



In Situ burning of Arctic marine oil spills

Ignitability of various oil types weathered at different ice conditions. A combined laboratory and field study

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In situ burning of Arctic marine oil spills

Ignitability of various oil types weathered at different ice conditions. A combined laboratory and field study



Janne Fritt-Rasmussen

PhD Thesis

**Department of Civil Engineering
2010**

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In situ burning of Arctic marine oil spills

Ignitability of various oil types weathered at different ice conditions.

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Janne Fritt-Rasmussen



SINTEF



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Arctic Technology Centre
Department of Civil Engineering
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Preface

This thesis is submitted for the degree of Philosophiae Doctor at the Technical University of Denmark. The focus of the thesis has been to increase the knowledge regarding in situ burning of oil spills in arctic ice-covered waters.

The project was carried out from November 2007 until October 2010 and funded by the Commission for Scientific Research in Greenland (Kalaallit Nunaani ilisimatuutut misissuineranut kommissioni - Kommissionen for Videnskabelige Undersøgelser i Grønland). Additional funding was also granted by the Commission for Scientific Research in Greenland.

The work has been conducted at ARTEK - Arctic Technology Centre, Department of Civil Engineering, Technical University of Denmark; SINTEF Materials and Chemistry, Marine Environmental Technology; UNIS - The University Centre in Svalbard and CERE - Center for Energy Resources Engineering, Department of Chemical Engineering, Technical University of Denmark. Field experiments were carried out at SINTEF's field research station in Svea, Svalbard and in the broken ice in the Barents Sea east of Svalbard. The supervisors were Head of Section, Professor Arne Villumsen (ARTEK), Senior Scientist Per Johan Brandvik (SINTEF) and Director Professor Erling H. Stenby (CERE).

The PhD-project was an integrated part of a Joint Industry Program (JIP), called "Oil in Ice" coordinated by SINTEF. The overall objective of the program was to develop knowledge, methods and technologies for environmentally beneficial oil spill response strategies for ice-covered waters. The "Oil in Ice" JIP was funded by the oil companies AGIP KCO, Chevron, ConocoPhillips, Shell, Statoil, Total and the Norwegian research council. The JIP summary report (Sørstrøm et al., 2010) gives an overview of the total program and the technical reports written.

Kongens Lyngby, November 2010

Janne Fritt-Rasmussen

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- The sponsors of the Oil-in-Ice Joint industry program: the Norwegian Research Council and the six oil and gas companies: Agip KCO, Chevron, ConocoPhillips, Shell, Statoil and Total.

List of papers

This thesis is based on laboratory and field work. The results from these experiments are described in the following papers which are the basis of this dissertation. Two additional papers have been written in Danish popular science magazines. They are mentioned here due to their relevance in relation to communicating the research to a wider audience. However, the articles are not included since they are published in Danish and most importantly they have not been through a scientific review process.

- [1] Brandvik, P.J., Fritt-Rasmussen, J., Daniloff, R. & Leirvik, F. 2010. Using a small scale laboratory burning cell to measure ignitability for in situ burning of oil spills as a function of weathering. Proceedings of the 33rd Arctic Marine Oil Spill Programme (AMOP) Technical Seminar on Environmental Contamination and Response, Environment Canada, vol. 2, pp. 755-771.
- [2] Fritt-Rasmussen, J., Brandvik, P.J., Villumsen, A. & Stenby, E.H. 2010. Comparing ignitability for in situ burning of oil spills for an asphaltenic, a waxy and a light crude oil as a function of weathering conditions under arctic conditions. Submitted to Cold Region Science and Technology.
- [3] Fritt-Rasmussen, J. & Brandvik, P.J. 2010. Measuring ignitability for in situ burning of oil spills weathered under Arctic conditions. From laboratory studies to large-scale field experiments. Submitted to Marine Pollution Bulletin.
- [4] Brandvik, P.J., Fritt-Rasmussen, J., Reed, M. & Bodsberg, N.R. 2010. Predicting ignitability for in situ burning of oil spills as a function of oil type and weathering degree. Proceedings of the 33rd Arctic Marine Oil Spill Programme (AMOP) Technical Seminar on Environmental Contamination and Response, Environment Canada, vol.2, pp. 773-786.
- [5] Fritt-Rasmussen, J., Ascanius, B.E., Brandvik, P.J., Villumsen, A. & Stenby, E.H. 2010. Composition of in situ burn residue as a function of weathering conditions. Submitted to Marine Pollution Bulletin.

Related papers which have not been included in the thesis

- [6] Fritt-Rasmussen, J. & Brandvik, P.J. 2009. Oliespild i Arktis bekæmpes med ild. Polarfronten, no. 3, pp. 8 (in Danish).
- [7] Fritt-Rasmussen, J., Villumsen, A., Brandvik, P.J., & Stenby, E.H. 2010. Ilden på havet. Aktuell Naturvidenskab, no. 3, pp. 6-9 (in Danish).

Abstract

Oil exploitation is gaining attention in the Arctic with the opening of new fields and exploration activities. The warmer climate and melting of sea ice also results in increasing ship traffic, and thus the risk of oil spills in the Arctic is expected to increase. Oil spills in Arctic waters are connected with great challenges and are more difficult to handle than oil spills in open waters. This is primarily due to the ice, as it makes conventional methods less efficient and complicates the accessibility to the spill site. The typically remote location of the spill, darkness for many months of the year and lack of infrastructure also add to the challenges of dealing with an oil spill in Arctic marine waters. The ice can also contribute to reduce the spreading and weathering of the oil, and thus enlarge the window of opportunity for the oil spill response. The oil spill contingency plan and tools need to be adapted for such conditions to respond in the best possible way and limit the damages from an oil spill to the vulnerable arctic ecosystems. For removal of oil spill in ice-infested waters in situ burning is a response technique with good affiliation and one of the available techniques with the highest potential.

In short, in situ burning is about igniting the oil at the spill site and thereby removing large amounts of the oil by converting it into CO₂, water, soot and other combustion products. Burning effectiveness higher than 90 % has been found under the right circumstances (fresh oil and thick oil slick) but also weathered oils can be ignited with high removal effectiveness. In spite of the research during the last 30-40 years there is still a need for more knowledge regarding burning of emulsions and burning of different oil types to make in situ burning an operational method. The purpose of this PhD study was to find the ignitability of oil spills as a function of oil type and weathering degree for laboratory and field experiments, to determine the window of opportunity for in situ burning.

A specially designed burning cell was used to test the ability of different oil samples (100 mL) to ignite. This new burning cell is a complete unit with cooling water, exhaust system and temperature measurement system. During the PhD study more than 220 burnings were performed in the burning cell with different oil types as a function of weathering degree and ice conditions. The oil for the burning experiments were weathered in a flume basin at the laboratories at SINTEF (9 L) with 0, 50 and 90 % ice cover, in a flume cut in the fjord ice at SINTEFs field research station on Svalbard (200 L) with 0, 50 and 90 % ice cover and finally as a large-scale weathering experiment in the Barents Sea with 70-90 % ice coverage (7000 L). Samples were taken continuously during the weathering experiments and were all tested for ignitability in the burning cell. Also large-scale in situ burnings (200-450 L and one 2000 L) were performed to validate the results from the burning cell.

The measured ignitability found with the burning cell was in agreement with the large-scale field experiment, thus the burning cell can be used to measure ignitability of oil as a function of oil type and weathering (time, ice). The weathering conditions are of great importance for the ignitability of the oil. Ice

will dampen the weathering and spreading of the oil, thus enlarging the window of opportunity for in situ burning. The composition of the oil is also very important for the window of opportunity, especially the ability to form water-in-oil emulsions. Oils that rapidly form stable emulsions, even with little energy in the system (dense ice), will have a shorter window of opportunity than oils which form unstable emulsions that are easily broken by heat. Furthermore, the remaining amount of volatile components in the weathered oil also influences the ignitability. Five different crude oils were tested in the experiments, Kobbe, Norne, Grane, Statfjord and Troll B, all with very different properties and thus windows of opportunity for in situ burning. Analysis of the residue from a series of burning experiments showed that the weathering time does not influence on the composition of the residue, but the weathering condition (no ice vs. ice) does; where presence of ice seems to affect the burn residue by less removal of hydrocarbons.

On the basis of all the data it was possible to develop a new algorithm that predicts ignitability as a function of oil composition and weathering degree, which has been implemented into the SINTEF Oil Weathering Model. This is a very important tool to have in a real oil spill scenario, as the model can help determine if in situ burning is a valid option that could be considered as a response method. The burning cell has also been found to be usable in the field i.e. it can be used to measure if a real oil spill is ignitable.

Resumé

Risikoen for oliespild i Arktis forventes at stige, da det varmere klima, med smeltning af havis til følge resulterer i flere offshore aktiviteter, hvor udforskning af uopdagede olie- og gasressourcer og øget skibstrafik udgør en særlig risiko. Oliespild i arktiske farvande er forbundet med store udfordringer og er vanskeligere at håndtere end oliespild på åbent hav. Dette skyldes primært tilstedeværelsen af is, da isen resulterer i at konventionelle metoder, til at fjerne oliespild, er mindre effektive og at adgangen til olien er mere besværliggjort. Andre udfordringer i forbindelse med oliespild i arktiske farvande er, at oliespildet ofte sker i afsidesliggende områder, hvor der er mørke flere måneder om året og infrastrukturen er begrænset. Isen kan dog også bevirke at spredningen og forvitringen af oliespildet reduceres, hvorved tidsrammen for olieberedskabet øges. Som følge heraf er der brug for olieberedskabsteknologier, der er særligt udviklet og designet til isfyldte arktiske farvande, for at kunne håndtere et oliespild på den bedst mulige måde og derved begrænse skaderne, som et oliespild ellers vil påføre det sårbare arktiske miljø. Metoden med størst potentiale for oliespil i arktiske isdækkede farvande er "in situ afbrænding".

I korte træk består in situ afbrænding af at brænde olie direkte på spildstedet og derved fjerne store mængder af olien, der omdannes til CO₂, vand, sod og andre forbrændingsprodukter. Under de rette forhold (frisk olie og tyk oliefilm) er det påvist, at afbrænding kan fjerne mere end 90 % af olien. Til trods for den forskning, der allerede har fundet sted de seneste 30-40 år, er der stadig brug for at udvide den viden som findes, særligt med hensyn til at brænde emulsioner og forskellige olietyper for at gøre in situ afbrænding mere operationel. Formålet med dette ph.d.-studie var at undersøge et oliespilds antændelighed som funktion af olietype og forvitningsgrad fra laboratorie- og felteksperimenter, for at kunne bestemme tidsrammen for in situ afbrænding.

En særligt konstrueret enhed blev benyttet til at teste forskellige olieprøvers (100 mL) evne til at brænde. Denne nye "brændecelle" er en komplet enhed med kølevand, udsug og mulighed for at måle temperaturer i forbindelse med afbrændingen. I løbet af ph.d.-studiet blev mere end 220 afbrændinger udført i brændecellen med forskellige olietyper som funktion af forskellige forvitningsforhold og isdækker. Oliene til afbrændingsforsøgene var forvitret i et bassin i SINTEFs laboratorier (9 L) med 0, 50 og 90 % isdække, i et bassin skåret i fjordisen ved SINTEFS forskningsstation på Svalbard (200 L) med 0, 50 og 90 % isdække og afslutningsvis som et stor-skala forvitringseksperiment i Barentshavet med 70-90 % isdække (7000 L). Prøverne blev taget løbende fra forvitringseksperimenterne og testet for brændbarhed i brændecellen. Afslutningsvis blev stor-skala afbrændingsforsøg (200-450 L og 2000 L) udført for at validere resultaterne fra brændecellen.

Brændecellen kan benyttes til at bestemme antændeligheden af olieprøver som funktion af olietype og forvitningsforhold (tid, is); dette er verificeret ved at sammenholde resultaterne fra stor-skala brændeforsøgene med resultaterne fra brændecellen. Forvitningsforholdene er af stor betydning for

tidsrummet for in situ afbrænding. Tilstedeværelsen af is vil reducere forvitringen og spredningen af olien, hvorved tidsrummet for oliens antændelighed øges. Sammensætningen af olien er også meget vigtig for tidsrummet, især evnen til at forme emulsioner (vand i olie). En olie, som hurtigt danner stabile emulsioner, selv med lidt energi i systemet (tæt isdække), vil have et kortere tidsrum sammenlignet med olier, der danner ustabile emulsioner, der let brydes ved tilførsel af varme. Endvidere er indholdet af lette forbindelser, tilbage i den forvitrede olien, også af betydning for antændeligheden. Fem forskellige råolier blev benyttet til eksperimenterne: Kobbø, Norne, Grane, Statfjord og Troll B. Det er råolier med meget forskellige egenskaber og derved forskellige tidsrum for in situ afbrænding. Analyser af restproduktet fra afbrænding af en serie af prøver viste, at forvitringstiden ikke har indflydelse på residuets sammensætning. Derimod har forvitningsforholdene (is eller ikke is) betydning, hvor det lader til, at tilstedeværelsen af is betyder et højere indhold af olieforbindelser i restproduktet fra afbrændingen.

På baggrund af alle de data var det muligt at lave en ny algoritme, som kan forudsige antændeligheden som funktion af oliesammensætning og forvitningsgrad. Denne algoritme er implementeret i SINTEF Oil Weathering Model. Dette er et meget vigtigt værktøj at have i forbindelse med et virkeligt oliespild, da modellen kan hjælpe med at forudsige, om in situ afbrænding i et bestemt tilfælde er en reel mulighed som bør tages med i overvejelserne i forbindelse med planlægningen af valg af beredskab. Brændecellen har også vist sig at være anvendelig i felten, derfor kan den også bruges til at bestemme, om en prøve fra et virkeligt oliespild er antændbar.

Uteqqiineq

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Naatsumik oqaatigalugu sumiiffimmi ikuallaaneq tassaavoq aniatitsiviusumi uulia ikuallallugu. Taamak isilluni uulia annertoq CO₂-mut, imermut, paamut, sinnikunullu allanut allanngorneratigut piiarneqassaaq. Periarfinni pitsaasuni (uulia nutaajutillu uuliallu qaava kinertillugu) ikuallaanikkut uuliap 90%-ia sinnerlugu piiarneqarsinnaasoq ersersinneqarpoq. Ukiuni kingullerni 30-40-ni ilisimasassarsiorneq pisimagaluartoq sulii ilisimaneqartut annertusarneqarnissaat pisariaqartinneqarpoq, pingaartumik akuliuffigineqarsimasut (emulsionit) uuliallu assigiinngitsut pillugit, tassuunatigut sumiiffimmi ikuallaaneq periusissatut atorsinnaanngorniarlugu. Ph.D.-tut (ilisimatuutut) ilinniarnep massuma iluani anguniarneqartoq tassaavoq uuliamik aniatitsisoortoqarsimatillugu uuliap qanoq ittuunera, qanorlu aasimatiginera tunngavigalugit laboratoriami piviusumilu misiliinikkut ikuallaanissamut piffisarititaasup ersersarnissaa.

Atortoq immikkut sanatitaq atorlugu uuliat assigiinngitsut (100 mL-ikkaat) ikummarissusaat misissorneqarput. “Ikuallaaveeraq” nutaaq imermik nillartaartitsisussamik, silaannamik milluaasussamik, ikuallaanerullu ingerlanerani kiassutsimik uuttuutissamik atortulersugaavoq. Ph.D.-tut ilinniarnep ingerlanerani ikuallaanerit 220-it sinnerlugit uuliat assigiinngitsut, assigiinngitsumik aasimasut, assigiinngitsunillu sikumik qallersimasut atorlugit ikuallaaveeqqami pisimapput. Uulia aasinneqarsimavoq SINTEF-ip laboratoriaani imiisivimmi (uulia 9 L) sikumik 0%-mik, 50%-imik 90%-imillu qallersimasumi, SINTEF-ip Svalbardimi ilisimasassarsioarfiani kangerluup sermianut kilitami (uulia 200 L) sikumik 0%-imik, 50%-imik 90%-imillu qallersimasumi, kiisalu Barentip Imartaani (uulia 7000 L) sikumik 70-90%-imik

qallersimasumi misileraanikkut. Uuliat misileraassutissat piffissaq misileraaviusup ingerlanerani tigoorneqarsimapput ikuallaaveeqqallu iluani ikummarissusaat paasinialugu ikuallanneqartarsimallutik. Naggataatigut annertuunik sumiiffimmi ikuallaasoqarsimavoq (200-450 L aamma 2000 L) ikuallaaveeqqamiit inernerit ilumuussusaat qulakkeerniarlugit.

Ikuallaaveeraq atorlugu uuliamik misileraassutissat ikummarissusaat uuliap qanoq ittuunera qanorlu aasimassusaa (piffissamik sikumillu) najoqqutaralugit aalajangerneqarsinnaapput. Tamanna ikuallaaveeqqamiit, annertuumillu ikuallaanerni inernerisat assersuunnerisigut qulakkeerneqarpoq. Uuliap aasimanagera sumiiffimmi ikuallaanissap piffisarititaanut assut pingaaruteqarpoq. Sikoqartillugu uuliap aasimanagera siaruaaneralu annikillisarneqartarpoq, taamatullu uuliap ikuallassinnaaneranut piffisarititaasoq sivitsornerqartarluni. Aamma uuliap qanoq ittuunera piffisarititaasumut pingaaruteqarpoq, pingaartumik uuliap imermik akuliuffigineqarsimanagera. Uuliap sukkasuumik imermik akuliuffigineqarsinnaasoq, uuliamiit imermut akuliuffigiuminaatsumut ikummarissumut naleqqiullugu, sikoqarlualu artillugu ikuallanniarnissaanut piffisarititaasoq annikinneruvoq. Aammattaaq uuliap aasimasup pitaatsunik atassutilinnik imaqassusia ikummarissusaanut pingaaruteqarpoq. Misileraanerni uuliat akuiagaangitsut assigiinngitsut tallimat atorneqarsimapput: Kobbe, Norne, Grane, Statfjord kiisalu Troll B. Uuliat akuiagaangitsut taakku assigiinngitsorujussuarnik piginnaasaqarput taamaattumillu assigiinneqisunik sumiiffimmi ikuallaanissamut piffissaqartitsillutik. Ikuallaarenerup kingorna misissuinikkut paasineqarpoq qanoq sivistigisumik aasimanagerat sinnikut katitissutaannut pingaaruteqanngitsaq. Uuliali sumi aasimanagera (sikoqarnera, sikoqannginnera) pingaaruteqarpoq, imaappasilluni sikoqarnerutillugu ikuallatat sinneri uuliartaqarnerat annertunerorpasilluni.

Paasisarpassuit makku tunngavigalugit uuliap qanoq ittuunera, qanorlu aasimatiginera tungavigalugit, ikummarissusaanut siumoortumik kisiseriaaseq nutaaq pilersinneqarsinnaavoq. Siumut kisiseriaaseq una SINTEF Oil Weathering Modelimut ilanngunneqarsimavoq. Tamanna pingaaruteqartorujussuvoq, tassa arlaanni uuliamik aniatitsisoortoqavitsillugu sumiiffimmi ikuallaaneq upalungaarsimanermut ilumut periarfissatut ilanngunneqarsinnaaneranik eqqarsaaterseeqataasinnaammat. Ikuallaaveeraq aamma silami atorluarsinnaasuusoq paasineqarpoq, taamaammallu uuliamik aniatitsisoorfimmut nassarneqarsinnaavoq uulialu tassaniittoq misiliummik ikummarissusaa misissorneqarsinnaalluni.

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Chapter 1 Introduction

1.1 Background

The Arctic is the area covering the northern hemisphere, and is defined here as where the climate is cold and harsh, ice often occurs and there is a lack of light for many months of the year. The Arctic is also remote with a limited infrastructure. Since 1920 there have been sporadic oil and gas activities in the Arctic and the activities will probably increase in the future due to higher temperatures and melting of ice i.e. more accessible areas. Also more activities related to tanker traffic are expected, hence the increase in activities related to handling of oil will increase the risk of oil spills. When oil is spilled at sea the oil is weathered and the composition is changed depending on the environmental conditions and the oil type. An oil spill may add serious damages to the vulnerable Arctic environment. To counteract the negative effects from an oil spill it is important with proper oil spill contingency planning to improve the operational capability for handling oil spills in Arctic areas (Brandvik et al., 2004). Response to oil spill in the Arctic is in particular difficult due to the presence of ice, cold weather, darkness and lack of or limited infrastructure (i.e. logistics problems) (Brown and Goodman, 1986; Fitzpatrick, 1985), and most conventional response technologies require prompt action, and thus have a limited potential in the Arctic. Methods adapted for the Arctic should be simple, low tech, efficient and robust with no requirement of heavy material. One of the methods best suited for the Arctic is in situ burning, which can be very efficient (> 90 %) and have limited logistics demands.

Research regarding in situ burning has been performed previously including laboratory, tank- and field studies. Rules of thumb indicating maximum water content and maximum evaporative loss for in situ burning are established based on these experiments. Also research regarding the physics of in situ burning (flame spreading, slick thickness, burning efficiency etc.) has been performed. The concentration of ice will also influence the capability for in situ burning and from 30 % up to 90 % the ice will confine the oil gradually more and more. A proper igniter is also important especially if emulsions are to be ignited. However, a deeper and broader understanding of the relationship between ignitability and weathering for different oil types is needed to implement in situ burning in operational contingency planning and to predict window of opportunity for in situ burning. There is also a large need for operational large-scale field testing to verify findings from the laboratory and basins tests (Brandvik et al., 2004).

1.2 Objective

The objective with this work, performed during the 3 year PhD study, was to add new knowledge to the research field of in situ burning in Arctic waters. More specifically the aim of the project was to find a

better basis for deciding when to use in situ burning as an oil remediation technique for oil spills in ice filled waters. The objectives can be divided into the following points:

- Modify and refine a specially designed burning cell for testing ignitability of 100 mL oil samples (Paper [1])
- Establish a method to determine the window of opportunity for in situ burning as a function of oil type, weathering degree and ice conditions by using the new burning cell. This will contribute to in situ burning becoming a more operational tool. (Paper [1], [2] and [3])
- Verify the results found by use of the burning cell by performing field experiments in a large scale (Paper [3])
- Determine the ignitability as a function of weathering for a broad range of oil types. Implement new algorithms into the SINTEF Oil Weathering Model, to be able to predict the time window for in situ burning (Paper [2] and [4])

Great concern is often related to smoke production and residue; however, it is beyond the scope of the thesis to also cover these areas. In the thesis a literature overview of the smoke and residue research conducted is presented, additionally paper [5] presents analysis of residue samples from in situ burning of samples taken from weathering experiments performed in the fjord ice at Svea. The focus was to study the effect of the weathering conditions on the residue.

The thesis is not dealing with other response technologies i.e. chemical dispersions and mechanical recovery. The PhD-project was an integrated part of a Joint Industry Program "Oil in Ice", which also included experiments with dispersions and mechanical recovery methods. The JIP summary report (Sørstrøm et al., 2010) gives an overview of the total program and the technical reports.

1.3 Structure of thesis

This thesis consists of a chapter giving theoretical background information about in situ burning, a chapter explaining the experimental work, a chapter presenting the important results found during this PhD study, a chapter regarding oil spill in Greenlandic waters and concluding a chapter with a summary of the main results published. Finally, the three submitted papers to international journals and two papers published in conference proceedings presenting the major results from the PhD study are presented.

Chapter 2 In situ burning

In situ burning is the term used for controlled burning of oil “in the original place” and refers to a technique where accidentally spilled oil is ignited and burned directly on the water surface. The oil is removed from the spill site surface and turned into the combustion products: CO₂, water, soot and other compounds depending on the initial composition of the oil burned. The method is efficient under the right conditions, in general not very labour demanding and can easily be achieved. At flame out only a small percentage of the original amount is left, and it consists of a high viscous residue. Thus the need for physical collection is much reduced. Some of the drawbacks with in situ burning are the smoke production, risk of secondary fires, concern for the workers and possible settlements nearby. However, by burning the oil, the chances of shoreline pollution and contamination of biota is reduced (Evans, 1994). In situ burning is not restricted to be used on water entirely, but can also be used as a response to oil spills on e.g. tundra, marshes and open fields (Majors and McAdams, 2008; Zengel et al., 2003), as it can be less damaging, less costly and more effective than other methods (Zengel et al., 2003). For in situ burning to be successful some conditions are important, especially the thickness of the slick, the weathering of the oil, the type of oil and the ambient environmental conditions (temperature, wind, waves etc.) affects the burning success (Nordvik et al., 2003).

The first recorded in situ burning was in 1958 in the Northern Canada and the burn was carried out successfully on Mackenzie River with log booms as a response to a pipeline oil spill (McLeod and McLeod, 1974). The next major oil spill where in situ burning was attempted was in 1967 in the Torrey Canyon spill, although unsuccessful (Yoshioka et al., 1999). Since 1958, 21 in situ burnings have been used on actual spills, whereas 10 of these were in ice, thus in situ burning has not yet been widely used as a response technique (McKenzie and Lukin, 1998). Most recently in 2010, in situ burning was used in the Mexican Gulf as one of many response options to the Deepwater Horizon accident.

In the following the theory, regarding in situ burning, are presented.

2.1 Basics of in situ burning

2.1.1 Burning characteristics

When igniting a liquid fuel the fuel must be converted to the gaseous form and mixed with air to allow for ignition, since it is the vapour that burns (Buist, 2003). A liquid with a high vapour pressure usually indicates a liquid that easily vaporizes and forms ignitable vapours.

The minimum temperature where the vapour/air mixture can ignite is called the flashpoint (Drysdale, 2004). The flashpoint increases with increased weathering of the oil (Wu et al., 2000). However, the burning needs to be self sustained, and this requires a rise in temperature of the fuel to the fire point (Quintiere, 2006; Ross, 1994), which is the lowest liquid temperature where the evaporation rate is sufficient to create flammable vapour-air mixtures (Nordvik et al., 2003). Therefore, to secure self sustained burning the oil needs to be heated to a temperature (fire point) where the oil changes its state from liquid to gaseous form and where the heat from the burning itself can vaporize the oil.

The ignition of the oil is performed with an external source (see Section 2.3). When the igniter heats the oil slick, the warm oil begins to flow horizontally outwards away from the igniter. Colder oil from below is replacing the warm oil by convective flow (see Figure 2.1.1). The convective flow is decreasing with increasing viscosity of the oil; hence low viscous fuels are easier to ignite (Buist and Dickins, 2003). When the oil is ignited, flame spreading, if possible, will follow. Flame spreading are flow structures formed ahead of the flame front due to capillary motion (Wu et al., 2000), thus the flames, from a burning oil slick, spread outward along the oil layer. Flame spreading is also sustained by radiant heating from the burning (Buist and Dickins, 2003). In the beginning of the burning the flame spreading is low, but as sufficient heat is generated the spreading becomes more rapid (Brown and Goodman, 1986). In general, weathering decreases flame spreading, because the difference between the ambient water temperature and the flash point increases, thus more heat is needed to ignite the oil (Bech et al., 1992a; Buist, 2000; Buist and Dickins, 2003; Guenette and Sveum, 1995a). An increasing oil slick thickness however, will increase the flame spreading, because of the oil insulate from the cold water (Buist and Dickins, 2003).

The oil will burn by itself, if the oil slick is thick enough to insulate from the underlying cold water and thereby provides the necessary radiative feed-back (Buist, 2000; Buist and Dickins, 2003; Wu et al., 1996) (see Section 2.1.23). The burning reaches a steady state where the radiant heat from the combustion sustains vaporization of the oil and so forth (Buist and Dickins, 2003). However, time is needed to reach that state, as in the beginning all the heat transferred from the flame to the fuel is used for vaporization (Garo et al., 2006). The heat radiated back to the oil has been estimated to be around 1-3 % of the heat from the fire (Buist 2000; Fingas and MacKay, 2003; Torero et al., 2003). The heat radiation is absorbed close to the fuel surface (Garo et al., 1999a). The rest of the heat is carried away by the gasses (Buist and Dickins, 2003). Energy from the fire is also fed back to the oil slick by convection (see Figure 2.1.1). The dominant heat of transfer in the liquid phase is conduction (Garo et al., 1999a). The heat flux generated by an oil pool fire is varying with time and space. Guenette and Wighus (1996) measured 400 kW/m² as the maximum heat flux.

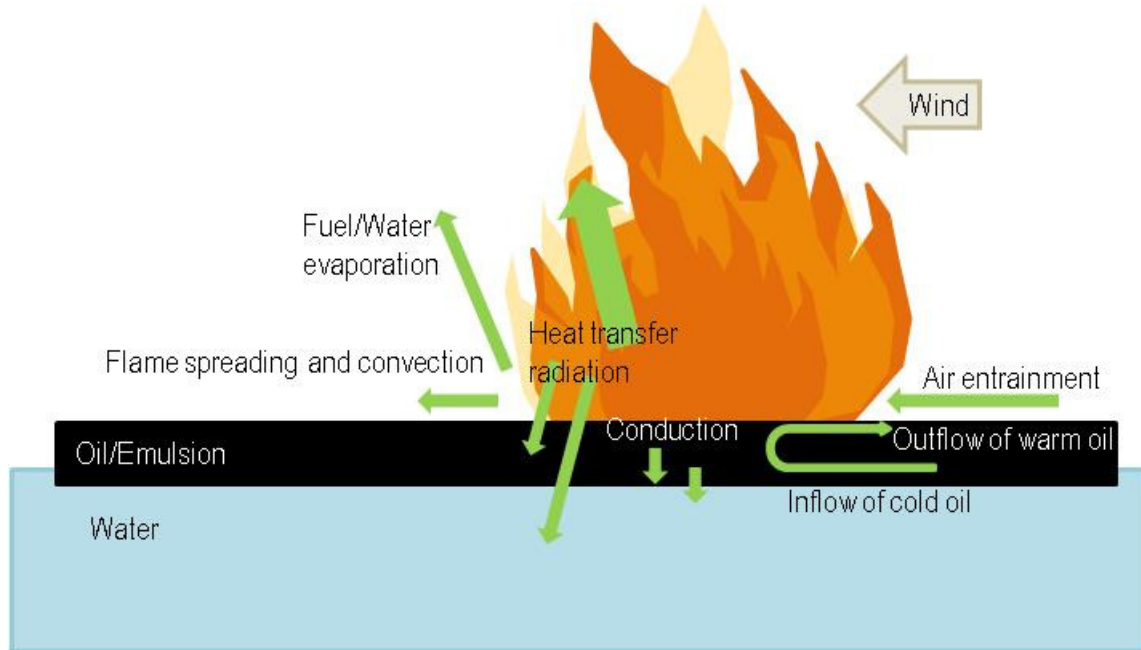


Figure 2.1.1 Conceptual outline of the heat transfer processes during in situ burning of an oil slick on water.

Combustion of oil is an exothermic (heat is generated) reaction, involving oxidation of fuel vapour by atmospheric oxygen and the combustion takes place in the region where vapour and oxygen is mixing (Nordvik, et al., 2003). When burning, an oscillation in the flame is seen (see Figure 2.1.2). This is because of instability at the boundary layer between the fire and the surrounding air, with origin close to the surface of the fuel, which gives rise to disturbances seen as axisymmetric vortex-like structures (Drysdale, 2004). Such large counter-rotating vortices entrain much of the fresh air and mix with and cool the combustion gasses (McGratten et al., 1997). Different flame regimes can be distinguished dependent on the size of the plume. With a pool diameter less than 0.03 m the flames are laminar, from 0.03 to 1 m a behaviour between laminar and turbulent is seen and plumes larger than 1 m the flames are turbulent (Drysdale, 2004).



Figure 2.1.2 Oscillation of the flames during burning Troll B crude oil in a basin cut in the fjord on Svalbard 2008. Snap shots from video filming of the burning.

2.1.2 Vigorous burning

Vigorous burning or thin-layer boil over are the terms used for the situation where the water under the oil slick starts to boil (Buist et al., 2003). Vigorous burning is related to an uncontrolled nature of the burning process (Garo et al., 1999b). When the oil layer is getting thinner and does not insulate anymore, the water beneath the oil will reach the boiling point and hence in some cases result in steam that vigorously mixes with the remaining oil layer and ejects oil droplets into the flames (Buist et al., 1999). The burning rate, flame height, thermal radiation output and foaming is increased by this (Buist et al., 1999). For thin oil layers vigorous burning will result in high energy losses. Vigorous burning has not been observed for burnings where a towed fire boom is used. This is probably because the water beneath the slick is not staying there long enough to reach the boiling point (Buist, 2000). The intensity of the vigorous burning is increasing with increasing fuel thickness, decreasing pool diameter and increasing boiling point of the fuel (Garo et al., 2004). Thicker fuels and super-heated water layers result in a stronger and faster ejection of the fuel to the flame i.e. a more explosive and hazard boil-over (Garo et al., 2004). In Figure 2.1.3 a picture illustrates how a vigorous burning can be seen compared with a normal burning.



Figure 2.1.3 *Burning of a fresh Troll B crude oil sample 2 minutes after ignition (left) and the vigorous phase at the end of the burning just before flame out (right).*

2.1.3 Initial and terminal oil slick thicknesses

The initial slick thickness is one of the most important parameters to determine if the oil will burn or not. A minimum thickness is necessary to insulate the oil from the underlying water and minimize the heat conduction and loss to the underlying water body. A way of calculating the heat loss to the underlying water is given by Bech et al. (1992a):

$$Q = \frac{\lambda(T_{oil} - T_{water})}{h}$$

Where Q is the heat loss to the underlying water, λ is the thermal conductivity for the oil, T_{oil} and T_{water} are the temperatures in oil and water respectively and h is the height of the oil layer.

Many studies have found different minimum initial thicknesses, depending on oil type and state of weathering. Walton (1998) found that 1-5 mm is required for ignition depending on the weathering of the oil. Potter and Buist (2008) report that the minimum thickness that can sustain burning is 1 mm for fresh crude oil on water, 2-5 mm for aged unemulsified crude oil or diesel and 10 mm for residue oils as Bunker C (IF-380). Day (1979) reports that 5 mm thickness is needed to permit ignition. To achieve the adequate thickness it might be necessary to use fire resistant booms to thicken the oil slick (Walton et al., 1998) (see Section 2.4). In situations with sea ice, the ice might prevent the oil from spreading, which will also result in a higher film thickness (Brandvik and Faksness, 2009). In loose pack ice herding agents (see Section 2.4) can be used to thicken the oil and prevent it from spreading (Buist et al., 2008).

The burning will stop when the slick thickness becomes too thin, hence the heat is transferred to the underlying water instead of the oil and the temperature of the slick drops below the fire point for the specific oil (Buist, 2003; Buist and Dickins, 2003). The flame out occurs quite fast (Fingas and Punt, 2000). The minimum thickness depends on oil type and weathering degree (Guenette and Wigus, 1996) and Buist and Dickins (2003) find that for thick crude oil slicks (initial 50 mm) the residue is 3-5 mm, for emulsified slicks the residue is much greater and for slicks from light and middle-distillate oils the residue thickness is 1 mm, regardless of initial thickness. For unemulsified oils, initial 10-20 mm, the residue can be 1 mm in thickness (Buist et al., 1999). In general, the thicker the oil the thicker the residue (Buist, 2003). For oil spill in ice Buist et al. (2003) have set some rules of thumb both regarding initial and terminal slick thickness. The minimum ignitable thickness for fresh oil slicks on brash or frazil ice is 1-2 mm and for evaporated crude oils it is about 3 mm on brash or frazil ice. The residue thickness in calm conditions and pack ice is 1.5 mm, but in situations with waves in brash or frazil ice the residue thickness is about 2 mm.

2.1.4 Burning efficiency

Burning efficiency is an expression of how much of the oil that has been removed during the burning and the burning efficiency can easily exceed 90 % (Guenette and Sveum, 1995a; Walavalkar and Kulkarni, 1996). The burning efficiency is primarily a function of oil spill volume, thus the larger the spill the higher

the burning efficiency, and for oil spills larger than 1 m³ ignited immediately the burning efficiency exceeds 90 % (Buist and Twardus, 1985). The initial thickness of the oil slick is another important factor for the burning efficiency, where thick oil slicks typically will have a higher burning efficiency, because the oil burns down to approximately 1 mm (see Section 2.1.3) (Bech et al., 1992a). Other factors of importance are the areal coverage of the flame and the herding of the slick (Buist, 2000). The degree of weathering will also have great influence on the efficiency where a small decrease in burning efficiency is seen with increasing weathering (Brown and Goodman, 1986; Guenette et al., 1994), thus the sooner the slick is ignited the higher the burning efficiency (Buist and Twardus, 1985).

2.1.5 Burning rates

Oil burning rate is a measure of the decrease in the oil thickness over the period of the burning and can be found in the following way:

$$\text{Burning Rate} = \frac{\text{Mass}_{\text{oil initial}} - \text{Mass}_{\text{residue}}}{\text{Density oil} \cdot \text{Area} \cdot (\text{Burning time})} \quad (\text{SLRoss, 1998})$$

Burning rate per unit area of fuel is known to initially increase with increasing pool diameter (Koseki and Iwata, 2000), this is due to the flame characteristics changing from laminar flow to turbulent flow regime (see Section 2.1.1). However, the burning rate reaches a plateau for large fires, at diameters larger than 6.88 m (McGratten et al., 1993). The burning rate is besides from fire size a function of slick thickness (a thick oil layer results in a longer steady burning phase and a rapid burning phase), oil type and ambient temperature (Buist and Dickins, 2003) and during the vigorous burning (see Section 2.1.2) the burning rate increases significantly (Buist et al., 1994). There is a linear relationship between the wind velocity and burning rates, which may be due to wind herding (Brown and Goodman, 1986). But there are conflicting data on whether or not wind speed increases or decreases burning rates and why, for pool fires greater than 0.2 m (Barrauskas, 1983). Waves will lower the burning rate (Buist et al., 2003). At the end of the burning the burning rate decreases due to increased heat loss to the water beneath (Walavalkar and Kulkarni, 1996).

Different burning rates have been reported. Brown and Goodman (1986) found burning rates between 0.5 and 2.5 mm/min dependent on wind and weathering for 3 mm thick Norman wells crude oil. Buist and Twardus (1984) report burning rates about 1-2 mm/min for 4-40 mm thick Alberta Sweet blend. Smith and Diaz (1985a) found burning rates of 0.2-0.4 mm/min for 2.5 - 10.5 mm thick fresh Prudhoe Bay crude oil. Walavalkar and Kulkarni (1996) found burning rates of typically 2 mm/min for heavy crude oils and 3 mm/min for lighter crude oils. Bech et al. (1992a) found that the burning rate decreases for evaporated oils, from more than 3 mm/min to 1.4 mm/min. Rules of thumb for burning rates are given by Buist (2000) and they are 3.5 mm/min for unemulsified crude oil on water and 4 mm/min for automotive diesel and jet fuel fires on water. For burning oil in ice Buist et al. (2003) report that Alaska North Slope crude oil had burning rates of 1.2 mm/min in frazil or slush ice and 0.3 mm/min for brash ice (burns on open water were

1.6 mm/min). Rule of thumb says that the burning rates in calm conditions are halved on frazil ice and halved again in brash ice compared to open water burnings (Buist et al., 2003).

2.1.6 Effect of wind and waves on in situ burning

The effect from wind on fires is complex as both positive and negative effects are seen.

Wind in certain amounts will have a positive impact on the flame spreading, as the wind deflects the flames downwind in the pool. This deflection is shown to be more important for flame spreading than the size of the fire (Guenette and Wighus, 1996). Also the flame temperatures are raised due to improved mixing and combustion (Babrauskas, 1983). Another advantage of the wind is that the wind can herd the oil against a barrier (e.g. ice floes) and thereby accumulate acceptable thicknesses to support combustion (ASTM F2230-02). Wind as little as 2 m/s can herd slicks against a barrier (Buist, 2000; Buist and Dickins, 2003) and with 1 m/s of wind a 2 mm thick oil, weathered for one hour, can herd to about 3 mm (Buist and Twardus, 1984). This is in agreement with the findings of Brown and Goodman (1986). Viscous oils are herded to greater thicknesses and wind herded oil could be ignited either up- or downwind with similar burning results (Brown and Goodman, 1987).

Too much wind, however, will affect the burning negatively by preventing the oil from igniting or by blowing out the burning. Wind velocities higher than 10 m/s make ignition difficult since the vapour-air mixture is diluted below flammable concentrations and the wind cools the oil surface (Bech et al., 1992a; Nordvik et al., 2003). The wind also results in a redistribution of the radiant heat fluxes thereby lowering the radiative heating and convective heat transfer to the oil slick (Babrauskas, 1983). Thus wind velocities must be less than 10-12 m/s (Guenette and Wighus, 1996; Nordvik, et al., 2003), but the maximum wind for burning an oil depends on the weathering degree of the oil (Brandvik et al., 2006).

Waves will also affect the burning. The burning efficiency and burning time will decrease, thus the residue amount will increase; this is especially for waves higher than 30 cm and longer than 3 m (Walavalkar and Kulkarni 1996). This is due to the fact that the waves will stretch the oil slick, thus the slick becomes thinner (Brandvik et al., 2006). In case of very large waves the burning might even be extinguished. Choppy and steep waves can also prevent the oil slick from igniting; this is especially for oil slicks that are difficult to ignite (Buist and Dickins, 2003). With waves present the energy in the system increases, which results in an increased burning rate (Buist et al., 1996). For the waves not to affect the ignition they have to be smaller than 1 m for unemulsified oils and even smaller for emulsions (Nordvik et al., 2003).

2.1.7 Temperatures during in situ burning

The temperature regimes during a burning vary significantly between the flame, oil slick and water. The temperatures measured in the flames during a burning are generally high and from different authors the following temperature ranges have been found: between 900°C and 1200°C on still waters (Buist 2003; Buist and Dickins, 2003), 1500°C 15 cm above the surface (Nordvik et al., 1995) and between 400°C

and 1370°C (Guenette and Wighus, 1996). With wind present the maximum flame temperature may be higher and when the right amount of air is supplied to the flames the highest possible flame temperature is achieved (Bech et al., 1992a). For weathered oils the flame temperatures are lower, this is according to Brown and Goodman (1986), who finds that the temperature measured during burning of 15 % weathered oil was greater than from 20 % weathered oil.

1-3% of the heat from the burning is radiated back to the surface; even so, the surface temperature may increase considerably (Nordvik et al., 2003). According to Buist (2003) the oil temperature is between 350°C and 500°C at the surface. With increasing water content in the oil (water in oil emulsion), the temperature in the oil is lowered, this is a result of the poorer insulation capacity of water compared with oil (Guenette et al., 1994). The temperature of the oil is also a function of the thickness of the slick, with higher temperatures for thicker slicks (Guenette et al., 1994). Through the oil slick there is a steep temperature gradient, this is due to the good insulation capacities of the oil (Guenette et al., 1994) and in the water/oil interface the temperature is never more than boiling point of water and is usually around ambient temperatures (Buist, 2003; Buist and Dickins, 2003).

The water temperature is shown to have an effect on the burning in some cases, however no clear trend is found in the literature. Smith and Diaz (1985a) found that for burning Prudhoe Bay crude oil the burning efficiency and burning rates decreased with lower water temperature. Buist et al. (1996) found that increasing the temperature from 3°C to 15°C resulted in more ignitable samples; however, this was not the case for all the oil types tested. Walavalkar and Kulkarni (1996) report that the temperatures in the water (-1°C to 17°C) showed to have a negligible effect on the burning of oil. The water temperature however, may have a positive impact on the spreading, as low temperatures result in higher viscosities which might result in reduced spreading (i.e. thicker oils slicks) (Bech et al., 1992a).

The air temperature during a burning has shown to have a negligible effect on the burning of the oil. This is according to Buist and Dickins (2003) and Walavalkar and Kulkarni (1996), who report that air temperatures from -11°C to 2°C and -31.5°C to 3°C (for burning oil in snow) respectively, did not affect the burning.

2.1.8 Safety issues

When in situ burning is performed concern about safety should be taken seriously. The thermal radiation from burning oil is used to predict the potential hazard to personnel and equipment operating near the burn (Evans et al., 1990). The safety distance to the fire is four times the fire diameters (Buist, 2000). Experiments have shown that oil pools next to a burning slick can ignite if the pool is located directly downwind (Guenette and Sveum, 1994) otherwise the heat from the fire has a negligible environmental impact (Buist, 2000). The risk of accidental ignitions and explosions should also be taken into consideration. The same goes for burning near communities and from MacDonald et al. (2009) this is recommend to be avoided. Human activity and physical installations should also be in focus and handled by well prepared and controlled in situ burning procedures (Brandvik et al., 2006).

2.2 Effect of weathering on in situ burning

When oil is spilled at sea several natural processes affect the oil and change the physical and chemical composition of the oil. These processes are spreading, drifting, evaporation, dissolution, photolysis, biodegradation and formation of oil-in-water and water-in-oil (w/o) emulsions (Faksness, 2008). The generic term for the processes is weathering and an illustration can be seen in Figure 2.2.1. The weathering changes the composition of the oil and the degree of the processes depends on initial oil type and environmental conditions e.g. temperature, wind, waves, ice etc. The different weathering processes influence on the oil spill also varies with time and the relative importance is shown schematically in Figure 2.2.2.

The effect of the weathering has a considerable influence on the in situ burning potential. The major processes that influence the ignitability and ability to burn are evaporation (amount of volatile compounds left in the residue), water-in-oil emulsification and spreading. Spreading results in a thin oil layer and as mentioned in Section 2.1.3, a thick oil slick is required to secure self sustained burning. During burning of crude oils the oil is not spreading appreciably faster or farther than cold oil (Buist and Twardus, 1984). In scenarios with ice present the weathering processes are slowed down, this means that the window of opportunity is increased for most response techniques (Singsaas and Reed, 2006).

In the following only emulsification and evaporation are described as these processes are the most important in direct relation to burning the oil, as they both decrease the burning efficiency (Bech et al, 1993) and shorten the window of opportunity for in situ burning.

