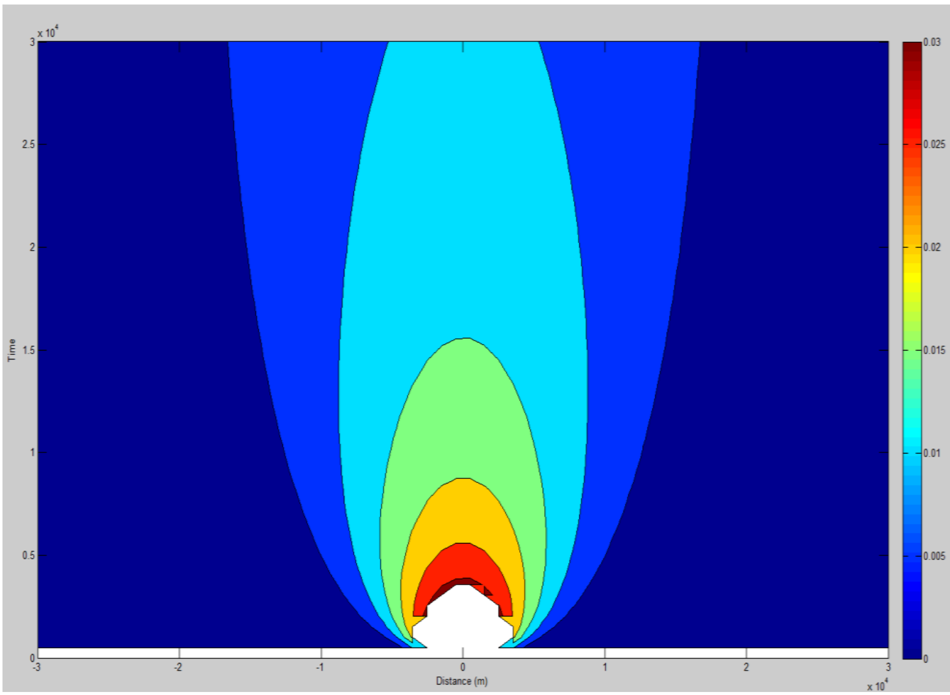

Figure 36: Concentration profile of spilled oil in time and space.

In Table 21, we see the ranking of the most polluted to the least polluted compartment is: sediment, water, ice and air. This is similar to observations in Yang et al. (2015) and Mackay (2001). In reality this might be different taking into account the effect of waves and currents and ambient temperature. The fugacities of these compartments also show that the reverse order is true. That is, the escaping tendency of the pollutant in air is higher compared to the other compartments. This means that the escape of pollutants in the sediment compartment is more likely to be delayed.

In Figures 37 and 38, the cumulative distribution of the exposure concentration in the water column and the sediment column, respectively, with a 90 percent certainty is shown. The median exposure concentration in the water and in the sediments are $3.6 \times 10^{-4}\ ppm$ and $4.2 \times 10^{-3}\ ppm$ respectively. The values, gives us an idea of the level of pollution in different media.These values cannot be used to make decisions unless they are compared to some standard value. The predicted values are comparable with experimental results of intentional spill reported by Brussaard et al. (2016). The study reported a naphatelene concentration in the water between $3 \times 10^{-4}\ ppm$ and $7.2 \times 10^{-4}\ ppm$ after an intentional release during an oil spill experiment. The results for the other compartments were not reported and so a comparison cannot be made. It should be noted that predicted concentrations are comparable to that in Brussaard et al. (2016) in terms of the order of magnitude but it is required to carry more study for further validation. Further the RQ which is the ultimate goal of this study compares the predicted concentration to the PNEC. No other current standard value for naphthalene exist for the Arctic. More research is needed to develop such a value.

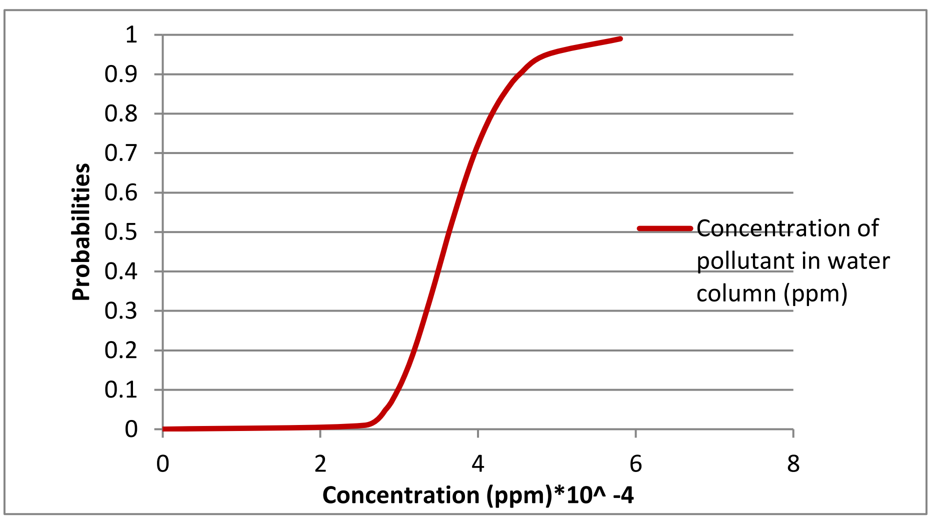

Figure 37: The cumulative distribution function for the exposure concentration in the water column.

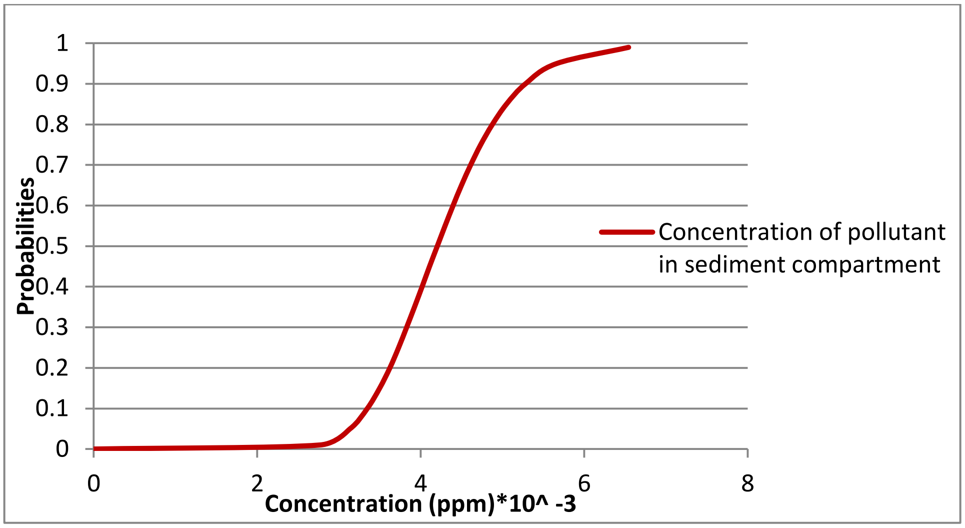

Figure 38: The cumulative distribution function for the exposure concentration in the sediment column

In Figure 39, the 95th and 5th percentile risk quotients are approximately 2.5×10^{-1} and 1.4×10^{-1} respectively. Figure 39 further shows that at 0.99 probability, the risk quotient would not exceed 1. This means that there is no chance of the risk exceeding 1. This makes the risk acceptable for the water column with respect to this particular scenario and indicates that the exposure concentration of the pollutant is acceptable in terms of the likelihood of adverse effects to the ecosystem. If the risk indicates the opposite, mitigation measures need to be put in place to lower the concentration of the pollutant.

