









REPORT

Oil in Ice - JIP

SINTEF Materials and Chemistry

Marine Environmental Technology



Preface

SINTEF has in cooperation with SL Ross Environmental Research Ltd and DF Dickins Associates LLC on behalf of the oil companies AGIP KCO, Chevron, ConocoPhillips, Shell, Statoil and Total initiated an extensive R&D program; *Joint industry program on oil spill contingency for Arctic and ice covered waters*. This program was a 3-year program initiated in September 2006 and finalized in December 2009.

The objectives of the program were;

- To improve our ability to protect the Arctic environment against oil spills.
- To provide improved basis for oil spill related decision-making:
- To advance the state-of-the-art in Arctic oil spill response.

The program consisted of the following projects:

- P 1: Fate and Behaviour of Oil Spills in Ice
- P 2: In Situ Burning of Oil Spills in Ice
- P 3: Mechanical Recovery of Oil Spills in Ice
- P 4: Use of Dispersants on Oil Spills in Ice
- P 5: Remote Sensing of Oil Spills in Ice
- P 6: Oil Spill Response Guide
- P 7: Program Administration
- P 8: Field Experiments, Large-Scale Field Experiments in the Barents Sea
- P 9: Oil Distribution and Bioavailability

The program has received additional financial support from the Norwegian Research Council related to technology development (ending December 2010) and financial in kind support from a number of cooperating partners that are presented below. This report presents results from one of the activities under this program.

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ConocoPhillips







R&D Partners





Cooperating Partners









oastal Response Research Center at the University of New Hampshire

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ABSTRACT		Zynny					
A large-scale field Fresh crude oil (7 and spreading in i	d experiment took p 7,000 liters) was rel ce and surface water	lace in the marginal ice zone in the Barents Sea in May 2009 (FEX2009). eased uncontained between the ice floes in order to study oil weathering					
GPS trackers, large-volume water samplers (KISPs), in situ oil-in-water monitoring systems and passive absorption devices (SPMDs) were all installed underneath ice floes in and around the oil slick to enable a detailed monitoring of oil-in-water dynamics and ice interactions throughout the six-day experiment. Meteorological and oceanographic data were recorded for the monitoring of wind speed and direction, air temperature, currents and ice floe movement.							
Sampling was performed from three stations in the oil slick area, and both KISPs and SPMDs have proven effective in detecting trace levels of organic contaminants from the water column. The monitoring shows low, but detectable concentrations in the range between 0.1 (background) to 1.5 ppb dissolved hydrocarbons and 4 (background) to 32 ppb total hydrocarbons from the KISPs, as well as between 0.6 (background) to 4 ppb dissolved hydrocarbons estimated from the SPMDs. The predicted acute toxicity, expressed as a hazard index, for the collected samples was well below a value of 1, indicating that the acute toxicity was low.							
Altogether, the da within biological in high ice covera	ata collected during effects, oil-in-water ge.	the field experiment constitutes a dataset for various follow-up analyses interactions and how the presence of ice affects the drift and spread of oil					

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TABLE OF CONTENTS

1	Intro	oductio	n	4
2	Exne	eriment	ลไ	
-	2.1	Instrur	nentation for sampling of MetOcean data	5
	2.1	2.1.1	AADI RDCP600 (Recording Doppler Current Profiler)	6
		2.1.2	AADI Seaguard recording current meter	6
		2.1.2	OCEANOR Seawatch Mini II Buov	
		2.1.3	Gyro Motion Sensor SMC S-108	7
		215	GPS systems	9
	2.2	Sampl	ing equipment for the monitoring of oil	9
		2.2.1	Large-volume water sampler	9
		2.2.2	Passive sampler (SMPD)	
		2.2.3	Online oil-in-water monitoring	
	2.3	Sampl	ing strategy	
	2.4	Collec	tion of samples	14
		2.4.1	Background samples	14
		2.4.2	Large-volume sampler	14
		2.4.3	Passive samplers	15
		2.4.4	Sampling during the dispersant experiment	16
		2.4.5	Online oil-in-water measurements (UVF)	16
	2.5	Prepar	ation of water accommodated fraction (WAF)	17
	2.6	Sample	e preparation	17
		2.6.1	Extraction of water samples	17
		2.6.2	Extraction of filter samples (from KISP)	
		2.6.3	Extraction of XAD resin (from KISP)	
		2.6.4	Extraction of SPMD	
	2.7	Chemi	cal analyses	
		2.7.1	Analysis of total petroleum hydrocarbons (TPH)	19
		2.7.2	Analysis of semi-volatile organic compounds (SVOC)	19
		2.7.3	Analysis of volatile organic hydrocarbons (VOC)	19
	2.8	Metho	ds for determining bioavailability	19
		2.8.1	Calculation of SVOC concentration in seawater from SPMD data	19
		2.8.2	Estimate hazard of dissolved oil in the water column	20
3	Resu	lts and	discussion	22
0	3 1	MetOc	rean time series	
	5.1	311	Meteorological data	
		312	Currents and ice drift	22
		313	Wayes and ice floe movements	32
	32	Chemi	cal monitoring	34
	2.2	3 2 1	Main oil release (7 m^3)	34
		322	Dispersant oil release	38
	3.3	Estima	ting acute toxicity using the hazard index	
4	Con	clusions		43
5	Acki	nowlodd	ramants	
5	Dofo	ronood	5-111-11-13	
U A	Refe	1 CHUES .		
Ap	pendi	x A:	Overview of components groups	
Ap	pendi	х В:	Input parameters estimated toxicity and sampling rates	
Ap	pendi	x C:	Chemical characterization of field samples	50



Appendix D:	Estimated toxicity in field samples53
Appendix E:	Chemical and toxicological characterization of laboratory experiments55
Appendix F:	Input to OSCAR
Appendix G:	Initial OSCAR simulations64

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1 Introduction

This study has been an add-on activity to the Joint Industry Program to develop and advance the knowledge, methods and technology for an oil spill response in Arctic and ice-covered waters (Oil-in-Ice JIP). The JIP summary report (Sørstrøm et al., 2010) gives an overview of the total program and the technical reports.

A large-scale field experiment in the marginal ice zone in the Barents Sea took place in May 2009 as a part of the Oil-in-Ice JIP. During the experiment, 7000 liters of Troll fresh crude oil were released uncontained between the ice floes to study oil weathering and spreading in ice. The processes for the drift, spreading and weathering of oil were monitored by multiple sampling throughout the six-day experiment. Meteorological and oceanographic data were collected for monitoring wind speed and direction, air temperature, currents and wave height. In addition, the recording of ice drift and ice field deformation was carried out by deploying a large number of GPS recorders on selected ice floes both in and around the oil slick. The recordings from the GPS systems on the ice floes, the position of the ship, and aerial surveillance from helicopter and field observations during sampling have all been used to estimate the spreading of oil-in-ice and the approximate dimensions of the oil slick. Data on the potential bioaccumulation of oil components in the water column were collected by passive absorption devices (semi-permeable membrane devices known as SPMDs), while dissolved hydrocarbons in the water column were sampled by in situ large-volume water sampler (Kiel In Situ Pump, KISP). These measurements were supplemented by online UV fluorescence measurements beneath and close to the oil slick.

The water soluble oil fraction (WSF) is of special interest since components dissolved (e.g. naphthales, phenanthrenes, dibenzothiophenes and phenols) in an oil slick or from the dispersed oil droplets beneath a slick are considered to be the major contributors to any ecological effects from oil spills and are given particular attention in the management of produced water discharges in Norway. Since the mid-1990s, there have been several studies conducted to monitor and model the fate and effects of produced water discharges in the Norwegian sector of the North Sea (e.g. Børseth et al., 1997; Durell et al., 2004 and 2006; Hylland et al., 2008; Johnsen et al., 1998; Neff et al., 2006; Utvik et al., 1999, and Utvik and Johnsen, 1999).

The objective of this comprehensive sampling program was to acquire more knowledge of how the presence of ice influences the distribution and spreading of oil on the surface and in the water column. The MetOcean parameters recorded will be used to improve and verify existing oil spill response and ice drift models. Initial OSCAR simulations have been performed and preliminary predictions have been presented. The chemical monitoring data collected will be used to perform a limited number of controlled experiments, with realistic exposure concentrations in the laboratory to compare the biological effects of various cleanup technologies, by measuring the body burden and biomarker responses (e.g. lysosomal stability in blood cells, MDA and catalase) on the Arctic amphipod *Gammarus oceanicus*.

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2 Experimental

The research vessel "Lance" was used during FEX2009, and 7000 liters of fresh Troll B crude (SINTEF ID 2009-0702) were released uncontained in 70-80% ice coverage on May 15th and followed for six days with a comprehensive sampling and monitoring regime. The sampling program involved oil weathering (Brandvik et al., 2010a) and oil-in-water studies, in addition to the monitoring of ice and oil distribution, drift and spreading. The mapping of ignitability (Brandvik et al., 2010b) and dispersibility (Daling et al., 2010) over time was also part of the test program. The slick was treated with chemical dispersants as a final response operation.

The processes for the drift, spreading and weathering of oil have been monitored by multiple sampling throughout the experiment, with some of the important measurements being:

- Data on the potential bioaccumulation of oil components in the water column were collected by passive SPMDs.
- Dissolved hydrocarbons in the water column were sampled by an in situ large-volume water sampler (KISP) that concentrates the dissolved hydrocarbons onto filters and XAD resins supplemented by online UV fluorescence measurements beneath and close to the oil slick.
- Oil droplet size distribution was measured by use of an online in situ laser diffraction instrument.
- Meteorological and oceanographic data were recorded for the monitoring of wind speed and direction, air temperature and pressure in addition to current, tide and wave height recordings.
- The recording of ice drift and ice field deformation was carried out by deploying a large number of GPS recorders on selected ice floes both in and around the oil slick.

An overview of the experimental program during field experiments (FEX2009) is given in Table 2.1 below. The complete field plan is available for more detailed information (Sørstrøm, 2009).

Date (in May 2009)	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Day						0	1	2	3	4	5	6				
Mob Longyearbyen and transport																
Large scale experiment (7000 L)																
In situ burning (2000 L)																
Dispersant experiment (2000 L)																
Sampling MetOcean and Chemistry																
Transport to and demob Tromsø																

Table 2.1Overall time schedule for large-scale field experiments 2009 (FEX 2009)

2.1 Instrumentation for sampling of MetOcean data

The MetOcean time series measured during FEX2009 is given in Table 2.2. The air temperature, wind speed and direction were recorded every 10 minutes by a weather station onboard the RV "Lance." The current speed and direction were measured by using a Doppler profiling device (RDCP) in one location and two single-point current meters (Seaguards) in another. Ice floe movements such as heave, pitch and roll were monitored using an accelerometer (Gyro motion sensor SMC S-108) and a Seawatch Mini Buoy.



Parameter	Source			
Air temperature [°C]	Lance			
Wind direction [^o]	Lance			
Wind speed [m/s]	Lance			
Water temperature [°C]	Seaguard RCM /RDCP600			
Salinity	Seaguard RCM /RDCP600			
Current speed [cm/s]	Seaguard RCM /RDCP600			
Current direction [°]	Seaguard RCM /RDCP600			
Ice floe movement [cm]	Gyro motion sensor SMC S-108/Seawatch Mini II Buoy			

Table 2.2MetOcean time series

2.1.1 AADI RDCP600 (Recording Doppler Current Profiler)

The RDCP600 (Figure 2.1) uses four acoustic beams to measure the Doppler shift and the subsequent current in the water column above/beneath the instrument. The instrument is equipped with compass, tilt, pressure, temperature and conductivity sensors as well as an internal recorder. The RDCP was deployed downward looking just below the ice floe, with the first good measurement taken from 5 m below the ice floe.