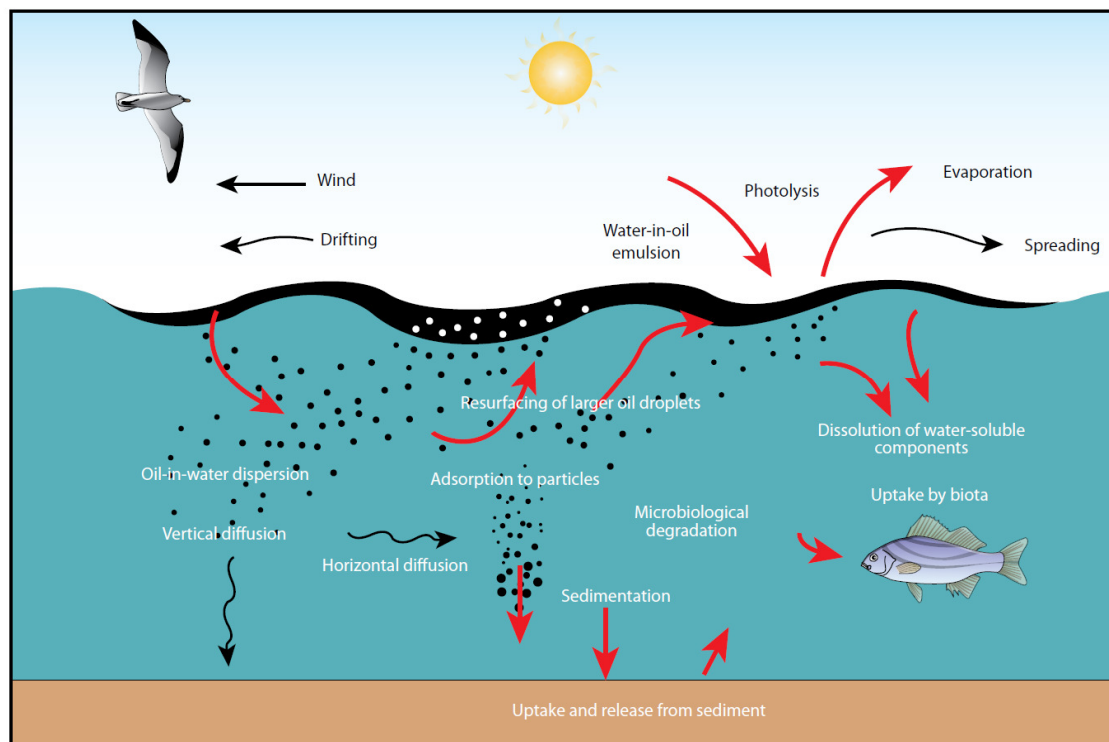


Figure 2.2.1 Weathering processes of oil that take place when oil is spilled on the sea surface (from SINTEF).

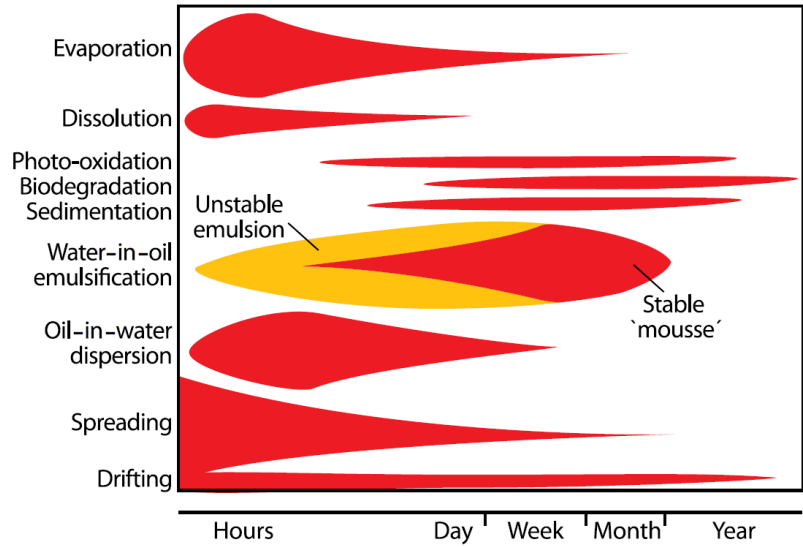


Figure 2.2.2 Weathering processes' relative importance with time (from Klungsøyr et al., 2009).

2.2.1 Evaporation

Evaporation is dependent on the vapour pressure of the oil and the ambient environmental conditions, and will start immediately after oil release and decreases with time (Figure 2.2.2). Evaporation is a surface phenomenon which is strongly dependant on the volume to surface ratio and the spreading of the oil slick (Brandvik et al., 2004). With ice present the evaporation is typically reduced due to a reduced area for the oil to spread. The remaining oil on the surface will have an increased flash point, boiling point, viscosity and density (Nordvik et al., 2003), changes that makes the oil more difficult to ignite. However, evaporated oils can easily be ignited and burn with high efficiency especially if the oil is water free (Bech et al., 1993). With increasing evaporation, results from Bech et al. (1992a) showed that the flame spreading and the burning rate decreased. Often the evaporative loss from an oil is given in the literature, however the most important in relation to in situ burning is the amount of volatile compounds left in the residue i.e. the flashpoint of the residue (Brandvik and Faksness, 2009). This is because a high amount of volatile compounds in the oil will ease the ignition and burning of the oil.

2.2.2 Water-in-oil emulsion

W/o emulsification means that the oil has taken up water and the water droplets are cooperated into the oil. The creation of emulsions is determined by the input of energy from breaking waves (Brandvik et al., 2004). Wind velocities above 2-3 m/s initiate emulsification, whereas ice and slush ice dampen the emulsification, due to the dampening effect from the ice on the energy in the system. In ice the emulsification can occur from pack ice, local wind in open fields and collisions between ice floes (pumping) (Løset et al., 1994). The appearance of the w/o emulsions can be very different as can be seen in the two examples in Figure 2.2.3.



Figure 2.2.3 Two types of emulsions: brown mousse and “salmon-egg” emulsion.

Four types of w/o emulsions are defined regarding the stability: stable, meso-stable, unstable and entrained. Entrained is not a real emulsion as no chemical stabilization is evident and the water is lost progressively (Fingas and Fieldhouse, 2009). In the beginning the emulsion is unstable, but becomes more stable with time (see Figure 2.2.2), dependent on the oil type and weathering conditions (Nordvik et al., 2003, Merlin and Poutchkovsky, 2004). Stability is obtained when the water droplet size in the emulsion is so small that the gravity force does not naturally separate them. Unstable emulsions drain off the water by gravity separation (Nordvik et al., 2003). The stability of the oil is dependent on the properties of the oil (McCourt et al., 1999) and especially the content of resins, waxes and asphaltene are very important (Merlin and Poutchkovsky, 2004). This is because these compounds form an interfacial film between the oil and water droplets that stabilizes the water droplets in the oil. Asphaltenes are in particular a major factor for the stability of the emulsion; however; too much asphaltene (more than 10 %) will increase the viscosity so that stable emulsions do not form (Fingas and Fieldhouse, 2009). W/o emulsions stabilized by resins are not as stable as for asphaltenes. If the content of resins is higher than the content of asphaltenes the emulsions become more stable, but the opposite destabilizes the emulsions (Fingas and Fieldhouse, 2009). The stability of the emulsion is also determined by the rheology of the oil and a high elasticity will increase the stability (Fingas and Fieldhouse, 2009). In cold conditions the emulsion stability will enhance due to the precipitation of the emulsions stabilizing waxes and asphaltenes. The same is evident for high mixing energy, as it will generate smaller droplets, which are less likely to coalesce and may create more viscous emulsions, which will lead to further inhibited emulsion separation (Guenette et al., 1994).

Emulsification is the most important weathering process in connection with in situ burning, because the water has to be removed from the oil before the oil can burn and this removal relates to the stability of the emulsion (Buist, 2000; Smith and Diaz, 1985b; Walavalkar and Kulkarni, 1996). The water either breaks or boils away. For the emulsion to break high temperatures are required. When the temperature in the oil increases, the viscosity is reduced and the internal molecular movement is increased. This in connection with a change in solubility of the compounds that creates emulsions leads to a break of the emulsion and the water is separated (Bech et al., 1992a). A layer of unemulsified oil will then float on top of the water (Buist, 2000; Buist and Dickins, 2003; Buist et al., 1999). To increase the break up emulsion breakers can be added to the igniter (see Section 2.3). If the water is boiled off, then the oil temperature will not exceed

100°C before the water is removed. For stable emulsions steam is also formed on the surface and thereby reduces the flame temperature and radiant heat to the slick (Nordvik et al., 2003). Hence w/o emulsification has a negative impact on in situ burning and the removal rate of the water is the controlling factor for burning emulsions (Buist et al., 1996).

When burning emulsions it is often quite violent with much spattering (similar to the vigorous burning phase) (Buist, 2000; Buist et al., 1999). Water droplets from emulsions can explode into vapour, making a loud sound and a light flash. Such micro-explosion is an unsteady burning process in which a sudden fragmentation of the droplet occurs (Ocampo-Barrera et al., 2001). In some cases, if these explosions are large enough, they can extinguish small fires (Fingas and MacKay, 2003). At the end of a burning foaming might result in that some areas are put out, but these might be reignited and result in sudden and rapid flare-up of flames (Buist, 2000; Buist et al., 1999).

Investigations have been made on in situ burning of emulsions and at what water content the emulsions cannot burn anymore. The most important findings are assembled in the following. Between 20 % and 30 % water has been found to be the limit for burning stable emulsions (Barnea, 1999; Buist, 2000; Buist, 2003; Potter and Buist, 2008; Twardus, 1980, in Payne et al., 1991). However, for paraffinic oils that create meso-stable emulsions, emulsions can easily be ignited at much higher water content than 25 % (Buist et al., 1999; Potter and Buist, 2008) and (Bech et al., 1992b) found that w/o emulsions with a water content of 40 % could be burned. Twardus (1980, in Payne et al., 1991) found that for ice covered areas the maximum water content is about 70 % for lighter and medium crude oils, but 30 % for heavy crude oils. These different results show that the maximum water content where ignition is still possible depends on the oil type and the stability of the emulsion. The conclusion must be as both Bech (1992b) and Buist (2003) also conclude that more investigations are needed to fully understand burning of w/o emulsions for various oils.

2.3 Igniter

Ignition of a surface is a function of the heat flux added by a thermal source on the surface, where the ignition time is decreasing with increasing pool diameter (Putorti and Tenysin, 1994). Thus the igniter is of great importance for the success of ignition. The oil must be heated to the fire point to ignite and therefore heavier oils require longer heating periods and warmer flames compared to lighter oils. It is also important that the igniter is applied upwind to secure the best conditions for flame spreading (Guenette and Sveum, 1995b) and if the winds are high the igniters should be applied close because the lateral flame spreading is limited (Guenette and Sveum, 1994). Igniters used to ignite emulsions must be able to first produce a water free oil layer of oil and then supply enough heat to secure that the oil is heated to its fire point.

Many igniters exist from handheld propane torches to sorbent pads soaked in diesel and gelled gasoline in plastic bags. Typically gasoline is used, but a mixture of diesel fuel, crude oil and gasoline could be used in connection with highly weathered w/o emulsions, since the heat flux produced is higher. For the

igniter fuel to be most efficient it should contain both light components, for a quick ignition, and medium and heavy components to provide the heat needed for ignition of the emulsions (Guenette and Sveum, 1995c). According to Bech et al. (1992b) and Guenette et al. (1994) crude oil is probably the best ignition promoter.

Several ways of igniting exist e.g. from vessels, ice edges or helicopters. For the helicopter primarily two types exist, namely the Dome igniter and Heli-torch igniter (Buist, 2000), where the Heli-torch is found to be the choice of igniter for in situ burning (Guenette and Sveum, 1995b; Potter and Buist, 2008). However, other types exist (Meikle, 1981). Aerial deployment of igniters can allow an accurate positioning on the slick, which is important when dealing with igniting stable emulsions or for oil spills in ice, where the oil can be found unconnected (Guenette and Thornborough, 1997).

Promising results have been found with the use of emulsion breakers added to the igniter (Guenette and Sveum, 1995b). An emulsion breaker is a chemical surfactant that lowers the oil-water interfacial tension and promotes the coalescence of water droplets in the w/o emulsions; this should ideally cause the emulsion to separate (McCourt et al., 1998). Adding emulsion breakers to the igniter also enhance the spreading over the surface of emulsions, thus oils with high water contents can be ignited (SL Ross, 1995). There appears to be an optimum for the concentration of emulsion breakers. If too much is added the emulsion breaker can hinder ignition or flame spreading due to a large amount of water released from the emulsion at once (Guenette et al., 1994). The emulsion breaker Alcopol has shown to be an efficient emulsion breaker (SLRoss, 1999). Even so, according to Guenette et al. (1994) the igniter technology needs to be improved. Besides from adding emulsion breaker to the igniter an anti-foaming chemical can enhance flame spreading due to reduced foaming in the early stages of ignition (Guenette and Sveum, 1994).

2.4 Fire booms and Herding agents

In cases where less than 30 % ice is present the oil will spread out and the thickness of the slick will reach the minimum required thickness rapidly. The use of fire resistant booms will prevent the oil slick from spreading and secure a sufficient oil slick thickness. The use of booms has been investigated both in open water and in ice since the beginning of 1980s. Using fire resistant booms to collect the oil for in situ burning requires less equipment than does collecting the oil for skimmer use (mechanical recovery) (Fingas et al., 1999). Several different booms exist, some constructed in steel, fire-resistant fabrics and others employing active water cooling (Buist, 2000). The oil is collected in either a horseshoe or catenary-shape and towed by two vessels. The oil is burned while the boom is being towed until nearly all the oil is burned. It is important that the boom can handle more than one burn (Walton, 1998) to enhance the field of application. Fire booms have a comparable performance, as other conventional non-fire resistant booms, with a first loss tow speed (when oil loss begins) of 0.85-1.0 knot; this is based on tests with five fire booms (Bitting and Coyne, 1997)

Herding agents are chemical surface-active agents that clear the oil from an open water surface; hence the oil slick will contract and thicken for a period of time, where the oil then might be burned (Buist et al., 2010). The herding agents work by reducing the surface tension of the surrounding water significantly. When this monolayer of surfactants reaches the thin oil slick, the balance between interfacial forces acting on the slick is changed and the oil is contracted into thicker layers (Buist et al., 2010). As opposite to wind herding, herding agents do not need a boundary to work against and can work well in open waters (Buist et al., 2010).

A part of the JIP was to test fire resistant booms in areas with broken ice and herding agents. More details about the reports can be found in Sørstrøm et al. (2010).

2.5 Burn residue

With a successful burn the majority of the oil is removed from the water surface and several experiments have shown that less than 10 % of the oil is left. During the burning both the light and heavy compounds are removed, but mostly the lighter lower boiling compounds, hence a concentration of the heavier compound is found in the residue. The precise chemical composition of the residue will depend on the parent oil (Buist, et al., 1999) and the physical texture of the residue also varies with oil type. A heavy bunker fuel will create very viscous and sticky residues, whereas residues from lighter crudes create semi-solid residues that are more easily removed. Examples of two different residues are given in Figure 2.5.1. The residue is assumed to contain no water as the water is removed during burning as written in (Section 2.2.2). A challenge exists on how to collect the residue. If the residue is in liquid form it might be possible to collect the residue with mechanical methods, for instance, a trawl or skimmer system. However, if the residue is semi solid other special methods must be used, which may be manual. In the case where the residue might sink, the residue must be collected before the residue cools down (this occurs quite fast), as the warm residue will often not sink (Buist, 2000). In the experiments performed in this PhD study 3M adsorption pads were used to remove the oil from the water surface (see Section 3.3.3 and Figure 2.5.1). The same method was used by (Brandvik and Faksness, 2009; Smith and Diaz, 1985 a; b). For oil spills in between ice floes this is an efficient way since it is possible to collect the residues even in small pockets. However, it is labour demanding because it must be carried out manually and in case of very large oil spills more efficient ways should be thought of. In the literature of oil burns in arctic ice-filled waters only few different techniques are presented for removal of residue. Brown and Goodman (1986) and Buist and Bjerkelund (1986) have reported the use of sieve shovels to lift the viscous residue and allow the water to drain of, before it is collected in plastic bags and Smith and Diaz (1987) used both sieves and absorption pads. Based on this, it seems as if there is a need to evolve this area and find some efficient methods that works for sticky and viscous residues even in the Arctic with ice.



Figure 2.5.1 Examples of burn residues from the laboratory (IFO-30) and the field (Statfjord) (right photo: Per Johan Brandvik).

2.5.1 Residue density

There is not complete agreement within the literature when it comes to whether or not the residue will sink. According to Moller (1992) the increase in density is a result of either burning of the oil or sediments incorporated in the residue. The latter is particularly an issue in coastal areas and is less important at open sea.

Some of the first studies of burn residue showed that the residue will not sink, and even though the density is increased, it is still lower than the density of water (Fingas et al., 1994; Norcor, 1975). This was also what Guenette et al. (1994) found, that in general the residue remained floating just below the surface. However, other studies have found that burn residue indeed can sink (Buist et al., 1995), when the residue has cooled down. Residues from thick oil slicks and heavier oils are more likely to sink due to the concentration of high molecular weight compounds as the burning continues (Buist et al., 1995). A rule of thumb says that oils, with an initial density higher than 0.865 g/cm^3 , will generate residues that will sink (Walton, 2003).

2.5.2 Toxicity of residue

An important issue is whether or not the residue is toxic. Daykin et al. (1994) concluded that the aquatic toxicity from in situ burning was minor and not beyond the effect already seen from the oil spill. The results are based on both field and laboratory experiments, where the laboratory experiments found the highest values (Daykin et al., 1994). The same was found by Blenkinsopp et al. (1997) and Gulec and Holdway (1999). Regarding poly aromatic hydrocarbons (PAH) early research of the burn residue showed no significant difference between the fresh crude oil and the residue (Buist and Bjerkelund, 1986). However, several recent researches have all concluded that the content of PAHs overall have decreased in the burn residue (Fingas, 1998; Fingas et al., 1994; Garrett et al., 2000; Li et al., 1992; Lin et al., 2005). Toxic compounds from the volatile lower boiling point fraction as benzene, naphthalene and

benzopyrenes are expected to be removed by the burning process; hence the residue is expected to be less toxic than the parent oil (Buist et al., 1999; Buist, 2000). Heavy metals were found only in the residue, and not in the soot, this concentration in the residue correlates well with the volatility of the metals (Fingas et al., 1994; Fingas et al., 1993). Analysis of the water column beneath the in situ burning site demonstrated that no compounds of concern were found at detection level (Fingas et al., 1994). From Mullin (2003) and Snider (1998), it is concluded that the behaviour and toxicity of the burn residue has been studied sufficiently and the experiments have shown that the residue should not be of any environmental concern.

2.6 Air emissions from in situ burning

Major concern exists regarding the smoke from burning of oil. This is because of the risks related to exposure of the black smoke plume (see Figure 2.6.1). Smoke may cause severe health problems if inhaled in high concentrations (Buist, 2000); however, other human exposure pathways such as dermal uptake, seafood ingestion and direct human contact are considered negligible (Westphal et al., 1994). When comparing in situ burning with other types of burnings such as forest fires or slash burns the toxic emission from in situ burning is modest (Barnea et al., 2001). The smoke plume may obstruct visibility and may pose safety hazard to ships, aircrafts etc. (Buist, 2000). Many studies have been published regarding emissions from in situ burning, this also includes literature reviews (Fingas, 2010; Fingas et al., 2001; Fraser et al., 1997) and the areas within smoke emissions and trajectory models are well covered and do not need further work (Mullin, 2003).

From an ideal oil burning, the combustion products are carbon dioxide and water (NRT, 1995; NRT, 1992). If the burning is starved (incomplete) and not enough air/oxygen is drawn into the fire a black plume of smoke is seen as shown in Figure 2.6.1 (Smith and Diaz, 1985a). The smoke from an in situ burning consists of partially burned by-products namely particulate matter, either solid (soot) or liquid and gaseous products (NRT, 1995; NRT, 1992; Suo-Anttila et al., 2004). The burn products are typically divided as follows: 75 % CO₂, 12 % water vapour, 10 % soot, 3 % CO and 0.2 % other products including PAHs (Tenneyson, 1994). The rapid near-end-burning that occurs in the vigorous phase of the burning, results in increased combustion of gases as well as particulate matter (Fingas, et al., 1993).

The smoke yield expresses how much smoke that is produced during a burning. A rough estimate of how the smoke yield can be calculated is as follows:

$$\text{Smoke yield (mass\%)} = 4 + 3 (\log_{10}[\text{fire diameter cm}]) \quad (\text{Fraser et al., 1997})$$

The smoke yield will increase with fire size diameter (Fraser et al., 1997), until the smoke yield reaches a plateau for fires with diameters above 2 m (Evans et al., 2001; Notarianni et al., 1993).



Figure 2.6.1 *Smoke plume from burning Troll B crude oil in a basin cut in the fjord ice, Svea, Svalbard, 2008.*

The smoke plume is sent high up in the air (Potter and Buist, 2008) and experiments with burning Alaskan North Slope crude oil showed that the plume height was of 400 and 550 m (McGratten et al., 1997). For large oil spills it is assumed that the plume will rise higher and disperse to a greater extent; hence the particulate matter spreads over a larger area (Evans, 1994). Under calm conditions the plume will presumably remain stationary forming a cloud, which will diffuse slowly horizontally and vertically between the ground and the top of the mixing layer (Day et al., 1979). The safe distance downwind of a 500 m² oil spill is 500 m for crude oils and 690 m for diesel burns (Fingas et al., 2001). Buist et al. (1999) have reported that the distance for the smoke plume to dilute below 150 µg/m³ (US National Ambient Air Quality Standard) ranges from 1-20 km depending on the terrain and atmospheric conditions. The time required to clear the air again depends on meteorology (mixing layer depth, closely related to the wind speed and temperature) and topography (terrain) (McGratten, 1997). However, it is expected that the air above 30 m in altitude will clear relatively fast, but it is difficult to predict how fast the air is clear at the surface due to variety in the terrain (McGratten et al., 1993). In general the air emission from burning of oil spills is not a serious health problem about 150 m from the fire site and 500 m from the fire very little is detected (Mullin and Champ, 2003).

2.6.1 Particulate matter - Soot

Soot consists primarily of carbon, but in large scale burnings also droplets of oil can be found (NRT, 1995; NRT, 1992). Soot is generated because the burn is inefficient and oxygen-starved and the carbon in the fuel does not completely oxidize with the oxygen in the air resulting in particulates, primarily inert elemental carbon (soot) (Barnea et al., 2001). The production of soot is poorly understood, but three distinct steps are known. First the nucleation where a particle is formed and molecules cling around. Secondly the particles grow to a spherical particle in size of 10-50 nm in diameter (Fingas, 2010) and finally the particles agglomerate to chains of several micrometers (Suo-Anttila et al., 2004). The diameter of the soot particle is increasing with the size of the burning (Mulholland et al., 1996). The greatest concern is the particles smaller than 10 μm , since they are considered respirable (Evans et al., 1994; Mullin and Champ, 2003). Most of the particles (90 %) from in situ burnings are 10 μm or less (Brandvik et al., 2006). Particulate matter however, is only of health concern close to the fire and directly under the plume (Fingas et al., 2001; Mullin and Champ, 2003).

Few methods exist to actually measure the soot production from large scale burnings since small scale methods are not applicable (Fingas, 2010). One way is to capture and weigh all the soot produced and compare with the initial oil weight. The disadvantages are that the method results in poor oxygenation and particles that otherwise would re-participate are collected, both leading to increased amount soot collected and finally only small experiments can be used with this method (Fingas, 2010). Another method is to take a soot sample and then extrapolate the sample weight to the total; however, extrapolation is difficult and is uncertain (Fingas, 2010). Light blocking is a third method where the light blocking is measured, typically with laser, over a passage in a chimney. Some problems however are connected to calibrate the system to yield an exact percentage of soot types (Fingas, 2010). A fourth method is by use of integration. Several models exist: integrating the whole length of the soot plume at the end of the experiment, integrating the soot deposition under the plume and integrating the soot deposition in the plume. Only the latter method has potential according to Fingas (2010). Additional estimations methods exist by use of the carbon balance. The percentage of soot is given by the percentage of carbon (sum of soot, carbon dioxide and carbon monoxide). This method assumes that carbon dioxide will stay in the plume, but the reality is that it will sink, which results in problems using this method as the carbon balance method will overestimate the soot production (Fingas, 2010). According to McGrattan et al. (1993) however, this is the only method that can be used both in the laboratory and in the field. Day (1979) finds that the amount of soot formed was 2-5 % of the original oil mass and from Fingas (2010) values from 1- 16 % are reported. There is a strong correlation between the amount of soot produced and the oil type. Larger molecules result in a higher soot production and compounds as rings and double and triple bonds have an important structure leading to soot production (Fingas, 2010). Presence of water will lower the particulate emission particularly in the case of medium heavy oil (Haynes and Wagner, 1981).

Combustion conditions, mainly the temperature, affect the fate of metals in the smoke. Secondly, the size of emitted particles (soot) is important for the fate of the metals. Particle size depends on the fuel and combustion conditions i.e. important in connection with the distribution of heavy metals. Where the heavy metals are found is dependent on the specific metal and its vapour pressure and volatilization temperature (Nerín et al., 1999). Fingas et al. (1993) find no detectable metals, however the soot samples were very small for the metal analysis, thus the authors suspect that some metals are transported in the soot.

2.6.2 Gaseous smoke products

The gaseous products consist of e.g. PAHs, carbon monoxide, carbon dioxides, sulphur dioxide, VOC (volatile organic compounds), benzene, toluene, xylene, dioxins and dibenzofurans (Fingas et al., 1993; NRT, 1995).

PAHs are largely consumed during the fire, hence PAHs have been found in lower amounts in the soot than in the initial oil (Benner et al., 1990; Fingas et al., 1993; Fingas et al., 1999; Fingas et al., 2001; Walavalkar and Kulkarni, 1996). But the concentration of PAHs with rings of five or more was higher in the smoke than in the crude oil (Benner et al., 1990; Fingas et al., 1999; Fingas et al., 2001), so the larger PAHs are either created or produce during the fire (Fingas et al., 1999). Overall the net loss of the larger PAHs in the smoke is lower after the burn (Fingas et al., 1993). The low doses of carcinogenic PAHs estimated for smoke inhalation and ingestion of particulate matter are not likely to produce a measurable increase in incidences of cancer (Westphal, et al., 1994).

CO₂, SO₂ and CO and other combustion gasses do not reach a level of concern (Fingas et al., 2001). The sulphuric acid concentration is proportional to the sulphur content in the oil (Fingas et al., 1999). The emissions of these gasses do not follow the smoke plume line but are separated over a broad area around the fire site. This shows that the compounds are widely diffused from the burn (Fingas et al., 1993). The emissions of volatile compounds are less from an actual fire, than from vaporization from a plume (Fingas et al., 1994; Fingas et al., 1993).

The concentrations of benzene, toluene, xylene etc. measured downwind of the burn were found in low concentrations (Mullin and Champ, 2003; Bowes, 1996). In general the concentration of VOCs is below human health limits (Fingas et al., 1999). When crude oil is burned the evaporated VOCs are destroyed in the burning process and thus are not of concern, however close to the fire the concentration might be high. VOCs measured from an evaporating oil slick are much higher than during in situ burning (Fingas et al., 2001; Mullin and Champ, 2003; Walavalkar and Kulkarni, 1996). Dioxins and dibenzofurans are very toxic products, but they are not produced during the fire and are not of concern (Fingas et al., 1993; Fingas et al., 1999).

2.6.3 Reducing of smoke

Experiments have been performed to investigate the possibilities of reducing the smoke production from in situ burnings. An important factor for the efficiency of the reduction is the composition of the hydrocarbon (Moir et al., 1993) and the composition of the emissions varies with the oil type and the size of the burn (Buist et al., 1999).

Metallic additives have been shown to be very effective in eliminating smoke emissions, however often the additives themselves result in air pollution (e.g. lead, manganese) or damaging effect (ferrocene) (Mitchell, 1991). Ferrocene is nevertheless an attractive additive since it is nontoxic, insoluble in water and the combustion by-products are CO and iron oxide. Ferrocene increases the burning temperature of the igniter fuels, but the flame spreading is not enhanced (Guenette and Sveum, 1994). Ferrocene is also very stable to heat and retains its structure up to 500°C; unfortunately it has a higher density than water, which might be a problem when applied in an oil spill situation, though ferrocene has shown very good results (Buist et al., 1999). Another additive, called RMS 9757, in liquid form has also showed promising results (Mitchell and Moir, 1992; Moir et al., 1993).

It is also possible to supply extra air during the burning to reduce the smoke production. Nordvik et al. (1995) tested two different air delivery systems for aeration of in situ burnings i.e. air jet aeration (also tested by SL Ross (1991)) and sub-surface bubble aeration. The air jet aeration system resulted in an increase in burning rate and notable reduction in smoke opacity and production; however, the system was very sensitive to wind resulting in a black smoke, when the wind pushed the flames to one side. The sub-surface bubble aeration was in general less efficient regarding smoke reduction, but the system was less sensitive to wind, hence more efficient with wind present, though the burning rate was decreased.

2.7 In situ burning in snow and ice

Oil spills in ice are much more complicated than on open water (Singsaas and Reed, 2006), and as can be seen from Figure 2.7.1, the distribution of oil in different ice scenarios can be very complex. Besides from the difficulties with handling oil in ice, ice can also be a threat to oil rigs, pipelines and vessels, resulting in a larger potential for oil spills, than in comparable environments without ice.

The research on burning oil in ice filled waters began in the 1970s with the Norcor (1975) experiments. A huge program was established to find fundamental data on the interaction of oil with Arctic sea ice. The program involved eleven discharges of a total of 56 m³ of crude oil, and the experiments were undertaken in a small bay (Cape Parry in Canada) (Norcor, 1975). The experiments also included burning of oils from melt pools. The burnings had great success, with 90 % burning effectiveness. The experiments also showed, that oil entrained in the snow, flowed into the burning pools due to the heat from the burning; however, the snow melt was not as much as expected. The research within in situ burning in ice increased in 1980s due to the increase in offshore production in Alaska and Canada.

2.7 In situ burning in snow and ice

The first recorded test of in situ burning in broken ice was in 1983 (Tier II) (Buist and Dickins, 2003). Buist and Twardus (1984) performed experiments in laboratory scale and meso-scale, where the purpose was to look at oil spreading, flame spreading and burning efficiencies. In 1984, 1985 and 1986 test burns were performed at OHMSETT (The National Oil Spill Response Research & Renewable Energy Test Facility) (Smith and Diaz, 1985b, 1987) with oil in broken ice, with ice covers ranging from 30-90 %. The results showed that oil can be burned in broken ice but that emulsification and increase of flash point (aeration) will inhibit the burning (Smith and Diaz, 1985b; 1987). Brown and Goodman (1986) performed tests with in situ burning of crude oil in ice leads in the test basins at Esso Research ice basin in Calgary, Canada. They found high burning efficiencies up to 90 % in moderate wind, if the oil was herded into long narrow leads. They also found that brash ice reduces flame spreading, lowers the burning rate and somewhat lowers the burning efficiency (Buist and Dickins, 2003). During the 1970s and 1980s the Arctic field experiments helped in situ burning become accepted as the most effective oil recovery strategy in ice covered waters, based on the body of knowledge on the fundamentals of burning in different ice types. At the end of the 1980s and beginning of 1990s several small-scale field tests and tank tests were performed in Svea, Svalbard in basins in fjord ice with fresh and weathered crude oil (Statfjord/Gullfaks). The main objective was, among others, to study the burning processes of emulsions, develop igniters and the influence of wind and waves (Bech et al., 1992a; Bech et al., 1993; Guenette and Wighus, 1996). Among other things they found that it was possible to burn emulsions, especially with the right igniter. From the mid 1990s until the middle of 2000 the activity level has been relatively low (Singsaas and Reed, 2006). There is still a need for new research on measures and techniques for expanding the operating window for burning oil in ice (Dickins, 2004). In Table 2.7.1 the use of in situ burning in ice-filled waters is listed for both experiments and as a countermeasure to accidental oil spills.

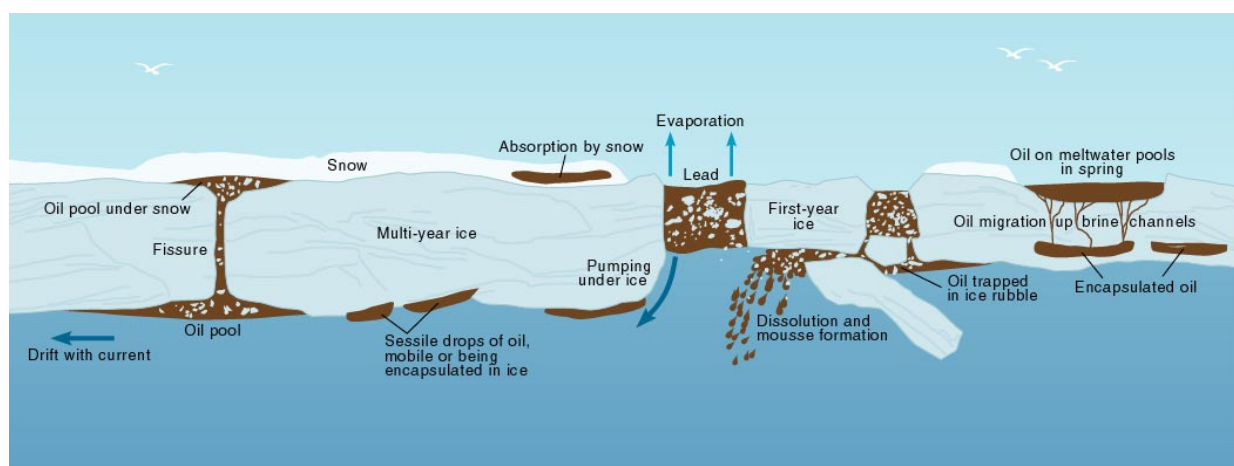


Figure 2.7.1 Illustration of the complex distribution of oil in different oil-in-ice scenarios (AMAP, 1998).

The types of test with burning oil in arctic conditions have primarily been burning of oil/snow mixtures, small and mid-scale tests in basins and test pans and mid-scale and large-scale tests as part of field trials (Buist and Dickins, 2003). The ice conditions have primarily been static pack ice. Only few tests have been performed in dynamic ice, but these studies have indicated that in situ burning is sensitive to movements, ice concentration/coverage, oil thickness and presence or absence of frazil ice, which can absorb the oil (Buist et al., 2003). Oil spilled in dense pack ice will drift with the ice (Løset et al., 1994). It has also been postulated that the interface between ice and oil is more efficient at transferring heat from the oil to the underlying ice than water (Buist and Dickins, 2003). Thus it was found that higher slick thicknesses were needed (double) to burn oil on ice compared to burning oil on water. No difference in slick thickness is found for different ice types. Both the burning rate and the burning efficiency are also lower for burning oil in ice than on water (Buist and Dickins, 2003).

In broken ice, the ice coverage is of great importance for the choice of response method. From open water up to 3/10 ice the oil will spread as in open water and open water techniques should be used. In ice from 3/10 to 6-7/10 the conditions are very difficult as the ice will reduce spreading and movement but not to an extent to contain the oil and use of booms in such conditions is very difficult. Above 6-7/10 to 9/10 ice cover and the ice might act as a natural containment and reduce weathering and spreading (Guenette and Wighus, 1996). Burning of oil in broken ice during break-up will be easier than during freeze-up. This is because of the darkness and slush ice during freeze-up and the light, less slush ice, deterioration of floes, melting and warmer temperatures during break-up (Brandvik et al., 2006). According to Buist and Dickins (2003) only one field experimental in situ burning in broken ice has been reported, and that was in 1986 at the coast of Nova Scotia, where two 1 m³ crude oil (Alberta Sweet Mixed Blend) were released in close pack ice (9/10 ice cover) with brash ice and burned with burning efficiencies of 93 % and 80 %. Thus large-scale field experiments in broken ice are very limited (Brandvik et al., 2004). Oil in snow (up to 70 %) can be burned with great success (Buist, 2000) and also for burning in brash ice and high ice concentration efficient results have been obtained (Buist and Dickins, 1987). The small pieces of brash, frazil or slush ice will accumulate with the oil against the larger ice floes and thereby control the thickness and spreading of the oil (Buist et al., 2003). Therefore, it is important to know the content of slush ice between ice floes, and not only the solid ice forms, as often reported, since the slush ice concentration can significantly slow and limit the oil spreading even in low to moderate solid ice concentration (Buist and Dickins, 2003). In situ burning can also be used in spill scenarios, where the oil is trapped beneath the ice, by cutting a hole in the ice where the oil can accumulate. In situ burning can also be used for piled ice (ridges, hummocks and rubble fields) and in rafted ice. When rafted ice is formed, one ice sheet slides upon another and forms natural pools for the oil (Morson and Sobey, 1979).

2.7 In situ burning in snow and ice

Table 2.7.1 *Accidental and experimental in situ burnings of oil spills from 1958 – 2009 in ice-filled conditions. Data from Buist and Dickins (2003); Buist et al. (1994) and Fingas (1998).*

Year	Location	Description	Event	Oil/Amount	Results
Accidents					
1969	Finland	M/T Raphael	Ice	200 T crude oil	85 %
1970	Sweden	Othello/Katelsysia	Packed sea ice	52000-90000 T Bunker C	Success
1970	Canada	Deception Bay	Sea ice and pools	1500 T diesel + gasoline	
1970	Canada	Quebec	Sea ice	2000 T diesel + gasoline	Success
1972	Sweden	Diesel fuel spill	Ice-choked river	600 T diesel fuel	400 T burned
1976	USA/Canada	Lake Huron	Oil melt out of ice	220 T diesel + gasoline	80-95 %
1977	USA	Bouchard #65	Broken ice	300 T No. 2 fuel	15 T burned
1979	Canada	Imperial St. Clair	Ice conditions		Success
1980	Canada	Edgar Jourdain	After ice melt	50 T marine diesel	Success
1983	Canada	Warwick Lake	Ice surface	59 T diesel	85 %
Experiments					
1974-5	Canada	Norcor – Cape Parry	Oil spill burned in melt-pools on ice	56 m ³ crude oil	Proved use of burning in ice
1983	USA	Beaufort Sea	Broken ice	Circo 4X light oil, Murban crude	55-73 %
1984-5	USA	Beaufort Sea	Various ice covers		
1984-6	USA	OHMSETT	In ice	Fresh/weathered Prudhoe Bay	
1985	Canada	Offshore Atlantic	Among ice		
1986	Canada	Esso Calgary	Slicks in ice leads	Aged Norman wells	
1986	Canada	Nova Scotia	Pack ice	Alberta crude	
1991-3	Norway	Spitsbergen	Meso-scale experiments in ice	16-4000 L Statfjord/Gullfaks crude	
2006	Norway	Spitsbergen	Melt-pools burn	3000 L Statfjord	>96 %
2007	Norway	Spitsbergen	Meso-scale burn	200-450 L Grane crude	
2008	Norway	Spitsbergen	Meso-scale burn	200-450 L Troll B crude	
2009	Norway	Barents Sea	Large-scale	2 m ³ Troll B crude	>90%

Chapter 3 Materials and methods

This chapter gives an overview of the materials and methods that underlie the burning experiments performed during this PhD study. Most of the burnings were performed in a specially designed unit named “burning cell”. The burning cell was used in the laboratory and in field situations. Furthermore, large-scale in situ burnings were performed at Svea and in the Barents Sea. The description of the actual burning experiments and the most important results are assessed in Chapter 4 and the Papers [1], [2], [3], [4] and [5].

3.1 Oil types

The selection of the crude oils for the experiments was made very carefully to secure utmost benefit of the results. An overview of the different oil types used in the experiments is given in Figure 3.1.1. This figure is based on previous characterisation of crude oils performed by SINTEF with respect to chemical composition and weathering properties. The five crude oils used in the experiments are highlighted with a blue circle and they represent a broad range of different oil types regarding chemical composition, thus they are expected to behave differently when spilled at sea. One crude oil (Balder) is marked with a green circle since this oil was used in the initial construction of and experiments with the burning cell presented in Paper [1], prior to the experiments performed in this PhD. All the crude oils used, originated from Norwegian oil fields.

Statfjord is a light paraffinic crude oil; hence it is rich in paraffins and saturated components and has a high evaporative loss. It has medium wax content and low asphaltene content. Statfjord was used in the laboratory flume weathering experiments. Statfjord was also used in the preliminary testing of the burning cell which included both experiments in the laboratory and in field (Paper [1]).

Kobbe is a light crude oil with a very high evaporative loss and a low content of heavier components (wax/asphaltene). However, the content of wax and asphaltenes are sufficient to form unstable w/o emulsions. Kobbe is from the Goliath field in the Barents Sea, thus a Norwegian Arctic crude oil. Kobbe was used in the laboratory flume weathering experiments. Results are presented in Paper [2].

Norne is a crude oil rich in waxes (higher saturated components $> C_{20}$) and with a high pour point, that results in solidification when released at the experimental temperatures (0-2 °C). The Norne Blend used in the experiments is from the Norne field, available from Mongstad refinery, and analysis of the blend showed that it mainly consisted of pure Norne crude which is very waxy. Norne was used in the laboratory flume weathering experiments. Results can be found in Paper [2].

Grane is an asphaltenic crude oil, rich in resins and asphaltenes and therefore forms stable w/o emulsions. The density is high and the evaporative loss is low. Grane was used in the laboratory flume weathering experiments and the results can be found in Paper [2]. Grane and Balder (another asphaltenic crude oil) were also used in the preliminary testing of the burning cell, which included both experiments in the laboratory and in the field as reported in Paper [1].

Troll B pure crude oil from Mongstad oil refinery is a naphthenic crude oil, rich in cyclic and branched saturated hydrocarbons. The pour point is very low due to the low wax content (naphthenic character) and a balanced blend of emulsion stabilising components (waxes, resins and asphaltenes), thus Troll B forms stable w/o emulsions. Troll B was used in the laboratory flume weathering experiments, in the field experiments in Svea (2008) and in Barents Sea (2009). Results with Troll B experiments are found in Paper [1], [3], [4] and [5]. In addition, Troll B was used in the preliminary testing of the burning cell, which included both experiments in the laboratory and in field as reported in Paper [1].

Besides from those crude oils mentioned, experiments with IFO30 and IFO180 were performed in the laboratory at DTU. IFO stands for intermediate fuel oil and refers to, a mixture of gasoil and heavy fuel oil, and 30 and 180 means that the viscosities are 30 and 180 centistoke at 50 °C, respectively. Those fuels were tested due to their use as fuels in tankers and thereby representing an actual risk of spill in Greenland. The fuels were provided by Trumf Bunker in Aabenraa, Denmark.

The physical and chemical properties for all the oils are listed in Table 3.1.1. It should be mentioned that refined products even within the same IFO grade can vary in properties depending on the refinery process and type of crude oil (Moldestad and Leirvik, 2005). The values provided for IFO180 and IFO30 are from the SINTEF Oil Weathering Model (Johansen et al., 2010), thus only giving an indication of the properties of such oils.

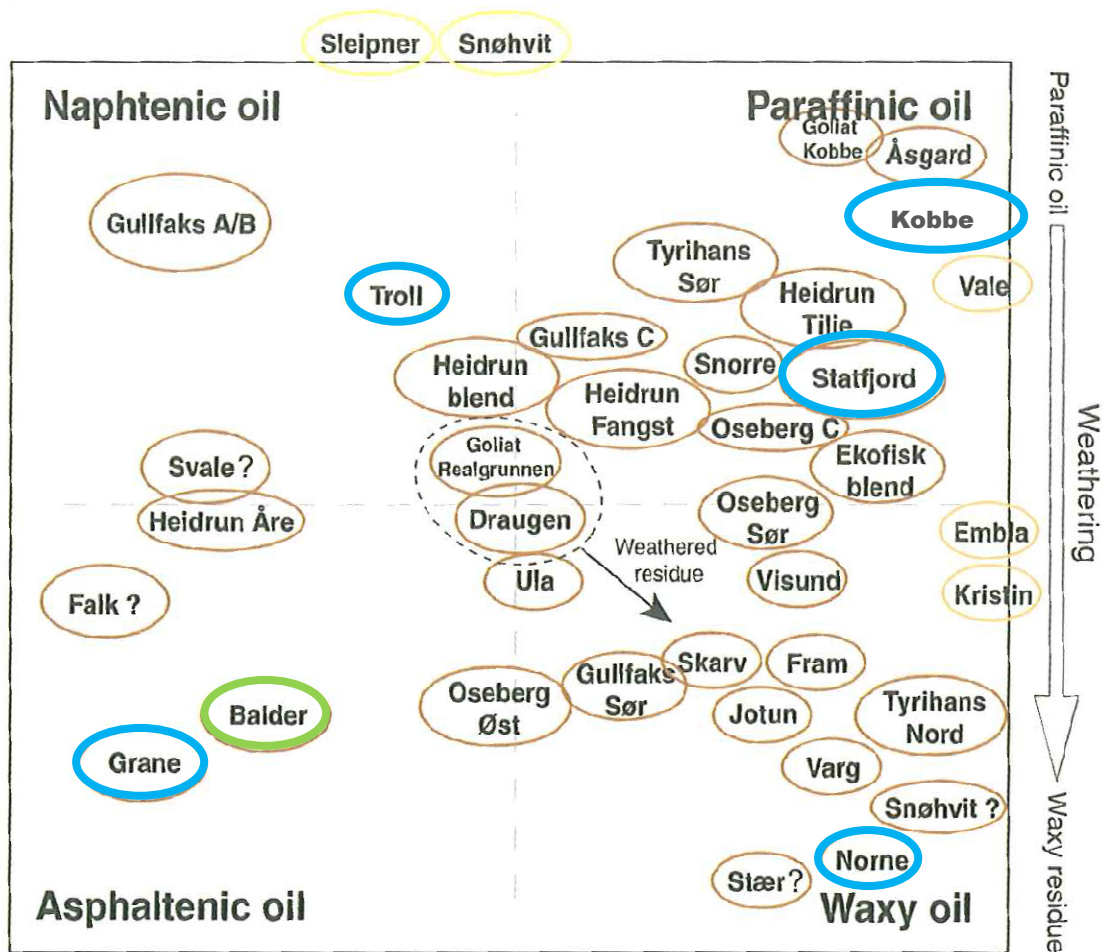


Figure 3.1.1 Categorization of different crude oils performed by SINTEF. The blue circles indicates the crude oils used in the experiments. The green circle marks an oil used in previous experiments.

Table 3.1.1 Physical and chemical properties for the fresh oils used in the experiments. Data from Brandvik et al. (2010a). Data for IFO180 and IFO30 from SINTEF Oil Weathering Model (Johansen et al., 2010). Viscosity data for Statfjord, Grane and Troll B from Faksness (2008), Kobbe from Sørheim and Moldestad (2008) and Norne from Singaas et al. (1998).