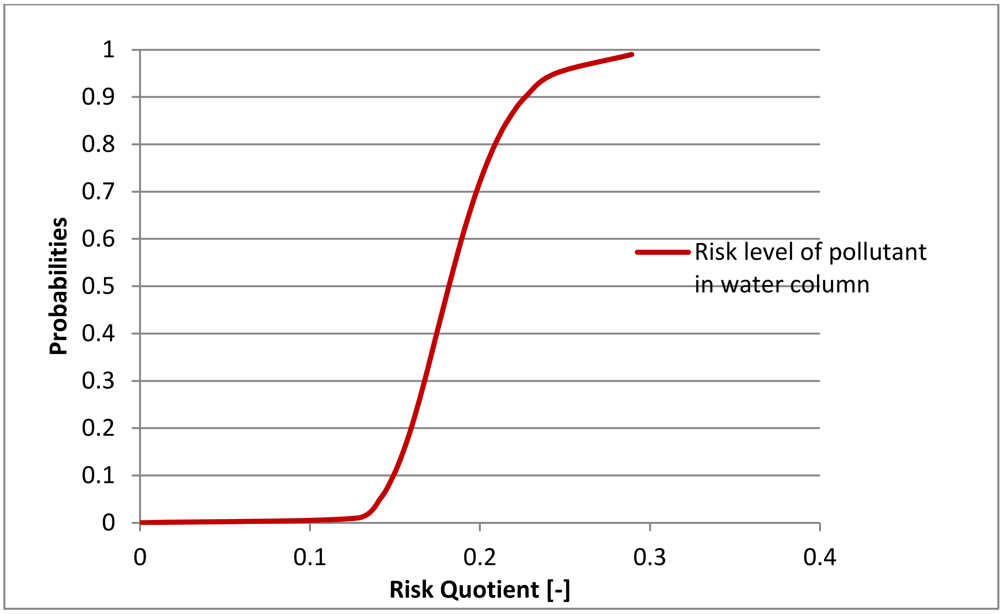

Figure 39: RQ profile in the form of cumulative distribution function of the pollutant under study.

While the current study does not aim to claim accuracy of quantities, it is hoped that it will provide a good tool for contingency planning for oil spill in waters where navigation is only beginning. Such waters are usually in environments where an accident has yet to occur. This means that in such regions, data is scarce and there are many unknowns. The Arctic is one such region. Testing effective response techniques and equipment for a terrain like the Arctic is still on going. Response efforts in such a terrain is made more difficult and complex by the limited infrastructure. It means institutions responsible for mitigating spills in such regions may not be totally equipped should there be an accident. This also means the species are likely to be at risk. This methodology can be used as a first step when making decisions on preparing for an oil spill in such regions.

4.5 Summary

This chapter proposes a model to analyze the ecological risk posed to Arctic marine ecosystems after an accidental oil release during Arctic shipping. The proposed model utilizes dispersion modelling, exposure assessment, and the results of ecotoxicological models to predict the risk profile of the pollutant. Since crude oil has a varying and complex composition, a surrogate (naphthalene) is used in the analysis. This approach allows for future modifications to different individual models that could be used, since dispersion modelling, and exposure assessment of pollutants in ice-covered waters are still evolving.

The risk profile produced by the proposed model provides information on the variability of risk quotient at different probabilities. The criterion used in this chapter is to evaluate if the risk is below or above 1. A risk quotient above 1 indicates that some actions need to be taken to reduce the concentration.

The methodology is probabilistic based, implying that some level of uncertainty is addressed. This is done through the use of distributions as input variables for the exposure model. Though this does not address all the uncertainties propagated in the model, and subsequently the result, it is a first step towards addressing such uncertainties. A Bayesian approach could be used to address some of the other forms of uncertainty that the frequentist approach adopted in this chapter may not have addressed. Bayesian approach might address the dynamic nature of the Arctic ecosystem as the method allows for the updating of information when data becomes available. This could be an area to explore in future research work.

There are still challenges to conducting a comprehensive ecological risk assessment for an accidental release during shipping in the Arctic. A lack of data remains one of the major challenges. Increased research in this area will be helpful to bridge the knowledge gap. The dispersion model also needs to be improved, to account for different ice conditions, which it does not account for at the moment.

More needs to be known about the entities that are in the different compartments, and the LC_{50} values for different Arctic species in those compartments. The dispersion model also shows that, in order to avoid a substantial damage, in the event there is an oil spill, there is need to respond in a timely manner.

By using a surrogate for the pollutant there is a likelihood of under or over evaluating the extent of pollution of the different compartments. There is a potential for the model proposed to be applied to a continous release. This will require the use of the appropriate source models. This is an area that can be explored for future work.

Readiness for an accidental release of oil in the Arctic, mainly from shipping activities, requires an improvement to shipping regulations to reflect the potential risk to the Arctic. A study such as the one presented in this chapter will be helpful in this regard.

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Appendix

Table 15: Physiochemical properties of Naphthalene (after Anon. (2003))

Parameter	**Value**	**Unit**
Molecular weight	0.1282	$\frac{Kg}{mol}$
Octanol-water partition coefficient (Log Kow)	3.70	$Unitless$
Vapor pressure at 298K	10.5	Pa
Melting point	353.15	K
Boiling point	491.15	K

Table 16: Inputs and distributions used for the probabilistic based fugacity model

Parameter	Symbol	Distribution
Gas Constant	R	Uniform
Temperature	T	Uniform
Air side MTC over ice-cover	τ_{va}	Triangular
Ice side MTC	τ_{vi}	Triangular
Aerosol deposition rate	ω_{di}	Normal
Flowrate in air	G_i	Normal
Reaction rate in air	α_a	Normal
Aqueous solubility	C_s	Point
vapor pressure	P_s	Point
Ice surface-air partition coefficient	K_{ia}	Point
Icing rate	ω_i	Normal
Reaction rate in ice	α_b	Triangular
Henry's constant	H	Uniform
Octanol-water partition coefficient	K_{ow}	Uniform
Volume fraction of suspended solids in water	ε_{ssw}	Lognormal
Volume fraction of suspended solids in sediments	ε_{is}	Triangular

Density of solids	ρ_s	Normal
Volume fraction of biota in water	ε_{qw}	Lognormal
Density of biota	ρ_b	Normal
Organic carbon of fraction	Q_{xy}	Lognormal
Melting rate	ω_m	Lognormal
Resuspension rate in water	ω_{rs}	Normal
Deposition rate in water	ω_{ds}	Normal
Advection rate in water	ω_w	Normal
Reaction rate in water	Kw	Normal
Volume of solids	V_s	Normal
organic carbon partition coefficient,	K_{oc}	Lognormal
Pore water in sediment	ε_{sw}	Normal
Water side MTC over sediment	τ_s	Lognormal
Sediment-water effective diffusivity	D_m	Normal
Sediment resuspension rate	ω_{rs}	Normal
Sediment burial rate	ω_{bur}	Normal
Reaction rate in sediment	α_d	Normal
Organic fraction for sediment	θ	Lognormal
Depth of sediment	h_d	Uniform
Volume fraction of water in water compartment	ε_{ww}	Lognormal

V_a,V_b, V_C, V_d are the volumes of air, water and sediments. The relations in Tables 3, 4 and 5 are taken from (Afenyo et al., 2016b; Nazir et al., 2008; Yang et al., 2015)

Table 17: Relations for calculating D-values

Compartment	D-values for	Relation
Air	D(ice-air) diffusion	$\dfrac{1}{\dfrac{1}{(\tau_{va}Z_{a-b}+\tau_{vi}Z_{b-a})}}$
	D(air-ice) diffusion	$\dfrac{1}{\dfrac{1}{(\tau_{va}A_{a-b}Z_{a-b}+\tau_{vi}A_{a-b}Z_{b-a})}}+A_{a-b}U_{di}\varepsilon Z_{a-c}$
	D(advection)	G_aZ_a
	D(reaction)	$\alpha_aV_aZ_a$
Ice	D(air-ice) diffusion	$\dfrac{1}{\dfrac{1}{(\tau_{va}A_{a-b}Z_{a-b}+\tau_{vi}A_{a-b}Z_{b-a})}}+A_{a-b}U_{di}\varepsilon Z_{a-c}$
	D(water-ice)	$A_{c-b}\omega_iZ_{c-c}$
	D(advection)	G_bZ_b
	D(reaction)	$\alpha_bV_bZ_b$
Water	D(ice-water)	$A_{b-c}\omega_mZ_{c-c}$
	D(sed-water)	$\dfrac{1}{\dfrac{1}{(\tau_sA_{c-d}Z_{c-c}+D_mA_{c-d}Z_{c-c}}}+A_{c-d}\omega_{rs}\rho_s\theta K_{oc}$
	D(water-ice)	$A_{c-b}\omega_i\dfrac{K_{ia}}{RT}$
	D(water-sediment)	$\dfrac{1}{\dfrac{1}{(\tau_sA_{c-d}Z_{c-c}+D_mA_{c-d}Z_{c-c}}}+A_{c-d}\omega_{ds}\dfrac{X_{ij}K_{oc}\rho_{ij}}{H}$
	D(advection)	G_cZ_c
	D(reaction)	$\alpha_cV_cZ_c$
	D(water-sediment) Deposition	$\dfrac{1}{(\dfrac{1}{(\tau_sA_{c-d}\dfrac{1}{H}}+\dfrac{0.5h_d}{D_mA_{c-d}\dfrac{1}{H}})}$
	D (Sed-water) diffusion	$\dfrac{1}{\dfrac{1}{(\tau_sA_{c-d}Z_{d-d}+D_mA_{c-d}Z_{d-d}}}+A_{c-d}\omega_{rs}\rho_s\theta K_{oc}$