The RDCP600's configuration:

Profiling interval:	10 min
Ping number:	150 Spread mode
Number of cells:	30
Cell size:	2 m
Blanking distance:	2 m
Overlap:	50 %

Figure 2.1 The RDCP600 recording Doppler current profiler from AADI

2.1.2 AADI Seaguard recording current meter

Two Seaguard recording current meters (Figure 2.2) were used. The current meters were placed 5 and 10 m below the ice floe during the experiment. These instruments transmitted four acoustic beams in order to measure the Doppler shift, which again was used to calculate the current at one point in the water column. The instruments are equipped with compass, tilt, pressure (only one of the Seaguards), temperature and conductivity sensors and an internal recorder.





The Seaguard's configuration:

10 min
150
1 m

Figure 2.2 The Seaguard recording current meter from AADI

2.1.3 OCEANOR Seawatch Mini II Buoy

The OCEANOR Seawatch Mini II Buoy (Figure 2.3) was intended for use in the sampling of ice floe movements such as heave, pitch and roll during the field experiment. However, due to little movement in the ice floe, it was not possible to obtain any data from this instrument.



Figure 2.3 OCEANOR Seawatch Mini II Buoy

2.1.4 Gyro Motion Sensor SMC S-108

A gyro motion sensor from SMC was installed in a steel tube and placed on an ice floe in order to measure ice floe movement (see Figure 2.4). This sensor measures six different parameters: Roll, pitch, yaw, surge, sway and heave (see Figure 2.5). The roll and pitch are the motion around the two horizontal axes, whereas the yaw is the motion around the vertical axis. All these parameters are given in degrees (as a fluctuation around zero). Likewise, the surge and sway are the displacement in the horizontal plane, while the heave is the displacement in the vertical. These three parameters are given in meters as displacement around zero.





Figure 2.4 The SMC S-108 sensor and the steel tube it was mounted in during the fieldwork



Figure 2.5 The six different parameters measured by the SMC S-108 sensor



2.1.5 GPS systems

The plan was to use two different GPS systems to track equipment and ice floes around the main oil spill release. A Garmin system (Astro 220) was the primary system, while a Trackstick system (Trackstick Pro) was planned as a backup system (Figure 2.6). After a few days of testing, the Garmin system demonstrated the best reliability and was used for the remainder of the test period.

The Garmin units on the ice transmitted their position (146 MHz) to the base station onboard the RV Lance every 30 seconds. The positions were logged on the base station's memory and downloaded every morning and evening. The memory in the base station has the capacity to store positions for 10 GPS trackers and for 4-6 hours on the vessel, which means the data is available for two six-hour periods per day.



Figure 2.6 GPS Garmin and Trackstick systems placed on the ice for testing before the oil release. The Trackstick unit is marked with T4 (in right box).

2.2 Sampling equipment for the monitoring of oil

2.2.1 Large-volume water sampler

The sampling of dissolved hydrocarbons in the water column was conducted with two largevolume water samplers of the Kiel In Situ Pump type (KISP, Figure 2.7), which is described in detail elsewhere (Petrick et al., 1996). In brief, a stainless steel Teflon gear pump draws in seawater through a Teflon tube, pumps it through a glass fiber filter (GF/C) which samples the particle-associated fraction and then through an absorber cartridge designed to remove the dissolved fraction of the components of interest. Next, the water passes through a rotating vane flowmeter before being discharged.

The KISP is equipped with an electronic control unit that allows the pump operation to be preprogrammed and record the flow data. The maximum pump capacity is 2 L water/min and up to 200 L of water was collected for each sample, depending on the content of the suspended particle matter of the water and the battery capacity.

Glass fiber filters (GF/C, Whatman no. 1822-15, 15 cm diameter) were employed to retain particle-associated oil components. The filters were pre-cleaned by heating them for 12 hours at 400 °C in a muffle furnace, after which they were wrapped in aluminum foil. After sampling, the filters were packed in aluminum foil and stored at -20 °C until extraction.



The resin XAD-2 (Supelco Supelpak-2SV, 13674U) was used to collect the dissolved fraction. The XAD-2 was delivered "super clean" from the supplier and did not require any pre-cleaning, but was wetted before use: A sufficient amount of methanol was added to the resin (covering the resin bed by 2-5 cm). The resin/methanol was gently stirred to ensure a complete mixing and then allowed to stand for 15 minutes. Most of the methanol was decanted off and replaced with distilled water. The mixture was then stirred and allowed to stand for 5-10 minutes. Approximately 2 cm of deionized water were added to the glass sampling cartridge (length 260 mm, diameter 50 mm, volume approx 500 mL). The resin slurry was slowly poured into the column and the excess water was drained through the bottom of the column, but the liquid level was not allowed to fall below the top of the resin bed. Enough resin to half-fill the glass sampling cartridge was added, and it was then filled with water, sealed and stored until use. Following sampling, the cartridges were resealed and stored until extraction.



Figure 2.7 KISP (large-volume water sampler)

2.2.2 Passive sampler (SMPD)

SPMDs have been widely used to monitor concentrations of non-polar components in aquatic systems primarily as a tool to determine relative concentration differences among sampling stations, either alone or in conjunction with caged mussels and/or large-volume water samplers (Durell et al., 2006; Utvik and Johnsen, 1999; Baussant et al., 2001).

The Semi-permeable Membrane Device (SPMD) mimics biological systems to provide a measure of bioavailable pollutants in the water. Its passive transport mechanism is similar to that of fish gills. The SPMD will accumulate oil components by diffusion and is composed of a lay flat, low-density polyethylene tubing containing a thin film of pure, high-molecular weight lipid (triolein). The polymer consists of transport corridors less than 10 Å in diameter. These pores allow for the selective diffusion of hydrophobic organic chemicals which are then sequestered in the lipid phase. Through SPMDs, it is possible to estimate the time-integrated dose of waterborne bioavailable pollutants to marine organisms (Est-lab, 2010). The length and width of the SPMD was 91.4 cm and 2.5 cm, respectively, with a wall thickness of 70-95 μ m. SPMDs with 99% ultra high pure triolein (EST Lab, Inc., Saint Joseph, MO, USA) were used.

The field deployment device was a stainless steel canister (Figure 2.8) and there were five SPMDs in each canister. The SPMDs were handled in as clean an environment as possible on the ship and were transported in clean tins from/to the lab and deployment/collection.





Figure 2.8 SPMD steel canister and the spider with the SPMDs (Photo: http://oceanexplorer.noaa.govl)

2.2.3 Online oil-in-water monitoring

An in situ UVF technique (ultra-violet fluorescence) was used to measure concentrations of oil in water, which can either be water soluble components leaking out from the surface oil or dispersed oil droplets in the water. The three instruments were individually calibrated with naphthalene (0.12 - 11.5 ppb) and chemically dispersed oil (0.16 - 10.5 ppm). These calibrations were used to offer semi-quantitative results during the field operation. These two groups of target analytes have a very different response on the UVF instrument and need different calibration curves. The usual approach has been to use the instruments to measure water soluble components in the early stages of an oil release, as well as in naturally dispersed oil (if the necessary energy is present) and chemically dispersed oil after the use of dispersants. Quantitative results were obtained by calibrating the UVF response with the field water samples analyzed after the field experiments.

Three UV fluorescence devices were installed on the ice floes in and around the oil slick area, a sensor was positioned at a 3 m depth and the measurements were stored in a control box placed on the ice (Figure 2.9). The measurements were averaged over a minute and stored locally, but also transmitted (2.4 GHz) to a base station onboard the RV "Lance."



Figure 2.9 The control box containing batteries, data logger and control unit for the submerged UVF sensor. The UVF antenna can be seen on top of the box.



2.3 Sampling strategy

The equipment was moored to the ice floes: Seaguards, RDCP (Recording Doppler Current Profile) and KISPs with chain assemblies fastened by several ice screws on the ice floes. Floating buoys were used for additional safety. A small anchor was attached to the SPMD canisters, and they were also moored to the ice floes with a chain assembly and ice screws. KISPs, SPMDs and UV fluorescence sensors were deployed approximately 3 m below the ice. An overview of the stations and deployed equipment is given in Table 2.3, Figure 2.10 and 2.11.

The current speed and direction were measured at several depths from two locations. In G5, two single-point current meters (Seaguards) were deployed, one at 5 m and the other 10 m below the ice floe, while in Station 1 a Doppler profiling device (RDCP) was deployed. The RDCP measured the current for every m from 5 to 30 m below the ice floe. The data from every meter between 5 and 10 m, and every 5 meters from 10 to 30, have been analyzed.

Ice floe movements such as heave, pitch, and roll were monitored using an accelerometer (Station 2) and a Seawatch Mini Buoy.

The Garmin system (Astro 220) was used to track equipment and ice floes both in and around the oil slick (as illustrated in Figure 2.10 and 2.11). The data has been used as input to the maps, showing the approximate dimensions of the oil slick and the position of equipment and sensors relative to the oil (see examples in Figure 3.12 and 3.13).

	Equipment	Comment
Station 1	UVF1	Located farthest from the oil release
	T1 + G1	Tracker and GPS
	RDCP	Recording Doppler Current Profile (Current profiling)
	SPMD	Four canisters deployed, sampled at Days 1, 3, 5 and 6.
Station 2	UVF2	Located between Station 1 and oil release
	T4 + G4	Tracker and GPS
	Accelerometer	Wave and ice floe movement
	SPMD	Four canisters deployed, sampled at Days 1, 3, 5 and 6.
	KISP	
Station 3	UVF3	Located between "Lance" and oil release
	T3 + G3	Tracker and GPS
	SPMD	Four canisters deployed, sampled at Day 1, 3, 5 and 6.
	KISP	
G5	Seaguard (2x)	5 and 10 m depth
	T5 + G5	Tracker and GPS
SMB	Seawatch Mini Buoy	Wave height recordings located close to the ship

Table 2.3Stations and deployed equipment prior to oil release





Figure 2.10 Overall sketch of the equipment on one of the monitoring locations. GPS and UVF data were transmitted to the "Lance" in real time.



Figure 2.11 Overall sketch of the oil slick and the various monitoring equipment immediately after the release of the oil

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2.4 Collection of samples

2.4.1 Background samples

Three days prior to the oil release (Tuesday, May 12th) background samples from the Barents Sea were collected: Two large volume water samples (200 L each), three passive samples (SPMDs), and three water samples (1 L). The sampling was performed approximately 3 m below the ice.

2.4.2 Large-volume sampler

The KISPs were programmed to pump 200 L of seawater. However, most of the samples were less than 200 L, which might be because of too high an algae concentration in the water (clogged filter), or that the battery capacity was too low due to poor recharging. KISP sampling with comments are given in Table 2.4. One sample was collected during the in situ burning experiments, with the remaining samples during the six-day large-scale oil spill.



Figure 2.12 Transport of KISP in the ice field

Table 2.4	KISP sampling:	XADs and filters.	Filters were	labelled A	and XADs B.
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SINTEF ID	Sample ID	Vol (L)	Comments
2009-0403	120509 ref st	200	From pos N7741.71 E03041.57
2009-0404	120509 ref st	200	
2009-0405	150509 St 3	186	Oil release from 08:25 to 08:50, sampling from 8:30
2009-0406	150509 St 1	0	No sample collected
2009-0407	160509 St 3	136	Moves mooring from St 1 to St 2. Surface oil sheen on St 3, moves mooring KISP 3-4 m due to ice floe
2009-0408	160509 St 2	200	
2009-0409	170509 St 2	0	Low air temp (-8) and near gale. MOB boat to stations took very long time. KISPs probably frozen prior to deployment.
	170509 St 3	0	Glass cartridge broken, no sample
2009-0410	180509 St 2	140	Oil on surface at St 2. Yellowish sample, but no smell of HC
2009-0411	180509 St 3	133	
2009-0412	190509 St 3	18	Sampled only for 14 min due to poor charging?
2009-0413	190509 burn exp	74	Sampled from 21:00 to 0:00.Burning from 22:15 to 22:35
2009-0414	200509 St 3	127	



2.4.3 Passive samplers

There were five SPMDs in each canister and the canisters were moored underneath the ice floes (Figure 2.13). The SPMDs have been handled in as clean an environment as possible on the ship (not in the same lab as the oil analysis) and were transported in clean tins from from/to lab and deployment/collection. However, oil sheen was observed on the surface at some of the samplings, but dispersant was added to remove the surface oil prior to sampling. SPMD deployment and collection is given in Table 2.5.