Oil type	Density (kg/m ³)	Pour point (°C)	Wax (wt. %)	Asphaltenes (wt. %)	Viscosity (cP)
Troll B	0.900	-36	0.9	0.04	299 at 2°C
Norne	0.860	21	10.8	0.3	1747 at 2°C
Kobbe	0.797	-39	3.4	0.03	51.2 at 2°C
Statfjord	0.835	-6	4.3	0.1	824 at 3°C
Grane	0.941	-24	3.2	1.4	22 at 5°C
IFO180	0.956	-12	n.a.	n.a.	10970 at 2°C
IFO30	0.936	6	n.a.	n.a.	236 a 13 °C

n.a. not available

3.2 Weathering experiments

All the samples for the burning experiments (described in Chapter 4) were taken from different weathering experiments, which are described below. The focus was on the oil in between ice floes and the weathering taking place there (see Figure 2.7.1). In Figure 3.2.1 the locations of the experimental work are shown. In the Barents Sea the large-scale field weathering experiments were performed and in Svea the meso-scale field weathering experiments were performed. The laboratory flume weathering experiments were carried out in SeaLab and the laboratory weathering experiments were performed at both SeaLab and DTU.

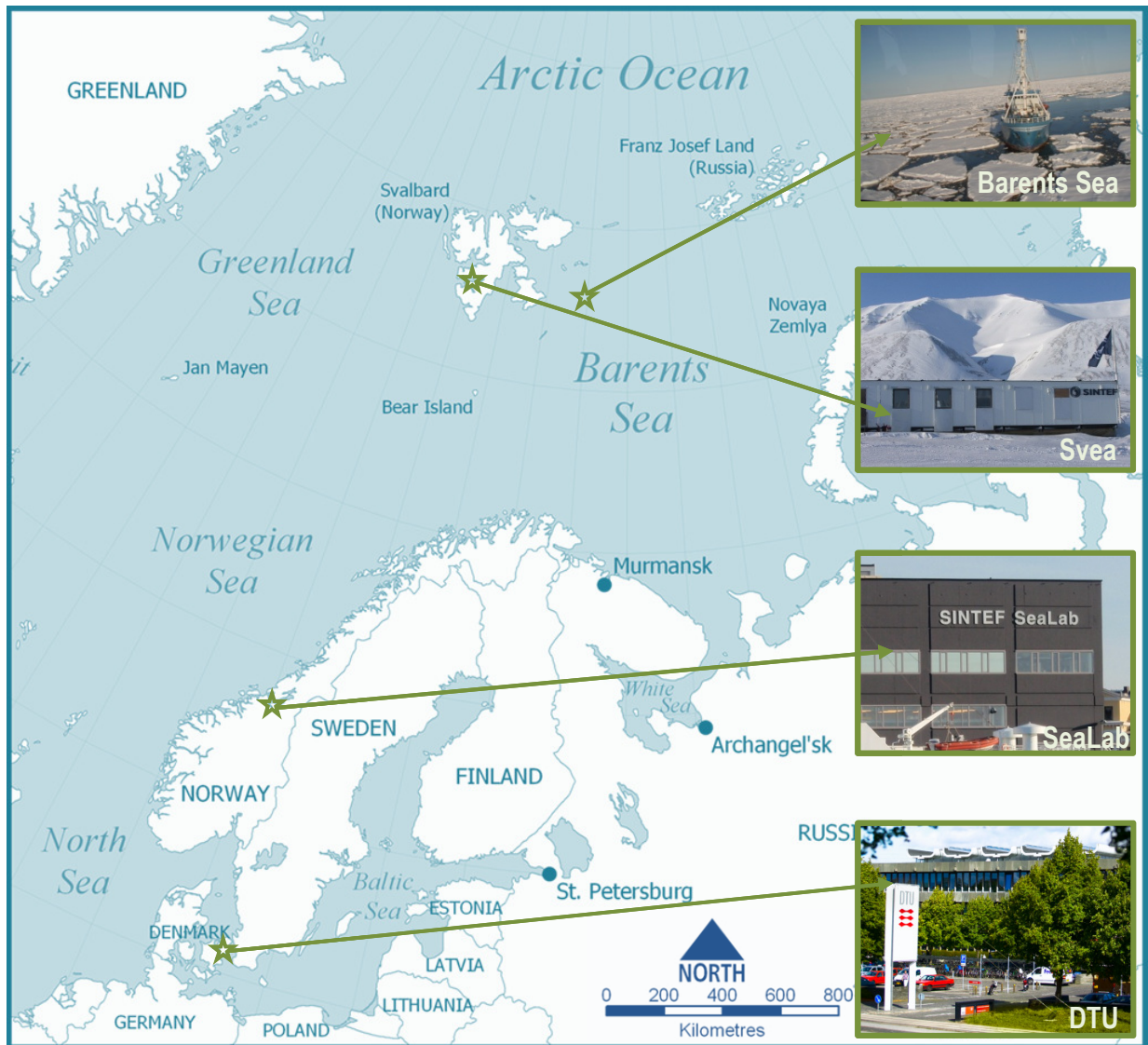


Figure 3.2.1 Overview of the locations where the experiments were performed (map: (Wikipedia, 2010) and bottom picture: ImageDTU).

3.2.1 Laboratory weathering experiments

A minor part of the samples was weathered stepwise by small scale equipment in the laboratories at SINTEF, SeaLab. However, it was not directly part of the PhD-work, but was performed during the initial construction of the burning cell and carried out as a Masters project (Daniloff, 2006). The oil was first distilled (topping) by use of a modified ASTM D86/82 distillation (Daling et al., 1990) thereby removing the light components. The distillate was emulsified, by the rotating flask technique, to simulate different scenarios with different water uptake (modified method based on Mackay and Zargorski (1982). This weathering procedure is also described in detail in Daling et al. (2003).

The laboratory weathering experiments performed in the laboratories at DTU with the bunker oils (IFO30 and IFO180), were emulsification without prior distillation. From the SINTEF Oil Weathering Model (Johansen et al., 2010) it was found that the evaporation from such oils is, as expected, very low (the products have already been treated), thus emulsification without prior distillation seems reasonable.

3.2.2 Laboratory flume weathering experiments

The majority of the samples for burning experiments were weathered in the flume basin at SINTEF, SeaLab (Singsaas et al., 1992). In the flume the weathering processes occur simultaneously and affect each other, thus simulate controlled arctic weathering conditions. The dimensions of the flume are given in Figure 3.2.2. Seawater was added the flume (4.8 m³) and the ambient conditions were controlled: 5-10 m/s wind speed at the surface, breaking waves if possible for ice, 15 cm/s current, water temperature at -1.8°C and room temperature between -1.5°C and 1°C. The weathering experiments were performed with different ice conditions: open water (0 % ice), 50 % ice cover and 90 % ice cover respectively. The crude oils used were Statfjord, Troll B, Norne, Grane and Kobbe. For each experiment 9 L of crude oil was used and the experiments lasted for 72 hours each. Samples were taken continuously from the emulsified surface for physical/chemical analysis and in situ burning. The free seawater was immediately drained off using a separate funnel before the sample was homogenized and divided into aliquots for further analysis. More details can be found in Brandvik et al. (2010a and b). The analyzed physical and chemical properties are given in Table 3.2.1.

Table 3.2.1 Physical and chemical analysis performed and units and methods used.

Property	Unit	Method
Water content of w/o-emulsion	Volume %	Daling et al. (2003)
Viscosity of weathered oil	cP (or mPas) at shear rate 10 s ⁻¹ at 3-6 °C	Daling et al. (2003)
Density of water free oil	g/mL at 15.5 °C	ASTM D4052-91
Evaporative loss	Weight %	Daling et al. (2003)

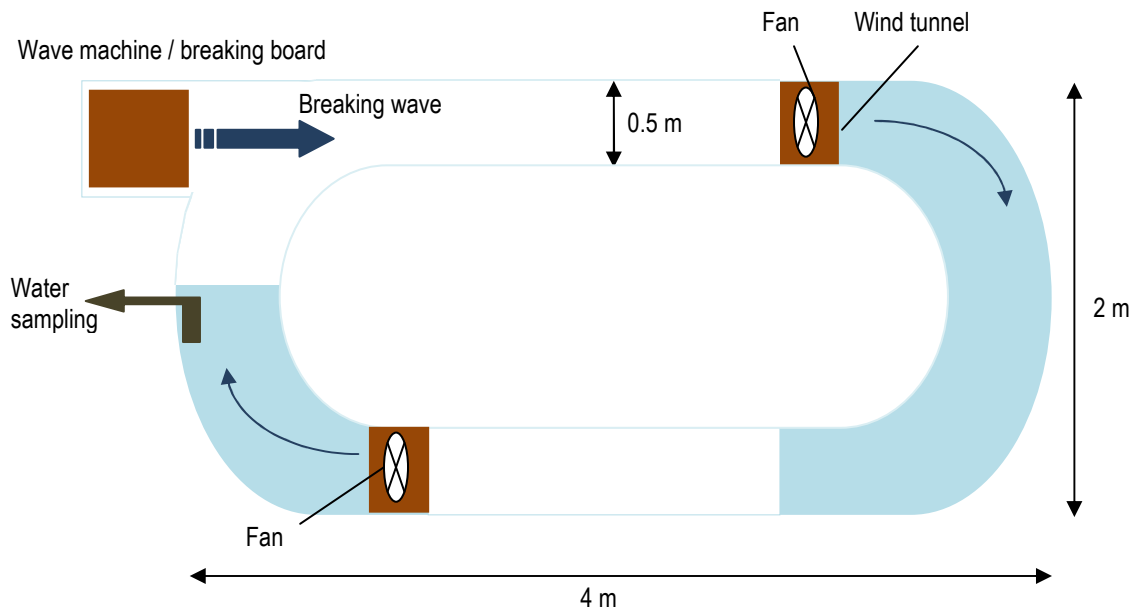


Figure 3.2.2 Outline of the flume for weathering at SINTEF SeaLab laboratories. The flume contained 4.8 m³ of sea water.

3.2.3 Meso-scale field weathering experiments

Meso-scale field experiments were performed at SINTEF field research station in Svea on Svalbard (N77.5, E16.4) in March/April 2008. A circular flume was cut in the fjord ice in Van Mijenfjorden and the dimensions are given in Figure 3.2.3. The depth of the flume was 0.5 m, thus not cut through the 1.10 m thick ice. Seawater from the fjord was filled in the flume and waves, current and air temperature were controlled. Three experiments were performed with open water (0 % ice cover), 50 % ice and 90 % ice cover, respectively. Each experiment lasted 72 hours and samples were taken continuously during the period from the emulsified surface oil. Surplus water was drained of and the samples divided into aliquots for different analysis (physical/chemical analysis and in situ burning). 200 L of Troll B crude oil was used for each of the experiments. In earlier experiments, prior to this PhD project, also Grane and Statfjord were used; these results are present in Paper [1] and Brandvik and Faksness (2009). Pictures from the meso-scale field weathering experiments illustrating the construction and use of the flume can be seen in Figure 3.2.4.

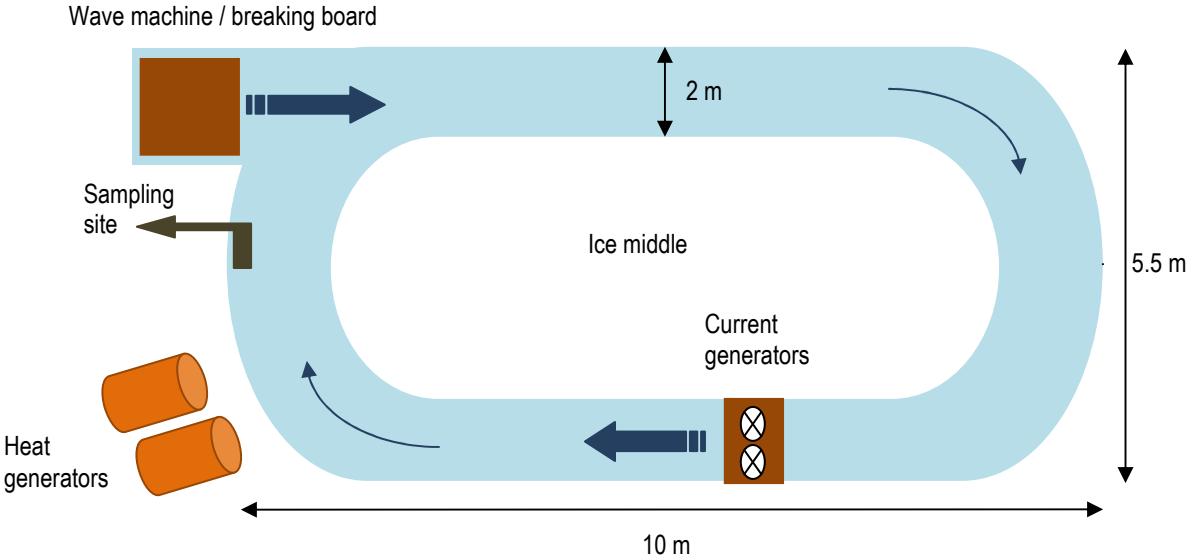


Figure 3.2.3 Outline of the flume cut in the fjord ice at Svea, Svalbard for meso-scale field weathering experiments.



Figure 3.2.4 Preparation of the weathering flume in the fjord ice (upper left). Tent placed over the flume to control air temperature (upper right). Oil applied to the flume (bottom left). 90 % ice cover weathering experiment (bottom right).

3.2.4 Large-scale field weathering experiments

A final large-scale field experiment was performed in May 2009 in the Barents Sea (N77.6, E30.9), in the marginal ice zone, with 70-90 % ice cover. The sea water temperature was around -1.8°C , the air temperature between -10 and -2°C , wind between 5-10 m/s, the visibility good and 24 hours of daylight (more details in Faksens et al. (2010)). 7 m³ of Troll B crude oil was released with a hose through an over-flow chamber placed on an ice floe. Samples were taken continuously during the weathering period from the bulk phase of the oil slick, surplus of water was drained of and the sample divided into aliquots for further analysis (physical/chemical analysis and in situ burning). The experiment lasted 6 days and pictures from the weathering experiments can be seen in Figure 3.2.5. Results from the experiments can be found in Paper [3] and Brandvik et al. (2010a).



Figure 3.2.5 Weathering experiment with Troll B crude oil in the marginal ice zone in the Barents Sea at the beginning of the experiment (top). Measuring the oil slick thickness (bottom left) and sampling (bottom right).

3.3 Quality control

3.3.1 Accuracy of burning cell results

Repeated burnings with the same oil were performed in the burning cell to control the accuracy of the burning cell, with regard to finding the same burning effectiveness. Four fresh Norne crude oil samples and three fresh Staffjord crude oil samples, all from the same batch, were burned consecutively. The results from the burning experiments can be seen in Table 3.3.1.

The Staffjord results show quite good replicates with a small standard deviation and very good repeatability. The repeatability is calculated as the variation in measurements when one person takes multiple measurements using the same instrument and techniques on the same analytes (standard deviation/average)*100). The 95% confidence interval is [63.7, 64.3] and all the values are within the interval.

The standard deviation for Norne is somewhat larger and the repeatability is also higher: 7.2. However, a rule of thumb says that a repeatability of ± 10 is good (Eriksson, 2006). The 95% confidence interval is [63.2, 72.8] with one sample outlying this interval. The poor accuracy of the results for Norne is expected to be a result of variations during the experiments, since an unknown amount of the oil flowed over the edge of the burning cell during burning for two of the experiments. This resulted in a forced increase in burning effectiveness. With that in mind the quality control of the burning cell seems to find that it is possible to replicate the results found within acceptable variation.

Table 3.3.1 *Replicates of burnings with Norne and Staffjord fresh crude oils.*

	Staffjord fresh - 3 samples			Norne fresh - 4 samples			
Burning Effectiveness [%]	64	63	63	65	63	69	74
Average Burning Effectiveness [%]	64			68			
Standard Deviation	0.6			4.9			
Repeatability [%]	0.9			7.2			

3.3.2 Ignition procedures

Two types of igniters were used in the burning experiments conducted during this PhD study. For the entire burning cell experiments a propane torch was used (Figure 3.3.1). The torch was held in the same position, a 30° angle approximately 3 cm from the oil surface, for 10 seconds of heating. Depending on whether or not the oil ignited the procedure was repeated up to two times more, with intermediate pauses of 10 seconds. If the oil did not ignite after 3 times of 10 seconds of heating the oil was classified as not ignitable. Sometimes extra heat was added after the standard procedure, to get an impression on how much more heat was required to ignite the oil sample, if possible. During some of the burning experiments in the laboratory at DTU, the propane torch was weighed before and after the ignition to roughly calculate the energy input from the igniter and thereby compare the energy input between the experiments. An overall increase in energy input was as expected seen for samples with a higher content of emulsified water; this is because emulsions are more difficult to ignite than fresh oils. For those samples that could not be ignited the energy input was higher than for those samples that could be ignited. This shows that the ignition procedure secures that the difficult to ignite samples have been tried ignited with high energy input.

For the large-scale in situ burning experiments 0.5 L and 1 L of gasoline or light crude oil (Statfjord) was added 4 % Alcopol O 60 emulsion breaker and gelled (Figure 3.3.2). The igniters were placed on the oil slick and ignited. For the large-scale burning experiment in the Barents Sea several igniters were placed around the slick. If the warmth from the igniter was enough to perform ignition of the oil slick and flame spreading, the slick was classified “ignitable”. This method has been proven earlier by Guenette et al. (1994) as an efficient method to ignite an oil slick. More specific details from the experiments can be found in the Papers [1] and [3] and in Chapter 4.



Figure 3.3.1 Applying (photo: Per Johan Brandvik), ignition (photo: Per Johan Brandvik) and burning of an oil sample in the laboratory burning cell.



Figure 3.3.2 Gelled gasoline in plastic bags ready for use, placed in the oil slick and ignited right (right photo: Per Johan Brandvik).

The propane torch can be characterized as a premixed flame, e.g. the gaseous fuel and air are mixed prior to ignition thus the rate of combustion is typically high (Drysdale, 2004). The gel igniter can however be characterized as a diffusion flame, where the fuel and air are initially separated and the combustion occurs where the gases mix in a favourable mixture for combustion (Karlsson and Quintiere, 2000). The two methods and the heat transfer processes are illustrated in Figure 3.3.3. The heat transfer from the propane torch to the oil is primarily by convective heat transfer, though some radiative heat is also expected (Karlsson and Quintiere, 2000). The heat transfer from the diffusion flames conducted by the gel burning to the oil is primarily by radiative heat from the flames, additional convective heat will occur if wind deflects the flames, however this is not expected to be the case in the laboratory, but could be the case in the field. A premixed flame is expected to burn with a higher efficiency (utilization of amount of fuel per time unit) as a result of the well adjusted fuel/air mixture. On the other hand the gel burns for a longer period than the 10 seconds of heating with propane torch. To compare the two ignition methods, experiments were performed in the laboratory using the burning cell with both methods. Table 3.3.2 outlines the experimental set-up and results.

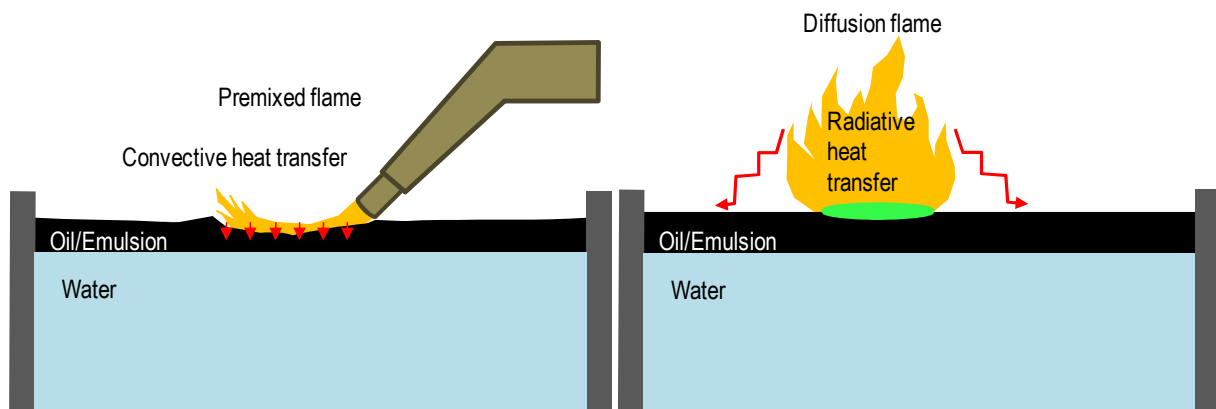


Figure 3.3.3 Ignition of a sample in the burning cell with propane torch (left) and gelled gasoline (right)

Table 3.3.2 Experimental set-up and results from testing of the two ignition methods in the burning cell.

Sample ID	Water content [%]	Evaporation [%]	Burning Effectiveness Corrected [%]		Ignition procedure	
			Propane	Gel	Propane	Gel
			Norne 1	11	9	53
Norne 2	21	9	57	50	1x10 sec. to ignite	1 mL gel to ignite
Norne 3	40	9	46	48	1x10 sec. to ignite	1 mL gel to ignite
Norne 4	27	13	50	49	2x10 sec to ignite	2 mL gel to ignite
Norne 5	50	13	48	44	3x10 sec. to ignite	3 mL gel to ignite
Norne 6	50	15	-	23	3x10 sec. No ignite	3 mL gel to ignite
Norne 7*	55	15	-	26	3x10 sec. No ignite	3 mL gel to ignite
Troll	30	19	64	75	3x10 sec No ignition	3 mL gel to ignite
Grane	52	4	-	-	3 x10 sec + extra No ignition	5 mL gel No ignition

*average of double ignitions, - not ignitable

The samples for the experiments were prepared in the laboratory (see Section 3.2.1). The same procedure was used for the propane torch as described above. The amount of gelled gasoline was scaled to fit the burning cell and 1 mL gelled gasoline with 4 % emulsion breaker was applied to the oil surface and ignited. The amount was gradually increased with one mL if the oil did not ignite. Although the numbers of experiments were limited a clear trend is seen between the two ignition methods (Figure 3.3.4). Two experiments (Norne 6 and 7) did not follow that trend. Here the 3 mL of gelled gasoline could ignite the samples but with a low burning effectiveness. The difference might be due to that the increase in amount of gel, supplying more heat for a longer period of time than a second or third ignition attempt with the propane torch. This indicates that the amount of gel recommended for a standard procedure with the laboratory burning cell should be 2 mL.

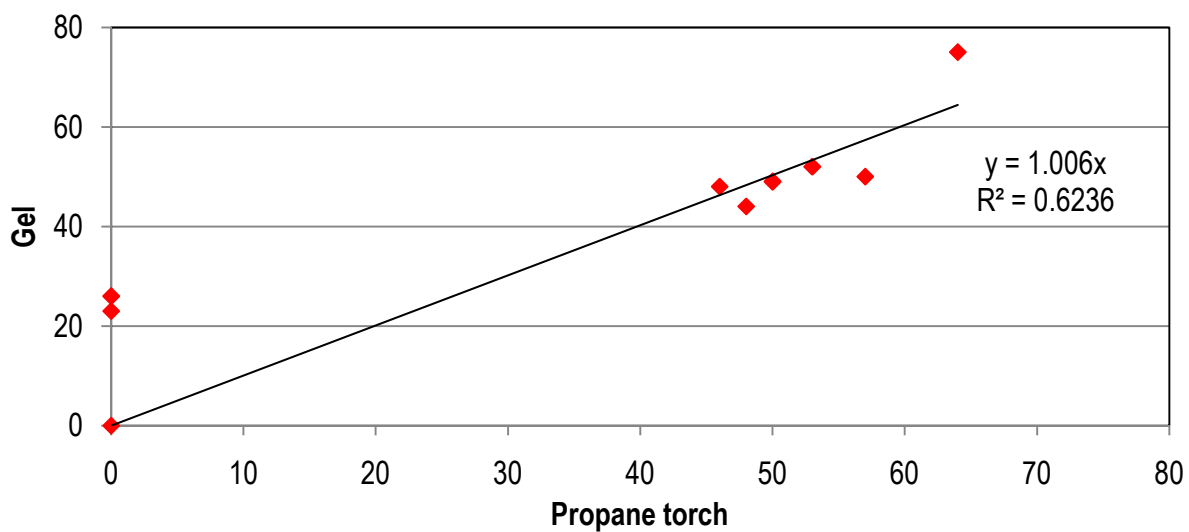


Figure 3.3.4 The correlation between the burning effectiveness results from igniting oil samples with gel and propane in the burning cell.

3.3.3 Oil absorbent pads

After each burning (field/laboratory) the residue was collected with oil absorption pads of the brand 3M. A picture can be seen in (Figure 2.5.1 and Figure 4.4.1). The pads are water repellent and thus very little water is collected with this method (less than 10 %), this is also what Smith and Diaz (1985a) found (+/- 2%). The amounts of oil left after treatment with the pads are also very small (less than 5 %).

3.4 Analysis of burn residue and soot

Soot and burn residue samples were taken from some of the burning cell experiments performed at DTU and analysed for metals, total hydrocarbons (THC) and poly aromatic hydrocarbons (PAH). Burn residue samples were taken from the burning cell experiments performed at Svea (Section 3.2.3) and analysed for THCs and PAHs.

The burn residue samples were taken with a small alumina spoon and transferred into a 1.5 mL GC-vial and stored for 5 °C until analysis. Soot samples were collected in a clean new alumina filter in the exhaust channel. Only enough soot was collected in few of the burnings.

3.4.1 Metal analysis

The metal concentration in the residue samples were analysed following NIST 1634b (Wondimu et al., 2000) with some modifications. Approximately 0.250 g of oil sample was transferred to the digestion liner and 8.00 mL concentrated HNO₃, 2.00 mL H₂O₂ and 0.5 mL HCl were added and digested in an Anton Paar Multiwave 3000 according to the following program: 800 W / 20 min, 30 min hold, ventilation 15 min. The resulting digest was filtrated and transferred to a 25 mL volumetric flask and the flask was filled to the mark with Milipore water.

The soot samples (approximately 0.25 g) were transferred to the digestion liner and 10.00 mL concentrated HNO₃ was added and digested in an Anton Paar Multiwave 3000 according to the following program: 1200 W / 30 min, 30 min hold, ventilation 15 min. The resulting digest was filtrated and transferred to a 50 mL volumetric flask and the flask was filled to the mark with Milipore water.

A filter sample was also analysed for the heavy metals. Approximately 0.50 g of oil sample was transferred to the digestion liner and 2.00 mL concentrated HNO₃ and 8 mL HCl were added and digested in an Anton Paar Multiwave 3000 according to the following program: 700 W / 5 min, 30 min hold, ventilation 15 min. The resulting digest was filtrated and transferred to a 25 mL volumetric flask and the flask was filled to the mark with Milipore water.

The metal content was measured by a Varian 720-ES ICP-OES. All analyses were made in duplicate.

3.4.2 Hydrocarbon and PAH analysis

Burn residue and soot samples from the laboratory experiments at DTU were diluted in dichloromethane (DCM) and spiked with recovery internal standards (RIS) prior to analysis on GC/FID (gas

chromatography/flame ionization detection) and GC/MS (gas chromatography/mass spectrometry). The GC/FID analysis was performed according to a modification of EPA Method 8100 (USEPA, 1986). THC (Total Hydrocarbons) was quantified by the method of internal standards using the baseline corrected total area of the chromatogram and the average response factor for the individual C₁₀ to C₃₆ n-alkanes. GC/MS analyses were performed according to a modification of EPA Method 8270D (USEPA, 2007) and the quantification of target compounds was performed by the method of internal standards using average response factors (RF) for the parent compounds.

The burn residues from Svea presented in Paper [5] were analysed in the following way. The oil samples were dissolved in DCM to a concentration of 10 mg/mL. GC/MS analysis was performed using a Hewlett-Packard combined Model 5890 gas chromatograph – Model 5972 mass selective detector. The GC column was a 30 m RESTEC Rtx-5sil MS (0.25 i.d., film thickness 0.25 µm). The temperature program applied to the GC oven was: 40 °C (10) – 5 °C/min – 320 °C (10). All the GC-MS results are presented as total ion chromatograms (TIC).

Chapter 4 Experimental work with in-situ burning

This chapter is an assessment of the experimental work and main results conducted in this PhD study with regards to in situ burning. The description of the weathering experiments of the oil used in the burning experiments can be found in Chapter 3, together with other information regarding materials and methods.

4.1 The burning cell

This section summarizes how the burning cell works and how the ignitability data produced with the burning cell is verified with field data. Furthermore, some words about the use of burning effectiveness and ignitability as terms are included.

4.1.1 Design of the burning cell

A burning cell has been constructed for testing ignitability of oil samples (100 mL) as a function of oil type, weathering time and ice conditions. The burning cell was initially constructed in 2006-2007 and modified and improved during the PhD study. The final design appears as shown in Figure 4.1.1, and is a complete unit with exhaust system, full temperature control and protection of the operator. The oil samples are burned upon sea water in a double layered cup, named burning cell on Figure 4.1.1. Cooling of the cup, by 10°C cold water circulating with a flow of 500 mL/min, is performed to prevent the system from overheating during burning and provide a more realistic system. The cooling temperature of 10 °C represents a broad range of conditions. Temperatures in the flame, oil and water just beneath the oil layer are measured with thermocouples (k-type). The design and use of the burning cell is described in more details in Paper [1]. The oil samples for the burning experiments came from the different weathering experiments described in Section 3.2. The samples were burned as soon as possible after collection and the early and unstable samples were burned within an hour, while the more stable samples could be stored until the next day. The ignition procedure and collection of the residue is described in Section 3.3.2 and 3.3.3 respectively.

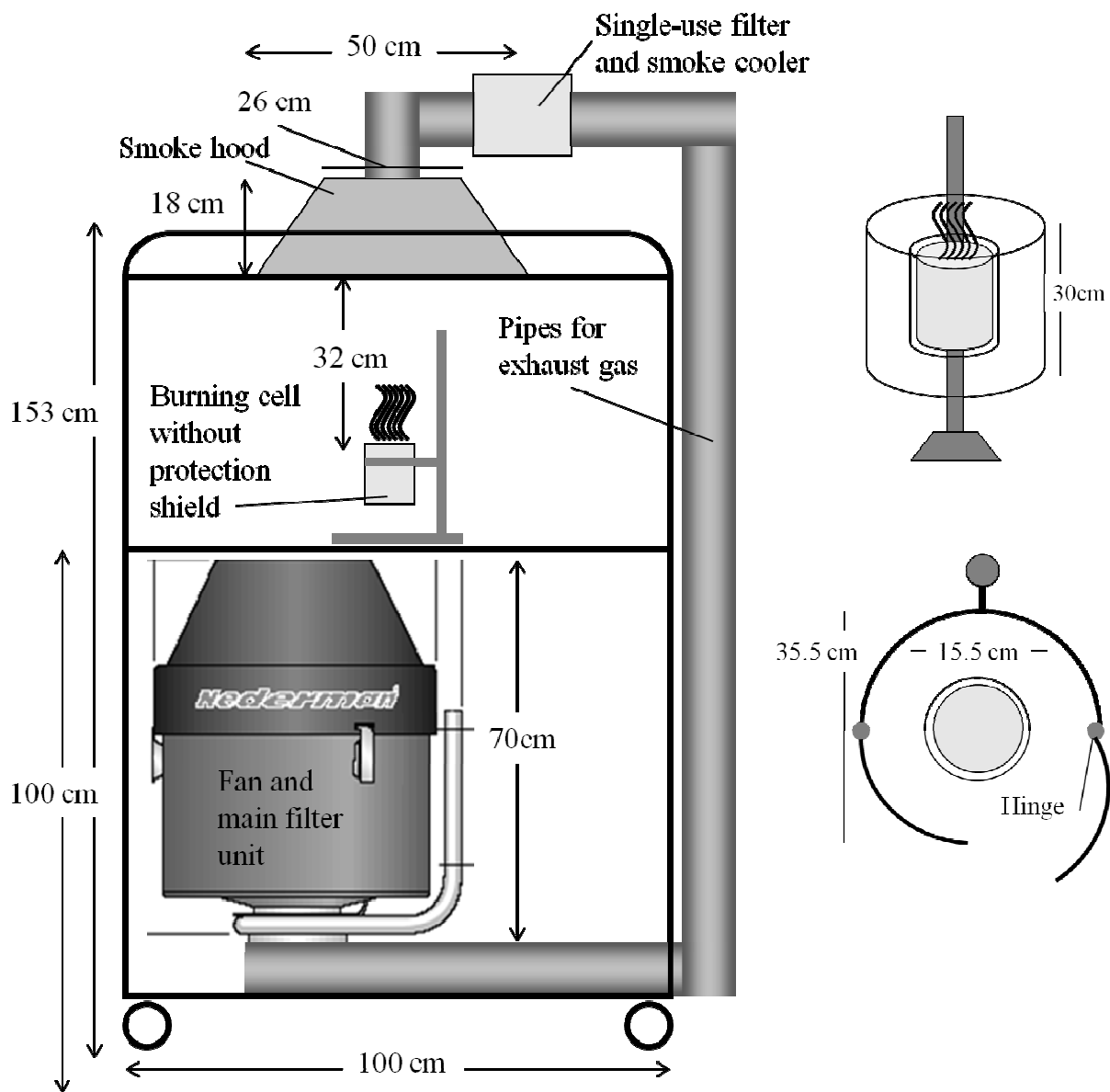


Figure 4.1.1 Conceptual outline of the burning cell. Details of the safety shield for protection of the operator is shown to the right.

4.1.2 Terms used to characterize the burning results

The burning effectiveness reported in the papers and in the thesis is calculated in the following way:

$$\text{Burning Effectiveness (BE\%)} = 100 \cdot \left(1 - \left(\frac{\text{mass of residue}}{\text{mass of initial oil}} \right) \right) \quad (1)$$

Next, the burning effectiveness is corrected for the water content measured in the weathered oil sample. This is done since the emulsified water is either broken or boiled out before the actual oil can be ignited and burned. Burning effectiveness corrected for water therefore gives a more precise picture of the actual amount of oil that has been burned. The calculation is as written below:

$$\text{Burning Effectiveness Corrected (BE\% - Corr.)} = 100 \cdot \left(\frac{1 - (100 - \text{BE\%})}{(100 - \text{WC\%})} \right) \quad (2)$$

WC% is the water content in the weathered sample.

The burning effectiveness is determined by the spill size (volume), oil thickness and ambient conditions and can thus vary a lot dependent on the circumstances for the in situ burning event. Therefore to describe the success of in situ burning, regardless of the circumstances, the terms “ignition” and “no ignition” are used and refer to whether or not it is possible to ignite the oil sample. The ignition/no ignition terminology are also used to determine the time-window for in situ burning, where the length of the time-window is defined as the midpoint between the last ignitable sample and the first not ignitable sample. In the graphic presentation of the BE%-Corr., an s-curve is sometimes plotted as well. The s-curve is a cumulative normal distribution function fitted to display the main trend in the BE%-Corr. results. The end of the in situ burning time-window is also visualized by a sharp drop in the s-curve.

4.1.3 Verification of the burning cell

The initial results obtained by use of the burning cell were verified with burning results from field experiments. The field experiments were performed at Svea, Svalbard in 2007, prior to this PhD study, and consisted of six meso-scale in situ burnings with 200-450 L (dependent on degree of emulsification) Grane crude oil. The oil was weathered for different periods of time and burned in a chamber cut out in the fjord ice (see Figure 4.4.2). The burning effectiveness results found by use of the burning cell and from the field experiments are plotted as a function of water content in Figure 4.1.2 and demonstrate a high correlation between the laboratory and field experiments. Especially in the area where the samples become not ignitable (sharp drop in s-curves), the correlation is very good. The variations in the burning effectiveness are of less importance since the burning effectiveness depends on the circumstances of the burning (volume, thickness, ambient conditions) as written in Section 4.1.2. This verification of the burning cell creates the basis for the further use of the burning cell as a tool for measuring ignitability and thereby maps the operational time-window for the use of in situ burning as a function of oil type and weathering conditions (time and ice).

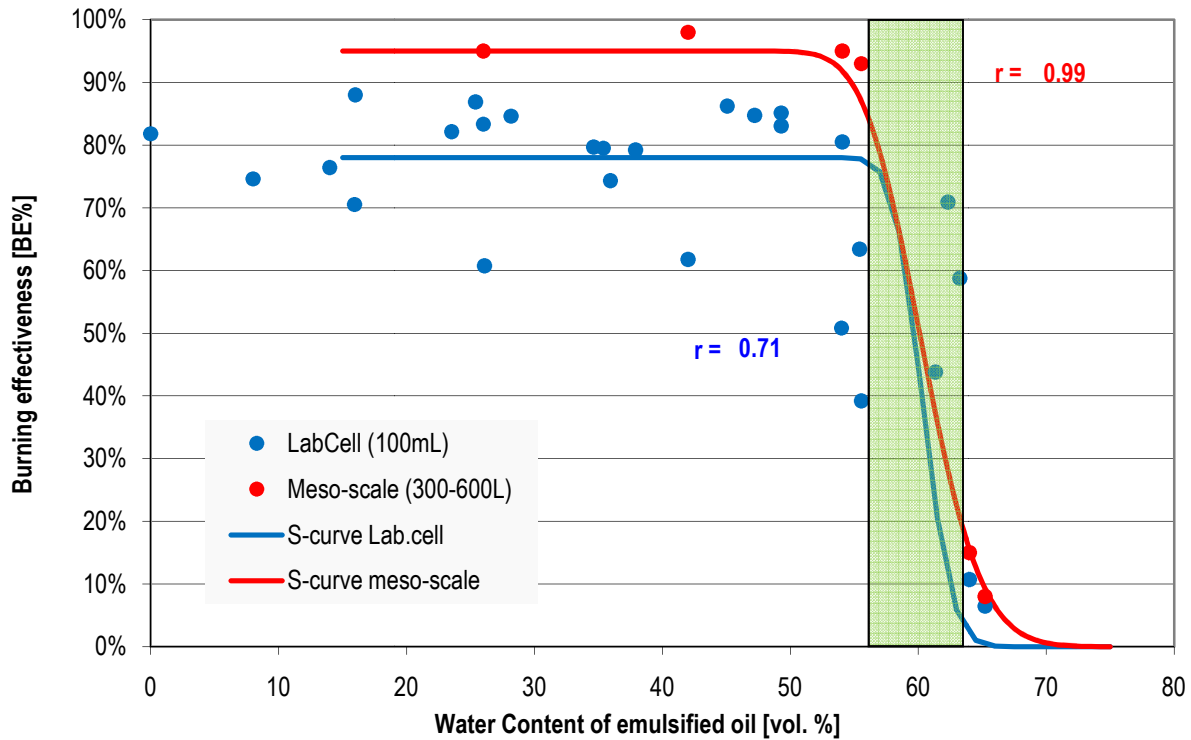


Figure 4.1.2 Burning effectiveness (BE%) measured with the burning cell (100 mL) and from meso-scale burning experiments (200-450 L) on Svalbard using Grane crude oil as a function of water content in the emulsified oil. The smoothed functions are s-curves fitted to the data and the correlation between the measured data and the functions are given on the figure (r). The green area indicates where the oil samples become not ignitable.

4.2 Laboratory experiments with the burning cell

For in situ burning to be an operational tool there is a need for better defining the potential and limitations regarding oil types and weathering degree. Laboratory flume weathering experiments were performed with Kobbe, Norne, Grane, Troll B and Staffjord crude oil as described in Section 3.2.2. The burning cell was used to measure the ignitability of the oil samples as a function of weathering conditions (0, 50 and 90 % ice cover) and thereby finding the time-window for in situ burning for such oil types. In Paper [2] the results with Grane, Norne and Kobbe can be found and in Paper [1] the results with Staffjord crude oil are presented. The results for Troll B crude oil are given in Paper [3] and will be presented in Section 4.5. In Figure 4.2.1 the burning effectiveness is shown as a function of weathering time for Kobbe, Norne, Grane and Staffjord. The results show that the ice conditions are of great importance for the time-window for in situ burning. In the experiment with no ice, the weathering processes occurred fast, due to a high level of energy in the system, thus a high water content and high evaporative loss were measured in the oil samples. With ice present (50 % and 90 %) the wave energy was inhibited, thus the weathering processes are reduced and the time-window for in situ burning is longer compared to an open water scenario.

4.2 Laboratory experiments with the burning cell

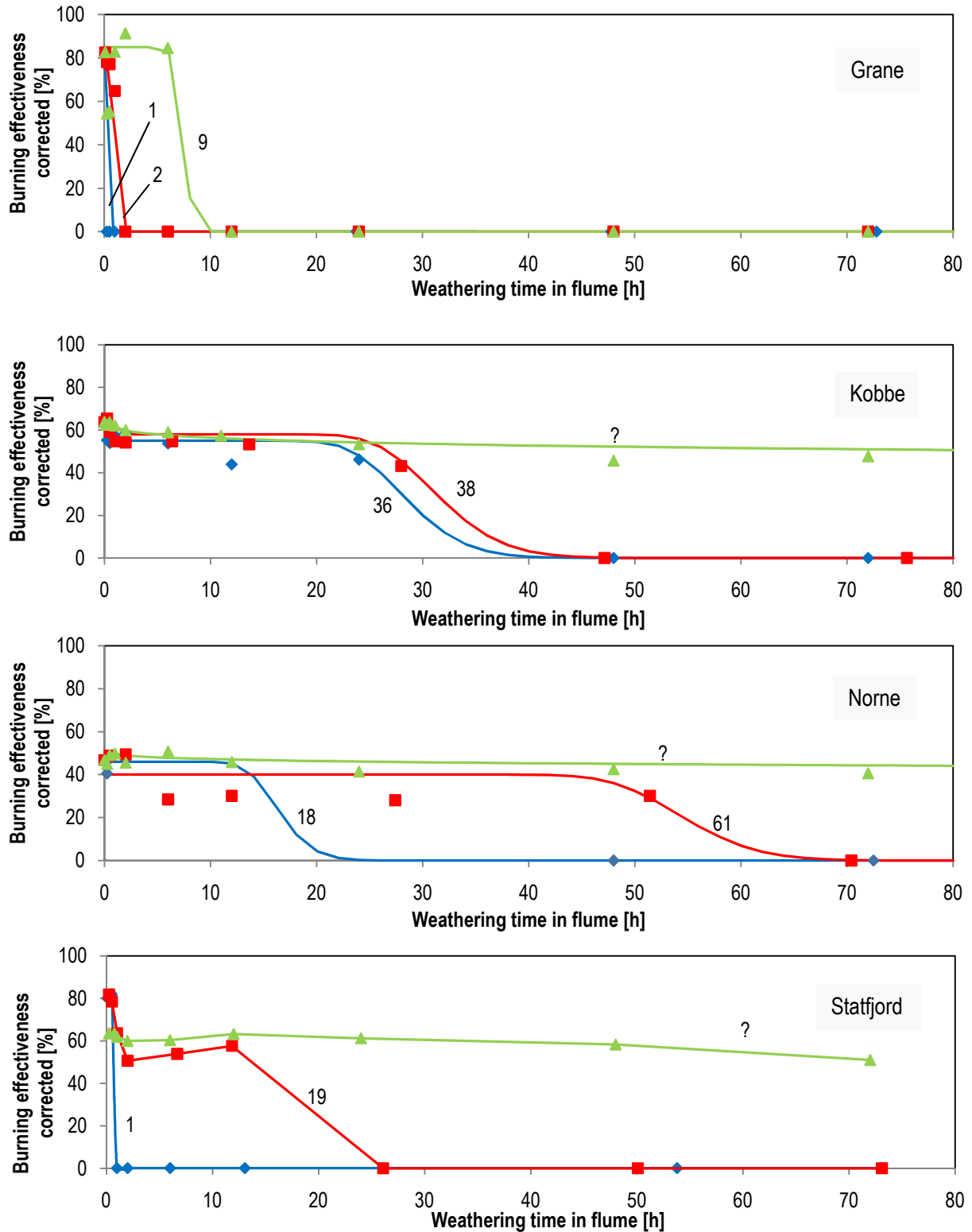


Figure 4.2.1 Burning effectiveness as a function of weathering time in the laboratory flume for Kobbe, Norne, Grane and Statfjord crude oil. ♦ Open water, ■ 50 % ice cover and ▲ 90 % ice cover. The estimated time-window for in situ burning (hours) are indicated as well.

The results also showed that the time-window for in situ burning varied largely between the oil types, due to the diverse chemical compositions. The chemical composition directly influences the weathering processes in particular the ability to rapidly form stable w/o emulsions and the content of residue volatile components in the residue.

The asphaltenic Grane crude oil had the shortest time-window, 9 hours or less, of all the oils tested. This is due to a low content of volatile components and a high content of emulsion stabilizing components, which contributes to a rapid formation of stable emulsion.

For the light Kobbe crude oil the time-windows for in situ burning were much longer for all three ice conditions compared to Grane. This is because Kobbe creates unstable emulsions that can easily be broken by heat. This is also the explanation for the little difference between the open water and 50 % ice cover experiments.

The waxy Norne crude oil had time-windows from 18 hours to more than 72 hours (for the 90 % ice cover experiment the weathering period was too short to find the time-window for in situ burning). Emulsions stabilized with wax are unstable and the formation depends on the energy in the system, thus a great variation in the time-windows for in situ burning, between the three experiments was found.

Statfjord crude oil also has a high content of wax, thus, as for Norne, the ice cover (energy in the system) has a great influence on the weathering processes and the number of ignitable samples, as can be seen from Figure 4.2.1.

Experiments with the bunker fuels IFO30 and IFO180 were conducted at the laboratories at DTU. Different emulsions were prepared and tested for ignitability in the burning cell (see Section 3.2.1). The results show that the higher water content in the oil the lower is the burning effectiveness (Figure 4.2.2). When these findings are compared with data from the SINTEF Oil Weathering Model (Figure 4.2.3), simulating how the oil is behaving when spilt at sea with different wind conditions, it is possible to find the time-window for burning the oil. For IFO30 with a wind speed of 5 m/s the oil was ignitable for 6 hours and for IFO180 the time-window will be even shorter (Fritt-Rasmussen et al., 2010).

From the results it can be concluded that in situ burning is a good response method for a waxy, a light and a paraffinic crude oil, however the time-window for an asphaltenic crude oil as well as bunker fuels is very short. This clearly shows that knowledge regarding oil composition and weathering in relation to in situ burning is important in connection with both contingency planning and during oil spill operations.