Sediments	D(sed-burial) D(Advection) D(Reaction)	$A_{c-d}\omega_{bur}Z_{c-d}$ G_dZ_d $\alpha_d \times V_S \times Z_d$

Table 18: Relations used for calculating Z values for the bulk compartments

Compartment	**Simplified relations**
Air	$\frac{1}{RT}$
Ice	$\varepsilon_{ww}\, Z_{b-c} + (\frac{A_{b-c}}{V_b})\, Z_{b-c}$
Water	$Z_{c-b} + \varepsilon_{ssw}Z_{C-C} + \varepsilon_{qw}Z_{C-d}$
Sediment	$\varepsilon_{is}Z_{b-d} + \varepsilon_{sw}Z_{d-c}$

Table 19: Relations for calculating Z values for the sub-compartments

Compartment	Relation
Air	$\frac{1}{RT}$, where $R(\frac{Pam^3}{mol})$ and $T(K)$ are the Gas law constant and the Temperature.
Water	$\frac{1}{H}$ or $\frac{C^s}{P^s}$ where H is the Henry's law constant $(\frac{Pa\, m^3}{mol})$, C^s $(\frac{mol}{m^3})$ and P^s (Pa) are aqueous solubility and vapor pressure respectively.
Solids	$\frac{Q_{xy}K_{oc}\rho_s}{H}$, where Q_{xy} is the organic carbon fraction, K_{oc} organic carbon partition coefficient, ρ_s is the density of solids $(\frac{Kg}{m^3})$
Aerosols	$\frac{6\times10^6}{P_VRT}$, where $P_V(Pa)$is the liquid vapor pressure
Ice-air interface	$\frac{K_{ia}}{RT}$, where K_{ia} is the ice-surface air partition coefficient (m)

Organic carbon in ice-cover ($\boldsymbol{Z_{bc}}$)	$0.41\frac{e^{\frac{InK_{ia}(12.5℃)+19.63-InK_{wa}}{0.68}}}{H}$
Biota	$\frac{0.048\rho_b K_{ow}}{H}$

Table 20: Exposure concentrations in the various compartments

Comaprtment	$(PEC_{95\%})\ (\ ppm)$
AIR	1.6×10^{-7}
ICE	7.2×10^{-6}
WATER	4.9×10^{-4}
SEDIMENT	5.62×10^{-3}

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Chapter 5: Arctic Shipping Accident Scenario Analysis Using Bayesian Network Approach††

5 Background

Increased shipping traffic in the Arctic may result in higher probability of accidents (Davidson et al., 2006; Anon., 2010). Transportation in the Arctic is faced with particular risk factors, including extremely low temperatures and drifting ice (Johansson et al., 2013; Goerlandt and Montewka, 2015). Responses to accidents in the Arctic can be slow because of the remoteness of the region (Jensen, 2007). In the review of Zhang and Thai, (2016), they pointed out that most shipping accidents are mainly low probability-high consequence in nature. It is therefore important to predict the chances of an accident in this region, which can inform countermeasure design to prevent and control such occurrences (Jensen, 2007).

Researchers have dedicated effort to understanding how and why accidents occur. As a result, theories and models of accident causation have been postulated (Katsakiori et al., 2009). Figure 40 shows the evolution and development of accident models over the past decades.

†† *This chapter is taken from the author's paper: Afenyo, M., Khan, F. Veitch, B., and Yang, M. 2017. Arctic shipping accident scenario analysis using Bayesian Network approach. Ocean Engineering. 133:224-230. I led the identification of the problem, performed the modeling and wrote the first manuscript with guidance from my supervisors: Profs. Khan, Veitch and Yang*

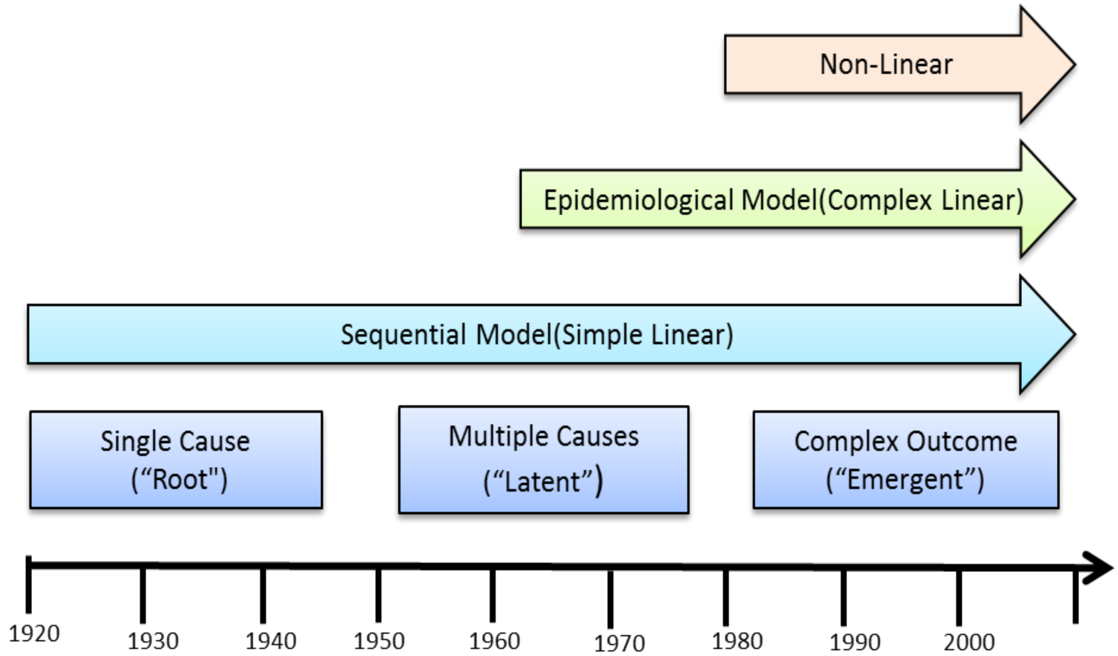

Figure 40: History of accident modeling (after Hollnagel, 2010)

Linear models depict accidents as a domino effect, in which one factor leads to the next factor and subsequently to another until it eventually results in an accident. Complex non-linear models describe accidents as a joint effect of multiple factors acting simultaneously. Epidemiological models consider an accident as the outcome of a combination of factors, some evident and some latent, that exist together in space and time (Anon., 2012). Table 22 summarizes the models that have been used over the recent decades. The importance of Table 22 is to show potential tools available for modeling accidents and how BN, Fault tree, FRAM and other probabilistic modeling tools have been implemented. Other popular models of accident causation include the SHEL (Software-Hardware-Environment-Livewire) Model, the CFAC (Contributing Factors in

Accident Causation) and MORT (Management Oversight and Risk Tree) (Lehto and Salvendy, 1991). While these accident models are detailed, they are complex and take a lot of time to build. As a first step to decision making, simpler, time efficient methodologies are required. The reviewed models also rely extensively on data for success, however in the Arctic there is lack of data.