Figure 2.13 Deployment of SPMD into the water

SINTEF ID	Sample ID	Out	In	Station	Time	Comments
2009-0416	SPMD ref	12-May	13-May	3m	Ca 16 hrs	Reference sample
2009-0417	SPMD ref	12-May	13-May	2m	Ca 16 hrs	Reference sample
2009-0418	SPMD ref	12-May	13-May	1m	Ca 16 hrs	Reference sample
2009-0419	SPMD#1	14-May	16-May	St 3	0-2 d	Deployed 15-18 hrs prior to release
2009-0420	SPMD#2	14-May	17-May	St 3	0-3 d	Deployed 15-18 hrs prior to release
2009-0421	SPMD#3	14-May	20-May	St 3	0-6 d	Deployed 15-18 hrs prior to release
2009-0422	SPMD#4	14-May	20-May	St 3	0-6 d	Deployed 15-18 hrs prior to release
2009-0423	SPMD#5	14-May	20-May	St 2	0-6 d	Deployed 15-18 hrs prior to release
2009-0424	SPMD#6	14-May	20-May	St 2	0-6 d	Deployed 15-18 hrs prior to release
2009-0425	SPMD#7	14-May	16-May	St 2	0-2 d	Deployed 15-18 hrs prior to release
2009-0426	SPMD#8	14-May	17-May	St 2	0-3 d	Deployed 15-18 hrs prior to release
2009-0427	SPMD#9	14-May	16-May	St 1	0-2 d	Deployed 15-18 hrs prior to release
2009-0428	SPMD#10	14-May	19-May	St 1	0-5 d	Deployed 15-18 hrs prior to release
2009-0429	SPMD#11	14-May	20-May	St 1	0-6 d	Deployed 15-18 hrs prior to release
2009-0430	SPMD#12	14-May	17-May	St 1	0-3 d	Deployed 15-18 hrs prior to release
2009-0431	SPMD#13	17-May	20-May	St 1	3-6 d	
2009-0432	SPMD#14	17-May	19-May	St 2	3-5 d	
2009-0433	SPMD#15	17-May	20-May	St 3	3-6 d	
2009-0434	SPMD#16	19-May	20-May	St 1	5-6 d	
	SPMD#17	19-May	Lost	St 2		Canister missing
2009-0415	SPMD#18					Not in water, blank sample

Table 2.5	SMPD deploymen	t and collection
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2.4.4 Sampling during the dispersant experiment

A 2 m^3 oil slick was dispersed with Corexit 9500 May 19th at 15:10, approximately 6 hours after release (described in Daling et al., 2010). Two hours later, measurements of oil-in-water were performed at 1, 2 and 3 m. Water samples (1 L) were collected simultaneously with *in situ* UVF monitoring and oil droplets measurements (LISST) at the same depths from the mob boat (Table 2.6).

SINTEF ID	Sample ID and depth	Time	Comments
2009-0274	Ref - 3 m I		Reference (3x at May 12th)
2009-0275	Ref - 3 m II		
2009-0276	Ref - 3 m III		
2009-0277 A	1-3m	16:27:30	Sampled after dispersant is applied
2009-0277 B	1-2m	16:29:00	
2009-0277 C	1-1m	16:31:00	
2009-0278 A	2-3m	16:40:30	
2009-0278 B	2-2m	16:37:30	
2009-0278 C	2-1m	16:38:30	
2009-0279 A	3-3m	17:07:00	Sampled after mixing of oil and dispersant (by Lance)
2009-0279 B	3-2m	17:08:15	
2009-0279 C	3-1m	17:09:00	
2009-0280 A	4-3m	17:26:30	
2009-0280 B	4-2m	17:27:15	
2009-0280 C	4-1m	17:28:15	
2009-0281 A	5-3m	17:33:05	
2009-0281 B	5-2m	17:34:05	
2009-0281 C	5-1m	17:34:40	
2009-0282 A	6-3m	17:36:27	
2009-0282 B	6-2m	17:38:10	
2009-0282 C	6-1m	17:38:41	

Table 2.6Water sampling during the dispersant experiment.

2.4.5 Online oil-in-water measurements (UVF)

Main oil release $(7 m^3)$

Three UVF stations were placed on the ice on the evening of May 14th (sensors at a 3 m depth) and background measurements were collected before the main oil release the next morning. Mainly water soluble conditions were expected under the ice due to the low energy conditions in the ice (calm weather and high ice coverage).

Data were recorded from the three UVF sensors in the period from May 14th until May 18th at 14:00 when two sensors (UVF3 and 1) were removed to be used in the two oil releases for dispersant and in situ burning. The sensor on the third remaining station was raised to a 1 m depth.

The locations for the three UVF units were coordinated with sampling/monitoring of oil components in the water column by two KISP units and several passive adsorption samplers.

In situ burning oil release $(2 m^3)$

The other UVF unit was located close to the oil release which was used as a control slick for the dispersant experiment and which later that same day was for in situ burning (described in Brandvik et al., 2010c). The sensor was in operation from the oil release (May 19th at 09:45) until three hours after the burn was terminated (May 20th at 01:30). This monitoring was coordinated with a KISP sampling of the water during the in situ burning of oil.



Dispersant oil release $(2 m^3)$

One of the UVF instruments (UVF1) was operated from a MOB boat with simultaneous measurements, with the LISST scatter instrument used to measure droplet size distributions and water sampling (1 L). The measurements were done after dispersant application (two series), and after energy was added, by using the Lance's thrusters to disperse the oil into the water (four series). Each series consists of simultaneous measurements at depths of 1, 2 and 3 m (see Table 2.6).

2.5 Preparation of water accommodated fraction (WAF)

A volume (1.75 L) of sterile filtered (0.2 μ m) natural seawater collected from a 90 m depth in Trondheimsfjord, yielding a water-to-air headspace ratio of ~4 to 1, was added to 2 L bottles. The oil was carefully applied to the water surface, and the oil-to-water loading was 1 to 40 (25 g oil/L seawater). The water was stirred so gently with a magnetic stirrer (< 200 rpm) that the oil film rested on the water surface without creating a vortex and without dispersing any oil droplets into the water. The preparation was carried out in darkness in a climate chamber, and samples for chemical analysis and toxicity testing were collected in glass vials with Teflon-lined caps, allowing no headspace in the vials. Samples for chemical analysis were acidified (hydrochloric acid to pH<2) immediately after sampling to avoid biodegradation during storage. The WAF was prepared at 2 °C with a mixing time of 4 days.

The WAF system illustrates a "snapshot" in the dynamic process of dissolution occurring during a spill situation. The test was performed with fresh oil using an oil-to-water ratio of 1 to 40 (25 g oil/L seawater), even though this ratio is considered to be unrealistically high. Still, the data generated gives a kind of "worst case scenario" condition: The solutions used are assumed to be "saturated" and therefore represent a conservative estimate of concentrations foreseeable in the field.

The acute toxicity was measured by the screening toxicology test method known as $Microtox^{\text{(B)}}$, which was chosen due to its sensitivity to the water soluble fractions of oils and because it is a rapid and easy test procedure that enables testing of a large number of samples compared to other standard toxicity tests. However, the $Microtox^{\text{(B)}}$ method is based on measurements of a single response for a primitive organism (the marine bacteria *Vibrio fisheries*), and is only suitable as an indicator of potential acute toxicity. For this reason, the ecological relevance of the test could be limited. In addition, the acute toxicity was predicted as a hazard index as described in Section 2.8.2.

2.6 Sample preparation

All samples (water, filter, XAD and SPMD) were added surrogate internal standards (*o*-terphenyl, naphthalene- d_8 , phenanthrene- d_{10} , chrysene- d_{12} , phenol- d_6 , 4-methylphenol- d_8) prior to processing and recovery internal standards (5 α -androstane, fluorene- d_{10} , and acenaphthene- d_{10}) prior to analysis on GC/FID (gas chromatography/flame ionization detection) and GC/MS (gas chromatography/mass spectrometry).

2.6.1 Extraction of water samples

The water samples for analyses of semi-volatile organic compounds (SVOC) and total hydrocarbons (TPH) were spiked with the appropriate surrogate internal standards and serially extracted with dichloromethane following a modification of EPA method 3510C (US EPA, 1996). The combined extracts were dried with sodium sulfate and concentrated to approximately 1



mL using a Zymark Turbovap® 500 Concentrator. The final extract was spiked with the appropriate recovery internal standards and analyzed on GC/FID and GC/MS.

2.6.2 Extraction of filter samples (from KISP)

The filter was cut into small pieces using clean stainless steel scissors and placed in a baked Pyrex glass bottle (100 mL) with a small amount of sodium sulphate for the extraction process and dichloromethane (DCM, 30 mL) as the solvent. The filters were fortified with surrogate internal standards and serially extracted 3 times (at approximately 12, 4 and 1 hour, respectively) using a shaker table. The solvent was carefully decanted off between each extraction. The combined extracts were concentrated to approximately 0.5 mL, spiked with recovery internal standards and submitted for GC/FID and GC/MS analysis.

2.6.3 Extraction of XAD resin (from KISP)

The extraction of the XAD-2 columns was performed in a modified Soxhlet extractor, and boiling chips were added to the boiling flask. Excess water in the sample column was drained off and transferred to an Erlenmeyer flask. Acetone (approximately 300 mL) was slowly poured into the XAD-resin bed and allowed to siphon into the boiling flask (500 mL). The XAD resin was spiked with surrogate internal standards, and the resin was extracted at a rate of approximately 4 cycles per hour (1 flush every 15 min) in approximately 2 hours. The acetone extract was poured from the boiling flask in to an Erlenmeyer flask, and fresh boiling chips were added if necessary. After pouring off the acetone, DCM (350 ml) was added to the XAD column and allowed to siphon into the boiling flask. The resin was extracted overnight.

The DCM extract was combined with the acetone/water from the first extraction in a separating funnel (the water is the upper phase, DCM and acetone are mixable), shaken for 3 minutes and then the DCM/acetone phase was removed. The water phase was extracted two more times with DCM (30 and 15 mL). The DCM/acetone extract was added sodium sulphate and allowed to dry for approximately 4 hrs. The extract was concentrated to 0.5 mL using TurboVap and added recovery internal standards. No clean-up of the extracts were required, and the extracts were submitted for GC/FID and GC/MS analysis.

2.6.4 Extraction of SPMD

Excess algae materials were wiped off the membranes in the field laboratory. Five SPMDs from each canister were placed in a Pyrex glass bottle (100 mL) and fortified with SIS compounds. The samples were serially extracted three times with hexane (60 mL) on a shaker table overnight (at 10 °C), and sodium sulphate was added to the samples which were concentrated using a Turbovap.

A leakage of triolein had occurred in some of the samples during the extraction, and these samples were re-extracted by saponification.

All extracts were cleaned up using gel permeable chromatography (GPC)/HPLC and the purified extracts were concentrated to 0.5 mL, spiked with RIS components and submitted to GC/FID and GC/MS for analysis.

2.7 Chemical analyses

The oils and their WAFs were analyzed for SVOC (PAHs and phenols) using gas chromatography/mass spectrometry (GC/MS), for TPH using gas chromatography/flame ionization detection (GC/FID) and for volatile organic compounds (C_5 - C_9), including BTEX (benzene, toluene, ethylbenzene, and xylenes), by Purge and Trap Gas Chromatography Mass



Spectrometry (P&T GC/MS). A list of the target analytes is shown in Appendix A. The P&T GC/MS analysis was only performed in WAF and oil samples, not in the field samples.

2.7.1 Analysis of total petroleum hydrocarbons (TPH)

A GC/FID analysis was performed according to a modification of EPA Method 8100 (US EPA, 1986). TPH (resolved plus unresolved TPH) 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 C_{10} to C_{36} n-alkanes. For the water samples from the dispersant experiment, crude oil Troll B was used to quantify the concentration of dispersed oil in the water.