4.2 Laboratory experiments with the burning cell

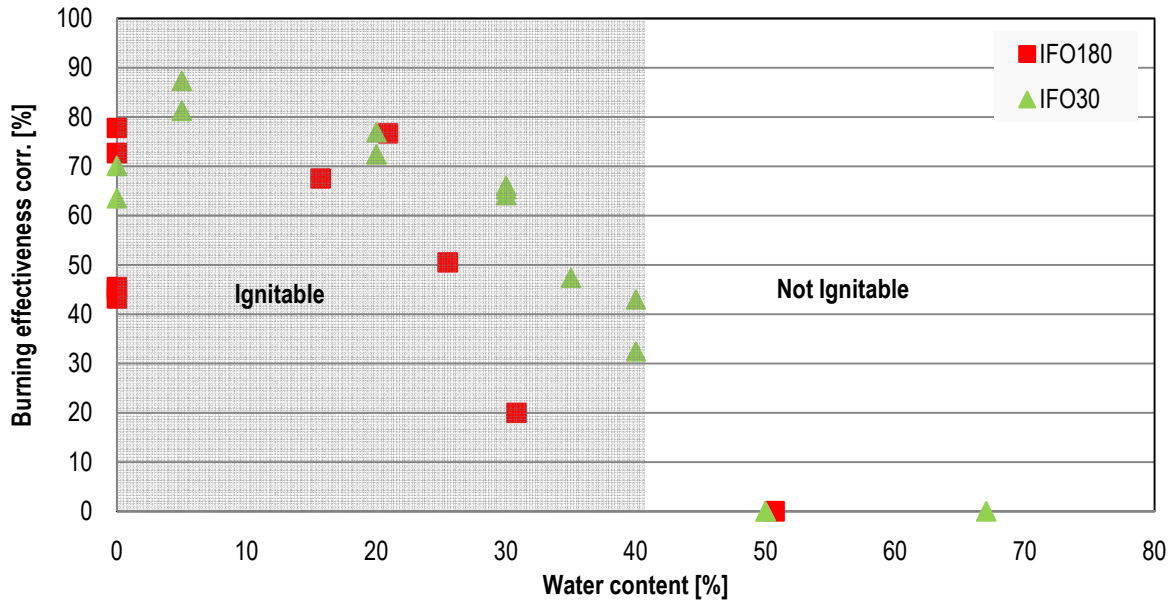


Figure 4.2.2 Burning effectiveness as a function of water content for IFO30 and IFO180. The gray shaded area indicates where the oil samples are still ignitable.

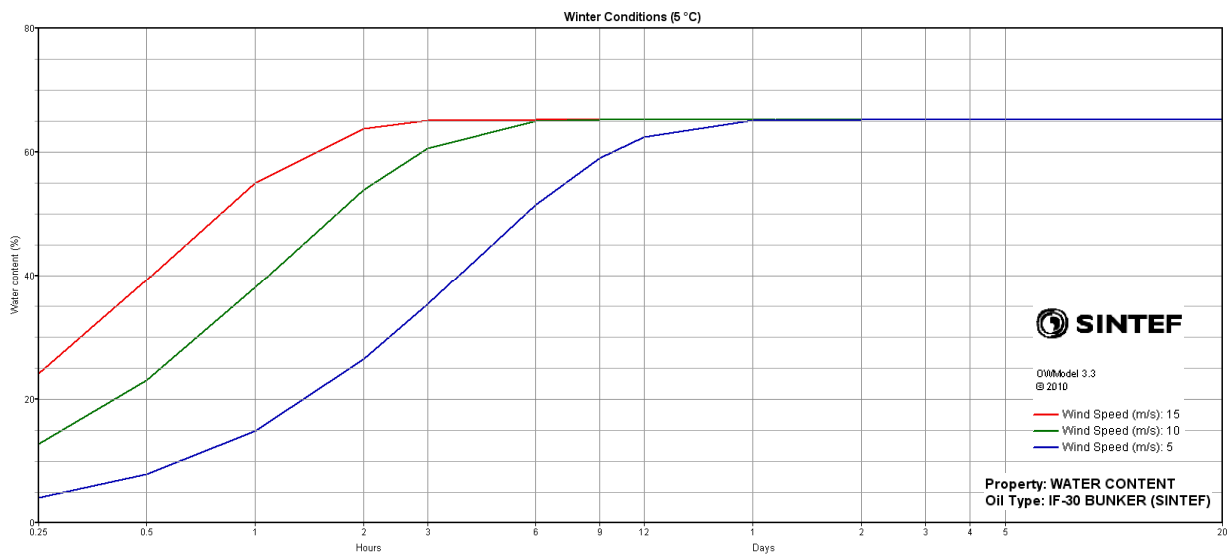


Figure 4.2.3 Water uptake as a function of weathering time for IFO30 for three different wind scenarios, 5 m/s, 10 m/s and 15 m/s. The figure is derived from the SINTEF Oil Weathering Model (Johansen et al., 2010).

4.2.1 Temperature measurements

During the burning experiments the temperature in the flame, oil and water beneath the oil layer was measured with temperature probes (type k). An example of the temperature measurements can be seen in Figure 4.2.4 for burning a sample of Grane crude oil weathered for 1 hour with 50 % ice cover.

The water temperature does not increase significantly during burning and even at the end the temperature does not exceed about 20 °C. Since the water temperature only slightly influences the ignition of the oil this increase in temperature is acceptable. This shows that the water cooling system works as expected and secures realistic burning. The oil temperature is increasing during the experiment as the oil layer thins out and the temperature probe, originally placed in the middle of the oil layer gets closer to the actual burning. The increase is also expected to be a result of heat conduction through the oil layer. The flame temperature expresses the nature of the burning. In the beginning there is a quite steep increase, from ignition (this oil had 2x10 seconds of heating to ignite) to self sustaining burning followed by a period with steady burning. Finally, the burning ends with a vigorous burning which increases the heat released during the burning (McGrattan et al., 1993; Evans et al., 1990). The flame height increased noticeably during the vigorous burning (see Figure 2.1.3). Burning of fresh crude oil sample for all the oil types was videotaped and from there it was found that the vigorous burning was different (length and how violent it was) between the varying oil types. The height of the flame also varied with oil type, with Statfjord and Kobbe having the highest flames. General for all the burnings was that flame out occurred quite fast; this can also be seen as the steep descent of the flame temperature (Figure 4.2.4).

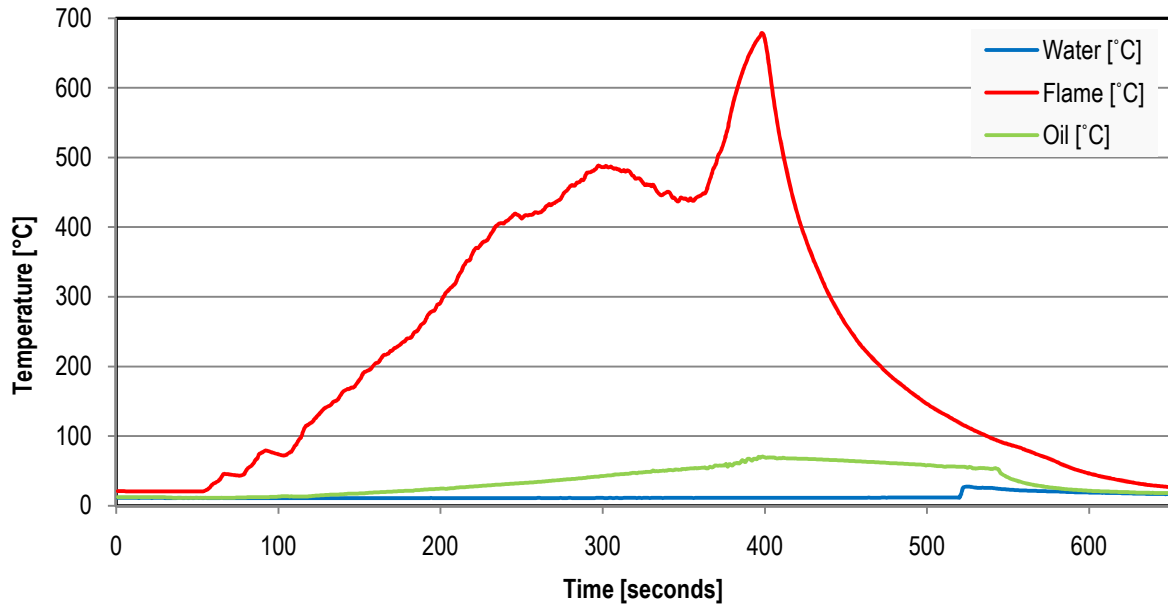


Figure 4.2.4 Example of temperature measurements in the water beneath the oil, in the oil layer and in the flame during a burning in the burning cell. The temperatures are measured for Grane crude oil weathered for 1 hour with 50 % ice coverage.

4.3 Use of burning cell in the field

The performance of the burning cell in different locations was tested, i.e. in the laboratory, and two different field situations: on the fjord ice at Svea and on board on a research vessel. Only the core unit of the burning cell along with the propane igniter, the water cooling system and the temperature measurement unit were used in the two field situations (see Figure 4.3.1). In the field a wind shield was needed and the hoses for the cooling system had to be warmed when temperatures were very low, to prevent from freezing.

The ignitability as a function of weathering for experiments carried out in the laboratory and in the field was investigated. The naphthenic Troll B crude oil was used in these experiments and was weathered in open water, 50 % ice and 90 % ice cover but in different scale: 9 L in the laboratory, 200 L in the field at Svea and 7000 L in the large-scale field weathering experiment in the marginal ice zone in the Barents Sea (70-90 % ice cover) (See Section 3.2). In Figure 4.3.2 examples of the BE%-Corr. results as a function of weathering time is shown for the three different weathering scales. More figures can be found in Paper [3]. It is clear from these results, that ignitability is very dependent on the weathering degree, ice conditions and oil composition. The burning results (ignitable/not ignitable) were in agreement as long as the samples had the same weathering degree. Where the weathering experiments and testing of ignitability in the burning cell were performed, laboratory or field, had no influence on the ignitability results. The use and performance of the burning cell directly in the field at Svea and on board the research vessel in the Barents Sea thus were very successful (Paper [3]).



Figure 4.3.1 Use of the burning cell in different situations. The burning cell used in the laboratory with the exhaust system and protection shield (left). The burning cell on the fjord ice at Svea, Svalbard (middle) and on deck of the research vessel in the Barents Sea (right). The wind shield and how the hoses for the cooling system were warmed can also be seen.

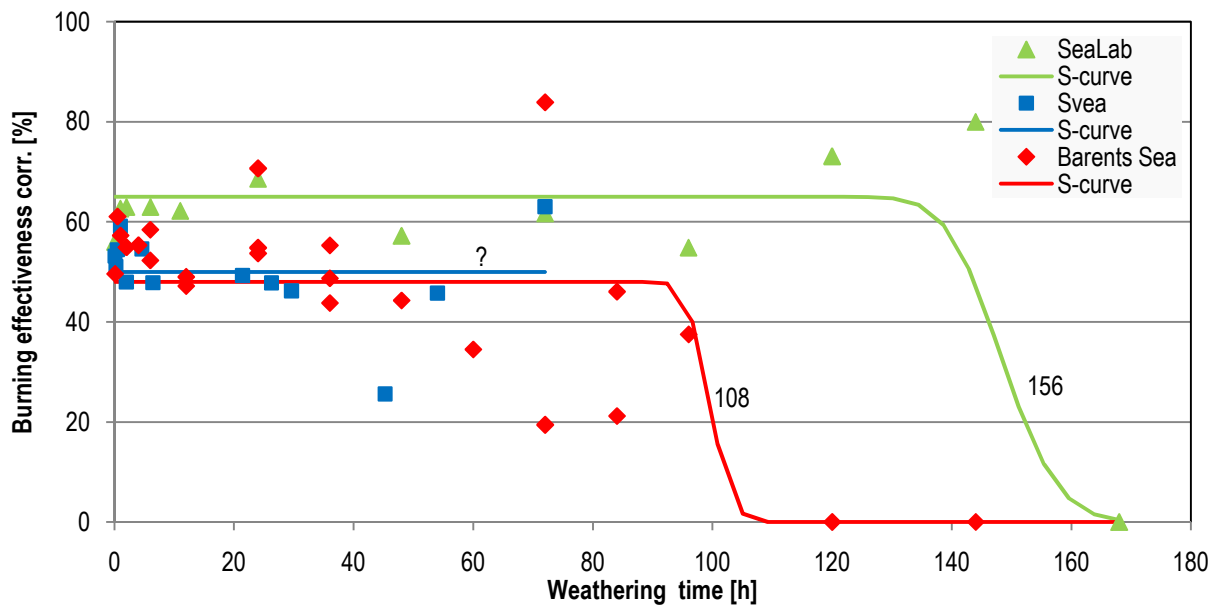


Figure 4.3.2 Burning effectiveness as a function of weathering time for weathering experiments performed in the laboratory (SeaLab, 90 % ice cover), meso-scale field (Svea, 90 % ice cover) and in the field in the Barents Sea (70-90 % ice cover), with Troll B crude oil. The time-windows for in situ burning are indicated as midpoints (hours) on the figure.

4.3.1 Uncertainties in field measurements

During the large-scale weathering experiment in the Barents Sea with the 7000 L of oil, the slick scattered as shown on Figure 4.3.3 and covered an area of approximately 100 x 3000 m at the end. Besides from the samples taken in the bulk phase, where the majority of the oil was found, some samples were also taken in the periphery of the slick. At these locations the oil layer was thinner, contained more slush ice and had had a different weathering history than the majority of the oil. The samples were all burned in the burning cell on deck of the research vessel and the results are presented in Figure 4.3.4. The results showed that the ignitability of the samples varied within the large oil slick and the samples taken on the periphery of the slick had shorter time-windows for in situ burning. This is important when planning where to collect the samples for analysis, as they should be sampled to be representative for the majority of the slick (Paper [3]).



Figure 4.3.3 The 7000 L oil spill in the ice in the Barents Sea at the end of the experiment six days after the release. The slick had spread out and covered an area of 100 m x 3000 m. The research vessel Lance is seen to the right in the picture.

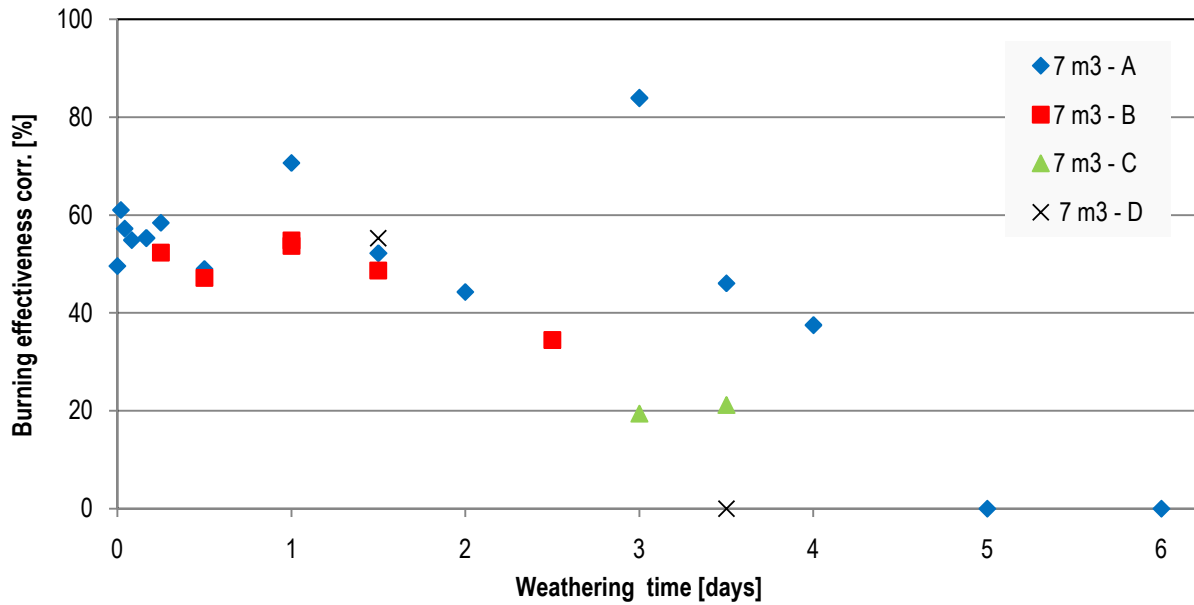


Figure 4.3.4 Burning effectiveness as a function of weathering time (days) for samples taken at different locations in the large-scale oil weathering experiment in the Barents Sea. A refers to the sampling spot in the main slick and B, C and D refer to samples taken on the periphery of the slick.

4.4 Large-scale burning experiments

One large-scale in situ burning experiment was performed with 2 m³ Troll B crude oil (details can be found in Paper [3]). The purpose was to validate the extensive data set found with the burning cell with an experimental oil release close to a real oil spill scenario. The Troll B crude oil was released in 70-90 % ice cover and was left for weathering for 12 hours during which it separated into two parts. The weather was calm with winds less than 5 m/s and air temperatures between -9 °C and -3 °C (Faksness et al., 2010). The thickness of the slick was 5-30 mm, which is enough to secure a sustainable burning. The slick was ignited with bags with gelled gasoline added 4 % emulsion breaker (Alcopol O 60) (see section 3.3.2). The residue was collected with 3M oil absorption pads and finally the area was treated with a sorbent (Sphagnum peat moss, NatureSorb from Nirom Peat Moss) to absorb the very last oil. Pictures from the large-scale burning are shown in Figure 4.4.1. The burning showed good results with >90 % burning effectiveness.



Figure 4.4.1 Large-scale in situ burning in the Barents Sea (top), collecting of residue with 3M absorption pads (lower left) and sphagnum peat moss applied to the area after the residue has been removed (lower right, photo: Per Johan Brandvik).

Three meso-scale burnings (between 250 and 400 L depending on degree of emulsification) were performed after each of the weathering experiments at Svea (Section 3.2.3). The emulsion was led to a 9 m² burning chamber by a simple boom arrangement assisted by shovelling of the surface oil (see Figure 4.4.2). For the last experiment the oil was burned directly in the weathering flume. The emulsions was ignited with 1 L gelled Statfjord crude oil added 4 % emulsion breaker (Alcopol O 60) (see section 3.3.2). The residue was collected by oil absorption pads and gravimetrically quantified to calculate the burning efficiency (> 90 %).

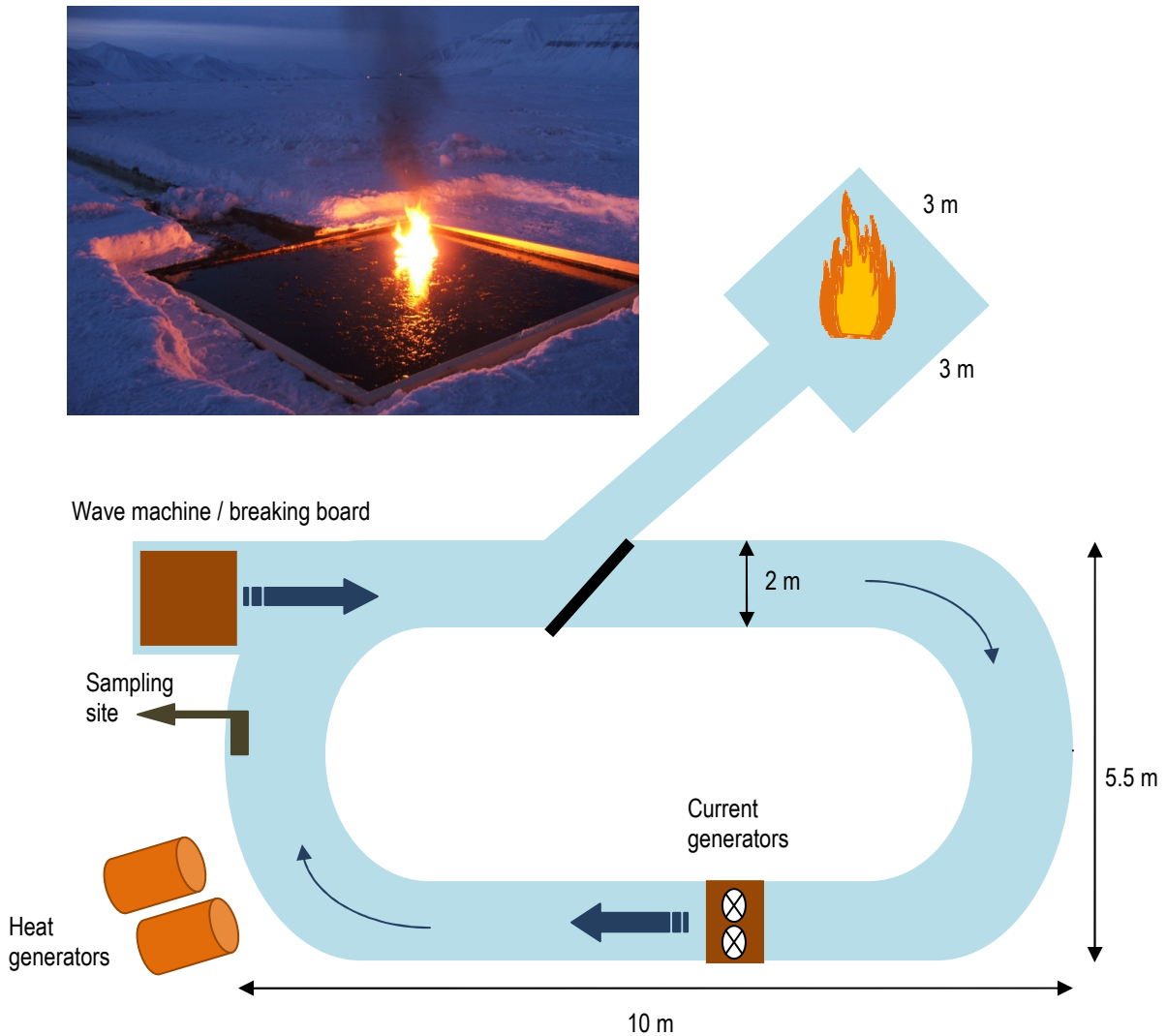


Figure 4.4.2 Outline of the weathering flume cut in the fjord ice at Svea, Svalbard and the burning chamber, where the oil was collected and burned. The picture at the top shows the initial stage of the in situ burning of the emulsions in the burning chamber.

4.5 Predicting ignitability

The burning cell has been used to generate a comprehensive dataset totalling 223 samples (taken from the burning cell experiments) with burning effectiveness as a function of oil type, ice conditions and weathering degree. So far the burning effectiveness corrected for water has been used to present the experimental data from the burning cell results, however the main objective is to present the ignitability of the samples as this is a parameter independent of spill volume/sample size. The burning effectiveness was thus converted to the Boolean variable “ignitable/not ignitable” (1 or 0). Samples with a burning effectiveness corrected for water above 25 % are determined as ignitable and the rest is determined as not ignitable. The dataset was used to develop and calibrate an algorithm for predicting ignitability of oil spills as a function of weathering. Regression analysis was used to build the multivariable regression

model to predict ignitability and the final model gave a correlation between predicted and measured values of 9.8 % in error (Paper [4]). The ignitability is expressed as a function of variables that describe oil type and weathering i.e. wax/asphaltene content, flash point, water content of emulsion, emulsion/viscosity, as these variables showed to be statistically significant (5 % level). Some variables were omitted due to low significance. These were evaporative loss (no information regarding the content of light components in the residual oil), wax content (no significant information), emulsion stability (the used approach to measure emulsion by settling was not useful here) and density (no significant influence on the ignitability). The ignitability results from the large-scale field weathering experiments from Svea and the Barents Sea were used to validate the predictions from the model. Figure 4.5.1 presents the entire development from the burning effectiveness data measured with the burning cell to the predicted ignitability values.

The algorithm developed in the multivariate regression study has been implemented as a subroutine in the SINTEF Oil Weathering Model (OWM) by which it is possible to predict the ignitability for oil spills in both open water and ice. An example of a possible output from the model is given in Figure 4.5.2. Being able to define ignitability as a function of oil composition, weathering and environmental conditions offers a significant improvement over the existing rules of thumb regarding time window for in situ burning (water content/evaporative loss/slick thickness). However, it is important to remember that the predicted values are for the bulk phase of the oil and certain igniter properties (temperature and burning time). Also, other operational factors have to be evaluated to be able to estimate the total effectiveness of a possible in situ burning scenario i.e. film thickness, volume, safety and environmental consideration (total reduction and environmental impact). These circumstances should also be evaluated against other options that might exist (mechanical recovery/dispersions) in case of an oil spill in ice.

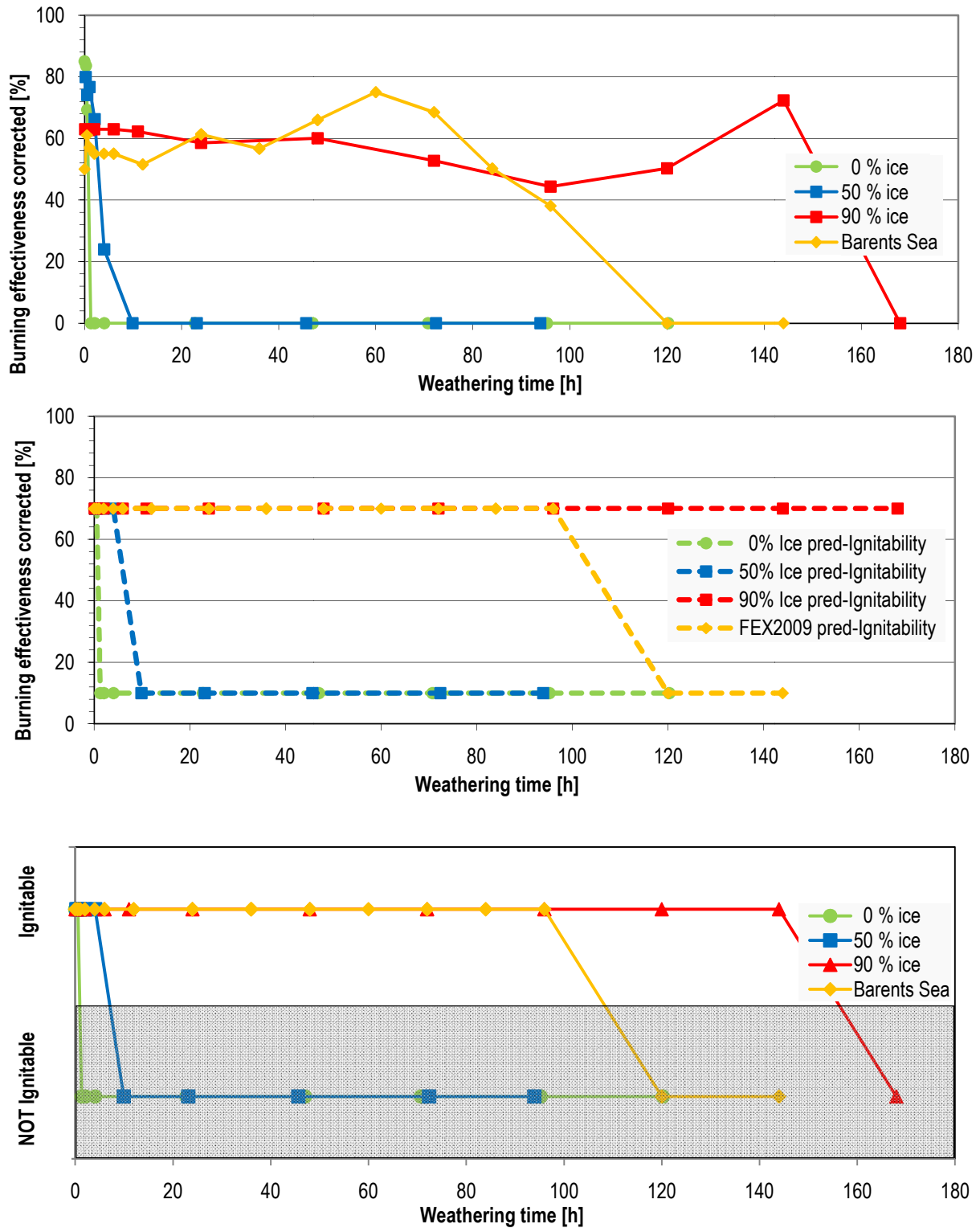


Figure 4.5.1 Top: Burning effectiveness as a function of weathering time for Troll B crude oil. Results from the burning cell, burning samples from weathering experiments performed in Svea (0 %, 50 % and 90 % ice) and in the Barents Sea (70-90 % ice). Middle: The burning effectiveness data converted to ignitability and for purposes of illustration plotted as 70% (ignitable) or 10% (not ignitable). Bottom: the same data, although all the data are now converted to ignitability (1 or 0). This shows how the ignitability of the weathered oil drops from ignitable and becomes not ignitable.

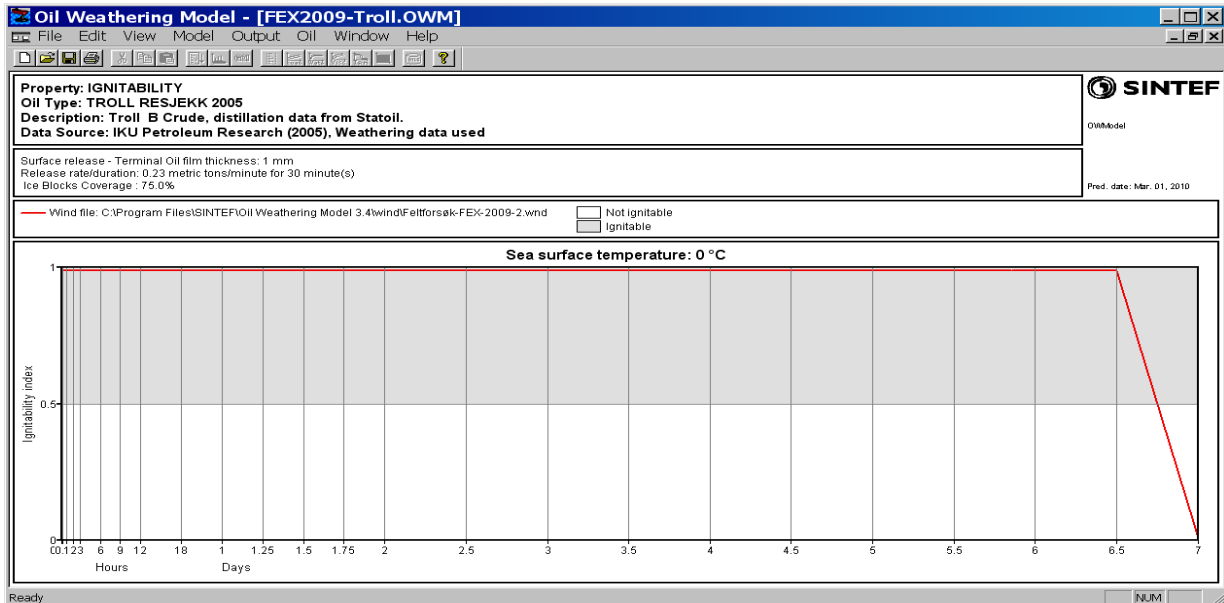


Figure 4.5.2 Example of a possible output from the SINTEF Oil Weathering Model (Johansen et al., 2010) for Troll B crude oil, with 75 % ice, illustrating the potential time-window for in situ burning.

4.6 Composition of residue and soot

Burn residue and soot samples were taken from some of the experiments performed in the laboratory at DTU (Section 3.2.1) and residue samples were taken from the experiments in the field at Svea (Section 3.2.3). In the following the results from the analysis of these samples are provided.

4.6.1 Soot and burn residue from laboratory experiments

From burning cell experiments at DTU residue samples and soot samples were taken and the samples were analysed for metals (Al, V, Cd, Cu, Fe, Ni, Pb and Zn), THC (total hydrocarbons) and PAHs (Polycyclic Aromatic Hydrocarbons). The methods are described in Section 3.4. The results are presented in Figure 4.6.1 and Figure 4.6.2.

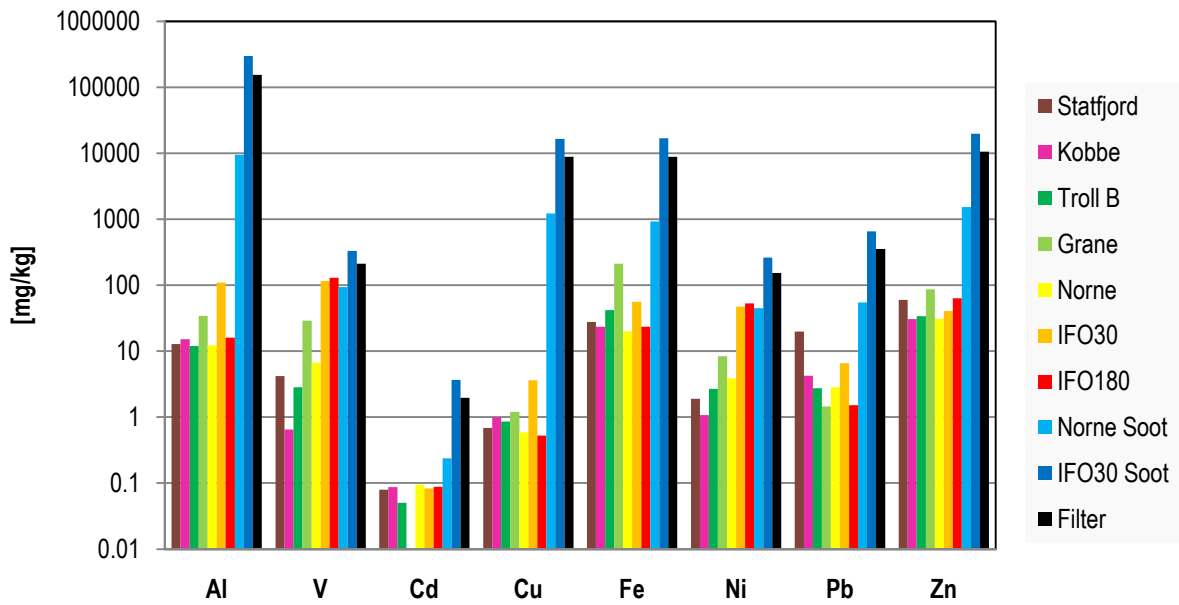


Figure 4.6.1 Content of metals in residue samples from burning of crude oils and two bunker oils. Two soot samples and the filter wherein the soot was collected is also included. The vertical axis is on logarithmic scale.

The variation in metal content between the different oil types is expected to be a result of the initial oil composition. The soot samples stands out having higher content of metals in general than the residue samples, however the very high values are found in the filter as well, where the soot samples were collected. Thus these high concentrations might influence the concentrations found in the soot. Especially since these relatively high values in the soot are contrary to other findings, for example Westphal, et al. (1994) state that metals are bound up in organometallic complexes that are largely retained in the residue and Fingas et al. (1993) which could not detect any metals in the soot and conclude that the metals concentrate in the residue. Ecotoxicological assessment criteria (EAC) for sediment concentrations were found to relate the residue values to guidelines of environmental character if the residue should sink (Table 4.6.1). None of the metal concentrations found in the residue exceeds the EAC values. This is in good agreement with what has been found in the literature and described in (Section 2.5) that the aquatic toxicity from in situ burning is minor and not beyond the effect from the effect already seen from the spill.

Table 4.6.1 Criteria for sediment concentration from EAC (Bignert, 2004)

		Lead	Cadmium	Cobber	Nickel	Zink
EAC sediment	mg/kg dw	5-50	0.1-1	5-50	5-50	50-500

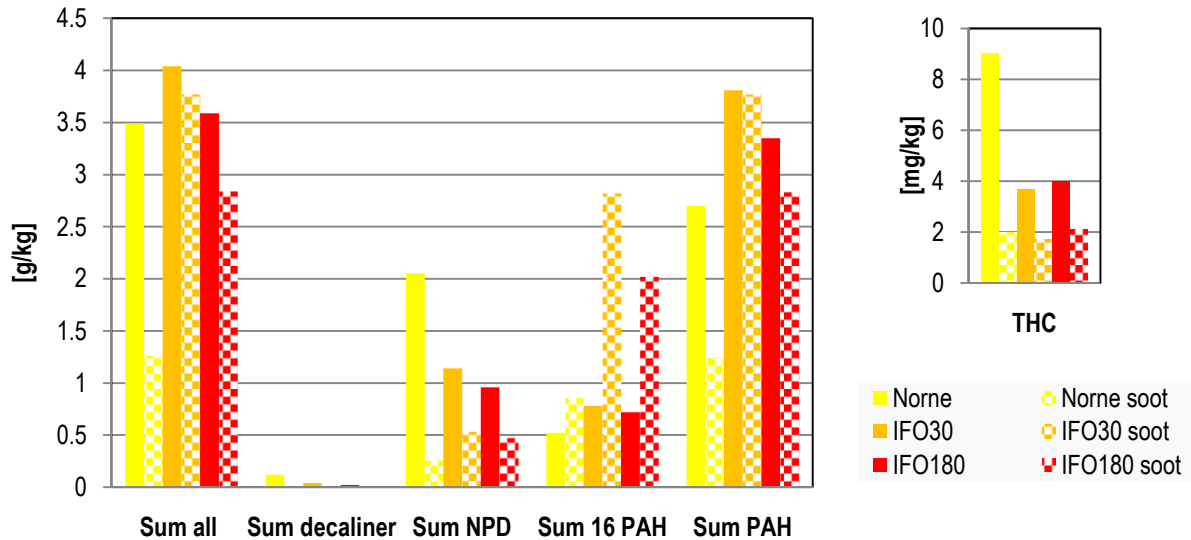


Figure 4.6.2 Content of THC and PAH for residue samples and soot samples.

The THC content in the soot is lower compared with the burn residue samples (Figure 4.6.2). Bowes (1996) reports that the measured THC content in air samples, during an in situ burning, was generally low with concentrations in the same range (or higher) as seen in Figure 4.6.2. The GC chromatograms are similar for the residue samples and the soot samples but the soot chromatograms are more reduced in light components and n-alkanes. This is in agreement with what Benner et al. (1990) write, that the soot sample is suggested to not contain large amounts of unburned crude oil.

The decalines (2-ringed cyclohexanes) are only found in the residue samples and not in the soot. The NPD components (naphthalenes, phenathrenes and dibenzothiophenes i.e. 2-3 ringed aromatic components) are found in both the residue and soot. The difference (between the soot and residue content) could be due to differences in boiling point, where the lighter components do not condensate on the soot at such high temperatures obtained during burning, but instead evaporate (Brandvik, 2010). The concentration seems highest for the residue samples and in particular for Norne samples, which might relate to the initial content of the crude oil. The "Sum 16 PAH" (16 PAHs according to the US EPA list) is higher for the soot than for the residue samples. However, this trend is not seen in the "Sum PAH".

4.6.2 Burn residue from field experiments in Svea

From the field weathering experiments in Svea (see Section 3.2.3) burn residue sample was taken from all the burn experiments and analysed for THC and PAHs. The variation of the content of the residue samples as a function of weathering time and different ice conditions was studied. From the total ion chromatograms (TIC) it was found that the compounds in the boiling range up to 230 °C were removed from all burn residues and up to 350°C a reduction was found. From Figure 4.6.3 it appears that the multi-component background is raised for 50 and 90 % ice cover experiments compared with the open water experiment. The results demonstrate that the presence of ice affect the composition of the residue and for weathering conditions with 50 % ice or more the removal of hydrocarbons was less than for oil weathered in conditions with no ice. The weathering time on the other hand seem not to affect the

residue composition, leading to the conclusion that when the oil is burned the prior weathering time is almost completely erased (see Figure 4.6.4). The identified PAHs (acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene) in the residue were either removed or reduced compared with a fresh crude oil sample; furthermore, all the compounds identified had boiling points below 340 °C, thus in the range where a relative removal of all components was found. Therefore it is concluded that the burning is not generating any PAHs. These results are presented in Paper [5].

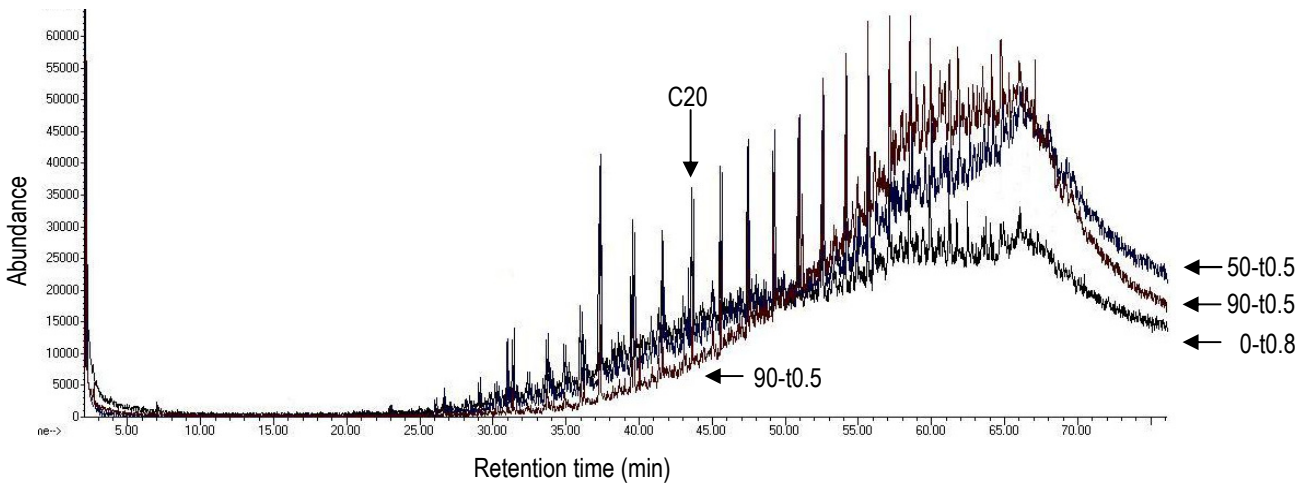


Figure 4.6.3 TIC of burn residue for samples with approximately 0.5 hour weathering time but different weathering conditions (open water, 50% ice and 90 % ice cover).

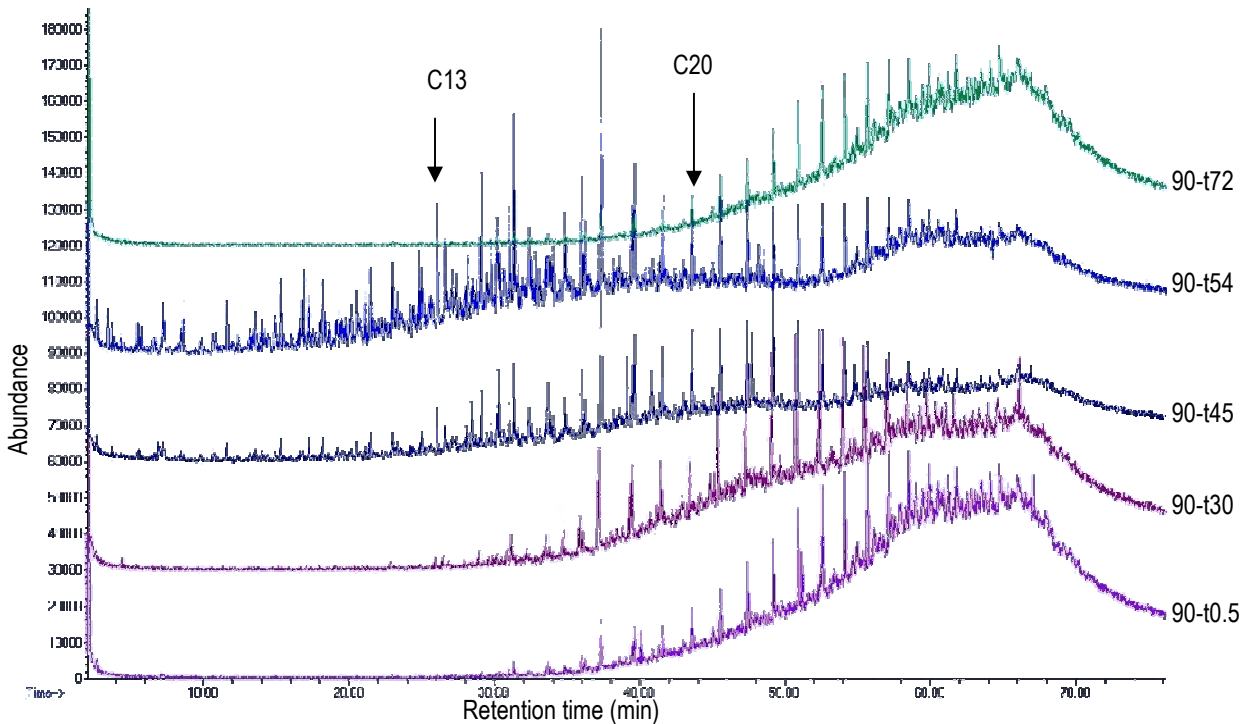


Figure 4.6.4 TIC of in situ burning residue for samples from the 90 % ice coverage series. Samples 90-t0.5, 90-t30, 90-t72 (samples taken after 0.5,30 and 72 hours of weathering respectively) did all burn, however 90-t45 and 90-t54 (samples taken after 45 and 54 hours of weathering respectively) were extinguished by the wind, thus more light components are seen.

Chapter 5 Risk for oil spill in offshore Greenlandic

This chapter focuses on the present situation in Greenland, considering shipping routes, ice occurrence and contingency plans all in relation to oil spills. A brief discussion of the future situation and the environmental concerns from an oil spill are given. The purpose of the chapter is to compile and give an overview of the above mentioned topics. This is to have a basis for, in connection with the research results found in this PhD-project, to decide if in situ burning could be used as a response technology for Greenlandic conditions.

5.1 Ships' routing, intensities and accidents

Greenland covers a large area – 2,127,600 km² - from Cape Farewell in the south to Oodaaq Island in the north and the long coast mainly consists of skerries. The climate is defined as arctic. The Greenlandic marine areas constitute about 2,000,000 km², this includes the Exclusive Economical Zone (EEZ) (Søfartsstyrelsen, 2007). Major parts of the Greenlandic marine areas are not mapped and occur as white spots. The data that do exist are not in digital form, except a few examples (IMO, 2009). An ongoing project is carried out to produce better charts with respect to topography, coastline and hydrography etc. These improved charts will be used to produce electronic navigation charts (IMO, 2009). No official recommended ships' routing exists at the moment, but the future focus will be on inshore routes from Upernavik to Cape Farewell, routing to seaports and routes relevant in connection with tourism and other industries (mining industry and offshore plants) (Søfartsstyrelsen, 2007). At the present the main traffic is expected to be between the large cities, villages, in the fishing and hunting areas and routes connecting to other countries. A risk assessment regarding areas of risks in connection with sailing in Greenlandic waters is about to be made by the Grønlands Kommando (GLK) (GLK, 2007).