In the review of Zhang and Thai, (2016), they pointed out that most shipping accidents are mainly low probability-high consequence in nature. This implies that, even though the accidents do not occur often, when they do the consequences are high.

In Friis-Hansen (2000), the possibility of using BN for risk analysis was studied. The outcome of the proposed model was compared to output from an event tree analysis. The proposed tool was applied to a helicopter landing on a cruise ship. In the same study, BN was applied to diagnose misfire and leakage in a marine diesel engine. The study also attempted to combine BN with structural reliability methods, and regression methods for requalifying a pipeline in the North Sea. Another application of BN in maritime operation is by Liwåg (2015), who applied BN to model the operation of Military Ocean Patrol Vessels (OPVs) with consideration of the potential threats during operations. The outcome of this study is essential information for ship design as it incorporated survivability and endurance. These are linked to operational risk. While the main aim of this study was to evaluate operational risk and show how both aleatory and epistemic uncertainty could contribute to the output of such a model, it is a good example of the efficiency of a BN application to a security problem. Priston et al. (2016) also presented a BN based model that seeks to estimate the probability of a ship getting hijacked off the east coast of Africa or off western India. The overall goal of this study was to provide a tool for stakeholders to make economic decisions in the context of ship operation. An elaborate BN for the Maritime Transport System (MTS) was also presented by Trucco et al. (2008). A study by Musharraf et al. (2013) applied a BN to a generic scenario of an offshore emergency evacuation in the context of estimating human error probability. The study shows the effectiveness of BN to estimating such probabilities. This study also shows the different dimension of applicability of the BN. In a study by Weber et al. (2012), the authors presented a review of BN and some notable applications in other industries. Readers may refer to this publication for more on BN and its applications. While these examples are not exhaustive of applications of BN in maritime and other industries, few studies have attempted to forecast accident scenarios from past accident data using BN in Artic marine environments, with the goal of identifying priorities for the allocation of resources for response. This is the focus of the present study.

This study is focused on presenting a methodology that is simple and easy to execute. It is to be used mainly as a first step for envisaging an accident, and making a decision on how to mitigate the potential consequences during shipping in the Arctic.

There are parallels between existing methodologies and the proposed, but this method aims at forecasting possible Arctic shipping accident scenarios from past accident data using a Bayesian Network based methodology. In this methodology, the probabilities can be updated as new information becomes available. Potential contributory factors can be identified and subsequently controlled through the use of relevant safety measures. The use of Bayesian Network provides the flexibility of considering interdependencies and conditionality of factors involved in the envisaged scenarios for Arctic shipping. It also provides the analyst with a tool to represent multivariate state of causal factors compared to binary states in a tool like the Fault tree. The modeler also has the flexibility of using expert elicitation. This is very important when data is scarce as is the case for Arctic shipping. The details of the advantages and the use of Bayesian Network are further elaborated in Zhang and Thai (2016).

Table 21: Accident models and description.

Model	Description
Heinrich Domino model	This model describes an accident as a linear one-by-one progression that occurs in a fixed and logical pattern. The premise here is that human errors cause accidents. The factor preceding the accident (the unsafe act or the mechanical or physical hazard) should receive the most attention (Weaver, 1971; Bird, 1974; Adams, 1976).
Kletz model	This is an accident investigation model. It involves the sequences of decisions and actions that resulted in the accident. It shows against each step, the possible recommendations from investigations (Kletz, 2001).
Swiss Cheese Model	This model describes an accident as the outcome of failures at several stages, a complex combination of unsafe acts by front line operators and latent conditions. The system is depicted as a stack of Swiss cheese. Each slice is a safety barrier and an alignment of the holes in the slice means failure of the system (Reason et al., 2006).
Offshore Occupational Accident Frequency Prediction Model	The idea behind this model is that occupational accidents come from unacceptable interaction between the worker and the working environment. The behavior of workers is influenced by corporate philosophy, workplace environment, and procedures (Attwood et al., 2006).

Human and Organizational Factor (HOF'S) model	This model is based on the idea that the cause of an accident is a result of a chain of errors. An individual error may not be sufficient to cause severe impact unless it is through a combination of multiple latent errors. The focus of this methodology is the demonstration of how root cause, trigger event, incident, accident, and consequence levels are logically related (Ren et al., 2008).
Loss Causation Model	This model is organized in such a way that it establishes a hierarchy of events relative to their respective precursor conditions. The analysis starts with the harm caused to a person and then goes back through a series of processes that resulted in the loss. A failure at any point in the model will result in the progression of loss (Kujath et al., 2010).
SHIPPS Model	The goal of the SHIPP methodology is to detect hazards, assess them, forecast, avert their occurrences, and continue monitoring the occurrences. The model relies on process history, accident precursor information, and accident causation modeling. A notable capacity of this methodology is its use to assess the risk of an entire process system and sub-systems. It is also a good tool for identifying the system's concealed interactions and their effects (Rathnayaka et al., 2011).
Functional Resonance	This is a complex non-linear model. It describes the non-sequential nature of accidents. It has been applied, for example in the aviation industry (Hollnagel, 2004).

Accident Model (FRAM)

5.1 Bayesian Network

In Friis-Hansen (2000), the use of BN for risk analysis was studied. The outcome of the proposed model was compared to the output from an Event Tree analysis. The proposed tool was applied to a helicopter landing on a cruise ship. In the same study, BN was applied to diagnose misfire and leakage in a marine diesel engine. The study also attempted to combine BN with structural reliability methods, and regression methods for requalifying a pipeline in the North Sea. Another application of BN in maritime operation was made by Liwåg (2015), who applied BN to model the operation of Military Ocean Patrol Vessels with consideration of the potential threats during operations. The outcome of the study was information for ship design to enhance survivability and endurance. While the main aim of the study was to evaluate operational risk and show how both aleatory and epistemic uncertainty contribute to the output of such a model, it is a good example of the efficiency of a BN application to a security problem. Priston et al. (2016) also presented a BN based model that sought to estimate the probability of a ship getting hijacked off the east coast of Africa or off western India. The overall goal of this study was to provide a tool for stakeholders to make economic decisions in the context of ship operation. An elaborate BN for the Maritime Transport System (MTS) was also presented by Trucco et al. (2008). A study by Musharraf et al. (2013) applied a BN to a generic scenario of an offshore emergency evacuation in the context of estimating human error probability. The study shows the effectiveness of BN for estimating such probabilities. In a study by Weber et al. (2012), the authors presented a review of BN and some notable applications in other industries, to which the interested reader may refer. The focus of the present study is using BN to forecast Arctic shipping accident scenario's based on past accident data. The goal of this approach is to enable identification of priorities for allocation of resources for response and mitigation.

The proposed method in this chapter, discussed later in section 3, is used mainly to forecast accident scenarios from past accident data. The advantages of making the method Bayesian based is discussed in the context of the advantages the BN has over tools like the Fault Tree and the Event Tree.

The Bayesian Network (BN) is a probabilistic graphical based network, mainly for describing knowledge uncertainty (Martin et al., 2009; Jensen et al., 2009; Ben-Gal, 2007). BN follows a Direct Acyclic Graph (DAG) structure and is made up of nodes and edges (arrows). The node is representative of random variables while the edges are the probabilistic relationships between these variables. The relationships in the BN describes dependency among the variables. In its simplest form, it is represented as two nodes which depict the random variables. These nodes are connected by directed edges. A line from Y_i to Y_j depicts dependence between the two variables. A simple interpretation of this connection is that the variable Y_i has an impact on Y_j. Y_j is called the child of Y_i. Y_i is the parent of Y_j.

The DAG is basically the qualitative description of the BN. The quantitative relationship is described using the conditional probability table (CPT) for discrete random variables. The basis of the Bayesian network is the Bayes theory, which is expressed as:

$$P(A|E) = \frac{P(E|A)P(A)}{P(E)} \tag{77}$$

where $P(A|E)$ is referred to as the posterior, thus how likely *A* is, given an evidence of *E*, $P(E|A)$ is the likelihood which represents how likely the evidence is true, $P(A)$ is the probability of *A* before observing the evidence *E*, and $P(E)$ is the normalisation factor (Zhang and Thai 2016).