2.7.2 Analysis of semi-volatile organic compounds (SVOC)

The semi-volatiles were quantified by modifications of EPA Method 8270D (US EPA, 2007). The mass spectrometer was operated in the selective ion monitoring (SIM) mode for optimum sensitivity and specificity. The quantification of target compounds was performed by the method of internal standards using average response factors (RF) for the parent compounds. The PAH and phenol alkyl homologues were quantified using the straight baseline integration of each level of alkylation and the RF for the respective parent PAH compound. The response factors were generated for all targets and surrogates versus fluorene- d_{10} .

A target analyte list of the parent and alkylated PAH and phenols is given in Appendix A. This list includes the recommended analytes given by Singer et al. (2000), and is a typical standard list of target compounds used during post-oil spill damage assessments.

2.7.3 Analysis of volatile organic hydrocarbons (VOC)

The volatiles were not analyzed in the field samples, only in WAF and fresh oil. A total of 35 target volatile analytes in the C₅ to C₁₀ range (Appendix A) were determined by P&T GC/MS (Purge and Trap Gas Chromatography Mass Spectrometry), using a modification of EPA method 8260C (US EPA, 2006). The samples were spiked with SIS (toluene- d_8 and ethylbenzene- d_8) and RIS (chlorobenzene- d_5). The quantification of individual compounds was performed by using the response factors of the individual compounds relative to the internal standards. All standards and samples were analyzed in a full scan mode.

2.8 Methods for determining bioavailability

2.8.1 Calculation of SVOC concentration in seawater from SPMD data

The analyte concentration in the SPMDs is calculated as μg analyte/g lipid. A linear model method developed by Huckins et al. (1993) uses SPMD concentration data to estimate the concentration of dissolved oil components in the water column (in μg analyte/L water). In the present study, the method described in Durell et al. (2006) is used, as the equipment and measured components are the same as in FEX2009. Assuming that equilibrium between the SPMD lipid and the water is not reached for a particulate analyte, the compound will still be in the linear uptake region. The concentration is then proportional to the SPMD sampling rate R_s, and the concentration of analyte in the water can be estimated:

$$C_{w} = C_{SPMD} / [(R_{s} \times F) \times t]$$
(1)

where

 C_w = Concentration of analyte in water (µg/L); C_{SPMD} = Concentration of analyte in SPMD (µg/g SPMD);



 R_s = SPMD sampling rate (volume of water extracted per day by an SPMD of a specific configuration (L/day));

F =Samping rate (R_s) correction factor, to adjust R_s for actual water flow;

t =Sampling/uptake time (days).

The sampling rates given in Durell et al. (2006) are used in this study (Appendix B), although the seawater temperature in their study was approximately 10 °C compared to the -1.8 °C in the Barents Sea. According to Booij et al. (2003) and Huckins et al. (2006), the water temperature does not have as much of an effect as the flow rates, so an adjustment was only made for the sampling rates.

The published sampling rates and the sampling rates estimated for additional compounds are based on a flow rate of 1 cm/s. The average flow rate in the Barents Sea during the exposure period was approximately 17 cm/s (Table 3.1). To calculate the correction factor, F, Durell et al. (2006) used equation (2) to determine the relationship between the flow rate and sampling rates. This relationship generates the following equation:

$$R_s = -0.0038 \text{ (flow rate)}^2 + 0.3132 \text{ (flow rate)} + 2.6906$$
 (2)

By entering the flow rate of 1 and 17 cm/s into equation (2), the R_s value for 17 cm/s was determined to be 2.3 times higher than for 1 cm/s, and the constant of 2.3 (i.e. F in Eq.(1)) was then used to adjust the R_s (Appendix B). The flow rate-based adjustment in Durell et al. (2006) was only applied for compounds with a log $K_{ow} > 4.2$, but since the deployment period in FEX2009 was six days or shorter, it is assumed that there was not an SPMD water column equilibrium concentration established.

2.8.2 Estimate hazard of dissolved oil in the water column

A hazard index (HI) is a simple approach which is used to predict LC_{50} (median lethal concentration) by comparing the estimated LC_{50} of the individual components to their measured exposure concentrations (e.g. Neff et al., 2000 and 2006). Other authors have used the term toxic unit (TU) (e.g. Di Toro et al., 2000 and 2007; French McCay, 2002; McGrath et al., 2004), although the definition is the same as for the HI. The method assumes toxicity by non-specific narcosis and that the effect of all components are additive, excluding antagonistic or synergistic effects (McCarty et al., 1992; DiToro et al., 2000).

The published values of $logK_{ow}$ (Neff et al., 2006) were used to estimate the acute toxicity to marine organisms of all the target decalins, PAHs, phenols and their alkyl-homologues.

Regression models have been used to describe the relationship between acute toxicity and the octanol-water partition coefficient (K_{ow}) for target chemicals in order to estimate the threshold value of the toxic concentration of each component. There appears to be a linear negative relation between the log LC₅₀ of the marine organisms and the log K_{ow} of the components that serve as the basis for toxicity by non-specific narcotic action (McCarty et al., 1992 and 1993; Di Toro et al., 2007). The equation is expressed as:

$$\log LC_{50} = m \log (K_{ow}) + b \tag{3}$$

The LC₅₀ (mg/L) is calculated for each component by the use of equation (3) and is given in Appendix B. The slope (m=-0.55), and the intercept (b=0.064) given in McCarty (1993) is used for the phenols and the slope, m=-1.162, and the intercept b=2.46 given in Neff et al. (2006) is used for the decalins and PAHs.



The hazard quotients for all the target organic chemicals in the samples can be summarized to produce a hazard index, which is equivalent to an estimate of the acute toxicity. The HQ for each component (i) was calculated for each sample:

$$HQ_i = C_i / LC50_i \tag{4}$$

 C_i is the concentration of component *i* in the sample and LC50_i is the estimated acute toxicity for component *i* calculated from the equations (4).

The HQs were totaled for each component group to produce an estimate of the acute toxicity known as the hazard index (HI), which is equivalent to the total hazard of the hydrocarbons. A value of HI > 1 implies toxicity, i.e. the concentration in the water is expected to cause a 50% mortality rate in the test organisms. A HI<1 does not imply that the oil is non-toxic in the environment, but only implies that the oil is not acutely toxic according to the predictions.

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3 Results and discussion

In this chapter, the results are primarily summarized in the figures. The detailed measurements from the chemical monitoring and estimated acute toxicity are given in Appendices C and D. Results from the laboratory WAF studies are presented in Appendix E, and the input data to OSCAR (chemical characterization of the oil) is given in Appendix F. The initial OSCAR simulations are shown in Appendix G.

3.1 MetOcean time series

An overview of the MetOcean time series measured during FEX2009 is given in Table 2.2.

3.1.1 Meteorological data

Figure 3.1 to 3.3 show the air temperature, wind speed and a stick plot of the wind measured by the weather station onboard the "Lance". The lines in the stick plot show which direction the wind was blowing toward (i.e. lines pointing downward denote winds from the north, the same as for the current direction).

The air temperature varied from -1 to -3 °C (Figure 3.1) and the wind was from light to a fresh breeze (1 - 10 m/s, Figure 3.2) in the first days (May 14 to 16). The weather and wind direction changed at Day 3 (May 17^{th}), while the air experienced a temperature drop from -2 to -9 °C and the wind speed increased to 23 m/s (a strong gale, Figure 3.2). The weather became calmer and warmer over the last days of the experimental period.



Figure 3.1 Air temperature measured during the experiment (15/05 indicates Day 1)

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Figure 3.2 Absolute wind speed measured during the experiment (15/05 indicates Day 1)



Figure 3.3 Stick plot of the absolute wind measured during the experiment (15/05 indicates Day 1)



3.1.2 Currents and ice drift

The current speed measured by the RDCP is shown in Table 3.1, which gives the data from every meter between 5 and 10 m and every 5th meter from 10 to 30 m.

The relative current speed is the current measured by the instruments, thus giving the current speed relative to the ice floe.

The absolute current speed is the real current, and will be used in data processing. It is the sum of the relative current speed and the speed (and direction) of the ice drift as measured by GPS.

The mean absolute current speed at a 5 m depth during the experiment was 16.7 cm/s, and varied from 0.2 cm/s to 50.7 cm/s. The maximum absolute speed was recorded on Day 3 (May 17^{th} , see Figure 3.4).The mean absolute current speed throughout the water column down to a 30 m depth was notably constant, varying only between 15 and 17 cm/s. The maximum speed altered between 41 cm/s at a 20 m depth and 51 cm/s at a 5 m depth. The two single point Seaguards were positioned at 5 m and 10 m below the ice floe, and the current speeds measured are given in Table 3.2. Figure 3.4 show a stick plot of the absolute current speed measured by the two Seaguard current meters.

The measured current speed and direction from the two locations give a good picture of the current conditions in the oil slick area during the experimental period.

In addition, the Seaguards measured temperature and salinity in the seawater. Mean seawater temperature during FEX2009 at a 5 m depth was $-1.81 (\pm 0.06)$ °C and $-1.78 (\pm 0.06)$ °C at a 10 m depth. Mean salinity was measured to $34.3 (\pm 0.1)$ psu at 5 and 10 m depths.

	_		-		-	
Magguramant	Minimum	Maximum	Mean	Minimum	Maximum	Mean
donth	relative	relative	relative	absolute	absolute	absolute
depui	speed	speed	speed	speed	speed	speed
	cm/s	cm/s	cm/s	cm/s	cm/s	cm/s
5	0.3	27.7	11.0	0.2	50.7	16.7
6	0.4	25.7	10.3	1.1	50.7	17.1
7	0.3	33.5	12.0	0.4	48.3	16.3
8	0.3	33.7	13.3	0.4	44.2	15.7
9	0.1	34.6	14.3	0.4	43.8	15.4
10	0.6	36.0	15.1	0.2	43.9	15.4
15	0.7	40.1	16.9	0.3	42.1	15.5
20	0.7	41.9	17.3	0.4	40.6	15.2
25	0.6	41.3	16.7	0.3	43.5	14.9
30	1.4	40.3	15.0	1.0	47.0	15.4

Table 3.1Current speed (in cm/s) measured by the RDCP during FEX 2009

Table 3.2Current speed (in cm/s) measured by the by the two Seaguards during FEX 2009

Measurement depth	Minimum relative speed cm/s	Maximum relative speed cm/s	Mean relative speed cm/s	Minimum absolute speed cm/s	Maximum absolute speed cm/s	Mean absolute speed cm/s
5	0.1	36.8	15.6	0.8	37.7	15.4
10	0.9	40.4	17.7	0.3	34.4	15.1





Figure 3.4 Stick plot of the absolute current measured at 5 and 10 m by the two Seaguard current meters (15/05 indicates Day 1).

The progressive vector diagram of the ice drift from the GPS data is given in Figure 3.5. A progressive vector diagram shows the path a particle would follow when the velocity vector is added for every time step. The measurement interval used during FEX 2009 was 10 minutes.

It can be seen from Figure 3.5 that the ice drifted 10 km NE during the first two days of measurements before it started to drift southwards on the evening of May 16th. The wind was quite strong on May 17th, resulting in a more rapid ice drift. When the wind speed dropped, the ice drift slowed down and the direction turned towards the SW. On May 19th, the ice drift changed direction again, now drifting towards the NE, before turning towards the SE on May 20th.





Figure 3.5 Progressive vector diagram of the ice drift from GPS data (15/05 indicates Day 1).

The ice drift and progressive vector diagram of the wind are shown for the entire measurement period and for each day separately in Figure 3.6 and Figure 3.7, respectively. The wind velocity is scaled down to 2.95% of the measured wind speed. This fraction is calculated from the following formula:

$$\frac{\overline{U}_{gps}}{\overline{U}_{wind}} \times 100\% = 2.95\%$$
⁽⁵⁾

This downscaling makes it easier to compare the ice drift to the wind. It is known that ice floes usually move at 2 - 3 % of the wind speed, which agrees with the observations from the "Lance".