Passenger liners, fishing boats, tank vessels and other cargo ships represent a risk of oil spills. In 2007 approximately 30 passenger liners called into port, this number is expected to increase, but no statistics otherwise exist on the ship intensities (Søfartsstyrelsen, 2007). There are three primary entrants regarding large shipping traffic in Greenland: Polaroil, Royal Arctic Line and Arctic Umiaq. The two last companies transport primarily goods and passengers, respectively and carry bunker fuel. Polaroil is responsible for the import, distribution and storage of oil products in Greenland, supplying fuels to towns, villages, mining places, airports, bunkering of large ships etc. 2-3 times per year. Two chartered tankers with capacity of 1925 m³ and 5200 m³ provide for the distribution. The routes used are not the same and depend on the consumption in each place and the ice conditions. The maximum capacity of liquid fuels is 281 million liters and in 2007 the consumption was 250 million liters (Polaroil, 2007). The oil products supplied by Polaroil are all specially made, to secure proper performance in the cold climate, and are primarily petrol, petroleum, Jet-A and the gas oils MGO-20 and AGO (Polaroil, 2007). In addition large

import ships are supplying the biggest installations in Greenland in Qaqortoq, Kangerluarsoruseq, Nuuk, Sisimiut and Kangerlussuaq (Søfartsstyrelsen, 2007).

The total number of accidents in Greenland involving ships was 38 from January 2000 to May 2006 (Søfartsstyrelsen, 2007). How the accidents are divided between the different types of ships is shown in Table 5.1.1, where also the main reason of the accident is listed, however the consequence of the accident is not mentioned (Søfartsstyrelsen, 2007). With special focus on oil spills, the Department of Infrastructure and Environment state that 36 oil spills were reported to the police from end of 1992 and until 2006. The majority of these spill occurred along the coast due to bunkering, piloting, collisions and grounding. Only a few oil spills are seen annually in the open High Seas (GLK, 2010).

Table 5.1.1 The types of ships involved in accidents from January 2000 to May 2006 (left) and the main causes of the accidents (right). (Søfartsstyrelsen, 2007).

Fishing ships < 20 Gross tonnage	4	Operational errors	20
Fishing ships > 20 Gross tonnage	13	Technical errors	10
Cargo ships	8	Ice	5
Passenger liners	10	Extreme weather	3
Other	3		
Total	38		38

5.2 Ice conditions in Greenland

Ice is often seen in Greenland even in the summer and together with insufficient maps the risks of oil spills due to difficult sailing conditions are increased in Greenland compared to other non-Arctic waters. From Table 5.1.1 it appears that ice is the reason for about 13 % of the accidents with ships in Greenland.

The Danish Meteorological Institute (DMI) is in charge of collecting information about the ice conditions in Greenland (Søfartsstyrelsen, 2007). DMI gets the information from satellites, ice reconnaissance by helicopter and observations from the shipping trade (DMI, 2007). In the Cape Farewell area the mapping is routine, but at the east and west coast areas the mapping is done as a result of the season and intensity of navigation (DMI, 2007). The ice at the east coast primarily comes from the Arctic Ocean; every second about 150,000 m³ of ice, up to three meters thick, flows out of the Fram Strait between Greenland and Svalbard (DMI, 2007; GLK, 2007). A combination of multiyear ice from the Arctic Ocean and first-year ice formed at the east coast is called “stor is” and transported with the East Greenland Current to Cape Farewell and the ice might also reach the area around Disko Bay (Cappelen et al., 2001). When the “stor is” reaches Cape Farewell the huge floes are typically reduced to less than hundred meters in diameter (Cappelen et al., 2001). The Cape Farewell area is very much affected by the harsh weather and in connection with a lot of icebergs and floes the area is one of the most dangerous in the world for the shipping traffic. The ice at the west coast of Greenland is typically first-year ice, about 0.5-1.5 m thick and covers the west coast almost south to Sisimiut (Cappelen et al., 2001). The

ice is mainly produced in the Baffin Bay during the winter and transported into the Davis Strait. Only a small amount of the first-year ice will survive to the next season. Multiyear ice from the Arctic Ocean might also reach the west coast of Greenland via Nares Strait, but this ice will typically follow the Canadian coastline towards the south. Another type of ice is the winter ice, which is produced each year in the fjords and coastal areas in most of Greenland. Also icebergs produced from the large glaciers, are seen in most of Greenland, and also represent a risk. The prevailing currents around Greenland can be seen in Figure 5.2.1 and indicate the drifting paths for the ice.

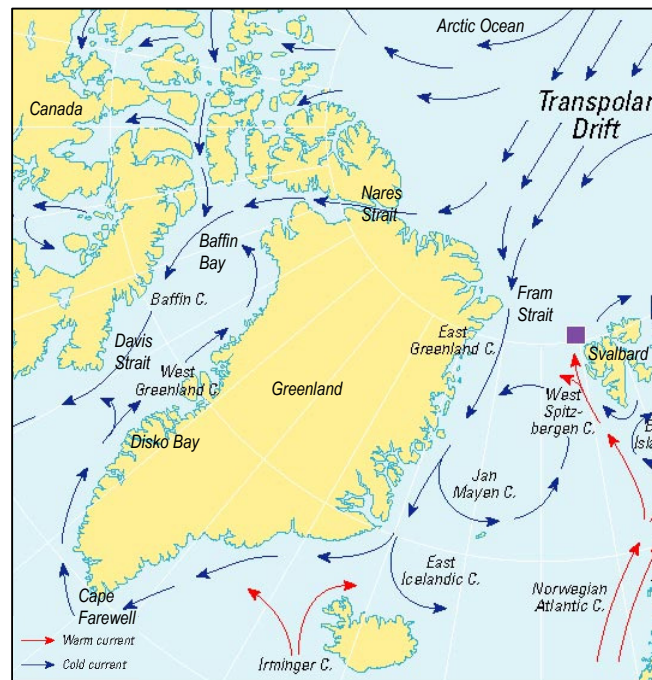


Figure 5.2.1 The general currents around Greenland (From AMAP, 1998 with some adjustments)

5.3 The Greenlandic contingency plan

The Government of Greenland and the Ministry of Defence in Denmark are sharing the tasks of preventing and cleaning up oil pollution in the Greenlandic marine areas. The areas are divided into different zones according to responsibility. The Government of Greenland has the responsibility for cleaning up pollution in the Internal Waters and the Territorial Sea (see Figure 5.3.1). Internal waters are the area from the coast to the Base Line (the low water level along the coast) and consist primarily of fjords, harbours etc. The Territorial Sea covers the area from the Base Line and three nautical miles (nmi) seawards i.e. The Ministry of Defence has assigned their responsibility to Grønlands Kommando (GLK). GLK is responsible for the area from 3 nmi from the base line to the 200 nmi from the base line, i.e. the end of the Exclusive Economic Zone (EEZ) or the dividing line between Greenland/Canada and Greenland/Iceland as shown in Figure 5.3.1 (GLK, 2007). There is a mutual obligation for the Government of Greenland and GLK to help each other if needed. In The High Seas no state has sovereignty, but in case of serious risk of pollution of the coasts a state can make the necessary arrangements (GLK, 2007).

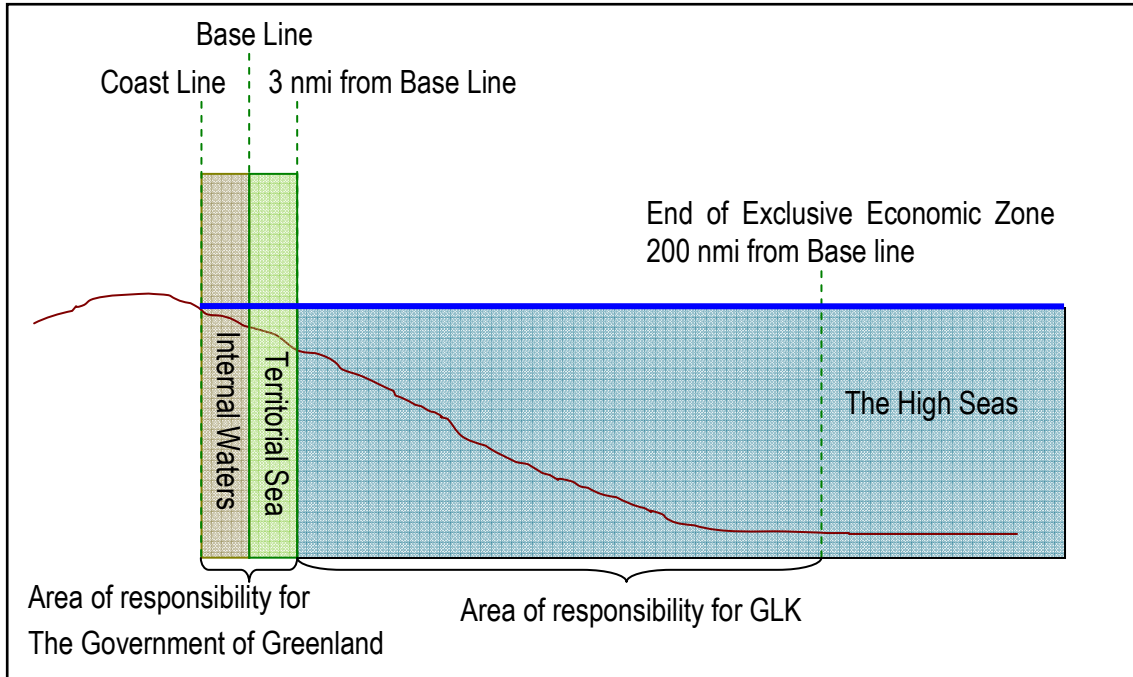


Figure 5.3.1 Conceptual overview of the responsibility areas for pollution combating in Greenland

The Government of Greenland has, via Department of Infrastructure and Environment, personnel and equipment placed in 12 towns along the coast, from Nanortalik in the south to Qeqertarsuaq in the north and in Tasiilaq/Kulusuk on the east coast. The equipment in the local areas is dimensioned for spill in size of up to 20,000 L. If a larger spill takes place it is necessary to transfer equipment between the local areas, or acquire it from Denmark, primarily by air freight (GLK, 2007). In case of large pollutions agreements with the surrounding countries i.e. Canada and Iceland, to help and cooperate exists (SOK, 2004). The method that is used for cleaning up oil spilled is a mechanical procedure with the use of booms and skimmers, which collect the oil and remove it from the water surface. Greenland does not have dispersants available, but if dispersants are to be used, a serious consideration should be made, concerning environmental and economical aspects. In-situ burning of oil is not yet practiced in Greenland, but is used in some other Arctic countries (GLK, 2007). Neither GLK nor the Danish Government is in possession of equipment for cleaning up pollution on the sea in Greenland, thus the response will be in cooperation between the Greenlandic authorities and e.g. civil flights (GLK, 2007). In spite of this, GLK are in possession of few ships and planes due to their task of maintaining the sovereignty, which might be used in case of oil spill. The available equipment is listed in GLK (2007).

5.4 Environmental concerns

The environmental consequences from an oil spill in arctic marine waters are many and can have negative effects to a broad spectrum of areas. The magnitude of the consequences will vary with the oil product, the size of the spill and where and when the oil is spilled. Many different oil products exist, all with different compositions, thus the fate of the oil at sea will be different as stated in Chapter 4. Light products will evaporate and degrade relatively fast whereas heavy oils will take a long time to degrade

and might be seen many decades after the spill took place. Large spills are considered to have the most serious impacts to the environment (AGO, 2007). However, regardless of the size of the spill the environment might be seriously affected if the timing of the spill is contemporary with seasonal aggregation and breeding of birds and mammals etc. (AGO, 2007). Thus the place and time for the oil spill is very important. If the spill occurs close to the shore there might be a great risk of the shorelines getting polluted as well.

Immediately after the spill has occurred the oil will typically be found as a thick layer upon the water body. The evaporation will in general be high from such an oil slick and be harmful to e.g. responders who have to approach the slick or to breathing mammals (AGO, 2007). The thick oil slick can add immediately and seriously damages birds, mammals and other organisms that live in the upper waters and are dependent on breathing, diving for food and the insulating capacity of fur or feathers. The toxic effects from an oil spill depend on the duration of the exposure and the concentration of the chemicals involved (Faksness, 2008). The most toxic components to aquatic organisms are the low molecular weight aromatic components and the PAHs (Faksness, 2008). The effects seen include narcosis, slowed growth, reproduction and death (Faksness, 2008). As the oil weathers and degrades the extent of the oil spill becomes less but even so the remaining products might have toxic effects on living organisms. The Arctic conditions with the cold temperatures will slow down the degradation and as already mentioned in Chapter 4, the weathering processes of an oil spill will be slowed down if ice is present. Oil can be entrapped in ice (see Figure 2.7.1) and transported over long distances and be released in an unexpected area. Thus the time and place for the spill is also important for the consequences and the fate of the spill.

Regarding the environmental sensitivity in connection with oil spill, The Danish National Environmental Research institute (NERI) has published several reports with this in focus e.g. (Mosbech, 2002) and the "Sensitivity atlas of the environmental effect from oil spills on the west coast of Greenland (58°N to 72°N)" (NERI, 2010). Greenland has vulnerable nature and a harsh climate. The production season is very short and the temperatures and light intensity are low, all conditions making the consequences of an oil spill evident. The contingency plan should take these environmental sensitive areas into consideration.

5.5 Contingency plan for the future

One of today's major topics is the climate changes. It is no longer an "if" the climate changes occur, but now it is "how will the climate changes appear and how can we as humans adapt to these changes". There is a great possibility that the ice in the Arctic Ocean within a few decades will disappear in the summer months. When the Arctic Ocean is open in the summer months, new shipping routes are made possible (See Figure 5.5.1). These new routes to the Far East are shorter and therefore cheaper than the existing routes, but on the other hand, this new unexplored ocean is not completely ice free, in spite of

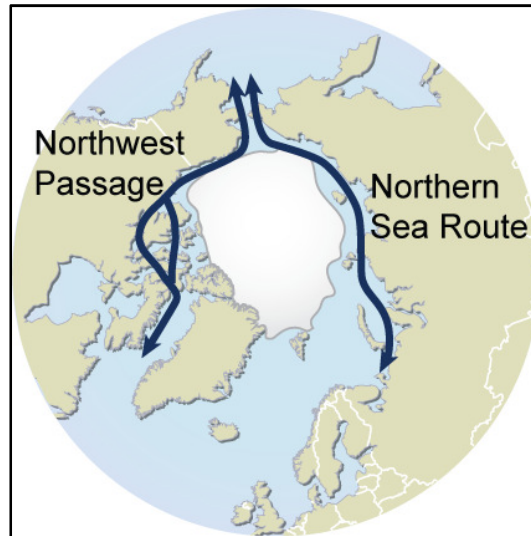


Figure 5.5.1 Ice smelting scenario. New routes crossing the Arctic Ocean to the Far East by the Northwest Passage and Northern Sea route (Grida, 2010).

the ice melting. Such new sailing routes via the Arctic Ocean are therefore connected with a great risk for oil spills. It is not only through the Arctic Ocean new routes might be possible; in the areas around the north of Greenland new routes could be expected in unknown areas for cruise ships etc. At the moment explorations are carried out to determine the possibility of oil production in Greenland and the first exploration drillings have been completed with oil and gas discoveries (Cairn, 2010). These activities and the potential oil production, increase the risk of oil spill now and in the future as well. GLK also expects to see an increase in accidents due to the increased tonnage in the Greenlandic waters (GLK, 2007). Other industries as mining and alumina production are expected to increase in the future, thus tanker transport of raw material will also represent a risk of oil spill. Therefore, it is important with knowledge about the oil types used in the tanker traffic and the potential crude oil products from possible Greenlandic oil fields. Especially knowledge regarding the weathering processes e.g. changes in pour point, flash point, viscosity of emulsion and water uptake in connection to response technologies is important to increase the operational capability for handling oil spills in Greenlandic areas.

From section 5.3 it is clear that almost no personnel or equipment exists north of Disco Bay or to a large extent at the east coast. The infrastructure in Greenland is generally very fragile complicating the possible sharing of equipment. All in all, there is very little material in Greenland for combating oil spill. If the oil spills are exceeding 20,000 L it is even more difficult. To make sure that Greenland is prepared for what the future might bring of potential oil pollutions the Greenlandic contingency plan should be adapted to the new situations that might occur. Based on the results from this PhD study and what has been found earlier by other researchers, in situ burning is expected to be a very useful method in many oil spill situations in Greenland, especially in cases with ice, where the time-window is enlarged. The requirements for equipment are also little, which is an advantage in Greenland as well, due to the limited

infrastructure and large distances. At the moment no other methods are competitive under such conditions. With that in mind it would be advisable if in situ burning with time is applied to the Greenlandic contingency plan with equal status as the other response methods included. In spite of the efficiency of in situ burning, the method should not be the single option as the results from this PhD study showed that in some situations, dependent on oil type and weathering conditions, the operational time-window is very short. Therefore, one should not rely on a single response method but have several, as it will probably result in the most efficient and effective clean-up after an actual oil spill.

Chapter 5 Conclusions

The main conclusions from the work carried out during this PhD study are summarized in the following and are primarily a conclusion of the five papers included in the thesis (Appendix [1]-[5]). At the end of the chapter a section with suggestions for further work is given.

5.1 Conclusions

This thesis adds important information to the present knowledge of in situ burning, regarding the time-windows for burning oil spills in Arctic marine areas with ice as a function of oil type and weathering conditions. This new knowledge furthermore, improves the basis for deciding when to use in situ burning in Arctic ice filled waters for a broad variety of oils at different weathering conditions.

The results are primarily based on experiments performed by use of a burning cell specially designed to test small samples (100 mL) for ignitability as a function of weathering and oil type. The burning cell was modified and refined in relation to the original design (from 2006) during the PhD study. The results found by use of this burning cell were verified with field burning experiments performed at Svea (200-450 L). The results showed good correlation and a large-scale field burning experiment (2000 L of oil) also contributed to these findings.

The samples from weathering experiments from the laboratory, the first year fjord ice in Svea and from large-scale field experiments performed in the Barents Sea were tested for ignitability in the burning cell. The oils used for the experiments had different characteristics and represented an asphaltenic, naphthenic, waxy, paraffinic and a light crude oil. From the results it was clear that the weathering processes affected the oil differently, thus the time-window and usefulness of in situ burning varied between the oil types. For the asphaltenic crude oil the ability to rapid create stabile emulsions was a limitation for the use of in situ burning. But for the four other crude oils in situ burning seems to have great potential within a reasonable period of time to be able to respond. From the ignitability results of the samples weathered in different scales (laboratory/field), the results showed that the scales had no influence on the ignitability results as long as the samples had the same weathering degree.

From the results it was evident that the ice content had a great influence on the time-window for in situ burning for all oil types. With 50 % ice coverage the time window was in most cases extended compared with an open water scenario and for many of the 90 % ice coverage experiments the experimental weathering time (72 hours) was too short to find the time window. These results clearly showed that the

weathering processes were slowed down with dense ice, i.e. the time-window for in situ burning was extended.

The analysis of the burn residue from some of the burning experiments showed that the density of ice during the weathering period affects the composition of the residue, as more ice results in more hydrocarbons left in the oil, however the weathering time does not affect the residue composition.

Based on the burning results from the experiments with the burning cell it has been possible to establish and obtain a better understanding of the operational time-window for using in situ burning. From this it appears that the burning cell now can be used in connection with a weathering setup to determine the ignitability of other oil types. Furthermore, the results showed that the burning cell can be used in the field e.g. in a real oil spill incident, as an operational tool to monitor ignitability of the oil spill.

The many burning results have been used to develop a new algorithm that has been implemented in the SINTEF Oil Weathering Model, hence it is now possible to predict the ignitability as a function of oil type, weathering conditions and time. This also contributes to obtain a better understanding of the operational use of in situ burning. When the output from the model is used, it is important to remember that it is the ignitability of the bulk phase of the oil that is given. The properties within an oil slick can vary significantly and results from this PhD study found that the ignitability varied significantly within an oil slick. Furthermore, ignitability of an oil spill is only one factor amongst many that needs to be evaluated before a decision is made regarding the choice of oil spill response method.

5.2 Suggestions for further work

In situ burning is considered an efficient method usable in many situations. One major challenge however remains to implement the method in existing contingency plans and make the method operational. In this connection factors of concern are how to educate the operators and secure their safety during an in situ burning operation. Guidelines should be made to determine in which areas the method should not be used due to e.g. a location too close to populated areas.

There is the challenge with the viscous burn residue and how to collect it in an efficient way, even though the amounts are much smaller than before burning. More experiments should be conducted to develop the most suitable method for dealing with the burn residue in Arctic marine areas with ice. Inspiration might be found from the area of mechanical recovery of heavy oil.

With special emphasis on Greenlandic conditions, still a lot of work needs to be done if in situ burning is to be implemented in the Greenlandic contingency plan as a response method on equal terms with the current method. This requires further experiments with oil relevant for Greenland, modelling of potential oil spills to determine the fate of the spill and education of the responders to be able to handle large oil spills.

In situ burning is not the only method; in spite of its efficiency and ease of use the results showed that in some cases the method has a very short time window. Focus should therefore also be on developing new and existing response technologies to be suited for Arctic conditions with ice, cold and limited infrastructure and remote locations.

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Appendix Paper [1]-[5]

Paper [1] Brandvik, P.J., Fritt-Rasmussen, J., Daniloff, R. & Leirvik, F. 2010. Using a small scale laboratory burning cell to measure ignitability for in situ burning of oil spills as a function of weathering. Proceedings of the 33rd AMOP Technical Seminar on Environmental Contamination and Response, Environment Canada.

Using a Small Scale Laboratory Burning Cell to Measure Ignitability for In Situ Burning of Oil Spills as a Function of Weathering

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Abstract

For the removal of oil spilled in ice-infested waters, in situ burning (ISB) is one of the response techniques with the highest potential for conditions with dense ice and snow. In order to make ISB an operational tool, there is a need to better define the potential and limitations regarding oil types and weathering degree.

A small laboratory scale burning cell has been constructed to perform a controlled experimental burn on a 100 mL scale (weathered and emulsified oil). This burning cell is a complete unit with cooling water, exhaust system, full temperature control and protection for the operator. After flame-out, the residue is collected and quantified to the calculated ISB effectiveness. The oils tested were Statfjord, Balder and Troll. The results showed that ISB time-window was the longest for Statfjord and dependent on ice conditions.

The laboratory scale burning cell has been verified against field ISB experiments performed at SINTEFs field station on Svalbard for Grane crude oil. The results from these large scale experiments (200-450 L of emulsified oil) with respect to the limit of burnability (water content/flash point) demonstrated a high correlation with the results from the laboratory experiments. The ISB time-window was the same for the large scale and laboratory scale experiments for Grane.

This work shows that the new burning cell can be used to map the operational "window of opportunity" for the use of ISB as a function of weathering.

1 Introduction

For the removal of an oil spill, ISB burning is one of the response techniques with the highest potential for conditions with snow, ice infested or dense ice waters as often found in Arctic areas. Experiments with ISB in recent years have shown removal efficiencies of up to, or in some cases even more than, 90% (Brandvik and Faksness, 2009; Brown and Goodman, 1986; Buist, 2003; Buist et al., 1999; Dickins et al., 2008; Dickins and Buist, 1999; Guenette and Sveum, 1995; Guenette, 1997; Guenette et al., 1995). The suitability of ISB burning depends on the initial characteristics and the weathering state of the oil, and several factors are important for a successful ISB operation:

A minimum slick thickness is required to both ignite the oil slick and obtain a high burning effectiveness. Different minimum thicknesses for ignition are reported: Buist et al. (2008) say 2-5 mm in loose pack ice, Fingas (1998) reports the prime rule of thumb as at least 2-3 mm and Guenette (1997) has found that a minimum of 1-3 mm is required for fresh crude oils, although more for weathered and heavier oils.

The wind speed should not exceed 10-12 m/s (Buist, 2003; Guenette, 1997), but even 9-10 m/s tends to have a negative effect on burning (Guenette et al., 1997). On the other hand, moderate winds tend to act as a herding agent for the oil (Guenette, 1997) and enhance upwind flame spreading (Guenette and Sveum, 1995). Evaporative loss is described in many studies as a critical factor because the oil slick must contain a sufficient amount of components that can evaporate and ignite. This is important since it is the gas above the oil slick that burns, so a rule of thumb has been introduced which states that the evaporative loss should not exceed 30% (Guenette, 1997).

Emulsification incorporates small water droplets into the oil and complicates ignition and reduces the potential of ISB. Heat from the igniter or burning oil is used to break the emulsion and thereby remove or boil off the water. Until this has been accomplished the temperature in the emulsion will not exceed 100°C, and for many weathered oils this is too low for ignition (Buist et al., 1999). Hence, both the water content and the stability of the emulsion are of great importance for a successful ignition.

Both the drift and spreading of the oil slick strongly influence the potential of ISB. Ice limits the spreading of the oil which results in a thick oil film and reduced evaporation, with such thick and continuous oil slicks increasing the burning effectiveness. The ice also has a wave damping effect, resulting in reduced emulsification, which is favourable for ISB (Brandvik and Faksness, 2009).

In order to improve ISB as an operational tool, there is a need to better define the potential and limitations with regard to oil type and weathering degree. Defining ignitability as a function of oil weathering (chemical composition, rate of emulsification, emulsion stability, flash point, etc.) would offer a significant improvement over the existing rules of thumb.

The objective with this study has been to develop a small scale laboratory burning cell for measuring ignitability. The upper limit of ignitability has been defined as the usual sharp drop in burning effectiveness at a certain weathering degree. The results from this small scale laboratory cell (100 mL) have been validated by comparison with field burns from large scale experiments (200-450 L).

This study has been an integrated part of a Joint Industry Program to develop and advance the knowledge, methods and technology for oil spill response in Arctic and ice-covered waters (Oil in ice JIP). The research program started in 2006, experiments were finalized in 2009 and final scientific reports issued in 2010. The JIP summary report (Sørstrøm et al., 2010) gives an overview of the total program and all the technical reports.

2 Materials and Methods

The burning cell used for the experimental work was developed in two stages. The initial development was performed in 2006-07 as an MSc project (Daniloff, 2007) in cooperation between SINTEF and the Norwegian

University of Technology (NTNU). This first version was later improved as part of a PhD project at the Denmark Technical University (DTU), which was coordinated as part of the Oil-in-Ice JIP.

2.1 Initial Construction of Laboratory scale Burning Cell

The laboratory scale burning cell consisted of a cup wherein the oil samples were burned on top of sea water. Cooling of the cup was performed by cold water flowing in body of the cup. Thermo elements were placed to measure flame, oil and water temperature. An exhaust system was placed over the burning cell. A conceptual drawing of the laboratory scale burning cell can be seen in Figure 1.

The initial testing of the burning cell confirmed that cooling was necessary in order to avoid the overheating of the system during burning, thus causing the water to boil. Furthermore, adding the cooling system to the burning cell provides a more realistic system because when burning oil in situ at sea, the water column is only heated to a minimal degree by the burning oil on top of the water column (Mullin and Champ, 2003). When testing the cell with a minimum of flow through the cooling system, the temperature of the water in the cell increased slightly, but stayed well below the boiling temperature for water. The flow rate was adjusted to ensure that the combustion was not inhibited (too high a flow) and to avoid boiling the water in the cell (too low a flow). With a rate of 500 ml/min, the returning cooling water from the cell started at 10°C and ended at approximately 20°C for the longest experiments. The 10 °C, was selected to be representative for a broad range of conditions. However, the water temperature only slightly influences the ignition of the weathered oil.

The functions in this early version which needed improvements and were later improved were:

- Better handling of the exhaust fumes, so it could be operated in an ordinary laboratory (see Chapter 2.2)
- Better system for temperature measurements and logging
- More reproducible ignition system
- More stable and reproducible system for cooling water
- Better protection of the operator against accidental bursts of hot water and oil
- All functions built into one unit – a “burning cell trolley”

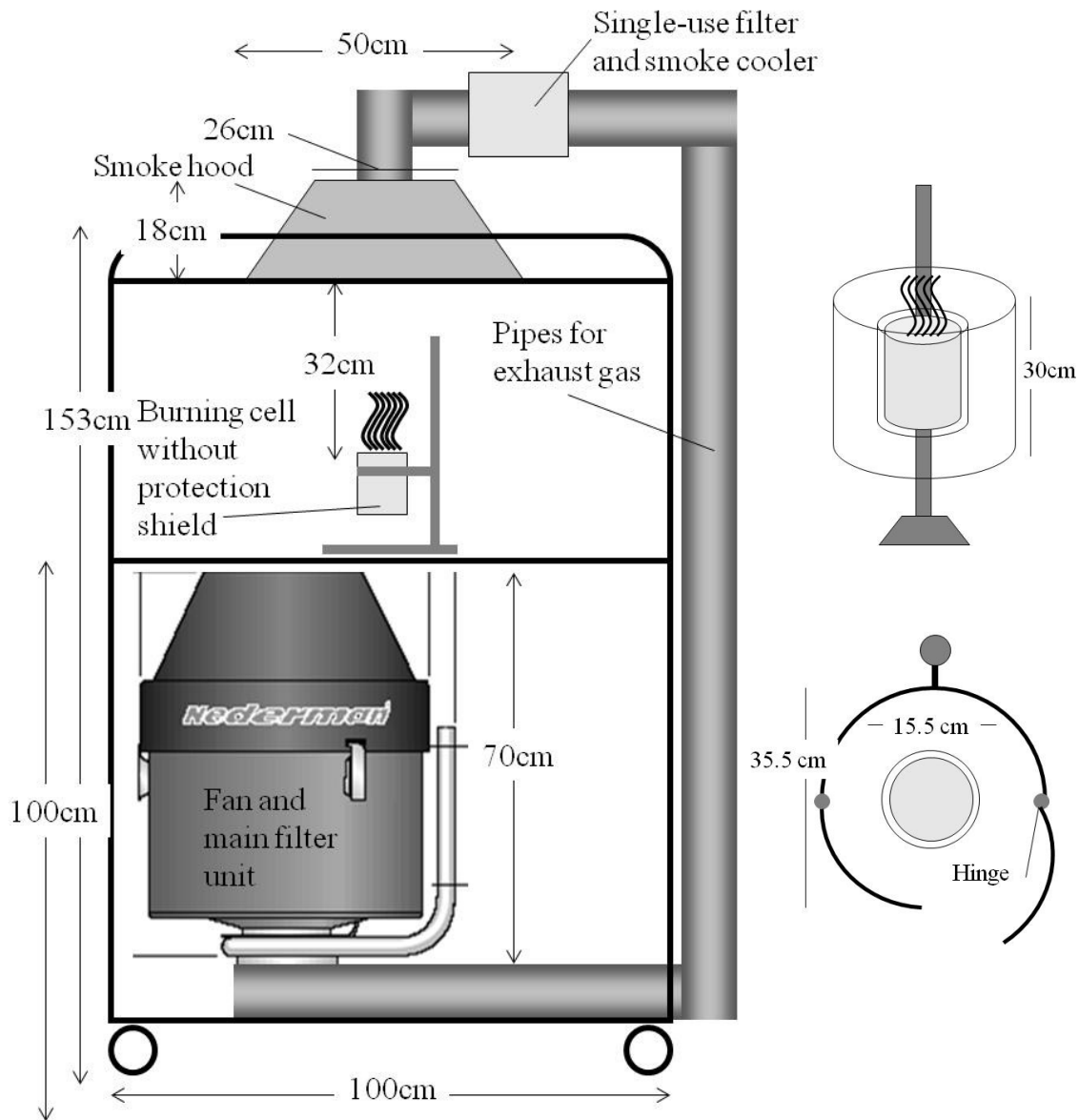


Figure 1 The laboratory scale burning cell with details of the safety shield around the burning cell (right).

2.2 Redesign/Modification of the Exhaust System

The smoke exhaust system had initially had a limited ventilation capacity and the expensive filters in the fan had to be changed rather frequently due to high soot production. The high temperature of the smoke also raised the temperature in the fan/filter unit above 120 °C, which we found disturbing. To deal with this problem, a cooling unit (tap water circulation, 5-10 °C) was mounted. This had the capacity to lower the exhaust temperature to a more or less ambient temperature during a burning session. The drawback of using this approach was that soot was now captured in the cold cooling ribs. However, the size of the cooling system made cleaning it in an ordinary laboratory sink manageable. To capture some of the soot before it entered the

cooling unit and the main (and expensive) filter in the fan unit, we mounted a filter holder (steel mesh filter) in front of the cooling unit.

2.3 Laboratory Use of Burning Cell

A short version of the burning procedure is given below. The full laboratory procedure for the operation of the laboratory scale burning cell is implemented as part of the laboratory procedures at SINTEF and described in the technical report from the Oil-in-ice JIP (Brandvik et al., 2010a).

2.3.1 Preparation

- Water flow adjusted to 500 mL/min
- Water temperature set to 10°C and controlled
- Exhaust fume filters and fan motor checked
- The temperature probes adjusted (in the water, in the oil layer and in the flame)
- Temperature logger turned on
- A fixed amount (approximately 120 g; the exact amount was found for each experiment) of fresh oil, evaporated oil or water-in-oil emulsion from the meso scale flume was added to the water surface in the cell

2.3.2 Ignition

Propane torch: A propane torch was used as the ignition source. The torch was held at a 30° angle to the oil for 10 seconds. If the oil did not ignite, the procedure was repeated two times after a break of 10 seconds. If no ignition was recorded after the third attempt, the oil was declared as “not ignitable”.

Gelled gasoline: Gelled gasoline (or crude oil) with an added emulsion breaker (4%, Alcopol O 60) was also used. The emulsion breaker was added to enhance breaking of emulsions and promote ignition (Guenette et al., 1995). Parallel experiments to study the correlations between these two ignition procedures were also performed. Only the experiments with the propane torch are reported in this paper.

2.3.3 Collection of Residue for Quantification

After termination of the burn, the residue was collected by adding a piece of pre weighted 3M adsorption pad that matched the inner diameter and shape of the burning cell. The warm residue soaked into the 3M pad and could easily be removed from the pad after cooling. Both the amount of water adsorbed to the 3M pad and the amount of oil residue left in the cell were typically marginal (<10%).

After each burn the cell was sufficiently cleaned by the removal of the residue. However, for more viscous or sticky residues, e.g. from heavy bunker fuels, a more thorough cleaning procedure might be needed. The water level was adjusted dependent on the amount of water in the emulsified samples, which was usually separated from the emulsion during the experiment and sometimes caused a rise in the water level.

2.3.4 Calculating Burning Effectiveness

The burning effectiveness (BE%) was calculated as given below:

$$\text{Burning Effectiveness (BE\%)} = 100 \cdot \left(1 - \frac{\text{mass of residue}}{\text{mass of initial oil}}\right) \quad (1)$$

However, the absolute value of the BE% is of less importance since the main use of this laboratory cell is to study the ignitability as a function of weathering in order to estimate the time window for in situ burning. The main area for the use of this apparatus is to quantify the sudden drop in BE% as a function of oil weathering, thus describing the upper limit for ignitability.

The absolute value of the BE% is also dependent on the scale of the laboratory equipment. Large scale burns will generally produce a higher BE% due to the generation of more heat and higher temperatures.

2.4 Ignitability Testing of Oil Samples Weathered in the Laboratory

The initial testing of the burning cell was conducted on samples weathered by small scale equipment. With these samples, the light components are removed by evaporation and then emulsified to simulate different weathering stages at sea. This was done by using a stepwise weathering approach used by SINTEF to study the weathering properties of oils and for preparing an “oil weathering manual” for the oil companies. The weathering procedures are described by Daling et al., 2003, and will not be discussed any further here.

Nevertheless, in an oil spill situation at sea, the weathering processes occur simultaneously and affect each other. It is therefore of great importance that the oils are weathered under realistic conditions when studying their behaviour when spilled on the sea surface. A meso scale flume basin (Singsaas et al., 1992) located at SINTEF is routinely used to simultaneously study the weathering processes under controlled conditions. Testing with the burning cell was performed on a series of weathered oil samples from the meso scale flume (see Chapter 0). Samples were taken from the emulsified surface oil for a series of physical and chemical analyses. The surplus, free seawater in the collected sample was immediately drained off using a separation funnel before the sample was homogenized and divided into aliquots for further analysis. The analysed physical and chemical properties are given in Table 1. Weathering experiments were performed using different oil types and ice conditions, and the details regarding these experiments are described in Brandvik et al., (2010b).

Table 1 Physical/chemical properties, units and methods

Property	Unit	Method
Viscosity of weathered oil	cP (or mP) at shear rate 10 or 100 s ⁻¹ at 3-6 °C	Daling et al., 2003
Water content of w/o-emulsion	volume %	Daling et al., 2003
Density of water free oil	g/ml at 15.5 °C	ASTM D4052-91
Chemical dispersibility of weathered oil	weight %	Concawe, 1988
Evaporative loss	weight %	Daling et al., 2003
Flash point of water free oil	°C	ASTM D93-90
Pour point of water free oil	°C	ASTM D97-87

2.5 Field Experiments to Verify the Laboratory scale Burning Cell

The field experiments were performed on the ice in Van Mijenfjord close to SINTEF's field research station on Svalbard. The field station is located at the mining community of Sveagruva (78°N) and is approximately 70 km from Longyearbyen, which is the administrative centre on Svalbard. A basin was cut out from the first-year ice in the fjord and used in a combined weathering and ISB experiment.

2.5.1 Oil Release Permits

All experimental releases of oil in both the laboratory and field experiments undertaken at Svea, Svalbard or in the Barents Sea were performed according to release permits from the Norwegian environmental authorities. All releases and cleanup operations were documented according to requirements in the release permit and reported to the authorities.

2.5.2 Large Scale Oil Weathering

A basin with circulating seawater was used to study the weathering of oil under different ice conditions. The flume dimensions and principal layout are given in Figure 2. The flume was cut out in the 110 cm thick fjord ice. The depth of the flume was 50 cm, hence the flume was not cut completely through the ice. Two propellers were used to control circulation and a wave generator to introduce wave energy (see Figure 3). A tent and two heat generators were used to control the ambient air temperature to prevent the seawater in the flume from freezing, and the duration of each experiment was from 2-8 hours. A comprehensive sampling and analysis program was performed similar to that described in Chapter 2.4. All analyses were performed on-site in a laboratory container placed on the ice close to the basin, with the variables measured given in Table 1. More details concerning the experimental set-up are given in Brandvik et al., 2009 and Brandvik et al., 2010b.

The weathering experiments were accompanied by small scale burning cell experiments and terminated with large scale ISB experiments (see the next two chapters).

2.5.3 Small Scale Ignitability Testing using the Laboratory Cell

The core unit of the burning cell was operated in “field mode”. Only the cell itself, the propane igniter, the cooling unit (pump, coolant and thermos) and the flame temperature unit/logger were operated in the field, see Brandvik et al., 2009 for details. The laboratory scale burning cell was operated behind a windshield outside the laboratory container close to the basin, and all samples collected from the flume were tested with the laboratory cell. The same procedure described earlier (Chapter 2.3) was used for the operation of the laboratory scale burning cell.

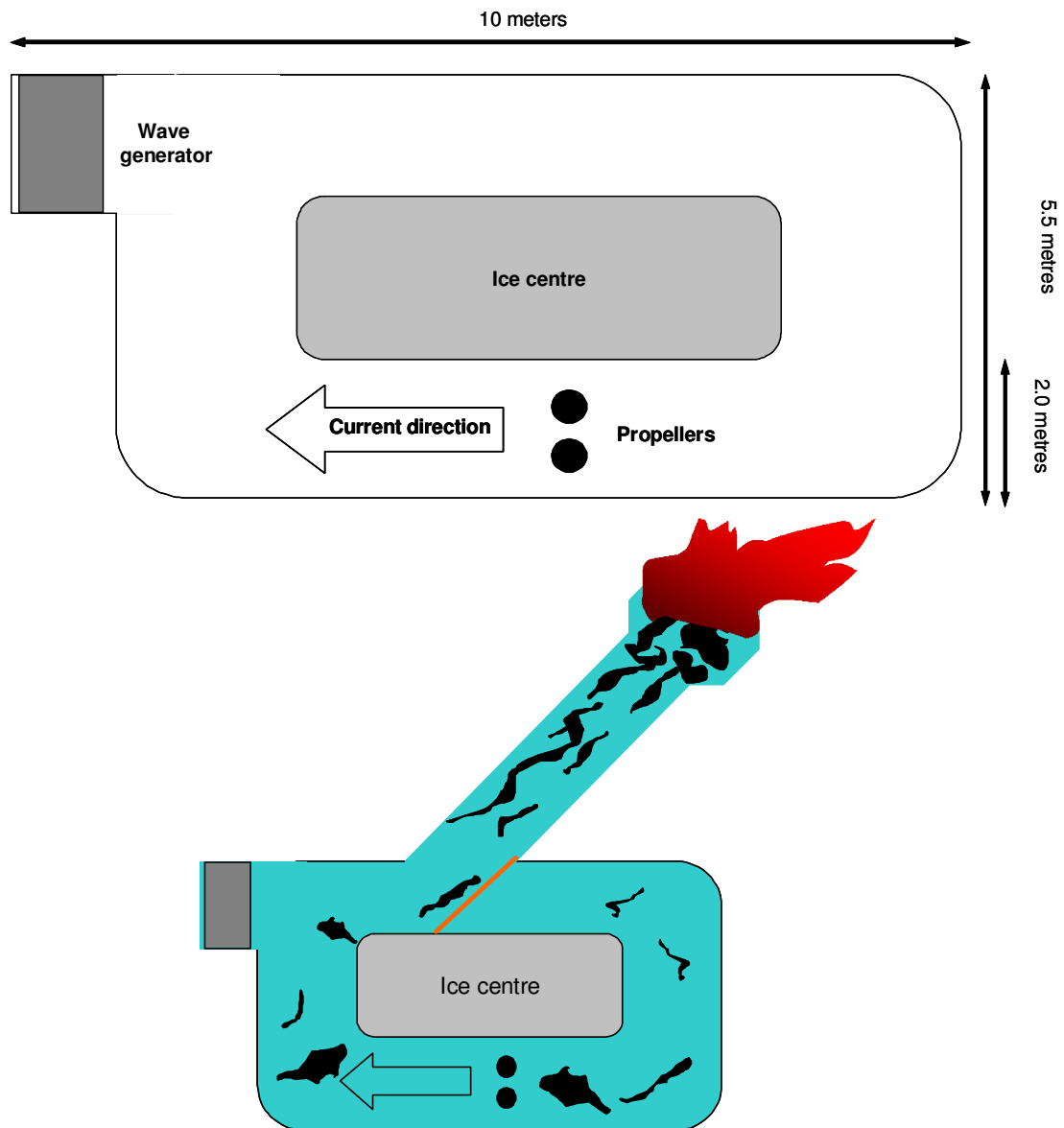


Figure 2 Overview of the weathering flume. After the weathering period, the channel was opened and the oil was led to the in situ burning basin.



Figure 3 Wave generator (left) and current propellers (right).

2.5.4 Large Scale Field Burning of Weathered Oil

The large scale verification of the ignitability measured with the laboratory scale burning cell (100 ml) was performed using a 300-450 L scale (dependent on emulsification). After each weathering experiment, the emulsion was led to the burning chamber (see Figure 2 and Figure 4) by a simple boom arrangement assisted by shovelling some of the surface weathered oil. The film thickness in the 9 m² burning chamber varied from 25 to 45 mm. The igniter was applied to the middle of the weathered oil and lit by a propane torch. The igniter that was used consisted of gelled crude (1L) added 4% emulsion breaker (Alcopol O60). If there was not a sufficient amount of flame spreading and initial burning taking place with the weathered oil during the burn time of the igniter (10 min), the weathered oil was classified as “not ignitable”. In cases where the weathered oil ignited, the residue was collected with adsorption pads and quantified gravimetrically.



Figure 4 ISB of weathered oil.

2.6 Oil Types

Statfjord, Balder, Troll crude and Grane crude (2007 field experiments) were used as the oil types for these experiments (laboratory and field). The relevant properties for the fresh crudes are given in Table 2.

Table 2 *Properties of Statfjord, Grane, Troll and Balder crudes*

Property	Statfjord 2008-0047	Grane 2007-1060	Troll 2007-0287	Balder 2000-0654
Wax content (wt. %)	4.3	3.2	0.9	2.1
Viscosity (cP, shear rate 100 s ⁻¹ , 13 °C)	7.0	640	27	219
Asphaltene content (wt. %)	0.1	1.4	0.04	1.1
Density (g/ml)	0.834	0.941	0.900	0.914
Flash point (°C)	<-39	26	3	15
Pour point (°C)	-3	-24	-36	-30
Loss at 150 °C (vol. %)	25.2	3.1	9.6	7
Loss at 200 °C (vol. %)	34.2	4.7	19.5	11
Loss at 250 °C (vol. %)	43.6	12.7	26.5	17

3 Results and Discussions

Four different types of experiments were performed in the development and verification of this laboratory scale burning cell. The first initial testing was performed with weathered oil samples (evaporative loss and emulsification) prepared with small scale laboratory apparatus (Chapter 3.1). Next, samples for burning experiments were generated using the meso scale weathering flume at the SINTEF SeaLab in Trondheim (Chapter 0). Finally, field experiments were performed at SINTEF's field station on Svalbard during the spring of 2007 (Section 3.3).

3.1 Initial Laboratory Testing

Samples were prepared using evaporation and corresponding levels of water content simulating realistic weathering of the three crudes - Statfjord, Troll and Balder - at 10 m/s wind. The weathering properties for the last ignitable samples are given in Table 3.

Figure 5 shows how the BE% results using the experimental cell vary as a function of the weathering time for these three very different oil types. The naphthenic Troll formed stable water-in-oil emulsions with a very high water content which revealed a very marked and quite early drop in BE% due to stable emulsions and a high water uptake. The asphaltenic Balder showed a similar behaviour, while the paraffinic Statfjord had a much longer time window for ISB. The Statfjord emulsion was still ignitable after one day of weathering with a high water content, evaporative loss and flash point due to the wax stabilization of the emulsion. Heat is a very efficient method for breaking emulsion where waxes are the main mechanism for stabilizing water droplets in the emulsion. The heat from the igniter has to break the emulsion so water free oil can be heated above the

flash point for both the ignition and burning of the oil. This process must continue after ignition, so heat from the burning oil can further break the emulsion and expand the burning area. This is a larger challenge for Troll and Balder emulsions (stabilized by a combination of wax, naphthenic and asphaltenic components), which are not so easily broken by heat.

Table 3 Weathering properties for the last ignitable samples in the series in Figure 5. All Statfjord samples in Figure 5 were ignitable.