To describe this mathematically, a BN, designated as *B* here, can be defined as a DAG that depicts a joint probability distribution (JPD), over the variables *V*. *B* is defined by the pair $\langle G, \Theta \rangle$. *G* is the DAG with nodes $Y_1, Y_2 \ldots \ldots \ldots \ldots . Y_n$ with the edges representing the dependency between the variables. Θ describes the set of parameters of the network. The set is made up of the parameter $\theta_{(Y_i|\pi_i)} = P_B(Y_i|\pi_i)$, that is for realising each of y_i of Y_i conditioned on π_i, which are the parameters of Y_i in G. Therefore *B* defines a special Joint Probability Distribution (JPD) over *V* (Ben-Gal, 2007). This relationship is shown as Equation 78.

$$P_B(Y_1, Y_2 \ldots \ldots \ldots \ldots . Y_n) = \prod_{i=1}^{n} P_B(Y_i|\pi_i) = \prod_{i=1}^{n} \theta_{(Y_i|\pi_i)} \tag{78}$$

Detailed principles of BN are explained in Jensen (1996), Pearl (1988) and Zhang and Thai (2016). Uncertainties exist in the use of BN to model scenarios. This may be in the form of the probabilities used, including those derived from expert opinions. Epistemic uncertainties are often addressed using probability density functions instead of using discrete probability values. Taylor series and Monte-Carlo simulation are some of the tools used to address uncertainties in BN based models (Liwåg, 2015). As Liwåg (2015) observed, the most effective way to identify the most important parameters in a BN based model is to perform a sensitivity analysis. This is one of the main objectives of the present study: to identify the most important factors in an accident scenario. While different approaches exist for doing this, the one adopted here is mainly to monitor the change in parameter before and after setting the top event to 100%. Details of this approach are presented in 3.5.1. While tools like the Fault Tree have the capability of allowing sensitivity analysis, the advantages of BN over traditional modeling tools makes it a better choice.

5.2 Proposed approach for Arctic shipping accident scenario modeling

Maritime transport is complex, and different factors are responsible for the causes of accidents. These factors include the state of the weather, selection of route, training of personnel, use of equipment, the specification of the vessel, and human factors (Zhang and Thai, 2016). In the Arctic, similar factors are likely to be responsible for the occurrence of accidents, in addition to the factors related to the presence of ice. Figure 41 represents the framework of the proposed methodology and the procedure is described from Sections 3.1 to 3.5.

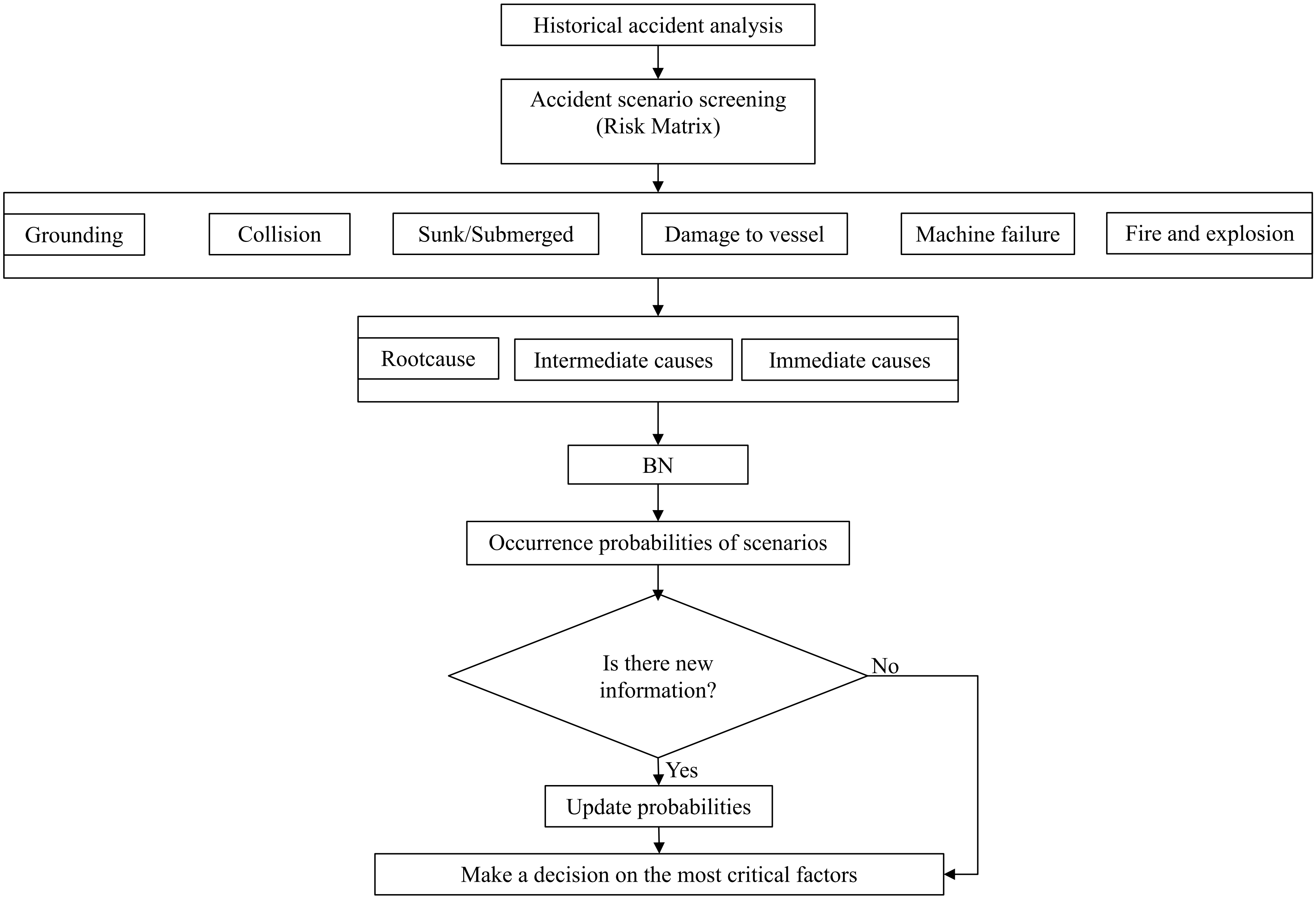

Figure 41: The proposed methodology.

5.2.1 Characterize possible accidents from historical data and literature

This step involves the analysis of past accident data. The goal is to categorise accidents into different groups for analysis. ArcticData (http://arcticdata.is/) is the main source of data used in this chapter. The information from ArcticData and other sources indicate that most shipping accidents are categorized as collision, grounding, fire and explosion, sunk and submerged, and damage to vessel.

5.2.2 Screen accidents using risk matrix

This is a qualitative approach used to highlight the most critical accident scenarios to be considered. The accident data for each category identified in 3.1 are screened and characterized. This is done by ranking them according to a risk matrix (see Figure 42). The matrix is constructed using Equation 79. Equation 79 calculates the risk for each scenario under consideration. The matrix can be customized to suit any industry or data available. The criteria used for the ranking are shown in Tables 23 and 24.

S/F	1	2	3	4	5
1	1	2	3	4	5
2	2	4	6	8	10
3	3	6	9	12	15
4	4	8	12	16	20
5	5	10	15	20	25

Figure 42: Ranking matrix

$$\text{Risk} = \text{Frequency} \times \text{Severity} \tag{79}$$

where S is the severity and F is the frequency

Table 22: Frequency of accident occurrence

Value	Description
1	Never occurred within the time frame for which accidents are considered (9 years).
2	Occurred once within the time frame for which accidents are considered (9 years).
3	Occurred in every 3 years within the time frame for which accidents are considered (9 years).
4	Occurred each year within the time frame for which accidents are considered (9 years).
5	Occurred once every month within the time frame for which accidents are considered (9 years).

Table 23: Severity of accident.

Value	Degree of severity
1	Minor vessel damage (e.g. scratch) recorded within a month after the accident occurred with a total damage amounting to less than $10000.
2	Extensive damage to the vessel, machinery, and other accessories amounting to more than $10000 within a week after the accident.
3	Minor injuries to humans within a month after the accident.
4	Life threatening injury to at least one person within a month of the accident.
5	Death of at least one person within the first three weeks after the accident.