Figure 3.6 and Figure 3.7 show that the direction of the ice drift is to the right of the wind direction during most of the measurement period. The angle differs somewhat from day to day, though this deflection to the right is in agreement with the theory of ice drift first described by Nansen and Ekman.

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Figure 3.6 Progressive vector diagram of the wind speed and ice drift. The wind speed is scaled down to 2.95% of the original speed. The red dot (in 0,0) denotes the start of the measurement period. Each midnight is marked by a dot. The distance is given for the ice drift.



Figure 3.7 Progressive vector diagram of the wind speed and ice drift on each day from 15th to 20th of May 2009. The wind speed is scaled down to 2.95% of the original speed. The distance is given for the ice drift.



The progressive vector diagrams of the absolute current measured by the RDCP are given in Figure 3.8 and Figure 3.9. The beginning is denoted by a red dot (in 0,0), and the midnight of each day is marked with a dot. These figures illustrate the movement of a water parcel at a specific depth assuming that the current field in the areas of measurements are uniform throughout the measurement period.



Figure 3.8 Progressive vector diagram of the absolute current at a 5 – 9 m depth.



Figure 3.9 Progressive vector diagram of the absolute current at a 10 - 30 *m depth.*



Figure 3.10 gives a stick plot of both the speed and direction of the ice drift throughout the measurement period. The ice field drifted nearly 80 km during the experimental period. It has been assumed that at ice coverage of less than 30%, the drifting of oil will be independent of the ice. At ice coverage larger than 60-70%, the oil will mainly drift with the ice (Vefsnmo and Johannessen, 1994), which is in accordance with the observations made during FEX2009: The oil drifted with the ice and remained contained between the ice floes, enabling continuous experimental work. The weather and wind direction changed on Day 3 (May 17). The wind speed increased to 23 m/s (strong gale), and the ship and ice field drifted more than 35 km in a southward direction over the next 24 hours.



Figure 3.10 Stick plot of the ice drift from GPS data (15/05 indicates Day 1).

The recordings from the GPS systems on the ice floes, the positions of the ship, aerial surveillance from helicopter and field observations during sampling have all been used to estimate the spreading of oil in ice and the approximate dimensions of the oil slick. Figure 3.12 to Figure 3.15 illustrate the changes in the ice field from Day 2 to Day 6, and the figures also show that the shift in weather and wind direction at Day 3 (see e.g. Figure 3.3) results in an enhanced spreading of the oil and changes in the ice field and position of the stations. Still, the oil drifted with the ice and remained contained between the ice floes.





Figure 3.11 Stations and deployed equipment during the oil release. The equipment deployed on the different stations is described in Table 2.3. The red diamonds indicate GPS receivers on the ice and SMB is the Seawatch Mini Buoy.



Figure 3.12 Stations and the approximate dimensions of the oil slick (shaded area) one day after the oil release (Day 2, May 16th).





Figure 3.13 Stations and the approximate dimensions of the oil slick (shaded area) two days after the oil release (Day 3, May 17th).



Figure 3.14 Stations and the approximate dimensions of the oil slick (shaded area) 3 days after the oil release (Day 4, May 18th).

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Figure 3.15 Stations and the approximate dimensions of the oil slick (shaded area) 5 days after the oil release (Day 6, May 20th). Lack of GPS data due to that several of the batteries had gone down.

3.1.3 Waves and ice floe movements

Waves and ice floe movements were monitored using an accelerometer (a Gyro Motion Sensor SMS S-108 installed in a steel tube, Figure 2.4) and a Seawatch Mini Buoy (Figure 2.3). The instruments were placed on two ice floes, but due to little movement of the ice floes, the Seawatch Mini Buoy yielded no results.

The gyro motion sensor measures six different parameters: roll, pitch, yaw, surge, sway and heave (see Figure 2.5). The results from the different days were fairly similar, and only data from May 17^{th} (Day 3) are given here. Figure 3.16 shows the heave of the ice floe, and indicates that there was little movement along the z-axis during the measurement period. Figure 3.17 and Figure 3.18 give the surge and sway of the ice floe, respectively. There was more movement along the horizontal plane than the vertical. The movement in the horizontal plane was in the range of -13 to +16 cm during the measurement period. The roll and pitch are given in Figure 3.19 and Figure 3.20, respectively. These figures show that there was little movement around the x- and the y-axis.

The measurements were all close to the lower measurement limit of the instrument, most likely due to the length of the distance from the ice edge and open water.




Figure 3.16 Heave of the ice floe on Day 3 (May 17th).



Figure 3.17 Surge of the ice floe on Day 3 (May 17th).



Figure 3.18 Sway of the ice floe on Day 3 (May 17th).





Figure 3.19 Roll of the ice floe on Day 3 (May 17th).



Figure 3.20 Pitch of the ice floe on Day 3 (May 17^{th}).

3.2 Chemical monitoring

The chemical monitoring data collected during FEX2009 will be used to perform a limited number of controlled laboratory experiments with realistic exposure concentrations and as input to models.

A large number of single components were quantified to describe the composition of the samples collected. The results are presented in component groups based on the grouping of compounds for the calculation of the environmental impact factor (EIF) as given by Johnsen et al. (2000). A detailed description of the component groups used in this project is listed in Appendix A.

Reference samples of XAD and filter (from 200 L water samples), water (1 L) and SPMDs were collected two days prior to the oil release and indicate the level of hydrocarbons in the area and the laboratory. In addition, laboratory blanks have been processed and analyzed. The data have not been corrected for background/blank concentrations.

3.2.1 Main oil release (7 m³)

Unfortunately, only two samples from the KISP were collected on Station 2, probably due to a too low capacity of the recharging unit for the batteries (the pump stopped immediately after being deployed in the water). The field results show measurements of low but detectable concentrations above background level (Table C 1 in Appendix C), and all given results are from the XAD resins, as the concentrations in the filter samples were below the detection limit. The concentration of total extractable hydrocarbons (TPH) in the seawater was in the range between 4



and 32 ppb (Figure 3.22), and the content of semi-volatile oil components was lower than 1.5 ppb (Figure 3.21). The water soluble fraction was dominated by the alkylated phenols, naphthalenes and 2-3 ring PAHs. The highest concentration was measured on Day 5 when an additional 4 m³ of crude oil was spilled into the area at approx 10 p.m. in connection with the in situ burning (Brandvik et al., 2010b) and dispersant experiments (Daling et al., 2010). Sampling taken during the in situ burning indicated an enhanced concentration of oil components in the water column (13 ppb TPH).



Figure 3.21 Semi-volatiles in large-volume water samples (from XADs) given in ppb (µg analyte/L water).



Figure 3.22 Total hydrocarbons in large-volume samples (from XADs) given in ppb (µg analyte/L water).



During the experimental period three UVF sensors were located as described in Table 2.3. The sensors only measured the water soluble components and were calibrated against naphthalene (see Section 2.2.3) in the laboratory. The field UVF-data from the three instruments (UVF1-3) and measured TPH in water samples (from KISP) are given in Figure 3.23. There seems to be a good correlation between these data for the first two days, but the measured TPH concentrations are some higher than the online monitoring at Day 4. The UVF3 instrument was captured in the ice close to the surface at the beginning of Day 3 (increased ice drift due to heavy wind) and did not give valid measurements after this.



Figure 3.23 Correlation of online oil-in-water monitoring and measured TPH in water.

The accumulated oil components from the passive samplers can be given as analyte concentration in the SPMDs (μ g/g lipid) as in Table C 2 or as the analyte concentration in water (Figure 3.24), as estimated and described in Section 2.8.1. The measured dissolved hydrocarbons estimated from the SPMDs were in the range between 0.6 to 4 ppb. The accumulated components are dominated by the naphtalenes, 2-3 ring PAHs and decalins. The results are also given in Table C 3 in Appendix C.

As illustrated by the results in Figure 3.24, the concentration level is highest on the first days in Stations 1 and 3, and decreases throughout the experimental period. The results also indicated that more oil components are accumulated in the SPMDs during the first three days (Days 0-3) than the last three days (Days 3-6). At the first sampling (Day 2), no oil was observed at Station 2, though on Day 3 Station 2 drifted more closely to the oil slick than Stations 1 and 3. This is very well illustrated by the results in Figure 3.24, and can also be seen in the photo in Figure 3.25.

The measured content of oil components in the water during the field experiment was low, but above background level. The large-volume samples from the KISP gave good indications about the concentration level in the water, but the recharging process for the KISPs was too slow and not reliable so a larger number of samples would have been preferable. Deploying SPMDs prior to the oil release and collecting samples at different time intervals seem to have resulted in good and interesting results accompanying the visual observations and the met ocean data during the experiment.





Figure 3.24 Semi-volatiles from passive samplers, estimated concentration in ppb (μ g analyte/L water) related to flow and exposure time in water. Days express the time the SPMDs have been in the water (e.g. 0-2 was deployed on Day 0 (prior to oil release) and collected on Day 2 (May 16th.).



Figure 3.25 Sampling at Day 4 (May 18th). Station 2 is located in the oil slick area and Stations 1 and 3 are outside the photo. See also map in Figure 3.14.



Studies after the "Exxon Valdez" summarized in Boehm et al., 2007 concluded that the petroleum hydrocarbons present in the water column of Prince William Sound at scattered locations shortly after the spill were elevated to levels that were probably high enough to cause harm to some individual marine organisms. However, the highest measured TPAH concentration after the Exxon Valdez was approximately 42 ppb, but only 9 out of 1,288 water samples taken during the first few weeks after the spill in 1989 contained more than 10 ppb TPAH (The State of Alaska's water quality standard for total aromatic hydrocarbons). All the samples collected during the large-scale field experiment in the Barents Sea are well below this concentration.

A few laboratory studies related to the Barents Sea have been published recently: Camus and Olsen (2008) exposed sea ice amphipods to WSF (1-55 ppm) for 30 days and observed total embryo aberrations from 4 to 29%. Nahrgang et al. (2010) exposed polar cod to WSF (15 to 40 ppb PAH) for four weeks and observed DNA damage at PAH concentration < 15 ppb. Both Barents Sea-related studies used oil concentrations well above the concentrations measured during the field experiment.

Other large-scale field experiments in ice-infested areas such as NORCOR (1975) performed a few measurements of the dissolved hydrocarbon content during the experiment. Their sampling locations were located just outside the oiled area, and the samples (1 L) were recovered just beneath the ice sheet. They concluded that the oil concentrations measured were low (below 5 ppm), although they were likely higher than the average for the water column.

3.2.2 Dispersant oil release

A 2 m^3 oil slick was dispersed 6 hours after release (Daling et al., 2010). Two hours later, measurements of oil in water were performed at 1, 2 and 3 m depths by the collection of water samples (1 L), online UV fluorescence and the simultaneous monitoring of oil droplet distribution (LISST).

Measurements conducted prior to the addition of mixing energy reveal that the concentrations were slightly above background level (Figure 3.26 and Figure 3.27). Mixing energy was added by ship thrusters, and after 30 min, measurements downstream to the oil slick were performed. The maximum concentration of oil in water was measured at 5.5 ppm (at a 2 m depth) with an oil droplet size smaller than 10 μ m. The oil droplet measurements indicate that effective chemical dispersion did indeed take place. However, after measurements on Station 6, the UVF monitoring indicated background level so no more samples were collected, as the plume had most likely drifted out of reach with the currents. The results are also given in Table C 4 and C 5 in Appendix C.





Figure 3.26 Dispersed oil in water (1 L) sampled during the dispersant experiment, given in ppm (mg/L water).



Figure 3.27 Semi-volatiles in water (1L samples) sampled after mixing of oil and dispersant (given in ppb (µg analyse/L water).

Figure 3.28 shows an example of in situ UVF transects taken under the slick. There is a fairly good correlation between the UVF response and oil concentration in the acquired water samples (yellow dots). The background concentration in the water column measured prior to the release was 0.04-0.06 ppm. After the dispersant treatment but prior to the mixing, the oil concentration at a 1-3 m depth was between 0.3 and 1 ppm. Measurements taken in the dispersed plume a few minutes after the mixing were measured at two different sites: At one site (time 17:04-17:10, see Figure 3.28), the dispersed oil plume concentrations were measured at 1.5-2 ppm (upstream). At the other site (time 17:32-17:40), concentrations of 2-5 ppm were measured (downstream).