Oil type	Weathering time (approx. hours)	Water content (vol. %)	Evaporative loss (vol. %)	Flash Point (°C)
Statfjord	24	75	44	150
Troll	1-2	67	10	70
Balder	2-4	50	7	60

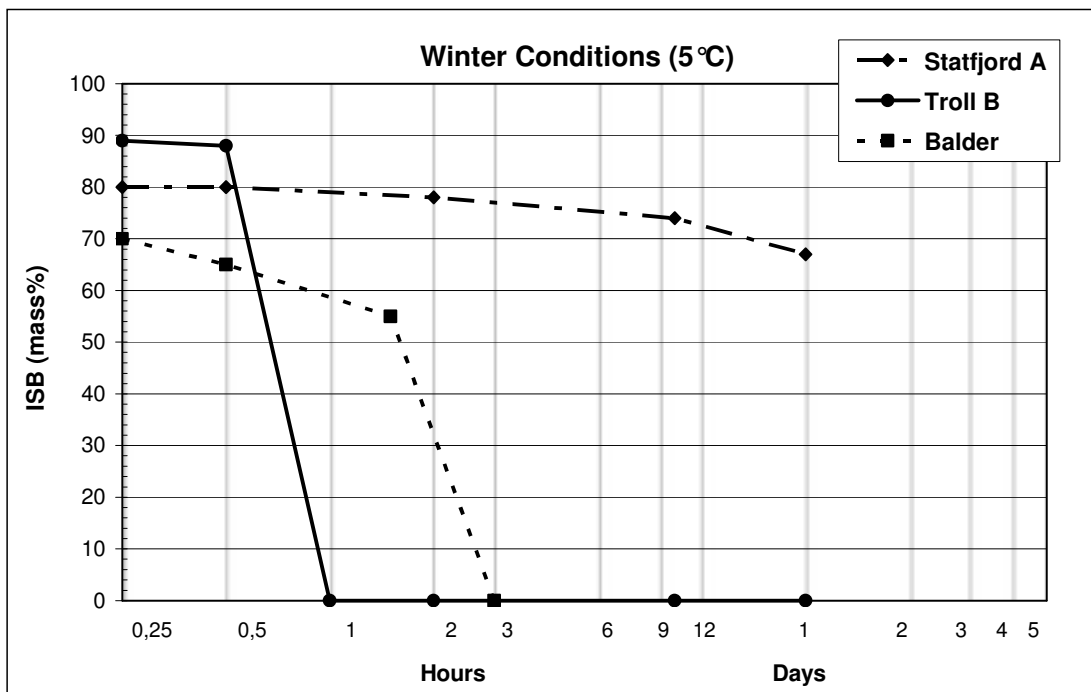


Figure 5 Burning effectiveness as a function of weathering (evaporative loss and emulsification) with three different oil types (Statfjord, Troll and Balder); data from Daniloff, 2007.

3.2 Laboratory Testing of Samples from the Meso scale Weathering (SeaLab)

The meso scale weathering concept is a very efficient approach for generating samples with an increasing weathering degree to be tested in the laboratory scale burning cell. The samples were burned as soon as possible after collection and the early and unstable samples were burned within an hour, while the more stable samples could be stored until the next day. Figure 6 shows the BE% from three series of meso scale

weathering experiments with open water, 50% ice cover and 90% ice cover (see Brandvik et al., 2010b for details). The Statfjord crude is a very waxy crude with a high water uptake rate. In open water (0% ice), the water uptake is fast and the ignitability drops during the first hour due to the high water content and very stable emulsions. As the amount of ice increases and weathering (especially evaporation and emulsification) is retarded, the drop in ignitability is delayed for 48h (50% ice) and still ignitable after 72 hours (90% ice).

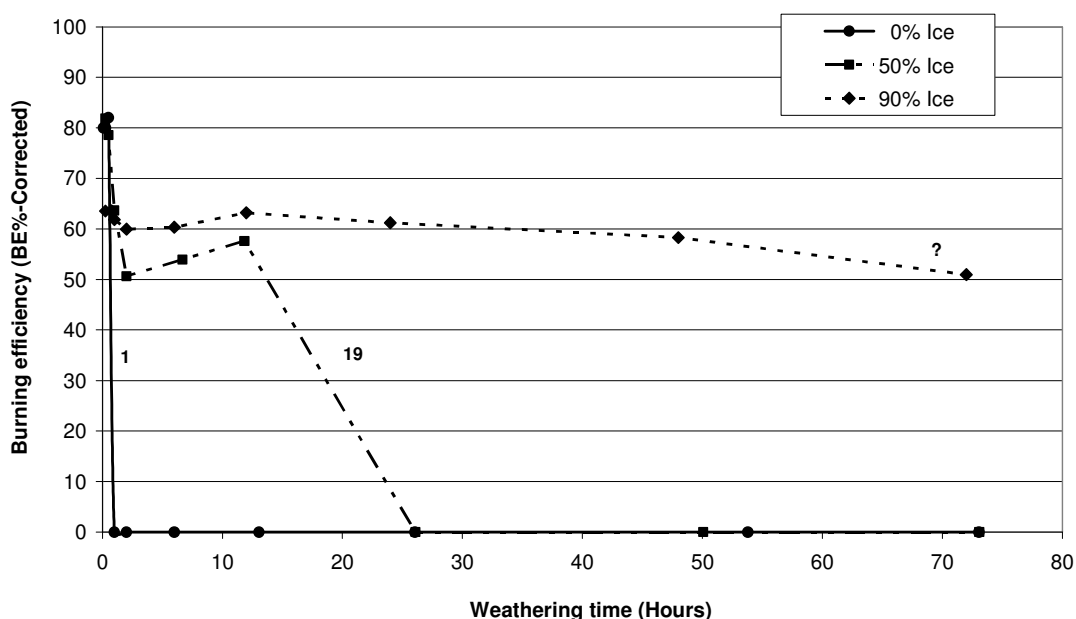


Figure 6 Burning effectiveness as a function of weathering time for the three different weathering experiments (0%, 50% and 90% ice coverage) with Statfjord crude. Maximum time window for ISB are indicated (hours).

A more complete selection of results using the new laboratory scale burning cell combined with the meso scale weathering basin as a function of oil types and ice condition are given by Fritt-Rasmussen and Brandvik, 2010.

3.3 Field Verification on Svalbard (Laboratory versus Field Experiments)

The main purpose of the fieldwork on Svalbard in April 2007 was to generate field data to verify the modified laboratory scale burning cell. A series of six meso scale experiments were performed with a varying weathering time from 2 – 8 hours. When planning the series of experiments, the aim was to spread the experiments with respect to weathering so that most of them were burnable, a few would show a reduced burnability and one or two should be not burnable. To keep the needed weathering time as short as possible, the asphaltenic Grane crude was selected for these experiments. This crude forms stable emulsions and becomes difficult to ignite after 6-8 hours of weathering.

To compare the burnability (BE%) from the laboratory scale burning cell and the meso scale basin burnings, the BE% from both these tests are plotted together as a function of water content in the emulsion (Figure 7)

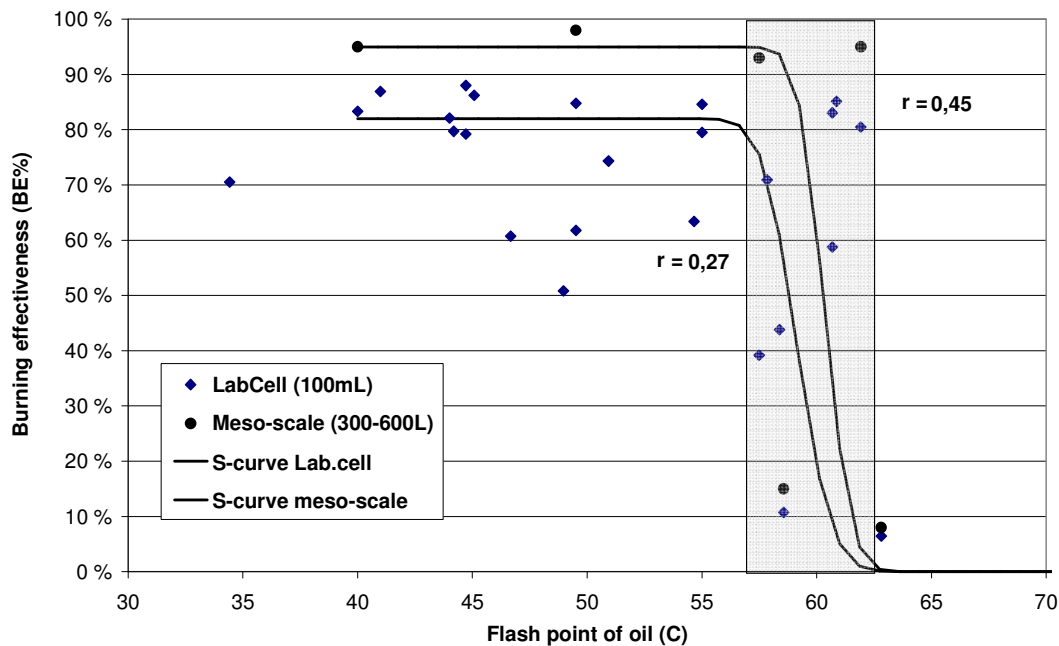


Figure 8 Comparison of burning effectiveness (BE%) measured with the laboratory scale burning cell (100 ml) and the meso scale weathering and ISB-basin (200-450 litres) on Svalbard with Grane crude oil. Effectiveness is given as a function of the flash point of the oil. The smoothed functions are S-functions fitted to the data and the correlation between the measured data and the functions are given on the figure (r).

4 Conclusions

The new laboratory scale burning cell has been used to measure ignitability as a function of weathering. The upper limit of ignitability (hours) has been defined as a sharp drop in burning effectiveness at a certain weathering time. The validity of these data has been verified by comparison with large scale burning experiments (200-450L) performed at Svalbard. The upper limit of ignitability for the use of in situ burning obtained with small scale laboratory cell and field experiments demonstrated a good correlation, which verifies the validity of the ignitability measured with the laboratory scale burning cell.

This small scale laboratory cell will be further used to measure ignitability as a function of oil type, weathering degree and environmental conditions, e.g. different ice conditions. This measurement will be done using the burning cell, together with basin weathering experiments performed at SINTEF.

5 Recommendations

The data generated by this measurement of ignitability versus oil types and weathering should be utilized to generate algorithms for predicting ignitability to determine the window of opportunity for ISB (Brandvik et al., 2010c).

6 Acknowledgements

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Comparing ignitability for in situ burning of oil spills for an asphaltenic, a waxy and a light crude oil as a function of weathering conditions under arctic conditions

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Abstract

In situ burning of oil spills in the Arctic is a promising countermeasure. In spite of the research already conducted more knowledge is needed especially regarding burning of weathered oils. This paper uses a new laboratory burning cell (100 mL sample) to test three Norwegian crude oils, Grane (asphaltenic), Kobbe (light oil) and Norne (waxy), for ignitability as a function of ice conditions and weathering degree. The crude oils (9 L) were weathered in a laboratory basin (4.8 m³) under simulated arctic conditions (0, 50 and 90 % ice cover). The laboratory burning tests show that the ignitability is dependent on oil composition, ice conditions and weathering degree. In open water, oil spills rapidly become “not ignitable” due to the weathering e.g. high water content and low content of residual volatile components. The slower weathering of oil spills in ice (50 and 90 % ice cover) results in longer time-windows for the oil to be ignitable. The composition of the oils is important for the window of opportunity. The asphaltenic Grane crude oil had a limited time-window for in situ burning (9 hours or less), while the light Kobbe crude oil and the waxy Norne crude oil had the longest time-windows for in situ burning (from 18 hours to more than 72 hours). Such information regarding time windows for using in situ burning is very important for both contingency planning and operational use of in situ burning.

Keywords

Oil spill, In situ burning, Weathering, Arctic, Laboratory experiments, Crude oils

1 Introduction

In recent years more investigations and explorations have been accomplished in the Arctic with the purpose to find and exploit oil and gas. Concurrently with this increased activity, the need for robust and efficient response technologies towards oil spills have grown. Several methods exist (mechanical and chemical) to combat oil

spills, but they have limited potential in the Arctic, with ice, coldness and limited infrastructure. In situ burning (ISB), a third response method, is in many arctic situations the only usable response technology; thus the method is named the “the Primary Arctic countermeasure” by Dickins and Buist (1999). The presence of ice inhibits the spreading of the oil i.e. the evaporation from the oil is reduced. During a burn it is the vapour that burns; hence it is important to have a high content of light components, and with a limited evaporation this might be achieved. According to Brown and Goodman (1986), Mullin and Champ (2003) there should be a sufficient initial oil film thickness to secure a sustainable burning; the authors suggest 2-5 mm at least to secure that the heat from the igniter is used to heat the fuel and not transferred to the underlying water. The reduced spreading of the oil, due to the ice, will have a positive impact on the initial oil thickness and could avoid the use of booms, resulting in a more efficient, simple and cost effective clean-up solution. The ice also inhibits the wave action i.e. the energy demanding emulsification process is slowed down. To burn the weathered oil the emulsion has to break and the water either boils out (Buist, 2003) or becomes a part of the sea water underneath the oil (Garo et al., 2004, Guenette et al., 1995). This depends on the stability of the emulsion (Nordvik et al., 2003). Low water content is therefore desirable. Ignition of an oil surface is a function of heat flux added by a thermal source (Putorti and Tennyson, 1994). As the degree of weathering increases the heat flux required for ignition and sustainable burning increases (Walavalkar and Kulkarni, 2003). All in all, the reduced weathering processes in the Arctic favour the conditions for ISB. Depending on the oil type, amount of oil spilled etc. A recovery between 30 % and 99 % has been found (Buist, 2003, Guenette and Sveum, 1995).

In spite of the research during recent years still more investigations are needed, especially to receive a better understanding of burning of emulsions including the understanding of window of opportunity (Buist, 2003). This is of particular importance when ISB is included in an oil spill contingency plan. Oil composition is very important for weathering of an oil slick thus the ignitability and time-window for ISB is different between oil types (McCourt et al., 1998). In the paper Brandvik et al. (2010a) a new laboratory burning cell is described and shows that the burning cell together with a laboratory weathering flume can be used to map the operational “window of opportunity” for ISB as a function of weathering. Our paper describes results from ISB experiments with three different crude oils, Kobbe, Norne and Grane using this laboratory burning cell to test ignitability as a function of weathering and oil types for oils weathered under simulated arctic conditions. The selected oils span over a large variation with respect to oil properties, which ensures that the results from this study can be interpolated and used for other oil types.

This study has been an integrated part of a Joint Industry Program to develop and advance knowledge, methods and technology for oil spill response in Arctic and ice-covered waters (Oil in ice JIP). The research program started in 2006, experiments were finalized in 2009 and final scientific reports issued in 2010. The JIP summary report Sørstrøm et al. (2010) gives an overview of the total program and the technical reports.

2 Experimental

The three crude oils, Kobbe, Norne and Grane, were chosen for the experiments since they have very different chemical compositions i.e. they represent a broad range of oil types. Kobbe crude oil is a Norwegian, arctic oil from the Barents Sea. It is a light, low density oil, but with some wax and asphaltene compounds. Unlike a

condensate, Kobbé crude oil can form water-in-oil emulsions, due to the content of these heavier components. Norne is a low density North Sea crude oil rich in waxes (saturated hydrocarbons, $>C_{20}$) and with a high pour point. At low environmental temperatures Norne will solidify due to formation of an internal lattice of precipitated waxes. This phenomenon is reflected in the high pour point. When Norne emulsifies, the waxes in the oil stabilize the water droplets by accumulating the droplets, hence the concentration of effective waxes will be reduced and the pour point and viscosity will decrease. The water droplets also disturb the formation of large and continuous wax lattices, which are needed to solidify the oil. The North Sea crude oil Grane is an asphaltenic crude oil with a high content of polar compounds like asphaltenes and resins, thus Grane crude oil creates very stable emulsions, due to these emulsion stabilizing compounds (waxes, resins and asphaltenes). Grane has a high density and the evaporation from the oil is low. The properties of the three crude oils are shown in Table 1.

2.1 Weathering of the oils

The crude oils, Kobbé, Norne and Grane, were weathered in a laboratory flume basin where arctic conditions were simulated. Three different ice cover experiments, open water, 50 % and 90 % ice cover respectively, were carried out for each oil. For each experiment 9 L of crude oil were added to the flume basin and each experiment lasted for 72 hours. Samples for burning and physical/chemical analysis were taken continuously during the experiment at the same place. The samples were tested for ignitability in the burning cell as soon as possible after sampling. A fresh oil sample from all three crude oils was also burned. An overview of the physical and chemical analysis performed can be seen in Table 1. More details about the weathering experiment can be found in Brandvik, et al. (2010b).

2.2 Burning procedure

The oil samples were tested for ignitability in a specially designed laboratory burning cell described in detail in Brandvik et al. (2010a), thus only briefly mentioned in the following. The burning cell consisted of a double layered cup wherein cooling water flowed. The cup was filled with sea water on which the oil was burned. Temperature probes measured the temperatures in the water, the oil and the flame. Approximately 120 g of samples were applied to the burning cell, corresponding to an initial thickness of $10 \text{ mm} \pm 2 \text{ mm}$. The ignition procedure was 10 s of heating with a propane torch. If the oil did not ignite, the procedure was repeated after a 10 s break. If the oil did not ignite after a third 10 s of heating, the sample was classified as “not ignitable”. No trend was found in the terminal thickness of the residue regardless of oil type or weathering degree. Burning effectiveness (BE) was calculated without including the emulsified water; this resulted in a lower burning effectiveness than if the water had been included. Since the emulsified water is removed before burning (Buist, 2003, Garo et al., 2004, Guenette et al., 1995), the burning effectiveness calculated without emulsified water is more realistic. It should be mentioned that there is a difference between burning effectiveness data obtained in the laboratory and in the field with large oil amounts. If the oil burns, it is most often possible to find very high burning effectiveness ($>90 \%$) for field experiments due to the large amount of oil burned (Buist and Twardus, 1985). The most important is, therefore, whether or not the oil sample is ignitable since the burning

effectiveness varies with spill size, ambient conditions etc. The equations for calculating the burning effectiveness corrected for water are given below.

$$\text{Burning Effectiveness (BE\%)} = 100 \cdot \left(1 - \left(\frac{\text{mass of residue}}{\text{mass of initial oil}} \right) \right)$$

$$\text{Burning Effectiveness Corrected (BE\% - Corr.)} = 100 \cdot \left(\frac{1 - (100 - \text{BE\%})}{(100 - \text{water content\%})} \right)$$

When plotting BE%-Corr. as a function of weathering time (Figure 1, 2 and 3) an s-curve is plotted in the graphs as well. The s-curve is a cumulative normal distribution function fitted to display the main trend in the BE%-Corr. results. Furthermore, a number indicates the length (in hours) of the time-window for ISB. The length of the time-window is defined as the midpoint between the last ignitable sample and the first sample that could not be ignited. The end of the ISB time-window is also visualized by a sharp drop in the s-curve.

3 Results and Discussion

3.1 Kobbe crude oil

Samples with different weathering degrees from the open water (0 % ice), 50 % ice and 90 % ice weathering experiments were ignited and if possible burned in the laboratory burning cell. The burning effectiveness (BE%-Corr.) measured with the laboratory burning cell is presented in Figure 1 for Kobbe crude oil. From Figure 1 an overview of the water content in the emulsified oil, viscosity and evaporative loss as a function of weathering time in the flume is also provided.

From Figure 1 it appears that the burning effectiveness decreased continuously from 64 % to around 45 % for all three experiments, but that the 90 % ice cover experiment had the least sharp slope. The fall in burning effectiveness was consistent with the increase in water content, since more and more water has to be removed before the oil can burn. As mentioned earlier Kobbe is a light crude oil with a small content of emulsion stabilizing compounds only sufficient to create unstable emulsions with low viscosity, hence the emulsification is much dependent on high mixing energy. Thus the ice conditions are important for the creation of emulsions since a dense ice cover will dampen the waves, and thus the energy in the system. Therefore significant differences are observed between the three weathering experiments with the highest water uptake for the open water experiment, with 65 % water, and the lowest water uptake for the 90 % ice cover experiment where less than 10 % water was measured in the samples. The viscosity measured in the open water experiment is lower than expected. It is even lower than the measured viscosity for the 50% ice cover experiment. This is probably caused by the rapid and high water uptake forming very unstable emulsions, which collapse during the viscosity measurements. The low viscosity for the 90 % ice cover experiment is mainly a result of the very low water uptake but also the low evaporation from this weathering experiment.

The window of opportunity for ISB was more or less the same for the open water and 50 % ice cover experiments and from Figure 1 time-windows of 36 and 38 hours respectively can be seen. This is as expected, as the emulsions are unstable and are easily broken by the heat from the igniter. The weathering experiment performed with 90 % ice coverage did not last long enough to find the time-window, and the oil was still ignitable after 72 hours.

As expected, since Kobbe is a light crude oil, the highest evaporative losses of the three tested oils were found from the weathering experiments with Kobbe. The high evaporative loss also results in a fast increase in the pour point. Though, it would have been expected that the open water experiment had a higher evaporative loss compared to the 50 % ice cover experiment. As described earlier the water uptake for the open water experiments was much higher compared to the 50 % ice cover experiment. This high water uptake results in thick emulsified oil patches, reducing surface to volume ratio and evaporative loss compared to the 50 % ice cover experiment. The low evaporative loss for the 90 % ice cover experiment is as expected since dense ice coverage results in little spreading and large film thickness and such conditions reduce the evaporative loss.

3.2 Norne crude oil

Figure 2 provides an overview of the burning effectiveness as a function of weathering time in the flume for the waxy Norne crude oil. The figure shows that Norne crude oil had the lowest burning effectiveness of the oil types tested ranging from 28 % to 51 % for all three ice conditions and the overall tendencies for the flame temperatures for Norne were also lower than for Grane and Kobbe.

In addition Figure 2 presents the water content in the emulsified oil, viscosity and evaporative loss as a function of weathering time in the flume. The high wax content in Norne crude oil is the main compound for stabilizing water in the oil. Such wax-stabilized emulsions are often unstable and the formations are dependent on the energy available in the system i.e. the ice cover as already described for Kobbe. This can be seen from Figure 2 (water content) as a clear difference is seen in the water uptake for the three weathering conditions. The difference in water uptake is also reflected in the measured window of opportunity for ISB, as highly emulsified oils are more difficult to ignite. Even so, Norne was the crude oil of the three tested that had the longest operational time-windows. For the open water experiment the time-window was 18 hours, for the 50 % ice cover experiment the time-window was 61 hours and for the 90 % ice cover experiment the oil was ignitable at least as long as the experiment lasted (72 hours). Oils with a high wax content (as Norne) and low asphaltene content usually create emulsions that are unstable at elevated temperatures (below 100 °C) and ignitability is not affected as much by emulsions as other oil types (Buist et al., 1994). The results in our paper confirm that wax stabilized emulsions are easily broken by the heat from the igniter. That waxy oils also break more easily by settling has been proven earlier by Strøm-Kristiansen et al. (1995).

As opposite to Grane and Kobbe and what is normal, the viscosity for Norne crude oil decreased in the beginning of the experiments. This is due to the high pour point, which, as described earlier, results in a solidification and high viscosity. The initial formation of unstable emulsions reduces the viscosity. However, as the emulsification continues the water droplets become smaller, the emulsion more stable and thus the viscosity increases again. The semi solid behaviour of Norne is expected to reduce the spreading, resulting in

a thick oil film, which is a key factor that needs to be fulfilled to secure a successful in-situ burning as mentioned earlier.

The evaporative loss from Norne (Figure 2) was low compared with Kobbe crude oil, but in the same range as Grane, even Norne is lighter than Grane and a higher evaporative loss would have been expected. This is caused by the high pour point which results in a stiff and thick oil slick which will remain thick as the oil gradually emulsifies, thus spreading is limited and the evaporation becomes low.

3.3 Grane crude oil

Figure 3 provides an overview of the burning effectiveness, water content in the emulsified oil, viscosity and evaporative loss as a function of weathering time in the flume for the asphaltenic Grane crude oil.

The burning effectiveness was between 54-91 % for all the experiments. The four samples that burned for the 50 % ice cover experiment had a clear decrease in burning effectiveness with weathering time and in correlation with the increase in water content, decreasing from 83 % to 65 %. For the 90 % ice cover experiment most of the samples had a high burning effectiveness.

The water uptake was rapid and high; the highest of the three oil types included in this paper. Even for the 90 % ice coverage experiment, with least energy in the system, the water content reached maximum (70 %) at the end of the experiment. This indicates that a high content of natural emulsion stabilizing components (waxes, asphaltenes and resins) is the significant factor for the rapid emulsification and lower dependency of energy conditions. The low pour point for Grane is also important, since it keeps the oil fluent at these low temperatures, thus easing the emulsification. The corresponding water content in the first samples that did not burn was 34 %, 62 % and 20 % for open water, 50% ice cover and 90 % ice cover conditions respectively. This indicates that the water content is a limiting factor, but is not the only factor that determines whether or not the oil will burn, as the water content varies. The viscosity increase during the experiments was correlated with the water uptake. The viscosity was the highest for the oils in this study; this is due to the high water content and high stability of the formed emulsion. The evaporation was low for all three ice conditions due to the low content of volatile components in Grane. The evaporative loss was highest for the 50 % ice cover experiment and not the open water experiment as one might expect. This is, as earlier explained for Kobbe, due to the high emulsification for the open water experiment that results in thick oil patches, which inhibit the evaporation. The low evaporation in the 90 % ice cover experiment was, as already explained for Kobbe, due to the high concentration of ice and thereby little energy in the system and a limited area for the oil to scatter.

The ability to rapidly create stable emulsions and the low content of volatile compounds corresponds well with the very short operational windows of opportunity for ISB. The time-window for ISB was 1, 2 and 9 hours for open water, 50 % and 90 % ice cover experiments respectively.

Grane crude oil had the highest density (0.952 g/mL at the end of the open water experiment) of all the oils tested; as the density never exceeded the density of sea water for any of the oils, the oil did not sink due to weathering. The burn residue was examined visually after the burning and no sinking or submerging of any of the residues were observed either.

4 Conclusion

From the results with the three very different crude oils, the chemical composition of the oils clearly has a major influence on the ignitability, as the composition directly influences the weathering of the oil. In particular, the ability to rapidly form stable water-in-oil emulsions with high water content will decrease the window of opportunity for ISB. Emulsification is nevertheless not the single decisive factor for the success of ignition and should be seen in association with all the other factors that influence ignitability e.g. amount of volatile components (flash point). The viscosity followed the emulsification in most cases, except where the composition of the oil (high pour point) resulted in a semi solid oil slick. Dense ice coverage reduced the evaporation from the oil slick, but the evaporation was also reduced when the emulsification resulted in thick oil patches. The ice cover also had a major influence on the degree of emulsification and thus ignitability. Open water with no ice resulted in high emulsification and shorter ISB time-windows. Dense ice covers, where the wave energy was inhibited thus reduced the weathering processes, resulted in longer window of opportunity for ISB. Grane crude oil had very narrow operational time-windows: 9 hours or less. Norne and Kobbe had longer time-windows and for the 90 % ice cover experiments the last ignitable sample was not found within the 72 hours the weathering experiment lasted.

Knowledge regarding oil composition and weathering and the use of ISB is important in connection with both contingency planning and during oil spill operations. This study shows that ISB has a large potential for light and waxy crude oils like Kobbe and Norne based on the measured time windows for ignition. However, the potential is limited for asphaltenic crudes like Grane (time-window of 9 hours or less), due to a rapid formation of very stable emulsions with high water content and a low content of volatile components. Data from a large number of experiments with this laboratory burning cell and two additional crude oils have been used to establish a general algorithm linking oil composition and ignitability as a function of oil weathering (Brandvik et al., 2010c). Another important operational consideration regarding burning oil spills is the fate of the burn residue. No analyses were done on the residues as a part of this study, but visual examination did not reveal any sinking or submerging of the residues. Further characterizations of soot and burn residues are performed in a separate study (Fritt-Rasmussen et al., 2010).

5 Acknowledgement

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Table 1 Properties for Grane (Singsaas et al., 2005), Kobbe (Sørheim and Moldestad, 2008) and Norne fresh crude oils (Singsaas et al., 1998).

	Density [g/mL]	Pour point [°C]	Viscosity [cP]	Max water uptake [%]	Wax content [wt %]	Asphaltene content [wt%]
Kobbe	0.797	-39	22 at 5°C	75	3.4	0.03
Norne	0.860	21	824 at 3°C	50	10.8	0.3
Grane	0.942	-26	1747 at 2°C*	65	3.2	1.4

* Grane viscosity from (Faksenss, 2008)

Table 2 Physical/chemical properties, units and methods

Property	Unit	Method
Viscosity of weathered oil	cP (or mP) at shear rate 10 s ⁻¹ at 2-6 °C	Daling et al., 2003
Water content of w/o-emulsion	volume %	Daling et al., 2003
Density of water free oil	g/mL at 15.5 °C	ASTM D4052-91
Evaporative loss	weight %	Daling et al., 2003
Pour point of water free oil	°C	ASTM D97-87

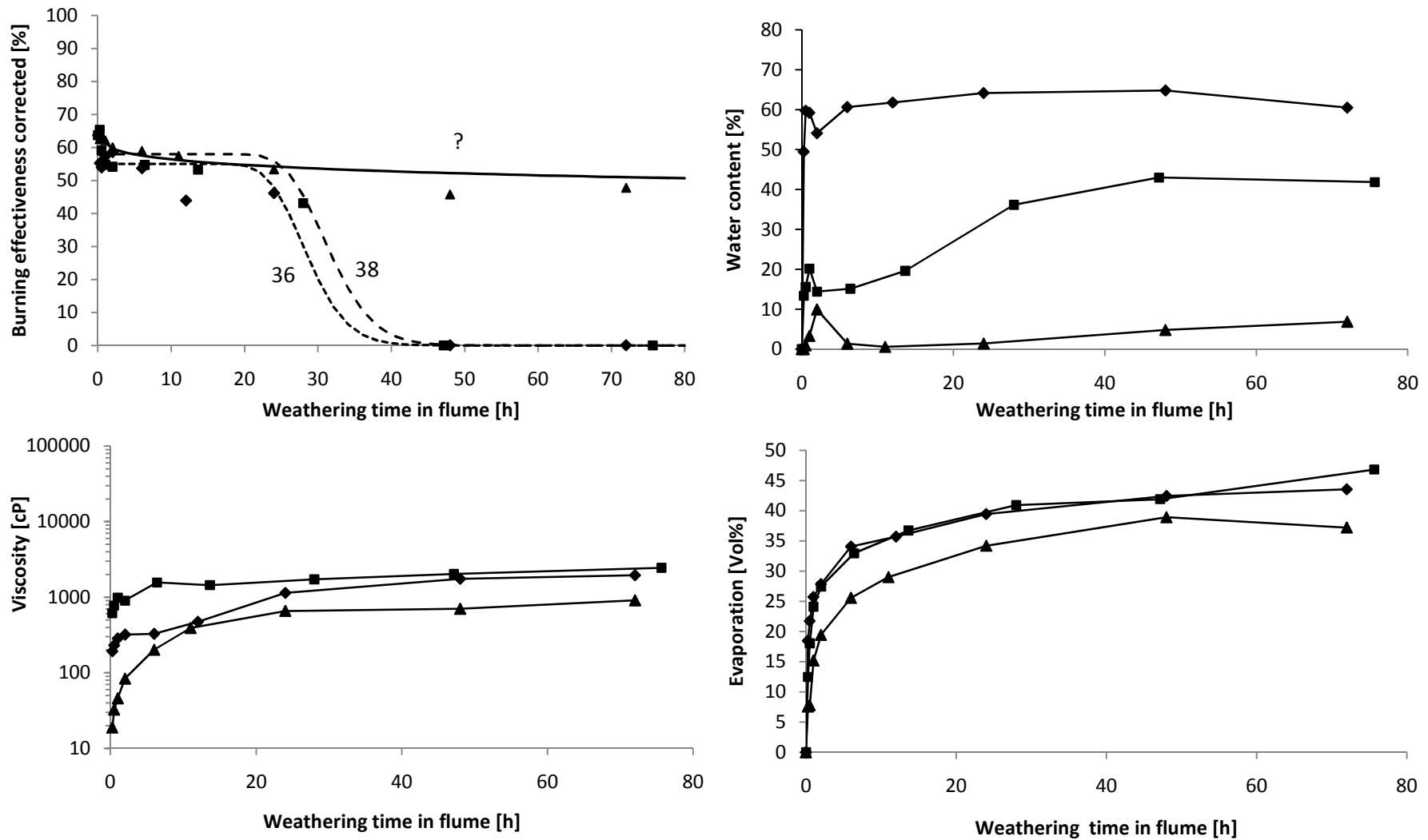


Figure 1 Burning effectiveness, water content, viscosity (cP at shear rate 10 s^{-1}) and evaporation as functions of weathering for Kobbe crude oil. \blacklozenge Open water, \blacksquare 50 % ice cover and \blacktriangle 90 % ice cover. In the burning effectiveness figure, the s-curve is shown together with the estimated time window for ISB (hours).

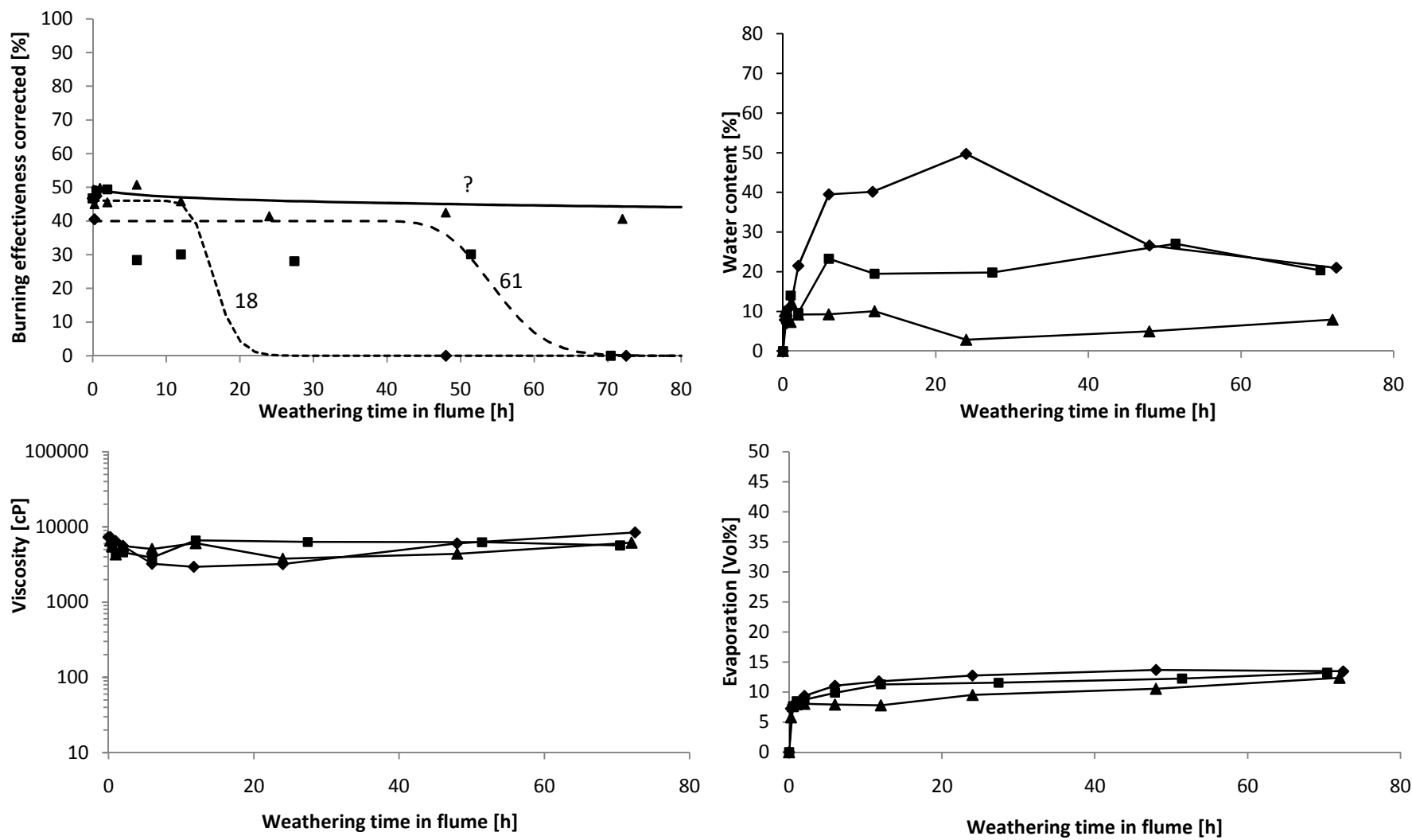


Figure 2 Burning effectiveness, water content, viscosity (cP at shear rate 10 s^{-1}) and evaporation as functions of weathering for Norne crude oil. \blacklozenge Open water, \blacksquare 50 % ice cover and \blacktriangle 90 % ice cover. In the burning effectiveness figure, the s-curve is shown together with the estimated time window for ISB (hours).

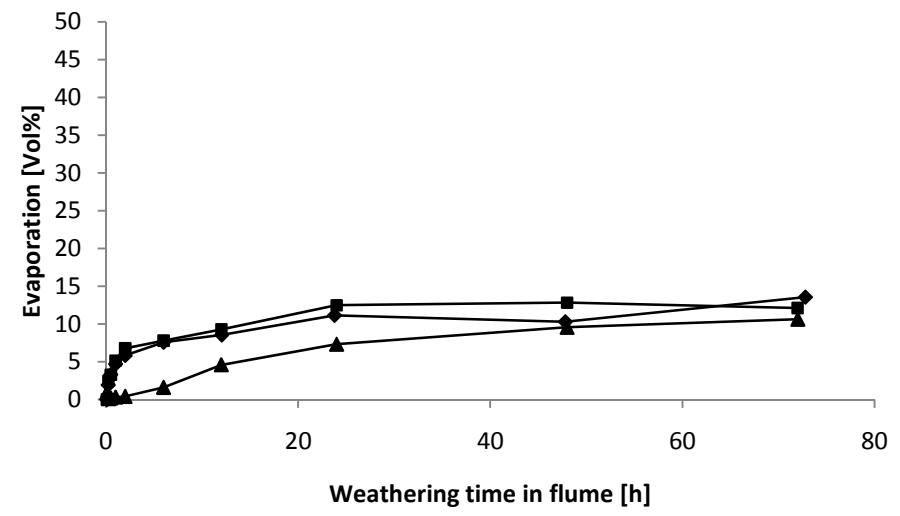
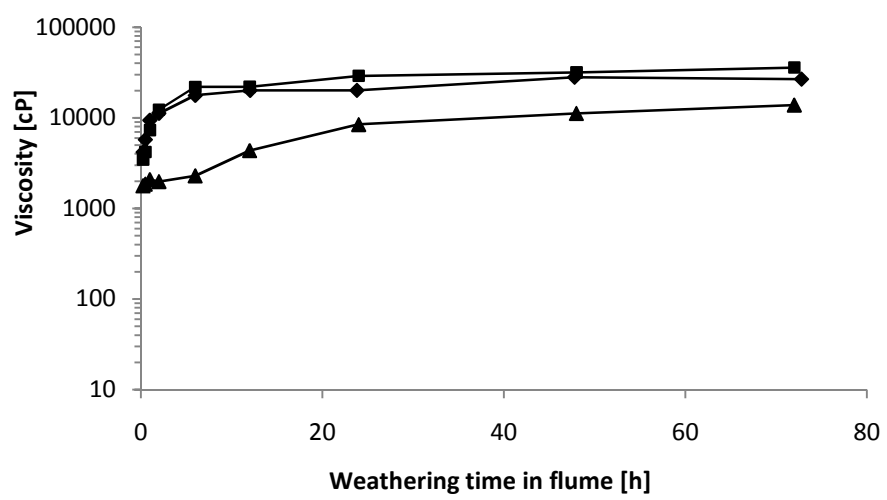
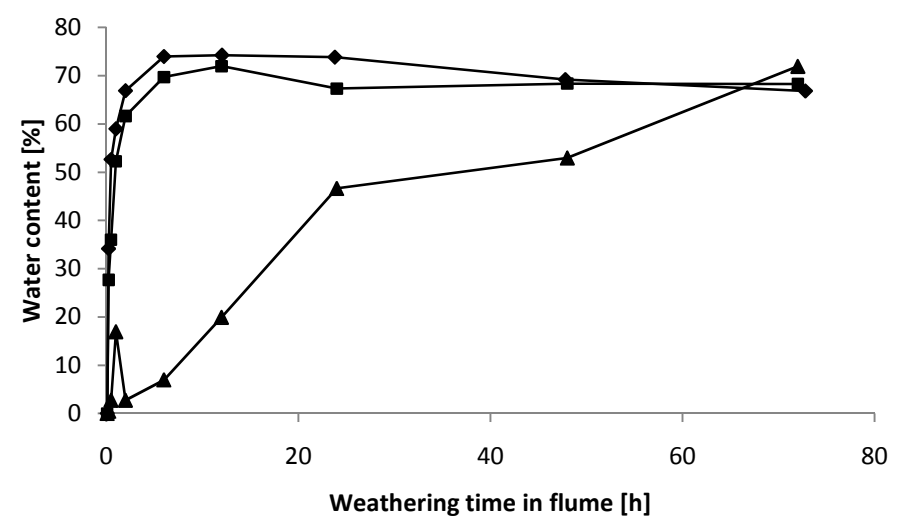
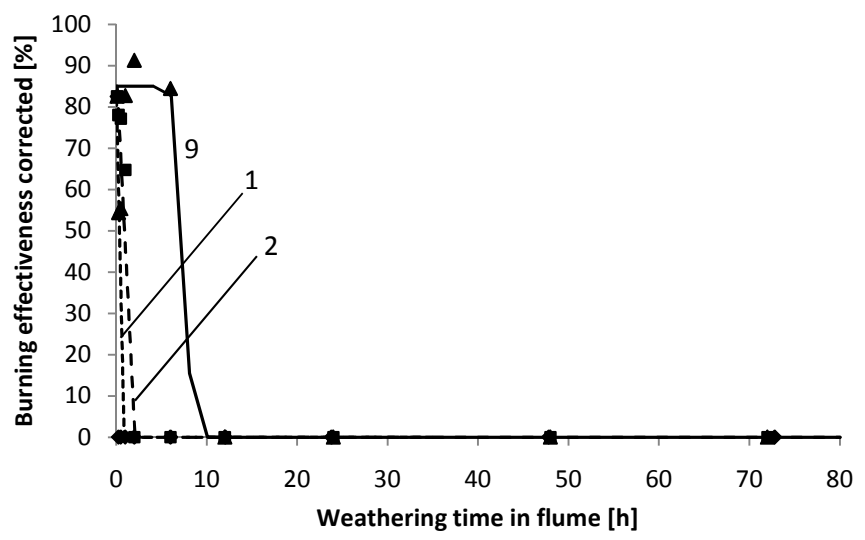


Figure 3 Burning effectiveness, water content, viscosity (cP at shear rate 10 s^{-1}) and evaporation as functions of weathering for Grane crude oil. ♦ Open water, ■ 50 % ice cover and ▲ 90 % ice cover. In the burning effectiveness figure, the s-curve is shown together with the estimated time window for ISB (hours).

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Measuring ignitability for in situ burning of oil spills weathered under Arctic conditions. From laboratory studies to large-scale field experiments

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Abstract

This paper compares ignitability of Troll B crude oil weathered under simulated arctic conditions (0, 50 and 90 % ice cover). The experiments were performed in different scales at SINTEFs laboratories in Trondheim, field research station on Svalbard and in broken ice (70-90 % ice cover) in the Barents Sea. Samples from the weathering experiments were tested for ignitability using the same laboratory burning cell. The measured ignitability from the experiments in these different scales shows good agreement for samples with similar weathering. The ice conditions clearly affect the weathering process, and 70 % ice or more reduces the weathering and gives a longer time-window for in situ burning. The results from the Barents Sea showed that weathering and ignitability can vary within an oil slick. This field use of the burning cell demonstrated that it can be used as an operational tool to monitor ignitability of an oil spill.

Keywords

Oil spills; In situ burning; Large-scale field experiments; Laboratory experiments; Weathering; Arctic

1 Introduction

In situ burning (ISB) is the term used for controlled burning of oil “in the original place” and refers to a technique where accidentally spilled oil is ignited and burned directly on the water surface. A significant amount of the oil is thereby removed from the spill site by converting it into combustion products, soot and residue. The method is, in general, not very labour demanding, can easily be achieved and is efficient e.g. efficiencies of 98 % (Allen, 1990) and 99 % (Guenette and Sveum, 1995) were found under the ideal circumstances (fresh oil and thick slick). After flame out only a small percentage of the original amount of oil is left; it consists of a high viscous/semi-solid residue.

The first recorded ISB was in 1958 in the Northern Canada (Fingas, 1998). Since then a series of burn and oil spill studies have been conducted; approximately 11 larger ISBs (accidental and experimental) in conditions with ice (Fingas, 1998). To secure a successful burning it has been found that two conditions are especially important: the thickness and the weathering of the oil. Of the weathering processes primarily water-in-oil emulsion is important (Bech et al., 1993; Guenette et al., 1995), however the amount

of light components left in the oil (Brandvik and Faksness, 2009) and spreading is also important. In addition, the type of oil and ambient conditions are crucial; e.g. too much wind will affect the burning negatively.

Some of the drawbacks with ISB are the smoke production and risk of secondary fires during a burn and the concern for the workers and possible settlements nearby. However, ISB may be the only method in ice-covered waters (Barnea, 1999), since conventional response technologies (mechanical and chemical) could have limited potential in snow, ice and cold, whereas ISB is strengthened under such conditions.

In the 1970s field trials showed that ISB had the potential of removing large amounts of oil on the ice surface (Norcor, 1975). Later experiments were performed with ISB in ice and snow primarily as laboratory and meso-scale experiments (tank or field tests). The focus has been on the burning physics (flame spreading, oil spreading, slick thickness, burning efficiencies) (Buist and Twardus, 1984) and studying burning processes of emulsions, development of igniters and the influence of wind and waves as small-scale field and tank tests (Bech et al., 1992; Guenette et al., 1994). In spite of the research conducted in the past decades the use of ISB as an operational response tool is still not fully developed. There is a need for large scale field experiments to compare and verify the results from the smaller scales, and an evaluation of certain techniques and tactics which can only be done in an actual oil burning situation (Walton and Jason, 1999). This paper contributes to the understanding of ISB as a contingency tool in Arctic areas. The main objective with this paper is to describe the ignitability and window of opportunity of a crude oil as a function of weathering in Arctic conditions with different ice scenarios (coverage of ice), and present the link between laboratory experiments and field experiments. As visualized in Figure 1, oil spilt in ice can be found in a variety of different places. The main focus for this study has been the continuous bulk phase of oil between the ice floes (white circle in Figure 1). To validate the results from the laboratory burning cell with a large-scale ISB has also been an important part of this study.