Table 23 illustrates the criteria for the frequency. It ranges from 1 to 5, where1 means the accident never occurred over the entire period the data is being analysed which is 9 years in this case, and 5 means the accident occurred once every month on average over the period. Table 24 is the criteria for the severity. It ranges from 1 to 5. For example minor vessel damage (e.g. scratch) recorded within a month after accident occurred, with a total damage amounting to less than $10000 is recorded as 1, and 5 at least death of one person within the first three weeks after the accident.

Table 25 is the criteria for ranking. A risk above 5 is considered a critical event that requires consideration. Scenarios with risk values from 1 to 4 are not considered for the next stage of analysis.

Table 24: Ranking Criteria for the accidents

$R \geq 13$	High critical accident scenarios when people die and property is irreparable.
$5 \leq R < 13$	Critical accident scenarios that can result in serious injuries and big damages to the property.
$1 \leq R \leq 4$	Accident scenarios that are not severe to people or property.

For instance, on November 1, 1995, on the Newfoundland-Labrador Shelf, a tug sunk killing 3 people. Only 1 of the 4 crewmen were rescued. This accident is ranked 5 in terms of severity and 2 in terms of frequency per the criteria in Tables 23 and 24. This gives a risk of 10, falling into the critical range: $5 \leq R < 13$ (see Figure 42 and Table 25). Another incident occurred on January 19, 1995 involving the grounding of a general cargo ship in the East Bearing Sea. It resulted in an 8 inch puncture at the bottom of the ship. It was repaired and the vessel returned to service the same day. The severity rank here is 2 and frequency 3 giving a risk of 6. The risk here again falls within the $5 \leq R < 13$ range, which indicates that the accident scenario is critical and may result in injury and extensive damage to property. It should be noted that these accident scenarios are located in the ArcticData database (Anon. n.d). Readers may consult the database for details of the accident. It is voluminous and is not included in this chapter.

5.2.3 Categorize potential failure factors and decide which categories to model

This step is similar to the hazard identification in the risk assessment framework. It aims to identify the potential contributing factors to each scenario for be analysed. Similar to studies conducted by Trbojevic and Carr (2000), the exercise also avoids multiple analysis of similar scenarios. The identified scenarios are reviewed and the failure factors are categorized and prioritized. A decision is made to select the most important contributory factors for each scenario identified. For example, grounding of a vessel is considered the outcome related to navigation error and ship manoeuvring in bad weather. Therefore, navigation error, maneuvering, and bad weather become factors to consider for a grounding scenario. As a guide for the criterion of selection, critical questions to consider while undertaking this exercise for the scenario selected are: i) which factors present the most threat for Arctic shipping, and ii) how often do they occur? These factors are further grouped into root cause, intermediate, and immediate cause factors for a better understanding of the hierarchy of contributing factors to a particular scenario.

5.2.4. Establish BN model

The purpose of this step is to obtain the probabilities of the scenarios under study. Each node of the network has two states: A "yes" and "no". "Yes" indicates a state of positive affirmation of cause due to that particular variable, while "no" is a negative indication of cause of a particular variable. These are illustrated in Figure 43 from part of BN for the collision of a vessel against an iceberg using the Hugin Expert 8.0 (Hugin, 2014). It involves the variable storms, fog, iceberg and bad visibility. Figure 43 is presented mainly for illustration purposes and the probabilities are assumed. For example, a state of having a snow storm is 10%, or 0.1, and not having a snow storm is 90%, or 0.9. It should be noted that this is simplified as there could be more states that could be added. The probability of the scenario for collision with an iceberg, which is presented latter, is discussed in the next paragraph.

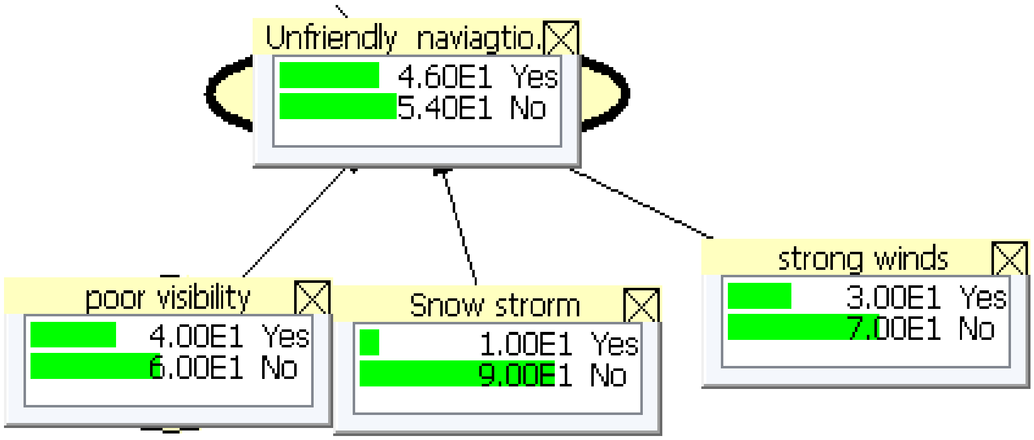

Figure 43: States for the nodes of the BN

In this chapter the prior probabilities are obtained from the literature. The prior probabilities used for the illustration of the scenario are taken from Apostolos et al. (2009), Amrozowicz et al. (1997), and Svein (2005). In Apostolos et al. (2001), the traditional methodology for calculating prior probabilities is used. In their approach, a Fault Tree was constructed and failure probabilities calculated. The Fault Tree is a major source of data for the illustration (Table 26) and Figure 44. Some of the probabilities used in this scenario are for similar events and not necessarily the exact same events. In Amrozowicz et al. (1997), the authors conducted a study of tanker grounding. This was done using the Fault Tree technique and a similar approach was taken as in Apostolos et al. (2009). This is another source of data for Table 26. Svein (2005) also served as a source for some of the prior probabilities. While probabilities obtained from publications are used directly in some cases, in other cases, some assumptions are made where an event does not occur in the three sources. However, the events in these sources serve as a guide to choosing reasonable probabilities for the illustration. The essence of the study is not to claim quantitative accuracy, but to illustrate the proposed methodology and have a qualitative view of how to make decisions in the event of a similar accident.

The BN model for ship collision against an iceberg is shown as Figure 44. Probabilities as well as the result of the sensitivity analysis are shown in Table 26. The main causes of a collision against an iceberg include technical failure during operation and the presence of an iceberg on the course of navigation. The presence of iceberg on the navigation course may also be due to the density of icebergs or the inaccurate prediction of the trajectory of the iceberg. The technical failure that occurs during operation can be attributed to navigational failure, or failure in communication among personnel involved in the voyage, or failure of the vessel's operation system. The causes of navigational failure, operation system failure, and communication failure are further broken down (see Figure 44).