Figure 3.28 In situ UVF transects and water samples taken under the $2m^3$ slick on May 19 at 16:20-18:00 local time (Daling et al., 2010).

3.3 Estimating acute toxicity using the hazard index

The acute toxicity to marine organisms of all target decalins, PAHs, phenols and their alkylhomologues was estimated as described in Section 2.8.2. The results are also presented in the tables in Appendix D.

An HI value below 1 indicates that the concentrations in the water are not high enough to possibly represent an acute toxicity to local marine biota. All HI values for water samples and passive samplers are well below a value of 1.0 (ranging from 0.0004 to 0.11), indicating that the acute toxicity is low. The main contributor to the HI in water samples is the group of 2-3 ring PAHs (Figure 3.29 and Table D 1). Among the passive samplers, the decalins contribute most to the HI (Figure 3.30 and Table D 2).

The HI was estimated in the range of 0.01 to 4.8 during the dispersant experiment. Due to the oil droplets, the 4-6 ring PAHs and decalins contributed mainly to the toxicity (Figure 3.31 and Table D 3).





Figure 3.29 Estimated toxicity expressed as hazard index in large-volume water samples (XAD). The hazard index is well below 1 in all samples.



Figure 3.30 Estimated toxicity in passive samplers (SPMDs) expressed as hazard index. The hazard index is well below 1 in all samples.





Figure 3.31 Dispersant experiment: Estimated toxicity expressed as hazard index. The red line indicate HI = 1.



4 Conclusions

Valuable information regarding the interactions between oil, ice and water, and how the presence of ice influences the distribution and spreading of oil on the surface and in the water column have been collected during the large-scale field experiment.

The recordings from the GPS systems on the ice floe, the positions of the ship, aerial surveillance from a helicopter and field observations during sampling have all been used to estimate the spreading of oil in ice and the approximate dimensions of the oil slick. The shift in weather and wind direction on Day 3 resulted in an enhanced spreading of the oil and changes in the ice field and position of the stations. Nonetheless, the oil drifted with the ice and remained contained between the ice floes, thereby enabling continuous experimental work.

Both large-volume water samples and SPMDs have proven effective in concentrating trace levels of organic contaminants from the water column. The chemical monitoring shows low but detectable concentrations above background level in the range between 0.1 to 1.5 ppb dissolved hydrocarbons, 4 to 32 ppb total hydrocarbons from the KISPs and in the range between 0.6 to 4 ppb dissolved hydrocarbons estimated from the SPMDs. The predicted acute toxicity, expressed as the hazard index, for water samples and passive samplers was well below a value of 1.0 (ranging from 0.0004 to 0.11), indicating that acute toxicity was low.

Altogether, the data collected during the field experiment constitutes a dataset for various followup analyses within biological effect, oil-in-water interactions and how the presence of ice affects the drift and spread of oil in high ice coverage.

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Appendix A: Overview of components groups

Overview of component groups used in tables and figures (SVOC: semi-volatile organic compounds, VOC: volatile organic compounds, TPH: Total petroleum hydrocarbons, UCM: unresolved complex mixture).

Group	Compound	Group	Compound
Decalins	Decalin	C0-phenol	Phenol
	C1-decalins	C1-Phenols	2-methylphenol
	C2-decalins		4-methylphenol
	C3-decalins	C2-Phenols	4-ethylphenol
	C4-decalins		2.4-dimethylphenol
Naphthalenes	Naphthalene		3.5-dimethylphenol
1	C1-naphthalenes	C3-Phenols	4n-propylphenol
	C2-naphthalenes		2,4,6-trimethylphenol
	C3-naphthalenes		2,3,5-trimethylphenol
	C4-naphthalenes	C4-Phenols	4n-butylphenol
2-3 ring PAHs	Biphenyl		4-tertbutylphenol
e	Acenaphthylene		4-isopropyl-3-methylphenol
	Acenaphthene	VOC	Isopentane
	Dibenzofuran	(incl BTEX and	n-C5 (Pentane)
	Fluorene	C3-benzenes)	Cyclopentane
	C1-fluorenes	,	2-methylpentane
	C2-fluorenes		3-methylpentane
	C3-fluorenes		n-C6 (Hexane)
	Phenanthrene		Methylcyclopentane
	Anthracene		Cyclohexane
	C1-phenanthrenes/anthracenes		2,3-dimethylpentane
	C2-phenanthrenes/anthracenes		3-methylhexane
	C3-phenanthrenes/anthracenes		n-C7 (Heptane)
	C4-phenanthrenes/anthracenes		Methylcyclohexane
	Dibenzothiophene		2,4-dimethylhexane
	C1-dibenzothiophenes		2-methylheptane
	C2-dibenzothiophenes		n-C8 (Octane)
	C3-dibenzothiophenes		n-C9 (Nonane)
	C4-dibenzothiophenes		n-C10 (Decane)
4-6 ring PAHs	Fluoranthene	BTEX	Benzene
C	Pyrene		Toluene
	C1-fluoranthenes/pyrenes		Ethylbenzene
	C2-fluoranthenes/pyrenes		<i>m</i> -xylene
	C3-fluoranthenes/pyrenes		<i>p</i> -xylene
	Benz[a]anthracene		o-xylene
	Chrysene	C3-benzenes	Propylbenzene
	C1-chrysenes		1-methyl-3-ethylbenzene
	C2-chrysenes		1-methyl-4-ethylbenzene
	C3-chrysenes		1,3,5-Trimethylbenzene
	C4-chrysenes		1-methyl-2-ethylbenzene
	Benzo[b]fluoranthene		1,2,4-trimethylbenzene
	Benzo[k]fluoranthene		1,2,3-trimethylbenzene
	Benzo[e]pyrene		
	Benzo[a]pyrene	ТРН	C10-C36
	Perylene	WAF	Sum of VOC and TPH
	Indeno[1,2,3-c,d]pyrene	UCM	TPH - SVOC
	Dibenz[a,h]anthracene		
	Benzo[g,h,i]perylene		



Appendix B: Input parameters estimated toxicity and sampling rates

Log K_{ow} and estimated toxicity (LC₅₀) of individual components based on the log LC₅₀/log K_{ow} regressions of Neff, 2006 (PAHs) and McCarty et al., 1993 (phenols). Log K_{ow} and R_s (sampling rate, L/day) are from Durell et al. (2006).

	Molecular weight	log K _{ow}	LC_{50} (mg/L)	$R_s(at 1 cm/s)$	R_s (at 17 cm/s)
Decalin	138	4.20	0.57	3.0	6.9
C1-decalins	152	4.60	0.22	3.3	7.6
C2-decalins	166	5.00	0.08	3.5	8.1
C3-decalins	180	5.40	0.03	3.5	8.1
C4-decalins	194	5.80	0.01	3.3	7.6
Naphthalene	128	3.37	4.87	1.9	4.4
C1-naphthalenes	142	3.87	1.42	2.6	6.0
C2-naphthalenes	156	4.37	0.41	3.2	7.4
C3-naphthalenes	170	4.90	0.11	3.5	8.1
C4-naphthalenes	184	5.30	0.04	3.5	8.1
Biphenvl	154	3.90	1.42	2.7	6.2
Acenaphthylene	152	4.00	1.07	2.3	5.3
Acenaphthene	154	3.92	1.34	2.7	6.2
Fluorene	166	4.18	0.72	3.0	6.9
C1-fluorenes	180	4.97	0.09	3.5	8.1
C2-fluorenes	194	5.20	0.06	3.5	8.1
C3-fluorenes	208	5.70	0.02	3.4	7.8
Phenanthrene	178	4.46	0.37	3.8	8.7
Anthracene	178	4.54	0.30	2.9	6.7
C1-phenanthrenes/anthracenes	192	5 14	0.06	3.5	8.1
C2-phenanthrenes/anthracenes	206	5 46	0.03	3.5	8.1
C3-phenanthrenes/anthracenes	220	5 92	0.009	3 3	7.6
C4-phenanthrenes/anthracenes	234	6 32	0.003	2.9	67
Dibenzothiophene	184	4 38	0.47	32	74
C1-dibenzothiophenes	198	4 86	0.14	3.5	8.1
C2-dibenzothiophenes	212	5 50	0.03	3 5	8.1
C3-dibenzothiophenes	226	5 73	0.02	3.4	7.8
C4-dibenzothiophenes	240	6 10	0.006	3.1	7.1
Fluoranthene	202	5 22	0.054	3.6	83
Pyrene	202	5.18	0.061	4.5	10
C1-fluoranthrenes/pyrenes	216	5 50	0.028	3.5	81
C2-fluoranthenes/pyrenes	230	5.80	0.013	3 3	7.6
C3-fluoranthenes/pyrenes	244	6.28	0.004	3.0	69
Benz(a)anthracene	228	5.91	0.010	3 2	74
Chrysene	228	5.61	0.022	3.7	8.5
C1-chrysenes	242	6 14	0.006	31	7.1
C2-chrysenes	256	6.43	0.003	2.8	6.4
C3-chrysenes	270	6.94	0.001	2.1	4.8
C4-chrysenes	284	7.36	0.000	1.3	3.0
Benzo(b)fluoranthene	252	5.80	0.014	2.8	6.4
Benzo(k)fluoranthene	252	6.00	0.008	2.9	67
Benzo(e)pyrene	252	6.44	0.003	2.8	6.4
Benzo(a)pyrene	252	6.04	0.008	3.2	7.4
Pervlene	252	6.25	0.004	3.0	6.9
Indeno(1,2.3-c.d)pyrene	276	7.00	0.001	3.0	6.9
Dibenz(a,h)anthracene	278	6.75	0.001	2.0	4.6
Benzo(g,h,i)pervlene	276	6.63	0.002	1.8	4.1
Phenol	94	1.50	16.3		
C1-Phenols	108	1.98	10.2		
C2-Phenols	122	2.35	7.21		
C3-Phenols	136	2.70	5.16		
C4-Phenols	150	3.31	2.63		

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Appendix C: Chemical characterization of field samples

SINTEF ID	Sample	Vol	TPH	Sum	Naph-	2-3 ring	4-6 ring	C0-C4	Decalins
	description			SVOC	thalenes	PAH	PAH	phenols	
		(L)	$(\mu g/L)$	μg/L	$(\mu g/L)$				
2009-0403	Ref st 1205	200	4.2	0.13	0.005	0.005	0.001	0.10	0.022
2009-0404	Ref st 1205	200	4.5	0.09	0.007	0.005	ND	0.07	0.007
2009-0408	St 2 1605	200	4.9	0.13	0.010	0.008	ND	0.11	0.010
2009-0410	St 2 1805	140	8.2	0.17	0.020	0.023	ND	0.11	0.014
2009-0405	St 3 1505	186	5.2	0.19	0.006	0.021	ND	0.15	0.012
2009-0407	St 3 1605	136	6.0	0.21	0.017	0.010	ND	0.17	0.014
2009-0411	St 3 1805	133	8.5	0.23	0.013	0.013	ND	0.19	0.015
2009-0412	St 3 1905	18	32	1.48	0.056	0.057	0.001	1.30	0.073
2009-0414	St 3 2005	127	10	0.54	0.080	0.038	ND	0.40	0.015
2009-0413	Burn exp	74	13	0.40	0.046	0.020	ND	0.31	0.021
	Labblank XAD	200	3.8	0.07	0.002	0.002	ND	0.06	0.004

Table C 1Total hydrocarbons (TPH from GC/FID) and semi-volatiles in large-volume water
samples (XAD) given in ppb (μ g/L)

Table C 2Total hydrocarbons (from GC/FID) and semi-volatiles in passive samplers (SPMDs) given
in µg analyte/g lipid (no phenols detected)