This study has been an integrated part of a Joint Industry Program to develop and advance knowledge, methods and technology for oil spill response in Arctic and ice-covered waters (Oil in ice JIP). The research program started in 2006, experiments were finalized in 2009 and final scientific reports issued in 2010. The JIP summary report (Sørstrøm et al., 2010) gives an overview of the total program and the technical reports.

2 Method and experimental setup

Experiments were performed at SINTEFs laboratories in Trondheim, Norway (SeaLab), SINTEFs field research station in Svea, Svalbard, N77.5, E16.4 (Svea) and as field experiments in the broken ice in the Barents Sea, north east of Hopen Island, N77.6, E30.9 (Barents Sea). Troll B crude oil was used for all the experiments and is a crude oil high in naphthenic components (cyclic and branched saturated hydrocarbons). This is caused by microorganisms that have degraded the linear hydrocarbons, yielding a very low paraffinic content and a relatively high content of naphthenic components. The Troll B has a very low pour point due to its low wax content (naphthenic character) and a balanced blend of emulsion

stabilising components (waxes, resins and asphaltenes), thus Troll B forms stable water-in-oil emulsions (Brandvik et al., 2010a). The low pour point is also important for the formation of water-in-oil emulsions, as the oil is fluent at the low experimental temperatures, and therefore is affected by the energy in the system. The properties for Troll B can be seen in Table 1.

2.1 Laboratory weathering experiments – SeaLab

9 L of Troll B crude oil were weathered in a flume basin at SeaLab. Open water, 50 % ice cover and 90 % ice cover weathering experiments were conducted. Samples were taken continuously during the 72 hours the experiment lasted (0.5, 1, 2, 4, 6, 12, 24, 36, 48, 60, 72) and the ignitability of the samples were tested as soon as possible after sampling in the burning cell (see section 2.4). More details about the weathering experiment can be found in (Brandvik et al., 2010b; Fritt-Rasmussen et al., 2010).

2.2 Meso-scale field experiments – Svea

The weathering experiments at Svea were performed in a flume cut in the fjord ice in the Van Mijenfjord. Three experiments were conducted with open water, 50 % ice cover and 90 % ice cover, with 200 L of Troll B crude oil for each experiment. Samples were taken continuously as in SeaLab during the 72 hours each of the experiment lasted. More experimental details can be found in (Brandvik et al., 2010b). The oil samples were tested for ignitability immediately after sampling in the burning cell (see section 2.4).

2.3 Field experiments – Barents Sea

The offshore field experiment was carried out in the marginal ice zone in the Barents Sea with 70-90 % ice coverage. Two experiments were performed: a weathering study with 7 m³ of Troll B crude oil (called P1.2, which is the name used in (Brandvik et al., 2010c)) and a large-scale burning experiment with 2 m³ of Troll B crude oil (called P1.1, as used in (Brandvik et al., 2010c)).

Samples from P1.2 for burning and physical/chemical analysis were taken continuously during the 144 hours the experiment lasted. The samples were applied to a 125 ml Nalgene flask and immediately tested for ignitability in the burning cell on board the research vessel (the burning procedure is described in section 2.4). More details about the P1.2 oil spill can be found in (Brandvik et al., 2010b, 2010c).

During the P1.1 large-scale ISB the weather was calm with winds less than 5 m/s and air temperatures between -9 °C and -3 °C (Faksness et al., 2010). During release the oil slick separated into two parts. The oil was weathered for 12 hours between the ice floes. An outline of the oil slick just before ignition can be seen in Figure 2. The left part of the slick was where the majority of the oil (bulk phase) was present as a continuous oil slick with oil thicknesses between 20 and 30 mm. The oil slick to the right was approximately 5 mm thick and contained a lot of slush ice. One sample for burning in the burning cell and one for physical/chemical analysis were taken from the left area. Plastic bags with 500 ml gelled gasoline added 4 % emulsion breaker, Alcopol O 60 were used as igniters. Addition of emulsion breaker was earlier proven by (Guenette et al., 1994) as an efficient method to ignite an oil slick. 12 igniters were placed around the slick and ignited with a handheld propane torch. The ignition was done downwind and flame spreading occurred within two-three minutes. The oil burned for 24 minutes with maximum intensity

after 12 minutes. Some areas needed to be reignited, due to discontinuous oil slick and high content of slush ice in the oil. After flame out and cooling the residue was collected with 3M oil absorbing pads and gravimetrically quantified to calculate the burning efficiency. The pads are water repellent thus the amount of water absorbed to the pad was found to be very little (less than 5 %), this is also what (Smith and Diaz, 1985) found (+/- 2%). The residue left was usually also marginal (less than 5 %). Finally, a sorbent (Sphagnum peat moss, NatureSorb from Nirom Peat Moss) was spread over the area to absorb and immobilize the last part of the burn residue.

2.4 Burning procedure

The burning cell consisted of a cup filled with seawater on which the oil sample (approximately 120 g taken from the weathering experiments; see chapter 2.1, 2.2 and 2.3) was burned. The cup was double layered, wherein cooling water flowed (500 ml/min at 10°C). Three thermo elements measured the temperature in the seawater, oil and flame. The burning cell in field mode (on the ice and on board the research vessel) was the same as in the laboratory. In field mode no exhaust system was used, however a wind protection shield was needed. For more details (Brandvik et al., 2010d) should be consulted. The procedure for testing the ignitability of the weathered oil samples was the same for all the experiments. The oil was ignited with a propane lighter for 10 s and if the oil did not burn after the third ignition attempt, the sample was classified as “not ignitable”. The burn residue was collected with a 3M oil absorbent pad. The burning effectiveness reported in this paper is corrected for emulsified water, as the water either boils out or breaks out and separates during a successful burning. If the water content was included the burning effectiveness would vary significantly dependent on the degree of weathering. The calculations of burning efficiency were as follows:

$$\text{Burning Effectiveness (BE\%)} = 100 \cdot \left(1 - \left(\frac{\text{mass of residue}}{\text{mass of initial oil}}\right)\right) \quad (1)$$

$$\text{Burning Effectiveness Corrected (BE\% - Corr.)} = 100 \cdot \left(\frac{1 - (100 - \text{BE\%})}{(100 - \text{Water Content\%})}\right) \quad (2)$$

3 Results and Discussion

3.1 Burning effectiveness versus weathering

Burning effectiveness (BE%-Corr.) measured with the burning cell is generally high and varies between 40-80 %, due to different degree of weathering and heterogeneity of the samples (Figure 3). It seems as if there is a tendency that the samples burned in the burning cell at SeaLab had a higher BE%-corr. than the samples burned in the burning cell in the field at Svea. A reasonable explanation appears to be the air temperature as a low air temperature can reduce burning effectiveness (Bech et al., 1992) and the burning due to a larger temperature difference between the flame and air temperature (the oil slick is heated primarily by radiative heat from the flame). In SeaLab the samples were burned at 10-20 °C, whereas in Svea the temperature was between -25 °C and -20 °C. Other authors report that air

temperatures from -11°C to 2 °C have a negligible effect on the burning (Walavalkar and Kulkarni, 1996) and Buist and Dickins (2003) do not report any effect of air temperatures from -31.5 °C to 3 °C of burning oil in snow. However, these findings are based on large-scale experiments which probably not had the same dependency on environmental temperature as the small scale burning cell experiments. Any difference there might be is therefore more distinct for the small (120 g) burning experiments.

The most important outcome of the experiments with the burning cell is however whether or not the oil is ignitable and it is important that this parameter is comparable for different sizes of experimental burns (small-scale/ large-scale). When oil burns it is the vapour over the oil slick that burns and not the oil itself, hence a sufficient content of light components in the weathered oil is important. A very low content of light components caused by weathering might result in a not ignitable oil slick. For an emulsified oil to be ignited and burn the water has to be removed first by breaking the emulsion. How easily the emulsion breaks depend on the stability of the emulsion, which is reliant on the content of emulsion-stabilizing components in the oil and the energy available in the system (wave action). Thus the ignitability of the oil is dependent on the initial composition of the oil and the weathering conditions (see Fritt-Rasmussen et al (2010) for further details). The point where the oil is not ignitable anymore is used to find the time-window for ISB and this endpoint is estimated as the midpoint between the last ignitable sample and the first not ignitable sample. The time-windows are indicated on Figure 3 and also visualized by a sharp drop in the s-curve (The s-curve is a cumulative normal distribution function fitted to display the main trend in the BE%-Corr. results). The time-window varied from 1 hour to 156 hours.

3.2 Ignitability versus ice conditions

Appearance and amount of ice have a significant impact on the weathering processes and thereby ignitability and time-window for ISB. Figure 3 clearly illustrates the relationship between ice cover and time-window for ISB in the different experiments: the more ice the longer the time-window. These findings correlate well with the findings of Brandvik and Faksness (2009). Troll B easily creates emulsions and therefore demands little energy to form stable emulsions. This is due to a well balanced content of waxes, resins and asphaltenes and a low pour point, i.e. the oil is fluent at low temperatures and easily takes up water. The importance of energy input becomes clear when the ice conditions reach 70 % or more, where a significant longer time-window is seen, 108 hours compared to 27 hours or less. The corresponding water content reported in Brandvik et al. (2010a, 2010c) is also much lower compared to the weathering experiments with less ice. For the 90 % ice cover experiments from Svea, no time-window is indicated since the experiment did not last long enough to find the time-window.

3.3 In situ burning experiments in different scale

Figure 3 compares the results from testing ignitability in the burning cell for samples weathered in SeaLab, Svea and in the Barents Sea. Some differences are seen for the time-windows for the two open water experiments, which are 1 and 11 hours for SeaLab and Svea respectively (Figure 3). The explanation for the variation is found when the weathering conditions reported in Brandvik et al. (2010b, 2010a) are examined. The water uptake is very similar for the two open water experiments. However, for

the laboratory experiments the water content becomes high (70 %) within the first two hours (half life, $T_{1/2}$: 0.35 h), whereas for the experiment performed in Svea the same water content was reached after 20 hours of weathering (half life, $T_{1/2}$: 1.5 h). This difference in water uptake is the explanation for the difference in the time-windows for ISB.

For the two 50 % ice cover experiments there is also a difference in time-windows between the results from SeaLab and Svea, 7 and 27 hours respectively. Brandvik et al. (2010a) reports that the water uptake was much faster in the SeaLab experiment than what was found from the experiment at Svea. This was seen when studying the water uptake rates (half life, $T_{1/2}$: 2.1 h versus 6.5 h). Therefore the weathering conditions were found to be different in SeaLab and Svea. The weathering conditions have great influence on the ignitability of the oil and because of the difference the time-windows for ISB had different lengths. The first not ignitable samples from the SeaLab and Svea weathering experiments did have water content, viscosity and evaporative loss in the same range.

For the 90 % ice cover experiments there is a good agreement between the experiments from SeaLab and Svea. The results from the field experiments in the Barents Sea with 70-90 % ice cover fit well into this picture with a somewhat shorter time-window, since less ice results in more accessible energy to drive the weathering processes.

On the basis of the above discussion it is clear that the field data from Svea and the Barents Sea verifies the data from the SeaLab experiments. The variations in the time-windows for ISB (Figure 3) are explained by variations in the weathering data, where especially the water content determines whether or not the oil is ignitable. Thus the weathering flume in SeaLab and the burning cell could be used to determine ignitability for different oil types.

3.4 Verification by large-scale field experiments

To present the link between the burning cell and a close to real scenario a 2 m³ large-scale burning experiment was performed in the Barents Sea (P1.1), see Figure 2. The large-scale ISB was ignited after 12 hours of weathering, where laboratory experiments had shown that the Troll B crude oil was still ignitable. The thickness of the slick (5-30 mm) was enough to secure a successful burning, and according to Potter and Buist (2008) the minimum thickness required to sustain ISB 2-5 mm for aged unemulsified oil. The burning was very successful with high burning efficiency >90 %. The calculation is based on the weight of the 3M absorption pads before and after the residue was collected and the total amount of oil released (2 m³) and the result of 90 % are conservative.

3.5 Uncertainties in field measurements

During the P1.2 weathering experiment in the Barents Sea the slick scattered and at the end of the experiment it covered a large area of approximately 3000 m times 100 m. An overview is given in Brandvik, et al. (2010b). Thus great variations in the slick are expected to be seen. Figure 4 shows BE%-Corr. as a function of weathering for samples taken different places in the P1.2 experiment. The samples presented in Figure 4 had varying burning effectiveness and this reflects the varying degree of weathering (water content, stability of emulsions and amount of volatile compounds) for samples taken at

the same time but at different places. Especially towards the end of the experiment the differences was enlarged. The time-window for the majority of the oil samples (named A in Figure 4), which represents the bulk phase of the oil, was between 4 and 5 days – interpreted it gives 108 hours of weathering before the majority of the Troll B crude oil could not be ignited anymore. For the samples that contained a lot of slush ice and were taken in the periphery of the slick (B, C and D) the time-window was shorter and ended between 1.5 and 3.5 days. Oil in ice can be found in many different places (see Figure 1) and therefore the degree of weathering and ignitability will be different within an oil slick, especially in ice. This is important knowledge to have when setting up a sampling strategy, to make sure that the samples taken are representative for the major part of the oil spill.

4 Conclusion

A specially designed burning cell was used to test weathered oil samples (120 g size), from SeaLab, Svea and Barents Sea weathering experiments, for ignitability. The burning cell was used with success directly in the field at Svea and on board the research vessel in the Barents Sea, as well as in the laboratory. The burning results (ignitable/not ignitable) from the different weathering experiments were in agreement when the samples had the same weathering degree. The scale (laboratory/field) had no influence on the burning results. The ignitability was dependent on the ice conditions, since the ice strongly influences the weathering. In general, the window of opportunity for ISB is extended with more dense ice conditions and less energy (reduced weathering). For the naphthenic Troll B crude oil, which was used in all the experiments, the importance and effect from ice conditions were clear with 70 % ice or more. The close to real large-scale burning performed in the Barents Sea with 2 m³ oil validated the results from the burning cell. This indicates that the burning cell could also be used as a part of a response operation as a tool to measure if the oil spill (bulk phase) is ignitable and if ISB could be considered as a potential response option.

5 Acknowledgements

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Table 1 *Properties for Troll B crude oil (Sørstrøm-Kristiansen et al., 1995).*

Property	
Density [g/mL]	0.900
Pour Point [°C]	-36
Viscosity [cP], shear rate 100 s ⁻¹ , 13°C	27
Max Water uptake [%]	75
Flash point [°C]	3
Wax content [wt. %]	0.9
Asphaltenes [wt. %]	0.04

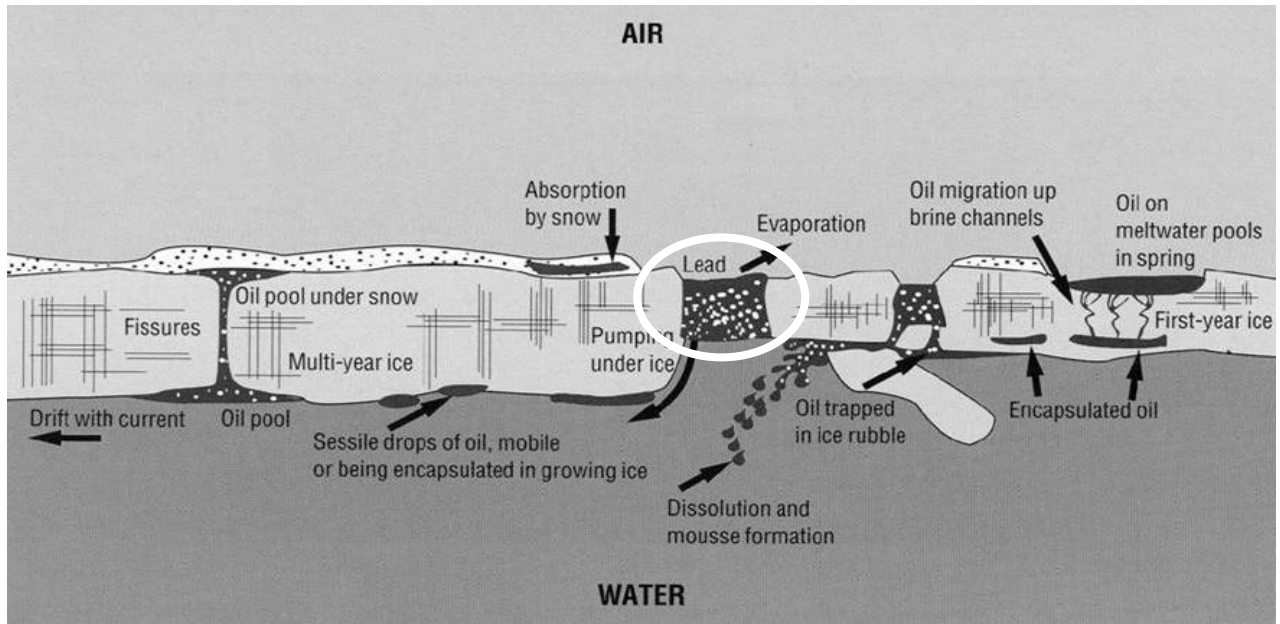


Figure 1 An illustration of the complex distribution of oil in different oil-in-ice scenarios (AMAP, 1998).

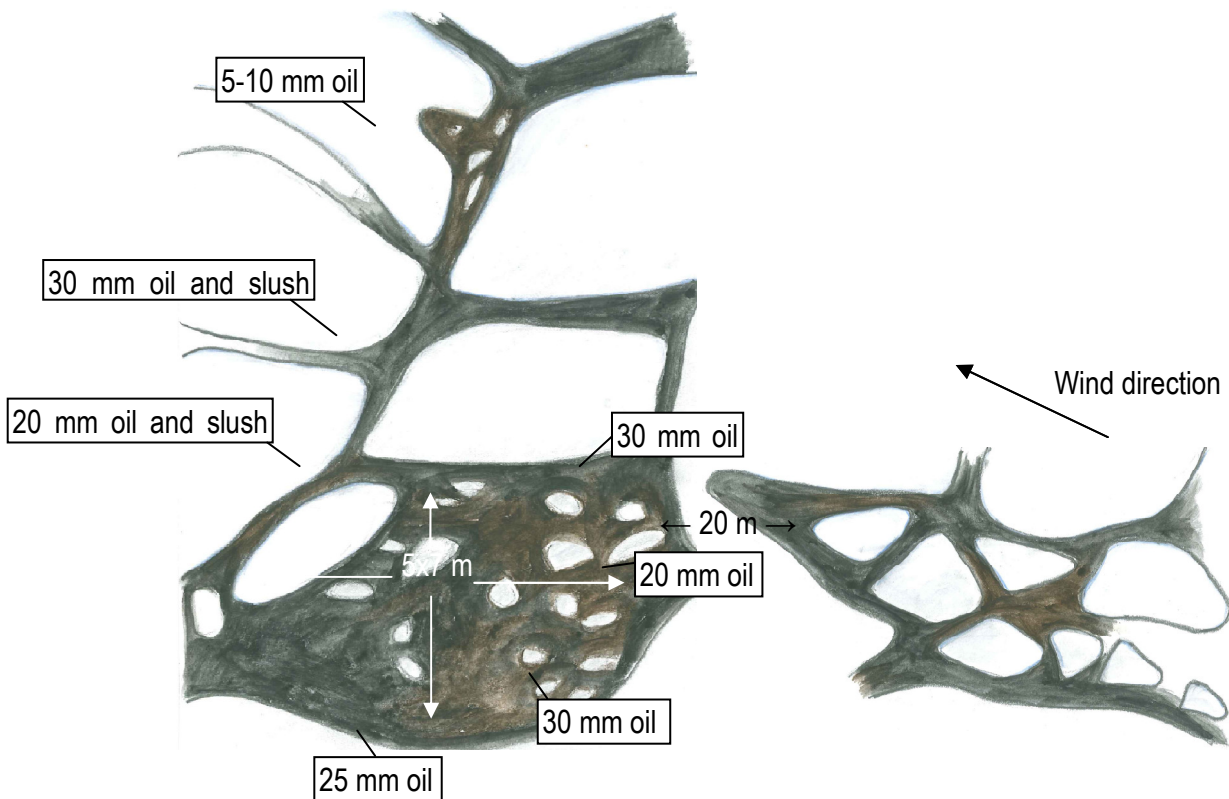


Figure 2 Outline of the 2 m³ Troll B crude oil spill in the Barents Sea (P1.1). The oil spill was separated into two slicks with approximately 20 m between.

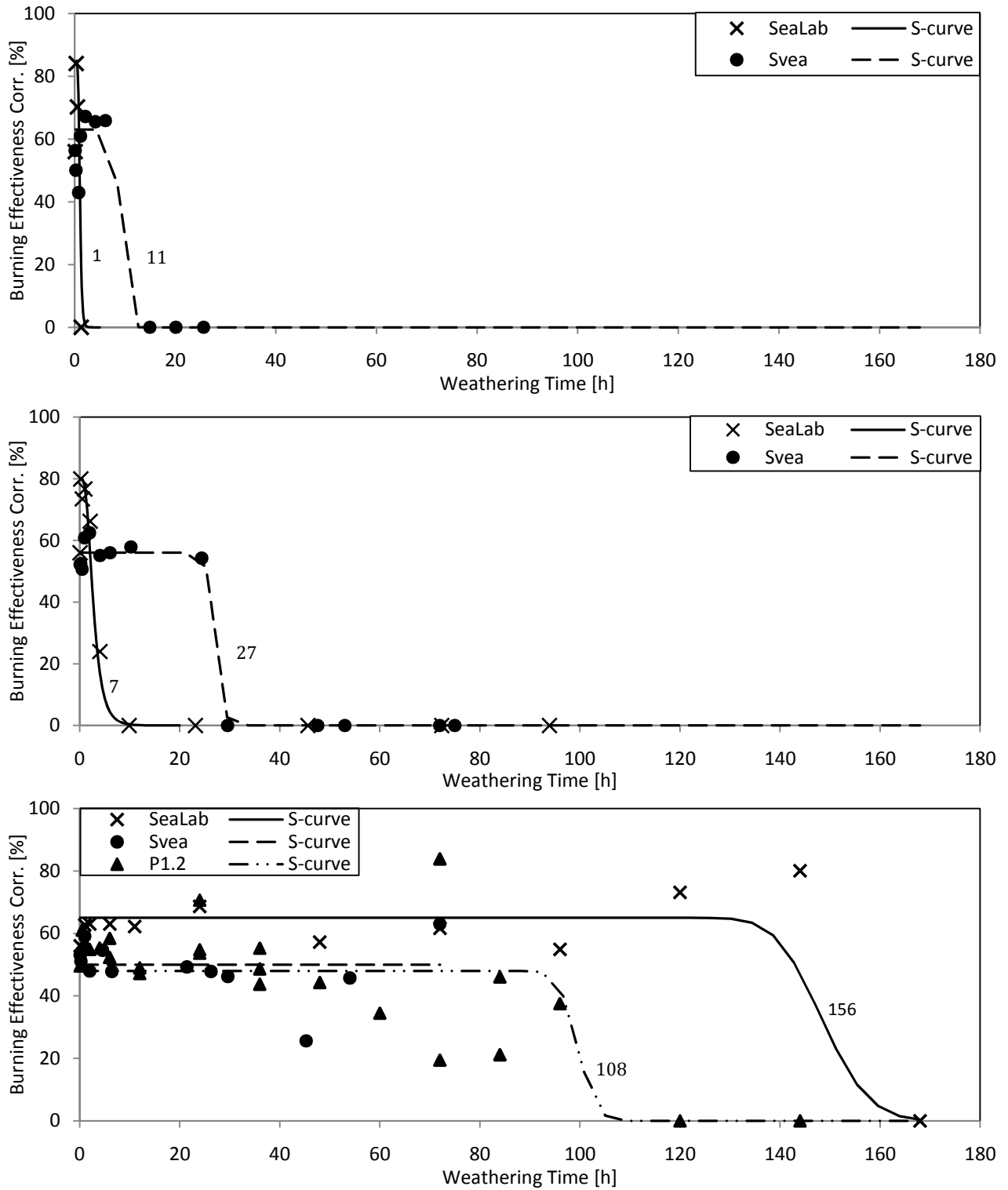


Figure 3 Burning effectiveness as a function of weathering time for experiments from SeaLab, Svea and the Barents Sea (P1.2). The “window of opportunity” for in situ burning is indicated as midpoints (hours). The upper figure is for open water, the middle 50 % ice cover and the lower is for 70-90 % (P1.2) and 90 % ice cover.

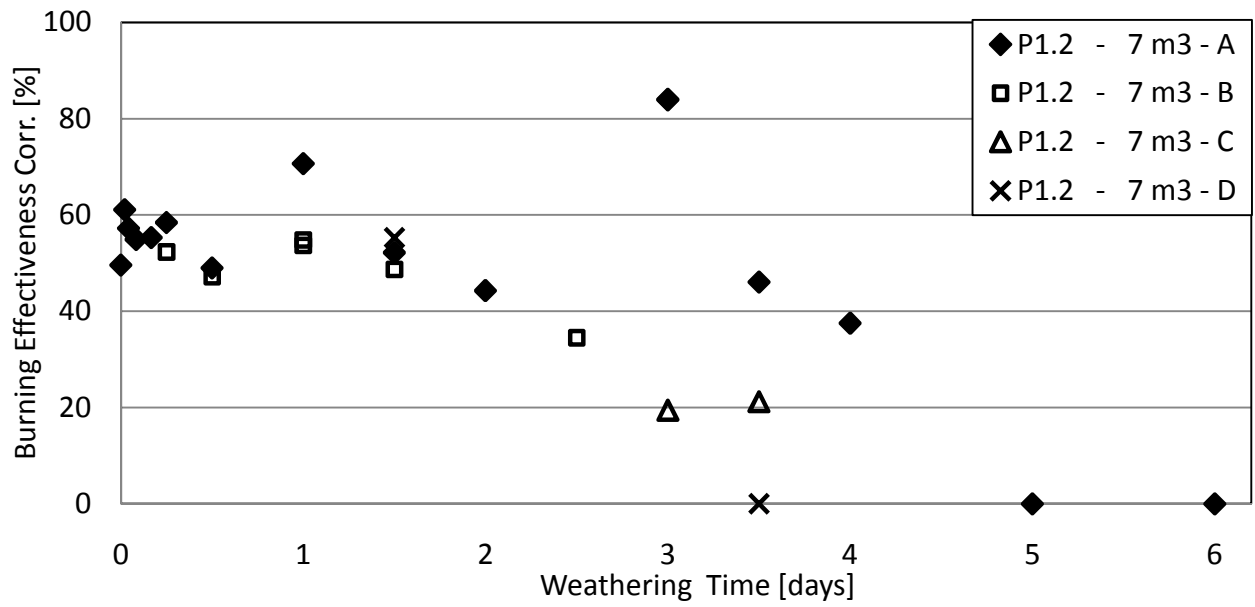


Figure 4 Burning effectiveness as a function of weathering for different samples in the P1.1 slick in the Barents Sea. A refers to the sampling spot in the main slick, B, C and D refer to samplings taken at the periphery of the slick.

Paper [4] Brandvik, P.J., Fritt-Rasmussen, J., Reed, M. & Bodsberg, N.R. 2010. Predicting ignitability for in situ burning of oil spills as a function of oil type and weathering degree. Proceedings of the 33rd AMOP Technical Seminar on Environmental Contamination and Response, Environment Canada.

Predicting Ignitability for In Situ Burning of Oil Spills as a Function of Oil Type and Weathering Degree

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Abstract

For the removal of oil spilled in ice-infested waters, in situ burning (ISB) is one of the response techniques with the highest potential for Arctic conditions, particularly in snow and dense ice. In order to make in situ burning more operational, there is a need to be able to predict the ignitability of oil spills as a function of oil type and weathering degree.

A new laboratory burning cell, which is described in a separate paper, has been used to generate a comprehensive dataset with ignitability/burning effectiveness as a function of oil type, ice conditions and weathering degree. These data are used to develop and calibrate an algorithm for predicting the ignitability of oil spills as a function of weathering. Ignitability is expressed as a function of variables that describe oil type, weathering and emulsion stability (wax/asphaltene content, flash point, water content of emulsion, emulsion viscosity).

The algorithms developed from this experimental data are implemented in SINTEF's Oil Weathering Model and used to predict the ignitability of oil spills as a function of oil type and weathering. This predicted time window for ISB is an important factor to evaluate the operational use of ISB.

1 Introduction

For the removal of an oil spill, in situ burning (ISB) is one of the response techniques with the highest potential for Arctic conditions, particularly in snow and dense ice. Experiments with ISB in recent years have shown removal efficiencies of up to, or in some cases even more than, 90% (Brandvik & Faksness, 2009; Buist, 2003; Dickins et al., 2008; Guenette et al., 1995). The suitability of ISB depends to a large degree on the initial characteristics and weathering state of the oil.

A new laboratory burning cell has been developed and used to measure ignitability as a function of weathering for several different crude oils. The upper limit of ignitability (hours) has been defined as a sharp drop in burning effectiveness at a certain point in the weathering process. The validity of these data has been verified by a comparison with large-scale burning with small-scale laboratory cell and field experiments demonstrated a good correlation, which verifies the validity of ignitability as measured with the laboratory burning cell (Brandvik et al., 2010a).

In order to improve ISB as an operational tool, there is a need to better define the potential and limitations with regard to oil type and weathering degree. Defining ignitability as a function of oil composition, weathering and environmental conditions would offer a significant improvement over the existing rules of thumb.

The objective of this study has been to use the data generated with the new laboratory burning cell (Brandvik et al., 2010a) in order to establish algorithms which describe the ignitability of the bulk phase of an oil spill as a function of oil properties, weathering and environmental conditions. If these algorithms can be implemented into operative weathering models, they could be used to predict the window of opportunity for ISB.

This study has been an integrated part of a Joint Industry Program to develop and advance the knowledge, methods and technology for oil spill response in Arctic and ice-covered waters (Oil-in-Ice JIP). The research program started in 2006, experiments were finalized in 2009 and final scientific reports issued in 2010. The JIP summary report (Sørstrøm et al., 2010) gives an overview of the total program and all the technical reports.

2 Experimental

This section contains a description of the experimental work performed in this study and the oils used.

2.1 Small Scale Laboratory Burning Cell

A new laboratory burning cell has been developed mainly for testing the ignitability of weathered oils. The operation of the cell, as well as the specifications and verification of the validity of the results is described elsewhere (Brandvik et al., 2010a), and only an overall description is given here. The cell contained a “cup” filled with seawater in which the oil sample was burned. The cup was double layered, and cooling water flowed (500 ml/min at 10°C) in to counteract the heat from the burning. Three thermo elements were placed in the cell to measure the temperature in the seawater, oil and flame. In the laboratory, an exhaust hood was placed above the burning cell and a protective shield was closed around the cup. In the field, a thermos was used to heat the hoses with cooling water to prevent them from freezing. The oil sample (approximately 100 ml from the weathering experiments; see Chapters 2.6, 2.7 and 2.8) was transferred onto the seawater surface in the burning cell. The sample container was weighed both before and after the oil was transferred to the burning cell to find the amount of oil/emulsion burned, and the oil was ignited with a small propane burner. The ignition procedure was 10 s of heating with an angle of 30° at one spot. If the oil did not ignite, the heating was repeated one or two more times, with intermediate pauses of 10 s to cool down the oil. If the oil did not burn after the third ignition attempt, the sample was classified as “not ignitable”. The burn residue was collected with an oil absorbent pad after the burning was completed and the pad was weighed before and after the residue oil was absorbed to find the amount of remaining oil. Temperature measurements were carried out during the burning and stored in a data logger.

An important feature of this laboratory burning cell is that it can be very effectively used on samples with an increasing weathering degree from standard basin weathering experiments (see Chapter 2.6). It can

also be easily modified for use as a field instrument in connection to experimental oil releases or real oil spills.

2.2 Calculating Burning Effectiveness

The burning efficiencies reported in this paper are corrected for the water content in the emulsions, which separates during a successful burn. If the water content was included, the calculated burning efficiencies would otherwise vary significantly depending on the degree of weathering. The calculations of burning effectiveness were as follows:

$$\text{Burning Effectiveness (BE\%)} = 100 \cdot \left(1 - \left(\frac{\text{mass of residue}}{\text{mass of initial oil}}\right)\right)$$

$$\text{Burning Effectiveness Corrected (BE\% - Corr.)} = 100 \cdot \left(\frac{1 - (100 - \text{BE\%})}{(100 - \text{WC\%})}\right) \quad (1, 2)$$

Nevertheless, the absolute value of BE% and BE%-Corrected are of less importance since the main use of this laboratory cell is to study ignitability as a function of weathering in order to estimate the time window for in situ burning. The absolute value of BE% is very dependent on the scale of the laboratory or field burn, and large-scale burns will usually produce a higher BE% due to the generation of more heat and higher temperatures.

2.3 Selected Oils for Testing

To ensure that a maximum amount of information could be drawn out of the laboratory and field tests, the oils used in this study were carefully selected. The selection of oils was made from among oils previously characterized at SINTEF with respect to weathering properties. Five oil types with varying composition and weathering properties were selected to represent a broad range of oil types. This will give general information in regard to the weathering behaviour of oil-in-ice and how this influences the time window for using ISB. The physical and chemical properties of the test oils are listed in Table 1, and further details can be found in Brandvik et al., 2010a.

Table 1 Physical and Chemical Properties of Oils used in the Experiments.

SINTEF Id	Oil type	Residue	Density (Kg/m ³)	Evap loss (Vol. %)	Pour point (°C)	Wax (wt.%)	Asphal- tenes (wt. %)
2007-0287	Troll B	Fresh	0.900	0	-36	0.9	0.04
		250°C	0.930	25.5	-27		
2007-0260	Norne	Fresh	0.860	0	21	10.8	0.3
		250°C	0.888	28.4	30		
2006-1061	Kobbe	Fresh	0.797	0	-39	3.4	0.03
		250°C	0.875	53.6	21		
2008-0047	Statfjord	Fresh	0.835	0	-6	4.3	0.1
		250°C	0.896	42.4	21		
2007-1060	Grane	Fresh	0.941	0	-24	3.2	1.4
		250°C	0.968	13	-6		

2.4 Data Describing Weathered Oil Samples

The weathered oil samples from the meso-scale weathering experiments performed at SeaLab (Chapter 2.6), in Svea on Svalbard (Chapter 2.7), and in broken ice in the Barents Sea (Chapter 2.8) were analysed for the properties given in Table 2. These data were used in the regression analysis to predict burning effectiveness and ignitability as a function of weathering time (Chapter 2.9).

Table 2 Physical/Chemical Properties, Units and Methods

Property	Unit	Method
Viscosity of weathered oil	cP (or mPas) at shear rate 10/100 s ⁻¹ at 3-6 °C	Daling et al., 2003.
Water content in emulsion	Volume %	Daling et al., 2003.
Density of water free oil	g/ml at 15.5 °C	ASTM D4052-91
Wax content	Volume %	Bridiè et al., 1980
Asphaltene content	Volume %	IP 143/90
Evaporative loss	Weight %	Daling et al., 2003.
Flash point of water free oil	°C	ASTM D93-90
Emulsion stability	Amount of expelled water after 24 hours	Daling et al., 2003.

2.5 Oil Release Permits

All experimental releases of oil field experiments performed at Svea, Svalbard or in the Barents Sea were performed according to release permits from the Norwegian environmental authorities. All releases and

cleanup operations were documented according to the requirements in the release permits and reported to the authorities.

2.6 Meso Scale Laboratory Testing with SeaLab

In an oil spill situation at sea, the weathering processes will occur simultaneously and affect each other. It is thus of great importance that the oils are weathered under realistic conditions when studying the behaviour of oil spills in ice.

A meso-scale flume basin (Singsaas et al., 1992) located at SINTEF is routinely used to simultaneously study weathering processes under controlled conditions. A new flume with updated instrumentation was built in 2006 at SINTEF's SeaLab. 4.8 m³ of seawater is circulated in the 10-metre-long flume, and the flume is located in a temperature controlled room (0±2°C). This allows for the conducting of weathering experiments under different ice conditions. Two fans placed in a covered wind tunnel allow for control of the wind speed, and the wind is calibrated to simulate an evaporation rate corresponding to a wind speed of 5-10 m/s at the sea surface.

Samples with an increasing weathering degree are collected from the basin experiments and tested for ignitability in the burning cell. The basin experiments also give a comprehensive documentation of the properties of the weathered oil samples (water content, viscosity, emulsion stability, chemical composition, etc.), which is important information for the interpretation of ignitability measurements.

Further details regarding the meso-scale experiments with oil-in-ice producing a significant part of the data used in this study are available in Brandvik et al., 2010a.

2.7 Meso Scale Weathering Svea, Svalbard

Combined weathering and in situ burning (ISB) experiments were performed on a larger scale to confirm the results from the laboratory burning cell. Only two of the oils (Grane/Troll) were weathered on a larger scale (200 L) and the entire batch of weathered oil (300-450 L) formed the basis for the testing of ISB ignitability. The results from these experiments are presented elsewhere (Brandvik et al., 2010a) and confirmed the findings (limits for ignitability) from the small-scale experiments with the laboratory cell.

2.8 Field experiment with Oil in Broken Ice (FEX2009)

The field study was performed east of Svalbard (78° North) and consisted of several experimental oil releases (releasing a total of 20 m³). The objectives of the field experiment were to study oil weathering, test new oil spill contingency equipment (dispersants, mechanical recovery and ISB), test the remote sensing of oil-in-ice and document the spreading of oil and water soluble components in the water. Further details regarding this experiment can be found in technical reports and publications. The summary report from the program offers an overview of the activities, objectives, main findings as well as a list of all reports from the program (Sørstrøm et al., 2010).

The experimental oil releases used for the weathering and ISB studies of free floating oil slicks (7 and 2 m³) were released in an area with 70-90% ice coverage. The oil type used was Troll B crude, which is a naphthenic crude oil with a low pour point. As a result, no solidification of the oil in the ice was either

expected or observed. The oil was released as a “single point release” with the vessel stationary, creating a (initial) circular oil slick. The spreading of the large oil slick after three days of weathering can be seen in Figure 1. The large oil slick was followed for five days and a comprehensive sampling/analysis program was performed (Brandvik et al., 2010b). The results from the testing of the burning effectiveness are included in this paper.



Figure 1 The spreading of the 7 m³ oil spill in ice three days after the oil release (Barents Sea, May 18th, 2009).

2.9 Multivariable Regression Analysis

The regression analysis to build a multivariable regression model to predict “Ignitability” was performed using a commercial software package for multivariate data analysis, Unscrambler® (v. 10). The analysis of the chemical/physical data for the weathered oil samples (X matrix) were more efficient using weighted data (divided by their standard deviation) to give all the variables equal (unit) variance (Var=1). The advantage of using this pre-treatment is that all the variables will be given equal importance in the multivariate analysis independent of their numerical scale (large or small). The focus is on their relevant systematic variation (information) which is extracted by the multivariate calibration. The use of Unscrambler® and multivariate statistics (partial least squares – PLS) to build and validate models for later prediction is well described in the literature and will not be discussed further in this paper. Further details regarding PLS are available from several excellent text books (e.g. Esbensen et al., 1994 or Nortvedt et al., 1996) and in tutorial publications e.g. Kvalheim (1988) or Höskuldsson (1988). A similar application using Unscrambler® and validation of models by crossvalidation is described in Brandvik and Daling, 1998 (regression analysis and PLS models).

3 Results and Discussions

3.1 Measuring Ignitability versus Weathering

The data used in this correlation study are from the combined meso-scale weathering and burning cell experiments. Samples with an increasing degree of weathering are analysed for their physical/chemical properties and tested for ignitability with the burning cell (see Table 1 and Table 2). The measured burning effectiveness for both Statfjord and Grane crude is presented in Figure 2 and Figure 3 below.

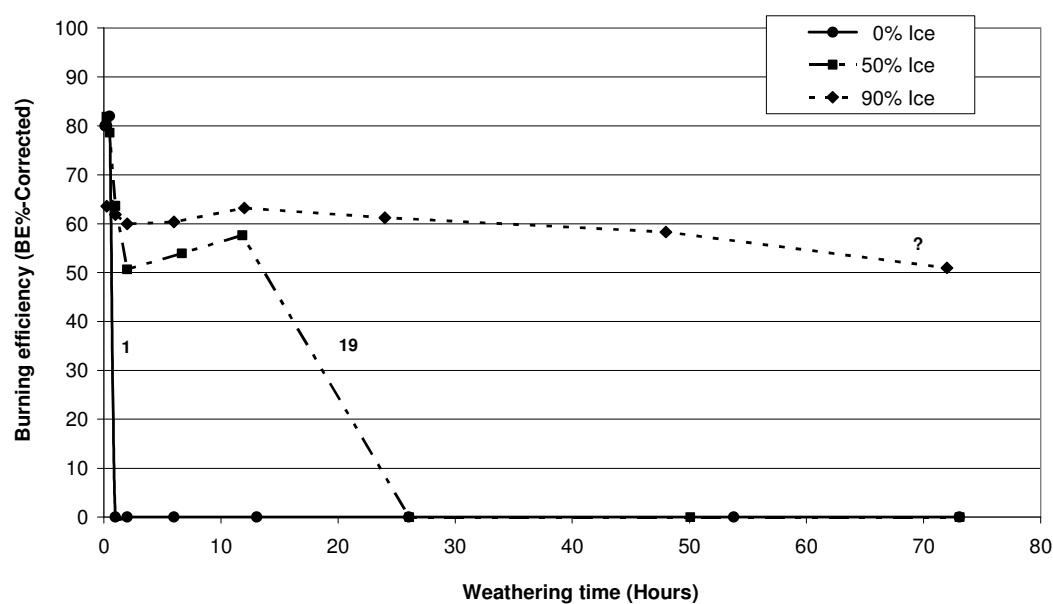


Figure 2 Statfjord crude. Burning effectiveness (BE%-Corrected) measured with the laboratory burning cell. Estimated time window for ignitability is indicated (hours).

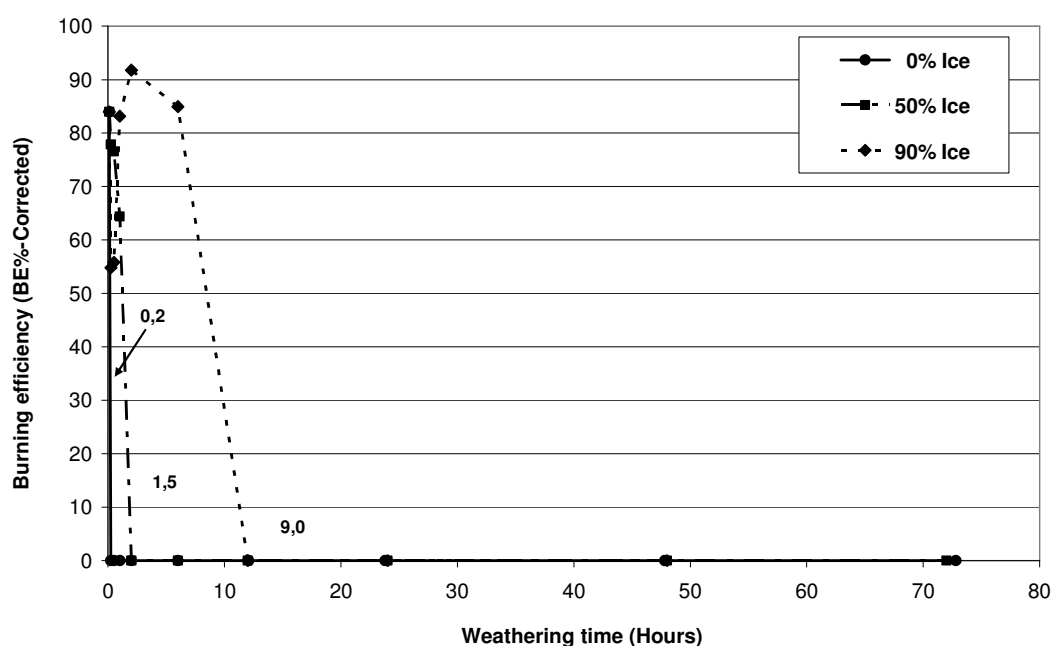


Figure 3 Grane crude. Burning effectiveness (BE%-Corrected) measured with the laboratory burning cell. Estimated time window for ignitability is indicated (hours).

So far, we have presented the experimental data from the laboratory burning cell as burning effectiveness BE%-Corrected. However, since the main objective of this paper is to study and predict “Ignitability”, the burning effectiveness data (BE%-Corrected) have been converted to the Boolean variable “Ignitability”. The weathered oil samples are regarded as “Ignitable” with a BE%-Corrected above 25%. The rest of the samples are assigned to the value “Not Ignitable”. The variable Ignitability (1 or 0) is used as the target or Y variable in the regression analysis described in the next chapter.

Data from 16 series of combined weathering-burning experiments are used in this regression analysis. In these experiments, five oil types were tested with different ice conditions, see Brandvik et al., 2010b for details. In total, this gives 223 corresponding measurements consisting of chemical/physical data that describe the oil sample (Table 2) and Ignitability. Basic descriptive statistics for these data are given in Table 3 below:

Table 3 Basic Descriptive Statistical Parameters for the Experimental Data Matrix, X matrix and y-variable (Ignitability).

	WC%	Visc	Evap%	Wax%	Asph%	FP °C	Stab	Dens	Ignitability
# of obs	223	223	223	223	223	223	223	223	223
# Missing	0	0	0	0	0	0	0	0	0
Min	0	3.7	0	0.9	0.03	-47		0.7970	0
Max	84	35894	46.8	12.5	1.6	159		0.9521	1
Mean	27	3387	15.0	4.1	0.3	70		0.8721	0.71
SDev	27	5611	11.4	3.6	0.5	39		0.14	0.45
Skewness	0.6	3.3	0.7	1.1	2.0	-0.48		-5.8	-0.93

3.2 Establishing Algorithms for Predicting Ignitability

In the initial phase of such a correlation or regression study, we are searching for correlation structures in the X-matrix to describe the properties of the weathered oil samples (X matrix, see Table 1 for details). This multivariate regression (PLS) searches for systematic information (correlation) in the X-matrix which explain the variation (correlates) with the y-variable (Ignitability, see Table 1). In traditional regression analysis, these x-variables need to be independent (no internal correlation), but in this case the multivariate regression can tolerate and even better utilize the internal correlation in the X-matrix. This is important since we know that the correlation or interactions between some of these variables are significant. For example, we know that the viscosity increase when the oils start to pick up water and form stable emulsions. We also know that the content of wax and asphaltenes are important for the rate of the water uptake, total water content and emulsion stability. In order to strengthen the regression model and include these interactions in the model, second-order interaction terms were included, e.g. Viscosity*Water-content or Viscosity², giving a total of 12 variables in the initial X-matrix.