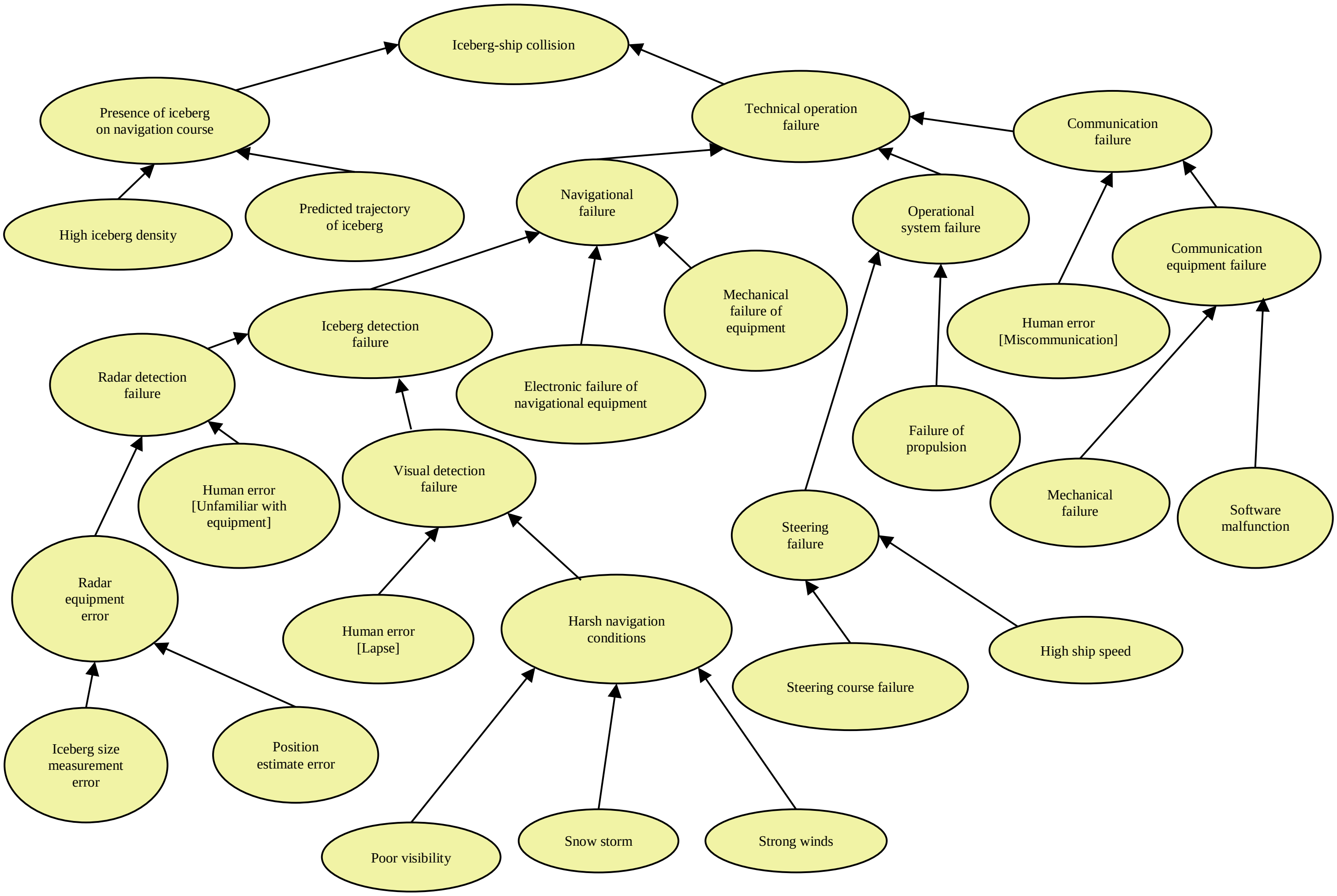

Figure 44: The BN for a collision of a ship with an iceberg.

A sensitivity analysis is conducted on the generic model presented. This is done in the context of identifying the most influential parameters as highlighted earlier. The next section describes the sensitivity analysis and the interpretation of the results. The basis for the calculation of the change ratio is Equation 80.

$$\left(\frac{Value\ after\ setting\ event\ to\ 100\%-Prior\ probability}{Prior\ probability}\right) \qquad (80)$$

Table 25: The prior and percentage changes when the top event is set to 100%.

Parameter	Prior	Change Ratio
High iceberg density	1.00×10^{-2}	9.85×10^{1}
Predicted trajectory of iceberg	1.00×10^{-4}	4.88×10^{1}
Iceberg size measurement error	2.00×10^{-5}	1.16×10^{1}
Position estimate error	8.00×10^{-5}	1.15×10^{1}
Human error [unfamiliar with equipment]	3.00×10^{-4}	1.16×10^{1}
Human error [lapse]	4.00×10^{-4}	5.98×10^{-1}
Poor visibility	7.00×10^{-4}	6.00×10^{-1}
Snow storm	6.00×10^{-4}	5.97×10^{-1}
Strong winds	6.00×10^{-3}	5.97×10^{-1}
Electronic failure of navigational equipment	2.00×10^{-6}	1.50×10^{3}
Mechanical failure of equipment	1.00×10^{-5}	1.50×10^{3}
Steering course failure	6.00×10^{-6}	0.00×10^{0}
High ship speed	1.00×10^{-6}	0.00×10^{0}
Failure of propulsion	1.00×10^{-4}	1.50×10^{3}
Human error [miscommunication]	1.00×10^{-4}	1.50×10^{3}
Mechanical failure	5.00×10^{-5}	1.50×10^{3}
Software malfunction	4.00×10^{-4}	1.50×10^{3}

5.2.5 Make a decision on the most critical factors

This step involves consideration of the most critical factors to the causation of an accident. While there may be more than one factor responsible, sensitivity analysis can inform decision making regarding the allocation of resources. The next section is dedicated to the description of sensitivity analysis and how it is used for decision making.

5.2.5.1 Sensitivity analysis and interpretation of the results

As discussed in the introduction section, as well as in section 2, the sensitivity analysis is performed to identify the most critical variables or factors in a scenario. This is done according to Equation 80. The results of the sensitivity analysis are shown in Figures 45. The probabilities of the most sensitive factors are higher relative to others. Only the most significant changes are shown in Figure 45. There is no guideline with respect to how much percentage change makes a particular factor worth considering. The criterion is subjective, and is guided by the probabilities of the other variables. It is highly dependent on the decision maker and not the analyst. It is therefore important to use this methodology as a first step to decision making and also knowing that it can be customized to suit the scenario that the analyst and decision maker is confronted with. This step is important for choosing the variables for prioritisation during intervention to prevent the occurrence of the scenario. It is also important for reducing the impact of an accident should it occur.

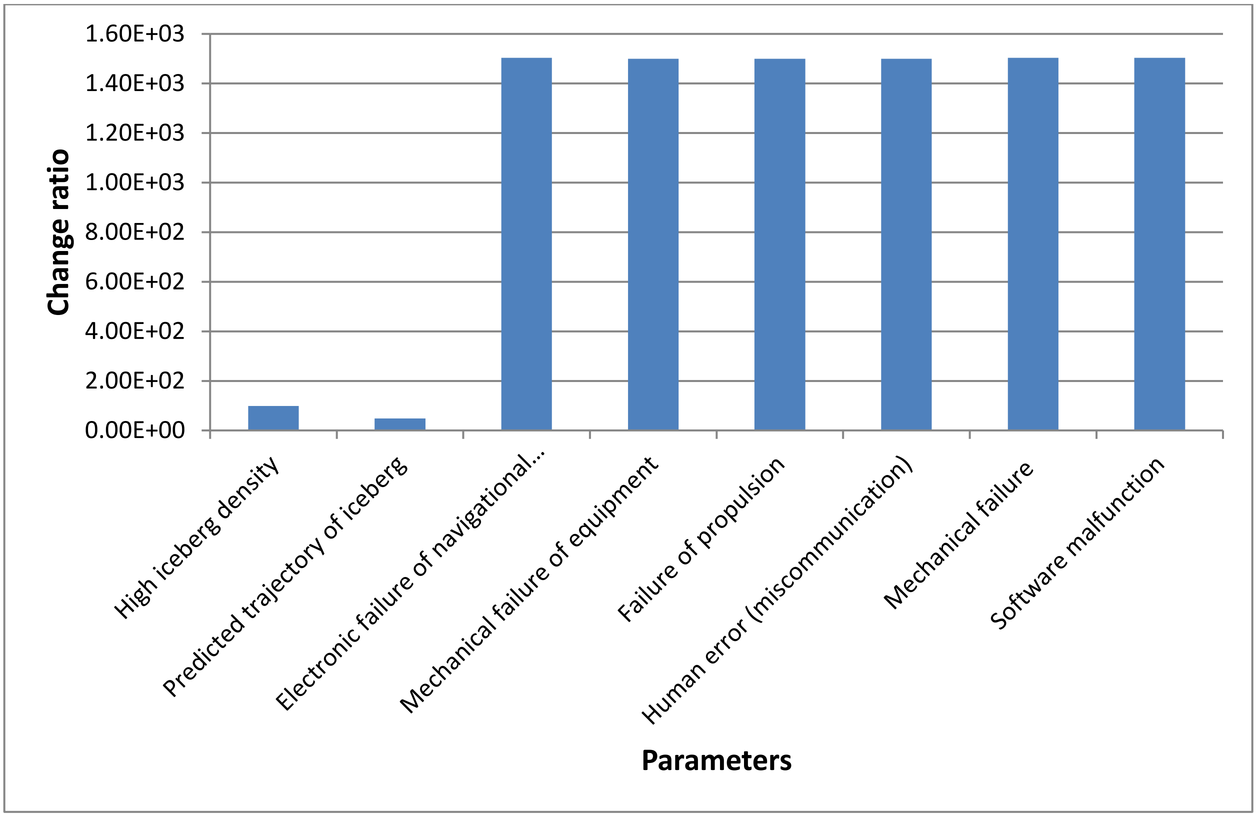

Figure 45: Change ratio of the casual factors of the collision against an ice-berg

5.3 Discussion

The analysis gives the probabilities of a vessel colliding with an iceberg. Figure 45 shows the results of the sensitivity analysis for collision of a vessel with an iceberg.