SINTEF ID	Sample	TPH	Sum SVOC	Naphthalenes	2-3 ring PAH	4-6 ring PAH	Decalins
	description	µg/g	μg/g	µg∕g	µg/g	µg∕g	µg/g
	Ref st 1205	23	4.54	1.24	0.11	0.01	3.19
2009-0427	St 1 Days 0-2	564	58.5	21.6	3.65	0.35	32.9
2009-0430	St 1 Days 0-3	575	34.1	12.1	1.80	0.10	20.2
2009-0428	St 1 Days 0-5	651	52.1	15.4	3.67	0.25	32.8
2009-0429	St 1 Days 0-6	638	48.9	14.7	4.20	0.57	29.4
2009-0431	St 1 Days 3-6	519	14.1	5.45	2.06	0.20	6.41
2009-0425	St 2 Days 0-2	264	11.0	3.58	0.24	0.00	7.15
2009-0426	St 2 Days 0-3	600	81.7	30.8	7.25	0.48	43.2
2009-0423	St 2 Days 0-6	1321	131	41.5	13.3	2.09	74.6
2009-0432	St 2 Days 3-5	356	34.1	8.47	2.63	0.26	22.8
2009-0419	St 3 Days 0-2	395	24.2	8.07	1.59	0.12	14.4
2009-0420	St 3 Days 0-3	443	28.8	9.27	2.17	0.22	17.2
2009-0421	St 3 Days 0-6	205	53.9	14.4	4.28	0.26	34.9
2009-0433	St 3 Days 3-6	561	23.2	7.90	3.66	0.24	11.4
	SPMD Blank	82	4.54	1.24	0.11	0.01	3.19



SINTEF ID	Sample	Sum SVOC	Naphthalenes	2-3 ring PAH	4-6 ring PAH	Decalins
	description	μg/L	μg/L	μg/L	μg/L	μg/L
	Ref station	0.78	0.27	0.02	ND	0.49
2009-0427	St 1 Days 0-2	4.88	2.02	0.30	0.03	2.53
2009-0430	St 1 Days 0-3	1.87	0.72	0.10	ND	1.04
2009-0428	St 1 Days 0-5	1.68	0.54	0.12	0.01	1.01
2009-0429	St 1 Days 0-6	1.31	0.43	0.11	0.01	0.76
2009-0431	St 1 Days 3-6	0.78	0.33	0.11	0.01	0.33
2009-0425	St 2 Days 0-2	0.93	0.36	0.02	ND	0.55
2009-0426B	St 2 Days 0-3	4.50	1.86	0.39	0.03	2.22
2009-0423	St 2 Days 0-6	3.53	1.21	0.35	0.06	1.92
2009-0432	St 2 Days 3-5	2.75	0.76	0.21	0.02	1.76
2009-0419	St 3 Days 0-2	1.99	0.75	0.13	0.01	1.11
2009-0420	St 3 Days 0-3	1.56	0.55	0.12	0.01	0.88
2009-0421	St 3 Days 0-6	1.44	0.42	0.11	0.01	0.90
2009-0433	St 3 Days 3-6	1.26	0.47	0.19	0.01	0.59
SPMD labblank 1		0.07	0.03	ND	ND	0.04
SPMD labblank 2		0.07	0.03	0.01	ND	0.03
SPMD labblank 3		0.07	0.02	ND	ND	0.04

Table C 3Semi-volatiles in passive samplers (SPMDs) given in µg analyte/L water (no phenols
detected)

Table C 4Dispersed oil in water from GC/FID analysis (External calibration Troll crude), sampled
during the dispersant experiment

SINTEF ID	Sample description	L (vol)	mg/L (ppm)	Comments
2009-0274	ref 120509 (3m)	0.98	0.06	Background level Barents Sea
2009-0275	ref 120509 (3m)	0.91	0.07	
2009-0276	ref 120509 (3m)	0.95	0.04	
				Prior to mixing of oil and dispersant
2009-0277A	St 1 - 3m kl 16:27:30	0.91	0.14	
2009-0277B	St 1 - 2m kl 16:29:00	0.93	0.36	
2009-0277C	St 1 - 1m kl 16:31:00	0.98	0.32	
2009-0278A	St 2 - 3m kl 16:40:30	1.04	0.22	
2009-0278B	St 2 - 2m kl 16:37:30	1.00	0.09	
2009-0278C	St 2 - 1m kl 16:28:30	1.02	0.25	
				After mixing of oil and dispersant
2009-0279A	St 3 - 3m kl 17:07:00	1.02	0.45	Upstream
2009-0279B	St 3 - 2m kl 17:08:15	1.06	0.38	
2009-0279C	St 3 - 1m kl 17:09:00	1.05	0.29	
2009-0280A	St 4 - 3m kl 17:26:30	1.12	0.08	Upstream
2009-0280B	St 4 - 2m kl 17:27:15	0.99	0.24	
2009-0280C	St 4 - 1m kl 17:28:15	1.11	0.25	
2009-0281A	St 5 - 3m kl 17:33:05	1.01	4.51	Downstream
2009-0281B	St 5 - 2m kl 17:34:05	1.06	3.89	
2009-0281C	St 5 - 1m kl 17:34:40	1.08	2.26	
2009-0282A	St 6 - 3m kl 17:36:27	1.05	0.09	
2009-0282B	St 6 - 2m kl 17:38:10	1.06	5.50	
2009-0282C	St 6 - 1m kl 17:38:41	0.97	3.53	



SINTEF ID	Sample	Sum SVOC	Naphthalenes	2-3 ring PAH	4-6 ring PAH	C0-C4 phenols	Decalins
	description	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L
	Ref st 3 m	1.00	0.83	0.13	0.005	0.04	ND
2009-0280c	St 4 - 1 m	2.44	1.23	0.58	0.083	0.04	0.50
2009-0280b	St 4 - 2 m	2.67	1.13	0.58	0.075	0.06	0.82
2009-0280a	St 4 - 3 m	0.90	0.47	0.21	0.020	0.03	0.17
2009-0281c	St 5 - 1 m	45.0	16.9	8.38	1.608	0.04	18.1
2009-0281b	St 5 - 2 m	80.9	30.3	16.4	2.982	0.16	31.1
2009-0281a	St 5 - 3 m	104	38.6	19.3	3.945	0.37	42.2
2009-0282c	St 6 - 1 m	77.1	25.8	13.6	2.642	0.77	34.3
2009-0282b	St 6 - 2 m	130	43.9	21.8	4.416	2.54	57.5
2009-0282a	St 6 - 3 m	1.01	0.47	0.33	0.025	0.03	0.16

Table C 5Semi-volatiles in samples from dispersant experiment given in µg analyte/L water

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Appendix D: Estimated toxicity in field samples

SINTEF ID		Decalins	Naphthalenes	2-3 ring PAH	4-6 ring PAH	C0-C4 phenols	Total HI
	Ref st	0.00015	0.00002	0.00010	0.00001	0.00001	0.0003
2009-0408	St 2 Day 2	0.00011	0.00002	0.00025	0.000004	0.00001	0.0004
2009-0410	St 2 Day 4	0.00015	0.00007	0.00092	0.000003	0.00001	0.0012
2009-0405	St 3 Day 1	0.00011	0.00001	0.00033	0.000005	0.00002	0.0005
2009-0407	St 3 Day 2	0.00014	0.00005	0.00035	0.000004	0.00002	0.0006
2009-0411	St 3 Day 4	0.00016	0.00004	0.00057	0.000049	0.00002	0.0008
2009-0412	St 3 Day 5	0.00078	0.00012	0.00192	0.000014	0.00017	0.0030
2009-0414	St 3 Day 6	0.00016	0.00026	0.00089	0.000004	0.00005	0.0014
2009-0413	Burn exp	0.00022	0.00011	0.00046	0.000006	0.00004	0.0008

Table D 1Estimated toxicity in large-volume water samples (XAD) expressed as hazard index

Table D 2Estimated toxicity in passive samplers (SPMDs in $\mu g/L$)) expressed as hazard index (no
phenols detected)

SINITEE ID	Sample	Deceline	Nanhthalanas	2.3 ring DAH	1.6 ring DAH	Total HI
SINTEFID	description	Decalifis	Naphthalenes	2-5 mg FAH	4-0 mig FAn	Total HI
	Ref st	0.015	0.000	0.000	0.0005	0.02
2009-0427	St 1 Days 0-2	0.076	0.006	0.005	0.0029	0.09
2009-0430	St 1 Days 0-3	0.036	0.003	0.001	0.0003	0.04
2009-0428	St 1 Days 0-5	0.030	0.002	0.002	0.0005	0.03
2009-0429	St 1 Days 0-6	0.026	0.002	0.002	0.0013	0.03
2009-0431	St 1 Days 3-6	0.011	0.002	0.003	0.0011	0.02
2009-0425	St 2 Days 0-2	0.016	0.001	0.000	0.0000	0.02
2009-0426	St 2 Days 0-3	0.083	0.007	0.009	0.0016	0.10
2009-0423	St 2 Days 0-6	0.059	0.006	0.009	0.0141	0.09
2009-0432	St 2 Days 3-5	0.074	0.003	0.005	0.0021	0.08
2009-0419	St 3 Days 0-2	0.034	0.003	0.002	0.0006	0.04
2009-0420	St 3 Days 0-3	0.030	0.002	0.002	0.0012	0.03
2009-0421	St 3 Days 0-6	0.033	0.002	0.002	0.0006	0.04
2009-0433	St 3 Days 3-6	0.022	0.002	0.004	0.0013	0.03

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		Decalins	Naphthalenes	2-3 ring PAH	4-6 ring PAH	Total HI
	Ref 3 m	0.000	0.000	0.002	0.000	0.002
2009-0280A	St 4 - 1 m	0.007	0.006	0.022	0.011	0.05
2009-0280B	St 4 - 2 m	0.025	0.005	0.021	0.010	0.06
2009-0280C	St 4 - 3 m	0.001	0.002	0.006	0.001	0.01
2009-0281A	St 5 - 1 m	0.602	0.091	0.347	0.396	1.44
2009-0281B	St 5 - 2 m	0.998	0.165	0.987	0.719	2.87
2009-0281C	St 5 - 3 m	1.334	0.211	0.815	1.440	3.80
2009-0282A	St 6 - 1 m	1.057	0.137	0.743	0.937	2.87
2009-0282B	St 6 - 2 m	1.724	0.242	1.329	1.471	4.77
2009-0282C	St 6 - 3 m	0.001	0.002	0.013	0.002	0.02

Table D 3Estimated toxicity during use of chemical dispersant expressed as hazard index (no
contribution from phenols)

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Appendix E: Chemical and toxicological characterization of laboratory experiments

The laboratory study of Troll fresh oil gives a detailed chemical characterization of the oil in addition to a chemical and toxicological characterization (Microtox[®]) of the water-accommodated fraction (WAF). The WAF represents the water soluble compounds with high bioavailability towards marine organisms and is relevant for both acute oil spills and regular discharges in terms of studying the toxic effect. The WAF can be considered to contain the highest possible concentration of dissolved petroleum hydrocarbons that can be expected from a spill. According to Singer et al. (1996), 1 to 40 is considered to be an unrealistically high oil-to-water ratio. However, the data generated documents a type of "worst case scenario" conditions, in that the solutions used are "saturated" and therefore represent a conservative estimate of concentrations foreseeable in the field and by virtue of the fact that chemically they are dominated by highly volatile components which might be expected to escape rapidly in a real surface water oil spill.

The GC/FID chromatograms of the fresh oil and the WAF are given in Figure E 1 and E 2. Troll crude is a naphthenic oil, which has been biodegraded in the reservoir and has a low paraffin content. A "hump" in the GC-chromatograms for the WAF and the oil can be recognized, which is often denoted as UCM (unresolved complex mixture). The UCM is not characterized, and contains particularly low molecular weight, slightly soluble cyclic alkanes and resins.

The detailed chemical composition of volatiles is given in Table E 1 and semi-volatiles in Table E 2. These data are also used as input to the OSCAR model.