Building a regression model is an iterative process in which an initially high number of x-variables are validated against their contribution to the predictive power of the model. The use of transformations and interaction terms are also important to utilize the relevant information available in the total X-matrix. Log transformations were used to improve the normal distribution of the data if the skewness was large (see Viscosity in Table 3). This will usually increase the contribution (explained variance) from this variable and strengthen the predictive capability of the model. In the process of refining a model, x-variables and interaction terms with little predictive power, i.e. a low contribution to the ability to predict Ignitability (1. 0) was omitted. Cross validation (ref) was used as an alternative to a separate test set in this validation. In this validation, each sample is sequentially kept outside the model and used for validation, producing a validation set of 223. The final refined PLS regression model used six principal components and explained 80% of the variance in the X-matrix and 65% of the y-variable (Ignitability). This gave a correlation between the measured and predicted Ignitability of 0.81, or a 9.8% error in predicting the Ignitability of the 223 samples used in this study (cross validation).

The x-variables contributing to the final refined model and their explained variance are given in Table 4.

Table 4

Weighted Coefficients of the x-variables in the Refined Model.

Variable	Coefficients (weighted)	Relative to mean (x-var)
Water Content %*	0,325*	1,2 %
Ln-Viscosity	0,115	3,8 %
Evaporative loss%	0	0,0 %
Wax content %	0	0,0 %
Asphaltene content	0,136	46,4 %
Flash point	-0,0816	-0,1 %
Density	0	0,0 %
Emulsion stability	0	0,0 %
Water Content * LnVisc*	-0,631*	-0,7 %
Water Content * Wax	-0,091*	-0,1 %
Evap * Flash point	0	0,0 %
Wax * Asph*	-0,188	-13,6 %

Only three coefficients were statistically significant (5% level, marked with an asterix in Table 4), however, further testing showed the including four other variables lowered the predicting error from 16 to 9.8% (cross validation).

The variables omitted during the interactive process of building the model were: Evaporative Loss, Wax Content, Density and Emulsion Stability (0 coefficients in Table 4), which is due to their low contribution to the predictive power of the model. We also wanted to keep the number of variables low for the sake of simplicity and only included variables with a clear significance. Evaporative loss was omitted since it contained no information regarding the content of light components (or flash point) in the residual oil. The wax content alone did not contain a significant amount of information. However, the interaction term between waxes and asphaltenes contained very significant information. Our approach to measuring emulsion stability by settling was not very useful for this correlation study (probably too influenced by wax content). The density was also not very informative for predicting the ignitability of the weathered oils.

3.3 Verifying Algorithms by Laboratory and Field Experiments

In addition to the experiments carried out in the basins at SINTEF, experiments were performed on a larger scale with the Troll crude at a basin cut in the first-year fjord ice in Svea (200 L crude) and as an field experiment in broken ice in the Barents Sea (7 m³ and 2 m³ crude). These experiments were used to validate the predictions from the model.

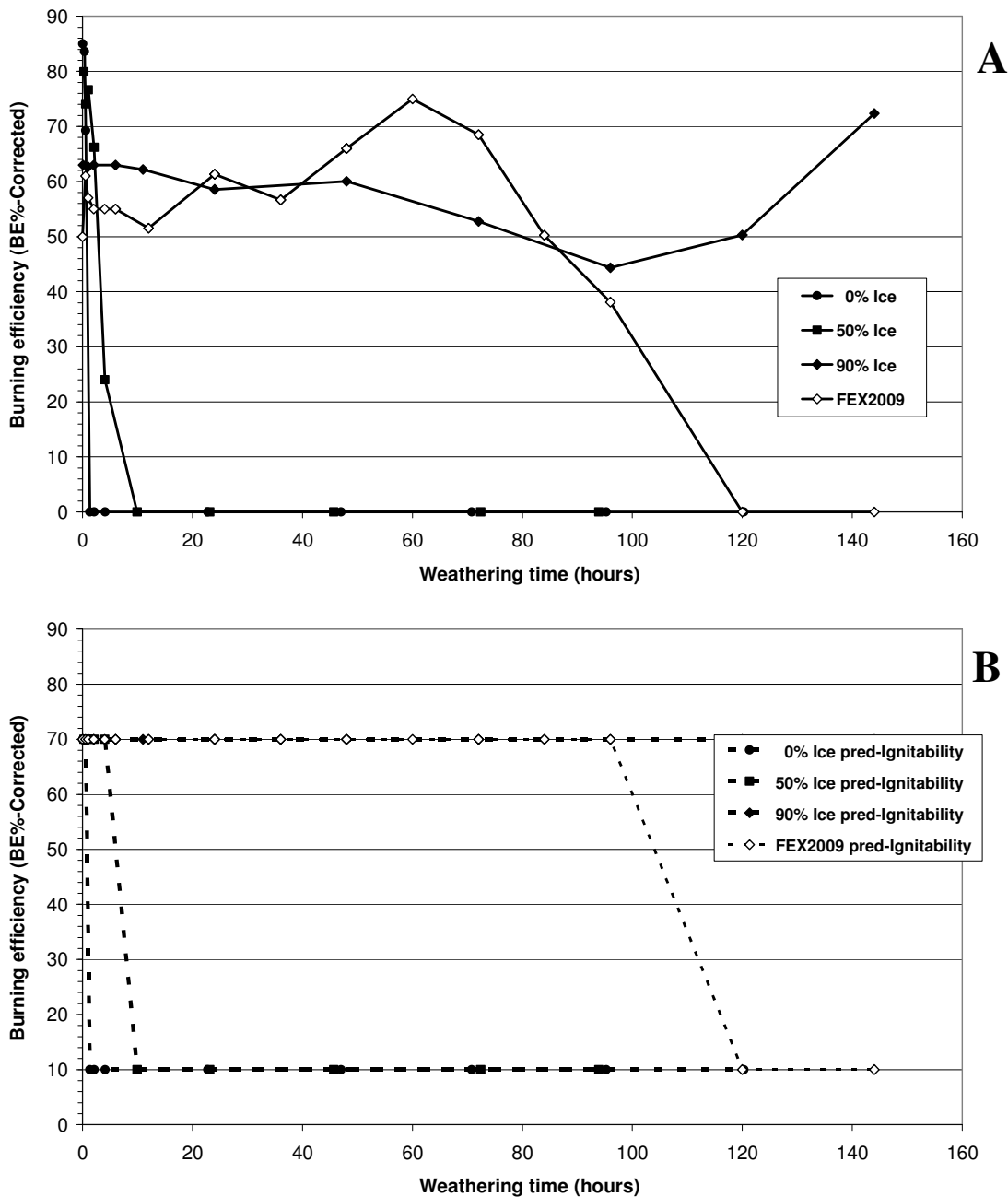


Figure 4 Measured burning effectiveness (BE%-Corrected) and predicted Ignitability as a function of ice coverage and weathering time. Experimental values from the burning cell (A: Solid lines) and predicted values (B: Dotted lines).

Figure 4 presents measured ISB effectiveness (BE%-Corrected) from meso-scale experiments under different ice conditions (0, 50 and 90% ice coverage) with the Troll B crude (circular, squared and diamond shaped symbols) and their corresponding predicted Ignitability (dotted lines). For purposes of illustration, the ignitability here is plotted in this figure as 70% (Ignitable) or 10% (Not Ignitable). In addition, the measured BE%-Corrected and the predicted Ignitability for the large-scale field experiment FEX2009 are given (open diamonds, predicted values with dotted line).

Figure 5 below presents the same data, although all the data are converted to Ignitability. This shows how the ignitability of the weathered oil in the large-scale field experiment drops from “Ignitable” after four days (96 hours) and becomes “Not Ignitable” after five days. Similar measurements of Ignitability from meso-scale experiments with Troll B from SINTEF’s Sealab are also shown in the figure below:

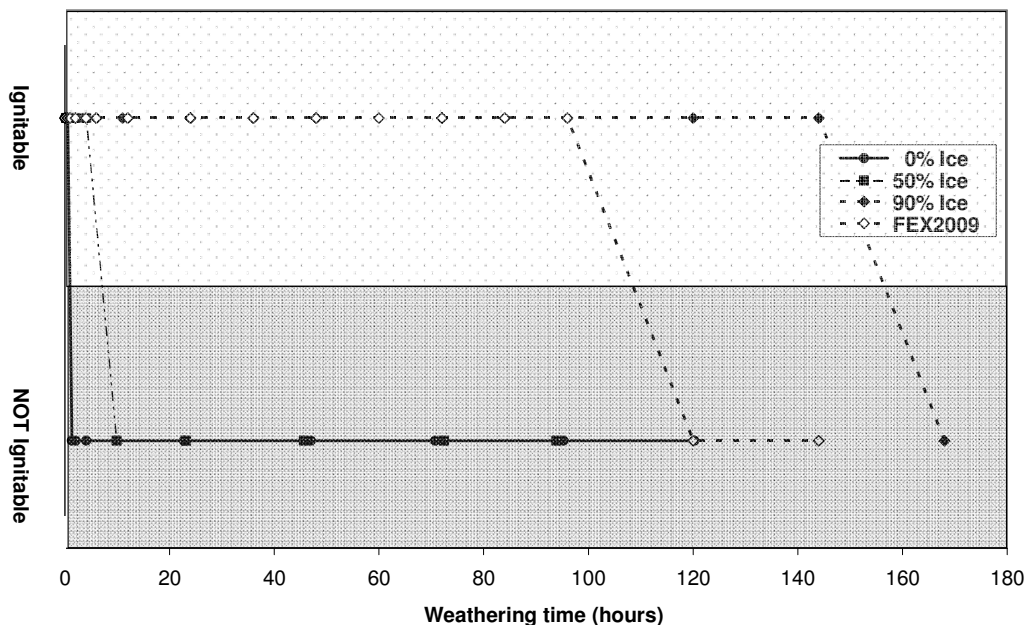


Figure 5 Ignitability measured with the laboratory burning cell as a function of weathering for the experimental oil slick and the meso-scale basin experiments with 0, 50 and 90% ice coverage. The absolute numbers, which are a function of conditions in the cell, are replayed with the classification “Ignitable” or “Not Ignitable”. Predicted values are given in Figure 4.

3.4 Implementing Algorithms into an Operational Oil Weathering Model

The algorithm developed in this multivariate regression study is now implemented as a subroutine in the SINTEF Oil Weathering Model (OWM). This enables users to predict the Ignitability for oil spills in both open water and ice. The information needed to describe the weathering state of oil (Table 2) for the prediction of Ignitability is supplied by other subroutines in the OWM.

An example of the user interface is given in Figure 6, and an example of a possible output from the model is presented as Figure 7.

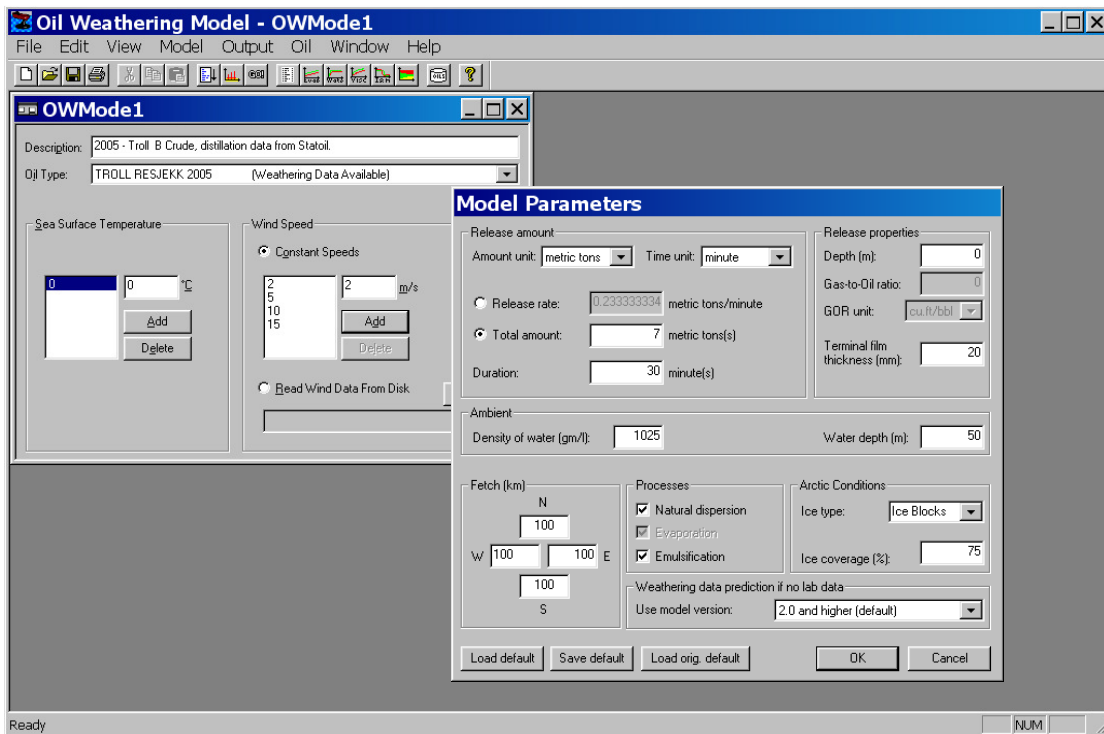


Figure 6 User interface from the SINTEF OWM, where the user selects oil type, environmental conditions and sets the model parameters for the oil release, selects weathering processes and ice conditions (ice coverage for a dynamic broken ice scenario).

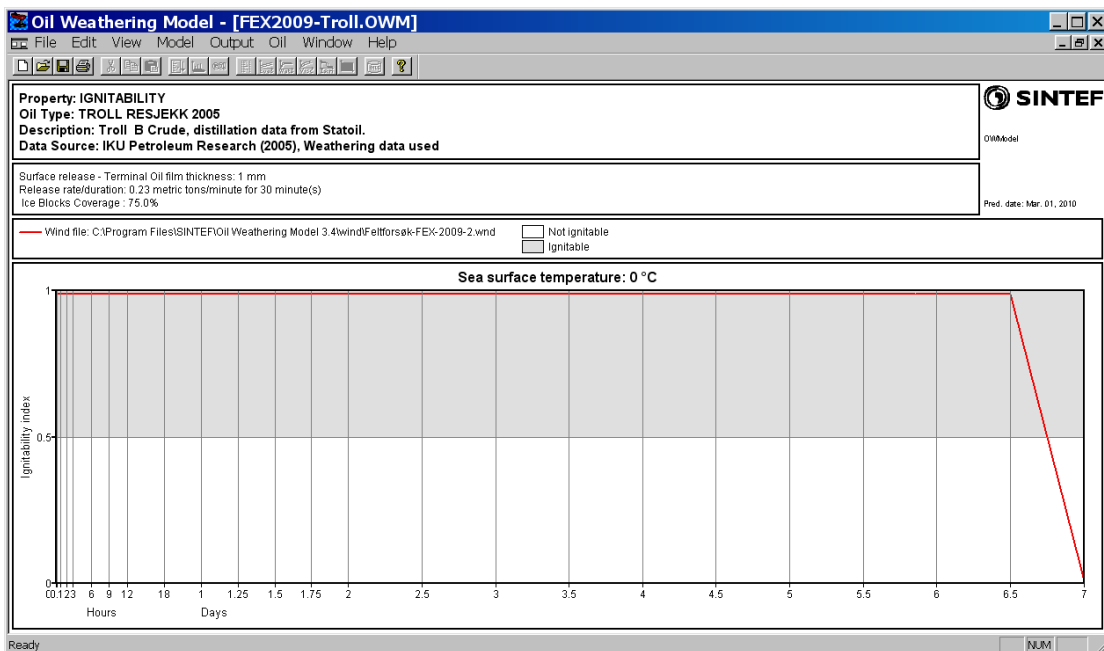


Figure 7 Ignitability as a function of oil type (Troll B), ice condition (broken ice, 80% ice coverage) and weathering time predicted by SINTEF's Oil Weathering Model. This illustrates the operational time window for ISB in this specific scenario, which is similar to FEX2009.

However, this prediction of Ignitability is based on properties for the bulk phase of the oil and certain properties of an igniter (temperature and burning time). Other operational factors have to be evaluated to better estimate the total effectiveness of a possible ISB operation, e.g. oil film thickness and total volume. In addition, both safety and environmental considerations also have to be taken into account. The total reduction on environmental impact using ISB has to be evaluated against all other options in case of an oil spill in ice (Net Environmental Benefit Analysis).

4 Conclusions

An algorithm predicting the Ignitability (1, 0) of the bulk phase of an oil spill as a function of oil properties and weathering has been established. This algorithm is based on the chemical/physical properties (water content, viscosity, content of waxes and asphaltenes, as well as flash point) of the bulk phase of the oil. The algorithm has been comparing predicted values with measured values from both the laboratory and the field. Of the 223 samples used in this study, only 9.8% were wrongly assigned (Ignitable/Not ignitable) by the new predicting algorithm.

This algorithm has been implemented into the SINTEF OWM and enables the model to predict the time window for the operational use of ISB.

However, it is important to remember that the ignitability of the bulk phase of the oil is only one of many factors that need to be evaluated before deciding on the use of ISB.

5 Acknowledgements

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Composition of in situ burn residue as a function of weathering conditions

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Abstract

Troll B crude oil was weathered under Arctic conditions with different ice coverage: open water, 50% ice and 90% ice respectively. Samples (100 mL) were taken continuously and tested for ignitability in a burning cell. From each burning a residue sample was taken and analyzed with Gas Chromatography/Mass Spectrometry. The burning process completely removes the light compounds before C13. No effect from the weathering time is seen in the burn residue composition. The burn residues from experiments with 50 % ice cover or more have a raised background of compounds, especially compounds with a boiling range above 350 °C, compared to the open water experiments. Therefore presence of ice seems to affect the burn residue. The PAHs identified (acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene) all had boiling points below 340 °C, i.e. where a relative removal of all components were observed, hence the burning seems not to generate additional PAHs.

Keywords

Oil spills; In situ burning; Burn residue; PAH; Arctic; Weathering

1 Introduction

In situ burning (ISB) of oil spills is a method with great potential, especially for oil spills in Arctic ice-filled waters. Experiments with ISB in recent years have shown removal efficiencies of up to 90 % or even higher in some cases (Brandvik and Faksness, 2009; Buist, 2003; Buist, et al., 1999; Guenette and Sveum, 1995; Guenette, 1997). The removal effectiveness and time window for ISB depends on the oil

type, the weathering conditions and the thickness of the oil layer. Some concern however, is related to the smoke produced during burning and the burn residue. In general, air emission from burning of oil spills is not a serious health problem about 150 m from the fire site, and very little is detected 500 m from the fire (Mullin and Champ, 2003). Furthermore, results by adding ferrocene as a soot-reducing agent has shown good results (Mitchell, 1991). Regarding the burn residues, focus has been on environmental concerns i.e. whether or not the residue will sink and if it is toxic. The aquatic toxicity from ISB residue was minor and not beyond the effect already seen from the oil spill (Daykin et al., 1994). The same was found by Blenkinsopp (1997) and Gulec and Holdway (1999). Guenette et al. (1995) burned Statfjord-Gullfaks crude oil blend (4:1) and the results showed that the residue was buoyant, with some of the residue below the surface. However, meso-scale burnings with Alaskan North Slope crude oil have shown that residue indeed can sink (Buist et al., 1995). In general, according to Buist et al., (1995), residues from thick oil slicks and heavier oils are more likely to sink due to concentration of high molecular weight compounds as the burning continues. A rule of thumb says that oils with an initial density higher than 0.865 g/cm³ will generate residues that will sink (Walton, 2003). The burn residues however, will only sink after cooling, since the density of the warm oil is less than the density of sea water (Buist et al., 1995). Regarding the composition of the residue Li et al. (1992) found from burnings of 7.6 - 19 m³ crude oils, that the burn residue had the same gas chromatographic (GC) profile as the fresh crude, but there was a notable depletion in the lighter components. Lin et al. (2005) found that the concentration of alkanes heavier than C₂₂ and PAHs with 4 or more rings was increased in the residue, probably caused by lower removal rates. Experiments with burning of Statfjord crude oil showed a decrease in all the PAHs on the list of U.S. Environmental Protection Agency and an increase in the pyrogenic compounds (compounds generated during the burn) due to the reduction in the total amount of oil during burning (Garrett et al., 2000). Garrett et al. (2000) also showed that the alkane C₃₀ was almost constant in the residue; hence the temperature in the residue had not exceeded 450 °C. Trudel et al. (1996) and Buist et al. (1997) studied small-scale burns of oil pools on water with 8 different oils as a function of oil thickness; two of the oils were weathered by aeration. The residue was characterized by fractionating into three ranges dependent on boiling point. The low boiling point fraction (<204 °C) was completely removed and the middle boiling fraction (204-538 °C) was reduced. The higher boiling fraction (>538 °C) was increased. The residue contained some solids and deviated from the fresh oil.

Even though a lot of research has been conducted with regard to the composition and toxicity of the residue, there is still a need to establish knowledge regarding the influence on the weathering degree (time) and weathering conditions (ice) on the residue. The purpose of this paper was to study the residue from a series of burns with Troll B crude oil, weathered at Arctic conditions, for different ice conditions and for different periods of time. The residue was analyzed by Chromatography/Mass Spectrometry (GC/MS) to find the composition of the samples and to clarify the influence of the weathering conditions (ice cover and time) on the burn residue composition.

2 Methods

Troll B crude oil was used for the experiments. Troll B crude oil is from the Troll field in the northern part of the North Sea. Troll B is high in naphthenic components (cyclic and branched saturated hydrocarbons). This is caused by microorganisms that have degraded the linear hydrocarbons in the reservoir, yielding a very low paraffinic content and a relatively high content of naphthenic components. The naphthenic Troll B has a low pour point due to the low content of wax (naphthenic character) and a balanced blend of emulsion stabilising components (waxes, resins and asphalthenes), thus forming stable water-in-oil emulsions (Brandvik et al., 2010a). The properties for Troll B can be seen in Table 1.

2.1 Weathering and burning of oil samples

Three weathering experiments were performed with open water, 50% ice cover and 90 % ice cover respectively, and for each experiment 200 L of Troll B crude oil were used. The oil was weathered in a flume cut in the fjord ice and filled with sea water. Waves, current, air temperature and ice cover were controlled. Samples (approximately 100 mL) for burning were taken continuously throughout the 72 hours each weathering experiment lasted. The samples consisted of oil and, as the weathering processes occurred, more and more water. More details about the weathering experiments can be found in (Brandvik et al., 2010b and Fritt-Rasmussen et al., 2010). The samples were tested for ignitability immediately after sampling in a specially designed burning cell, which can be seen in Figure 1. The burning cell setup is described in detail in (Brandvik et al., 2010c), thus only a short description is given here. The cell consisted of a doubled layered cup, wherein cooling water flowed and three thermo elements measured the temperature in the seawater in the cell, in the oil and in the flame. The hoses with cooling water were heated in a thermos to prevent them from freezing. The ignition procedure was 10 s of heating with a propane torch; if the oil did not ignite the procedure was repeated after a break of 10 s. If the oil did not burn after the third 10 s of heating the sample was classified as “not ignitable”. A small sample (1.5 mL) was taken from each of the residues, regardless of burning and stored at 5 °C for the majority of the transport time until GC/MS analysis.

2.2 Gas Chromatography/Mass Spectrometry analysis

The oil samples were dissolved in Dichloromethane (DCM) to a concentration of 10 mg/mL. Gas Chromatography/Mass Spectrometry (GC/MS) analysis was performed using a Hewlett-Packard combined Model 5890 gas chromatograph – Model 5972 mass selective detector. The GC column was a 30 m RESTEC Rtx-5sil MS (0.25 i.d., film thickness 0.25 µm). The temperature program applied to the GC oven was: 40 °C (10) – 5 °C/min – 320 °C (10). All the GC-MS results are presented as total ion chromatograms (TIC).

2.3 Water content analysis

The water content in the burn residue was measured by Karl Fischer titration with a 756 KF Coulometer Metrohm, hydranal coulomat AG-H.

3 Results and Discussion

3.1 Burning results

For the open water experiment the oil was ignitable until 20 hours of weathering, thereafter the oil was not ignitable within the standard ignition procedure (see Table 2). When the oil becomes not ignitable it is a result of weathering processes and oil composition. The weathering processes result in less insulation, due to the water in oil emulsion, and a reduced amount of flammable components in the oil caused by evaporation. Furthermore, the emulsion has to either break or boil out before the actual oil can burn (Guenette et al., 1994) and the stability of the emulsion is to a great extent determined by the composition of the oil (content of emulsion stabilizing compounds). The weathering processes are slowed down with less energy in the system (dense ice cover) (Fritt-Rasmussen et al., 2010), thus the number of ignitable samples was higher for the 50 % ice cover experiment, with the last ignitable sample after 30 hours of weathering. The ISB time-window was further expanded for the 90 % ice cover experiment, where all the samples burned during the 72 hours the experiments lasted, except one, which could not be ignited due to very windy conditions. More details regarding the ISB results can be found in Brandvik et al. (2010a) and Fritt-Rasmussen et al. (2010).

The water content in the burn residue was very low (between 0.05 and 0.6 %) and no correlation with the weathering time (i.e. emulsification) can be found. The results reflect that, for emulsions to burn, the water has to be separated from the oil, either by boiling out or by breaking, thus no water is expected to be found in the residue. It was observed that the emulsion in the not ignitable samples was broken and small droplets were observed in the bottom of the GC-vials. This is expected to be a result of gravitational separation that had time to occur, because of the long time (approximately 2 month) before the samples were analyzed in the laboratory.

3.2 Gas Chromatography/Mass Spectrometry results

Samples of the burn residues, non-ignitable oil samples and a fresh Troll B crude oil were all analyzed by GC/MS (Figure 2). The lightest part of the fresh Troll B crude oil sample had as expected a large content of molecules containing a cyclopentane or cyclohexane ring, i.e. naphthenes. The Troll B crude oil sample also contained a large portion of branched alkanes. The samples that were ignited and burned had complete removal of lighter components and no peaks prior to C13 are observed (corresponding to the first 25 minutes of the TIC). Due to the fact that these lower boiling point components had been removed the samples had a relatively large content of components with higher boiling points (after C21 i.e. 45 minutes) compared to the fresh Troll B crude oil (Figure 2). The samples, which could not be ignited, were also depleted in lighter components, especially of the light naphthenes (methylated cyclopentanes and -hexanes) which are very predominant in the fresh oil, but the removal was as expected not complete as seen for the samples that burned (Figure 2). This depletion was a result of the weathering processes, primarily evaporation. Because Troll B crude oil had already been degraded in the reservoir the difference between the TIC for the fresh oil and the weathered/burned samples would have been more distinct if an oil with a higher content of light components was used.

3.2.1 The effect of weathering time on the burn residue composition

Five 90 % ice cover scenario GC/MS TIC are presented in Figure 3. The samples 90-t0.5, 90-t30 and 90-t72 did all burn; hence the complete removal of light boiling point compounds up till 25 minutes is clearly seen. However, the 90-t45 and 90-t54 was extinguished by the wind (15 m/s) at different stages during the burning, thus more of the light boiling point compounds are seen here (Figure 3). An important notion is the similarity between all the samples which burned. Minor differences are found but no trend resulting from the weathering time was observed for the samples that burned. From this it is evident that the weathering time has a minor influence on the residue composition and the determining factor for the residue is whether or not the oil ignited and burned.

The simulated distillation type column used in the GC/MS analysis results in a linear relationship between retention time and the boiling point of the detected compounds. Table 3 lists the temperatures (boiling points) found by GC/MS and the temperatures in the oil measured during the burn experiments. These temperatures are related to the compounds detected in the GC/MS TIC. "No distinct peaks" means that no peaks are seen with a height more than 3 times the noise level. "Reduction" is defined as peaks with an area reduced to below 80% (area/area) of the fresh Troll oil. For boiling points above 216 °C (C12) only areas of normal alkanes have been calculated. To perform the calculations the TICs have been scaled by assuming conservation of hexacosane (C26). Hexacosane is the highest boiling component, which showed a distinct peak for all samples. Garrett et al. (2000) however, assumed conservation of 17 α -(H),21 β -(H)-hopane and found an almost complete conservation of triacontane (C30), but a reduction of approximately 20 % for hexacosane. The two experiments were performed at different conditions (arctic vs. temperate), two different oil types (Troll B (naphthenic) vs. Statfjord (light paraffinic)) and at different scales (100 mL vs. 1.25 L), where larger burns result in higher burning temperatures (Brandvik et al., 2010c). Due to these different conditions, the reduction of hexacosane will probably be smaller in our experiments and the complete conservation assumption seems realistic. From the TICs it is seen that the compounds in the boiling range up to 230 °C are removed from all burn residues. A reduction is seen for components with boiling points from 230 °C – 350 °C for the samples from the no ice cover experiments and from 230 °C – 370 °C for the samples produced with ice covers of 50 and 90 %.

The results correspond well with the findings in the literature. Buist et al. (1997) reports that the fraction of compounds with boiling below 205 °C is completely removed when burning crude oils and that the majority of the residue were compounds with boiling points higher than 538 °C. Buist et al. (1997) analyzed the samples by splitting them into 3 fractions by distillation, i.e. temperature ranges were not sample dependent but defined by their method. The experiments were performed at room temperature and with different crude oils and few artificially weathered (evaporation) samples. Garrett et al. (2000) found an almost complete conservation of C30 alkane and conclude that the residue could not have reached temperatures above its boiling point (450 °C). One very interesting fact is the similarity between all the temperature intervals between the burn series. For all the three different experiments (open, 50 % ice and 90 % ice) no distinct peaks are observed prior to tridecane (C13). After this point the relative profile of all the burned samples are remarkably similar and the weathering history is erased when the oil is ignited as also found by the visual examination of the TIC (Figure 3).

3.2.2 The effect of different ice covers on the burn residue composition

An important parameter investigated during the field study was the effect of the ice coverage on the weathering and therein the ignitability of the oil. This is discussed in detail in Brandvik, et al. (2010a) and Fritt-Rasmussen et al. (2010); in our paper we only focus on the effect seen on the residue composition. The raised background of the TICs is caused by the multi-component content of the residue samples. The samples contain a wide array of components with similar boiling points, but in too low concentrations to give a separate peak. The backgrounds are different between the three series of ice cover but not within the series. Samples from the open water experiments seemed to be depleted of the heavier components (boiling range above 350 °C) compared to samples proceeded with ice cover of 50 % or 90 % (Figure 3 and Figure 4). The composition of the residues varies however little, between 50 % ice and 90 % ice cover experiment. Since the major difference is seen between no ice and 50 % - 90 % ice, the presence of ice is thus found to affect the composition of the residue and result in a residue with a higher content of heavier hydrocarbons.

3.3 PAHs and aromatic components in burn residue

PAHs are of great concern due to their carcinogenic effects. The Agency for Toxic Substances and Disease Registry (ATSDR), U.S. Department of Health and Human Services has included 17 PAHs in their PAH profile (acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, benzo[g,h,i]perylene, chrysene, benz[a]anthracene, benzo[a]pyrene, benzo[e]pyrene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-c,d]pyrene, dibenz[a,h]anthracene). Of the PAHs only components with a boiling point below 340°C were identified by our method i.e. acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene were found. Since none of the identified PAHs has a boiling point above 350 °C, they were within the boiling range where a relative removal of all the compounds identified was observed for all residue samples (see Table 3). The burning procedure does not seem to generate additional PAHs in the burn residue; this is also what Garrett et al. (2000) find. Based on the temperatures (Table 3), which were reached during the burn procedure, this is reasonable. PAHs would be formed by destruction of complex molecules containing aromatic cores (asphaltenes and resins) or by naphthenes being dehydrogenated. It is generally accepted that these reactions will only take place at temperatures above 350 °C (Speight, 1991). But since the investigated PAHs have a boiling point below 350 °C there is a risk that any formation will be erased by subsequence burning.

Additionally the aromatic components toluene, ethylbenzene, p-xylene, 1, 2, 3, 4-tetrahydronaphthalene and naphthalene were included in the study due to their toxic nature. All the investigated 1 and 2 ringed aromatics were found in the fresh Troll oil. These components were completely removed from all the burn residues.

4 Conclusion

The analysis on GC/MS of the burn residue showed that all the light compounds with a boiling point up to 230 °C were removed during the burning and that the samples that could not be ignited had a less

significant depletion of compounds up to 150 °C. The PAHs identified (acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene) were only those with a boiling point below 340 °C. The burning procedure does not seem to generate more of the identified PAHs in the burn residue. The water content in all the samples regardless of ignitability was very low. The results show that when the oil is ignited, the prior weathering time is almost completely erased in the composition of the burn residue. However, it seems as if the ice content affects the composition of the residue. Less removal of hydrocarbons are seen for 50 % ice or more compared to the scenario without ice, judged by the composition of the GC/MS TIC for the residues.

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Table 1 Properties of Troll B crude oil from Strøm-Kristiansen et al. (1995). Viscosity from Faksness (2008).

	Density [g/mL]	Pour point [°C]	Viscosity [cP]	Max water uptake [%]	Wax [%]	Asphaltene [%]
Troll B	0.900	-36	299 at 2 °C	75	0.9	0.04

Table 2 Overview of weathering time in the flume, Ignitability of the samples and water content in the residue.

Sample ID	Weathering Time [h]	Ignitable	Sample ID	Weathering Time [h]	Ignitable	Sample ID	Weathering Time [h]	Ignitable
Open water			50 % ice cover			90 % ice cover		
0-t0.8	0.8	YES	50-t0.1	0.1	YES	90-t0.1	0.1	YES
0-t1	1	YES	50-t0.3	0.3	YES	90-t0.3	0.3	YES
0-t2	2	YES	50-t0.5	0.5	YES	90-t0.5	0.5	YES
0-t4	4	YES	50-t1	1	YES	90-t1	1	YES
0-t6	6	YES	50-t2	2	YES	90-t2	2	YES
0-t20	20	YES*	50-t4	4	YES	90-t5	5	YES
0-t26	26	NO	50-t6	6	YES	90-t6	6	YES
0-t67	67	YES*	50-t10	10	YES	90-t21	21	YES
			50-t24	24	YES	90-t26	26	YES
			50-t30	30	YES	90-t30	30	YES
			50-t48	48	NO	90-t45	45	YES**
			50-t53	53	NO	90-t54	54	NO*
			50-t72	72	YES*	90-t72	72	YES
			50-t75	75	NO			

YES*) ignition occurred due to extra heat supply, YES**) started to burn, but extinguished due to wind, NO*) no ignition due to very windy conditions

Table 3 Boiling range found by GC/MS and maximum temperatures measured during experiments.

Data series	Burn residue 0 % ice coverage	Burn residue 50 % ice coverage	Burn residue 90 % ice coverage	No ignition
No distinct peaks	90-230 °C	90-230 °C	90-230 °C	-
Reduction	230-350 °C	230-370 °C	230-370 °C	180 °C
Max oil temperature measured during burning	140 °C	225 °C	225 °C	-



Figure 1 Burning cell unit in the field, thermos to warm cooling water and temperature logger to the left.

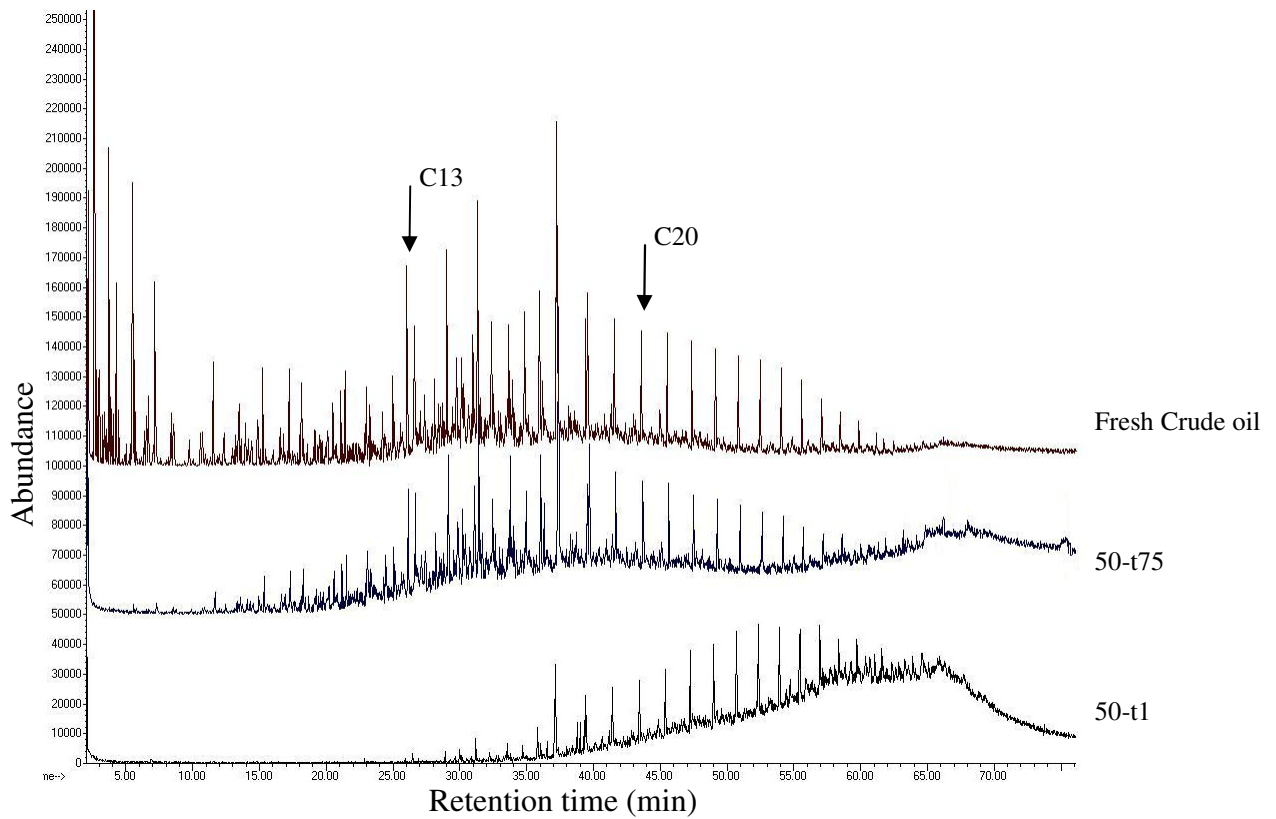


Figure 2 TIC of a fresh Troll B crude oil, a weathered oil sample that could not burn (50-t75) and a residue from burning (50-t1).

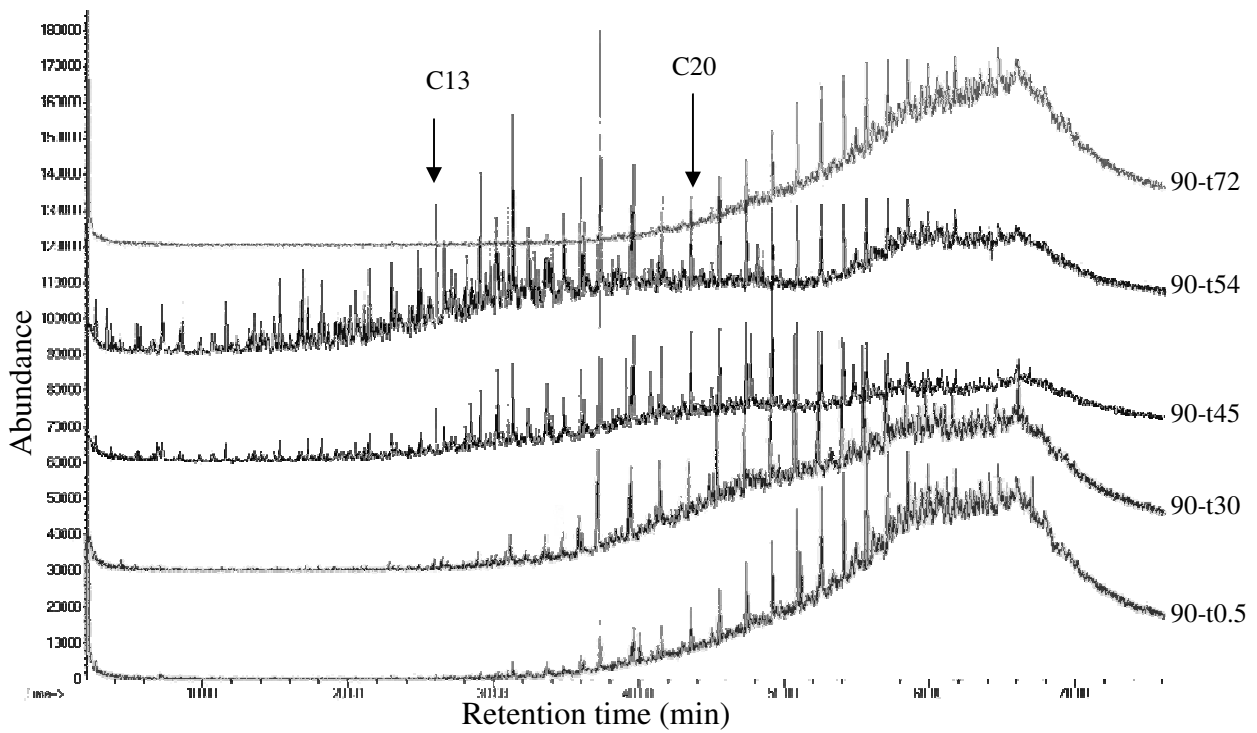


Figure 3 TIC of ISB-residue for samples from the 90 % ice coverage series.

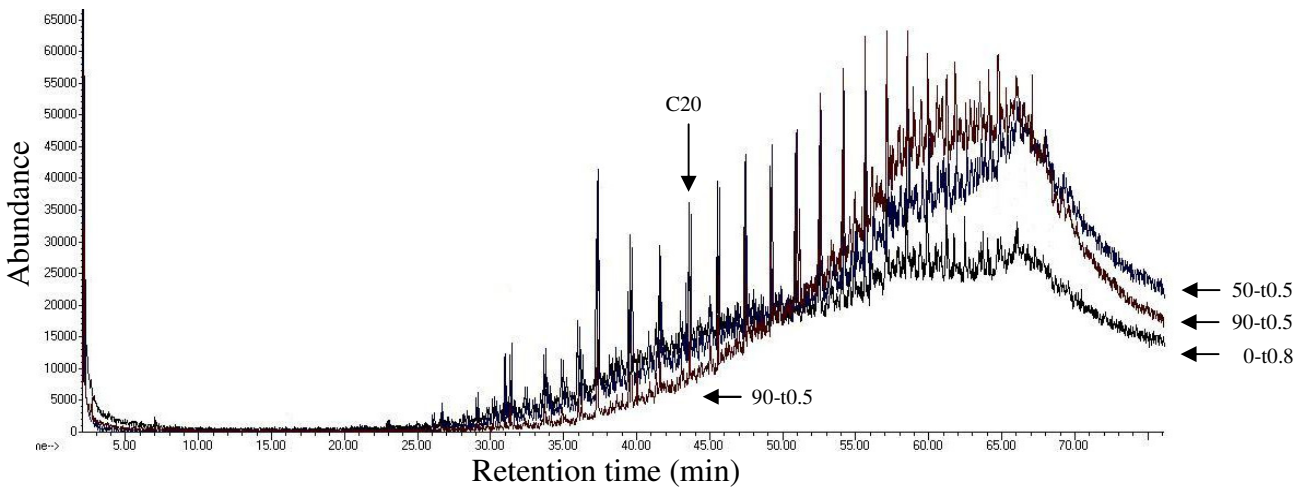


Figure 4 TIC of burn residue for samples with approximately 0.5 hour weathering time but different weathering conditions (open water, 50% ice and 90 % ice cover).

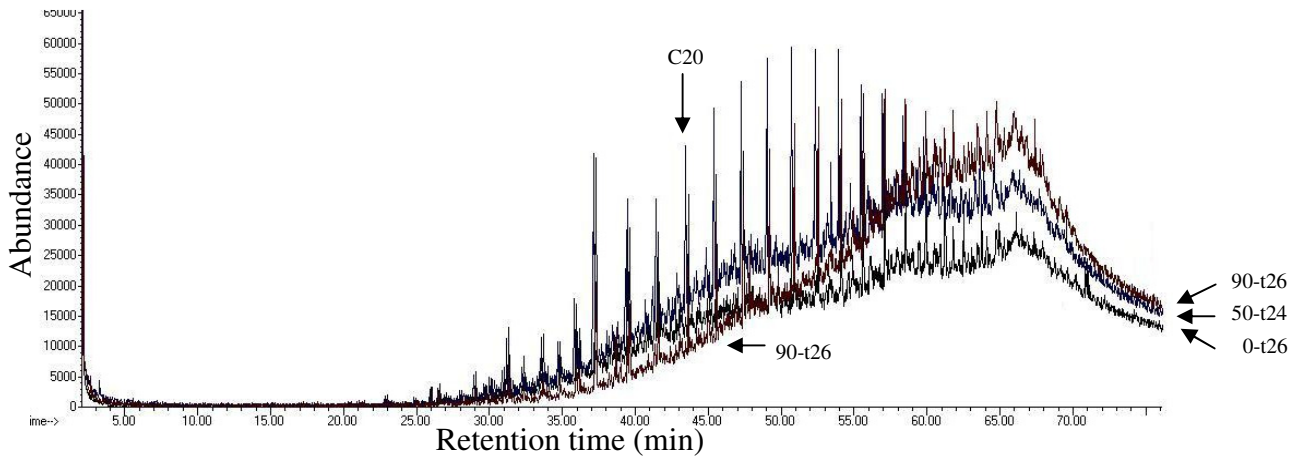


Figure 5 TIC of burn residue for samples with approximately 25 hour weathering time but different weathering conditions (open water, 50% ice and 90 % ice cover).

Oil spills in ice filled and Arctic waters poses other challenge for oil spill response compared to open and temperate waters. In situ burning has been proven to be an effective oil spill response method for oil spills in ice filled waters. This thesis present results from laboratory and field experiments where the ignitability of oil spill as a function of oil type and weathering conditions (time/ice) were tested. The results show that the composition of the oil and the ice cover are important for the in situ burning time-window.

The results were used to develop an algorithm that was implemented in a model, so it is possible to predict the operational time-window for in-situ burning.

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