The variables with significant changes include *electronic failure of navigational equipment, mechanical failure of equipment (Navigational), failure of propulsion, human error (miscommunication), mechanical failure (communication equipment), software malfunction.* It should be noted that it is only coincidence that the last six parameters have almost the same change ratios after approximation. Other variables with minor changes are *high iceberg density, predicted trajectory of iceberg.* These factors are a combination of different causes. For example, the high ice density is an environmental phenomenon, while miscommunication is a human factor. Mechanical failure may occur for a variety of reasons, including lack of maintenance. This means that different scenarios have peculiar dominant factors. It is therefore important to perform similar analysis for each potential scenario. Despite the diversity of the causes, generally doing the following will reduce the probability of occurrence of the accident and hence the associated consequences: i) adherence to navigation rules and proper preparation for bad weather, ii) the use of experienced captains, iii) giving the crew good training on reading navigation instruments, iv) adhering to navigational standards, and v) implementation of redundant design of critical components, as well as a good maintenance of these parts. It should be noted that while these recommendations are general, specific precautions need to be taken to address particular causes of failure. For example in Figure 45, mechanical failure of equipment identified as an important contributor to the collision of the vessel with an iceberg, can be reduced by adhering to a good maintenance culture. The sensitivity of other variables associated with the scenarios are negligible as compared to those presented in Figure 45. Probabilities obtained may not be accurate because of the challenges and uncertainties of estimating the prior probabilities, but it is a first step in making a decision on probable preventive and intervention measures for Arctic shipping. How much change ratio is significant? The answer is subjective and will depend on the decision maker. This is because different decision makers have different needs for particular problems. It will also be constrained by the availability of resources and to some extent by regulations. The actions to be taken for any scenario will also depend on how much premium is placed on safety. As stated earlier, sensitivity analysis remains one of the few methods available to achieve the ultimate objective of this study. It should also be noted that the case presented is a generic one and the model simplified. The states are discrete but a rigorous study may require the collection of more data and account for the complexity of operational scenarios. All the possible uncertainties that are likely to be observed in such a model may be addressed using, for example, Taylor series and Monte-Carlo simulation as proposed by Liwåg (2015).

5.4 Summary

Bayesian network based methodology for the analysis of probable accidents during Arctic shipping has been presented. The use of Bayesian network offers analysts the opportunity to model interdependencies among the casual factors, which is not possible in conventional methods like the Fault Tree. A scenario of a vessel colliding with an iceberg is analysed using the proposed methodology. A sensitivity analysis is performed to find the most contributory factors to a particular scenario for decision making purposes. The sensitivity analysis offers the best way to identify the most contributory factors to the scenario. The result is key to making a decision on the investment and allocation of resources for accident prevention for Arctic shipping. Observations from the analysis show that the most contributory factors to the top event are the most important. These factors require monitoring and should be given more attention to prevent accident occurrence. The present methodology relies on the inputs from literature for the probabilities. This remains a challenge to the accuracy of the BN. The methodology can be improved with advancement in the generation of conditional probability tables. The conditional probability table approach adopted in this study is very conservative and therefore may lead to over estimation of the probabilities of occurrence of the top event. The methodology offers a good first step for decision-making on resource allocation for accident monitoring and prevention. Uncertainties have not been addressed here. This could be addressed by adopting the suggestions of Liwåg (2015), where Taylor series and Monte-Carlo simulation was proposed. This could be an area for future work as well.

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Chapter 6: Conclusions and Recommendations

This thesis encompasses, a review of oil spill modeling in open and ice-covered waters, the application of fate and transport models of oil spills in ice-covered waters, a partition modeling of oil in different compartments (air, ice, water and sediment) during Arctic shipping, an ecological risk assessment of a potential oil release during Arctic shipping, and the forecasting of an accident scenario during Arctic shipping. The chapter (1), covering the state-of- the-art review of modeling oil spills in open and ice-covered waters identified gaps in knowledge for modeling oil spills in marine environments and proposed ways to address these gaps. The study on the modeling of oil spills in sea ice applied models for ice-covered waters to a case study involving shipping in the Arctic. The results show the limitation of open water algorithms and the capability of the refined model proposed. The dynamic partition model developed for predicting the concentration of oil spills in the Arctic marine environment was used for estimating the concentration of pollutants in different media of oil contact. In this case, air, ice, water, and sediment were the media under investigation. The model was applied to a case study of a ship involved in an accident going through the North West passage. The model predicted the level of contamination in the different compartments. The aforementioned models were integrated in an ecological risk assessment framework to predict the level of risk through the Risk Quotient for the media described. The framework was applied to a potential oil spill scenario in the Kara Sea. This area was chosen to draw readers' attention to a potential accident area in the Arctic when shipping. Some uncertainties (data) were addressed as well. The study on forecasting accident scenarios presents a tool for making decisions on how to envisage an accident during Arctic shipping and where to allocate resources when response operations are to be undertaken.

One critical use of the accident forecasting methodology work is that it gives the probability of occurrence of a particular scenario. This would be helpful to determine which scenarios are most critical for application of the models developed in the aforementioned studies. The approach adopted here is to use scenarios that could well represent real life occurrence. This is necessary because accidental oil spills in the Arctic have not occured, as the Arctic is only recently becoming navigable. The scenarios would serve as a good starting point for contingency planning. The key features, as well as the interactions of the models presented, are very helpful should a real life scenario occur. Further, owing to the limited data available, the scenario based approach serves as a more realistic approach to analyzing potential oil spills in a terrain like the Arctic. Limitations of the proposed models include the following: i) the algorithms for weathering and transport are very simplified. Some processes which are temperature dependent do not have a temperature parameter. Further, those that have a temperature parameter require correction for the cold environment, which may limit the capability of the models, ii) Salinity is not fully accounted for in the current models and this needs to be addressed as well, iii) a constant ice concentration, ice thickness, and wind speed are used in the simmulation, however this is not the case in real life. This also needs to be addressed by taking inputs from a comprehensive database, iv) the use of a surrogate to represent oil in the simmulation may also result in the underestimation or overestimation of the results.

Work from this thesis is intended to inform decisions on design, control, response and operational measures for addressing oil spills in the Arctic. Regulations restricting the intentional oil spilling for scientific experiment purposes means that it may be difficult to better understand the behavior of oil in ice. Some countries have done this in the past, but it is becoming increasingly difficult and expensive to carry out such studies. While this work is aimed at presenting a risk assessment framework for Arctic oil spill response, various components can be revised from time to time with improved algorithms and data when they become available to improve upon the results. Recent efforts by the oil companies in the Arctic response JIP has produced a comprehensive data base of oil spill work.

Suggested future work includes i) developing and integrating an encapsulation model in current oil spill modeling tools, ii) developing updated algorithms for weathering and transport processes (e.g. evaporation and emulsification) in ice-covered waters, iii) addressing model and other forms of uncertainties in the proposed models using the Bayesian approach, which offers the possibility of updating information when new data becomes available, iv) integrating current model with real life oceanographic data for ecological risk assessment in the Arctic, and v) liaising with regulators and operators to develop simplified tools to address critical Arctic oil spill issues as they evolve by considering control, design, operational, and response measures.