The chemical composition of the WAFs varies from oil type to oil type (Table E 3 and Figure E 4). The "chemical profile" of a WAF and the parent oil is very dissimilar due to different water solubilities of the various oil components, e.g. as illustrated in Figure E 3. Volatile components constitute a major part of the WAF from fresh oils, and the naphthalenes, phenols and the 2-3 ring PAHs are generally the dominating semi-volatile compounds. In addition, the WAFs may contain unresolved compounds. The WAF of Troll is compared with other oils (Table E 3 and Figure E 4) and exhibits a lower level of total WAF than, e.g. Goliat and Statfjord, but is higher than IFO180 and Grane.

The acute toxicity measured by $Microtox^{(e)}$ is reported as EC_{50} (Table E 4). A low EC_{50} indicates a high toxicity. In addition, the acute toxicity is predicted as a hazard index as described in Section 2.8.2 (Table E 4 and Figure E 5). An HI value below 1 indicates that the concentrations in the water are not high enough to possibly represent an acute toxicity to local marine biota.

The Microtox[®] measurements indicate that Troll is a relatively toxic oil compared to the WAFs of other oils in Table E 4. The calculations of predicted toxicity in WAF from Troll result in HI>1, meaning that the WAF may be acutely toxic to marine organisms. The HI indicates that Statfjord and Goliat are more toxic than Troll, while the measured toxicity indicates that Troll is more toxic. However, the part of the UCM content in the total WAF concentration of Troll is higher than in Statfjord and Goliat. The UCM is not characterized, so therefore the UCM and/or other non-analyzed components in the WAFs that are not included in the HI calculations may contribute to toxicity.





Figure E 1 GC chromatogram of Troll crude oil (2009-0702)



Figure E 2 GC chromatogram of Troll WAF 1:40



	Troll crude oil	WAF of Troll
	Fresh	Fresh 1:140
	g/kg oil	μg/L water
Isopentane	2.94	481
n-C5 (Pentane)	0.67	66.7
Cyclopentane	1.22	583
2-methylpentane	2.19	64.7
3-Methylpentane	1.39	52.2
n-C6 (Hexane)	0.35	11.5
Methylcyclopentane	4.77	485
Benzene	0.51	2322
Cyclohexane	8.18	1069
2,3-Dimethylpentane	0.87	5.81
3-methylhexane	1.40	5.77
n-C7 (Heptane)	0.06	3.57
Methylcyclohexane	18.4	449
Toluene	3.12	3484
2-Methylheptane	0.08	ND
n-C8 (Octane)	0.02	0.70
Ethylbenzene	1.79	563
m-Xylene	5.71	1579
p-Xylene	1.79	446
o-Xylene	1.80	600
n-C9 (Nonane)	0.02	0.31
Propylbenzene	0.63	42.0
1-Methyl-3-ethylbenzene	2.02	172
1-Methyl-4-ethylbenzene	0.66	50.6
1,3,5-Trimethylbenzene	1.25	89.8
1-Methyl-2-ethylbenzene	0.67	68.7
1,2,4-Trimethylbenzene	2.66	226
1,2,3-Trimethylbenzene	0.80	86.0
n-C10 (Decane)	0.11	0.23
n-Butylbenzene	0.23	3.34
1,2,4,5-Tetramethylbenzene	0.03	1.01
n-Pentylbenzene	0.12	3.36
C4-Benzenes	2.45	62.0
C5-Benzenes	4.23	9.20
Sum VOC	66.5	13014
Sum BTEX	14 7	8993
Sum DILA	17.7	0775
Sum OSCAR groups		
Benzene	0.51	2322
C1-benzene	3.12	3484
C2-benzenes	11.1	3187
C3-benzenes	8.69	735
C4- and C5-ben	0.38	7.71

Table E 1Composition of volatiles in crude oil and WAF from Troll fresh oil



		T 11 1 1	
		I roll crude oil	WAF of Iroll
		Fresh	Fresh 1:140
		g/kg oil	μg/L water
Decalin	DE	3.06	1.66
C1-decalins	DE1	4.77	0.82
C2-decalins	DE2	4.61	0.43
C3-decalins	DE3	3.37	ND
C4-decalins	DE4	2.40	ND
Naphthalene	Ν	0.97	94.5
C1-naphthalenes	N1	1.91	60.2
C2-naphthalenes	N2	2.37	22.2
C3-naphthalenes	N3	1.66	5.51
C4-naphthalenes	N4	0.99	1.18
Biphenyl	В	0.30	7.17
Acenaphthylene	ANY	0.01	0.05
Acenaphthene	ANA	0.03	0.50
Fluorene	F	0.14	1.92
C1-fluorenes	F1	0.33	1.34
C2-fluorenes	F2	0.47	0.59
C3-fluorenes	F3	0.38	0.21
Phenanthrene	Р	0.23	1.24
Anthracene	А	0.01	0.03
C1-phenanthrenes/anthracenes	P1	0.55	0.93
C2-phenanthrenes/anthracenes	P2	0.60	0.37
C3-phenanthrenes/anthracenes	P3	0.49	0.09
C4-phenanthrenes/anthracenes	P4	0.35	ND
Dibenzothiophene	D	0.03	0.23
C1-dibenzothiophenes	D1	0.10	0.44
C2-dibenzothiophenes	D2	0.15	0.27
C3-dibenzothiophenes	D3	0.12	0.31
C4-dibenzothiophenes	D4	0.07	ND
Fluoranthene	FL	0.01	0.01
Pyrene	PY	0.02	0.01
C1-fluoranthrenes/nyrenes	FI 1	0.14	0.04
C2-fluoranthenes/pyrenes	FI 2	0.17	0.01
C3-fluoranthenes/pyrenes	FL3	0.17	ND
Benz(a)anthracene	RA	0.01	ND
Chrysene	C DA	0.02	ND
Cl-chrysenes		0.02	0.01
C2-chrysenes	C^{1}	0.12	ND
C2 chrysenes	C_2	0.02	ND
C4 chrysenes	C_{1}	0.08	ND
C4-cill yselies Bonzo(b)fluoronthono	DDE	0.05	ND
Benzo(b)fluoranthene		0.01	ND
Benzo(k)nuorantinene	DED	ND 0.01	ND
Benzo(e)pyrene		0.01	ND
Denzo(a)pyrene		0.01	
Indona(1,2,2, a d) mercina		0.01 ND	
Dihong(a, h)orthogoca		ND	
Dibenz(a,n)anthracene		ND	ND
Benzo(g,n,1)perylene	BPE	ND	ND 1.22
Phenol	PH	ND	1.33
CI-Phenois	PHI	0.01	1.24
2-methylphenol		ND	0.66
4-methylphenol		0.01	0.80

Table E 2Composition of semi-volatiles in crude oil and WAF from Troll (SINTEF ID 2009-0702)



		Troll crude oil	WAF of Troll
		Fresh	Fresh 1:140
		g/kg oil	μg/L water
C2-Phenols	PH2	ND	26.4
4-ethylphenol		0.01	0.56
2,4-dimethylphenol		0.07	9.53
3,5-dimethylphenol		0.02	6.22
C3-Phenols	PH3	ND	50.6
4n-propylphenol		ND	0.68
2,4,6-trimethylphenol		ND	0.38
2,3,5-trimethylphenol		ND	7.03
C4-Phenols	PH4	ND	42.3
4n-butylphenol		ND	0.18
4-tertbutylphenol		ND	5.25
4-isopropyl-3-methylphenol		ND	0.90
C5-phenols	PH5	ND	12.1
		21.4	202
Sum SVOC (excl phenols)		31.4	202
Naphthalenes		/.91	184 15.7
4-6 ring PAH		0.89	0.09
C0-C4 phenols (single comp)		0.11	33.5
C0-C4 phenols (tot ion chrom)		0.16	122
Decalins		18.2	2.91
Sum OSCAR groups			
Napht-1		2.89	155
Napht-2		4.03	27.7
PAH-1		2.75	15.0
PAH-2		3.53	1.94
C0-C4 phenols		0.16	122

ND: Not detected (<0.01 ppb)





Figure E 3 Composition of semi-volatiles in Troll fresh oil (Fig. A) and WAF from Troll (Fig. B)

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Table E 3Chemical composition (in mg/L water) of WAF from Troll crude compared to other oils.Fresh oil and an oil-to-water ratio of 1:40 are used. The component groups are describedin Appendix A.

Oil type	BTEX	C ₃ - benzenes	Naph- thalenes	2-3 ring PAH	4-6 ring PAH	C ₀ -C ₄ phenols	WAF	TPH	UCM
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Troll	8.99	0.73	0.18	0.02	0.0001	0.122	15.5	2.53	2.20
Goliat	27.4	0.77	0.27	0.05	0.0005	0.167	37.5	5.58	5.10
Statfjord	31.0	0.67	0.15	0.01	0.0001	0.518	38.8	1.79	1.11
Heidrun Åre	1.36	0.20	0.16	0.02	ND	0.107	17.5	14.8	14.5
Grane	2.19	0.16	0.10	0.01	0.0001	0.010	4.45	1.30	1.18
IFO180	0.24	0.13	0.04	0.01	0.0001	0.147	1.31	0.87	0.66

ND: Not detected at <0.0001 ppm

Table E 4	Predicted hazard index (HI) and measured acute toxicity by Microtox [®] in WAFs. HIs are
	the sum of the hazard quotients (concentration in 100% WAF/estimated acute lethal
	concentration) for each analyte type. The component groups are described in Appendix A

		C3-	Naph-	2-3 ring	4-6 ring	C_0-C_4		HI excl	EC50
	BTEX	benzenes	thalenes	PAH	PAH	phenols	Total HI	MAH	%
Troll	0.646	0.275	0.197	0.121	0.005	0.035	1.29	0.37	4
Goliat	1.156	0.235	0.312	0.323	0.006	0.044	2.08	0.69	11
Statfjord	1.378	0.250	0.176	0.091	0.005	0.114	2.02	0.39	5
Heidrun Åre	0.089	0.078	0.210	0.227	0.004	0.020	0.63	0.46	9
Grane	0.131	0.068	0.132	0.086	0.002	0.005	0.42	0.22	10
IFO180	0.025	0.048	0.083	0.106	0.008	0.037	0.31	0.23	22

NM: Not measured





Figure E 4 Chemical composition of WAFs from fresh oils shown by selected component groups. The oil-to-water ratio was 1:40 for all oils.



Figure E 5 Estimated toxicity expressed as hazard index of WAFs from fresh oils. The oil-to-water ratio was 1:40 for all systems. The component groups are described in Appendix A. The red line indicates HI=1.



Appendix F: Input to OSCAR

The composition of Troll B fresh oil used as input to the OSCAR model is given in Table F1, and is a combination of experimental data and crude assay.

Group no **Group abbreviations** % distribution 1 C1-C4 gasses (dissolved in oil) 0.00 2 C5-saturates (n-/iso-/cyclo) 0.90 3 C6-saturates (n-/iso-/cyclo) 0.75 4 Benzene 0.05 5 C7-saturates (n-/iso-/cyclo) 1.50 6 C1-Benzene (Toluene) et. B 0.31 7 C8-saturates (n-/iso-/cyclo) 3.29 8 C2-Benzene (xylenes using O-xylene) 1.11 9 C9-saturates (n-/iso-/cyclo) 1.32 10 C3-Benzenes 0.87 11 C10-saturates (n-/iso-/cyclo) 2.70 12 C4 and C4 Benzenes 0.04 13 C11-C12 (total sat + aro) 4.55 14 Phenols (C0-C4 alkylated) 0.02 15 Naphthalenes 1 (C0-C1-alkylated) 0.29 16 C13-C14 (total sat + aro) 8.11 17 Unresolved Chromatographic Materials (UCM: C10 to C36) 000 0.00 37 metabolite 1 0.00 38 metabolite 2 0.00 18 Naphthalenes 2 (C2-C3-alkylated) 0.40 19 C15-C16 (total sat + aro) 7.40 20 PAH 1 (Medium soluble polyaromatic hydrocarbons (3 rings-non-alkylated <4 rings) 0.27 21 C17-C18 (total sat + aro) 7.43 22 C19-C20 (total sat + aro) 6.60 23 C21-C25 (total sat + aro) 7.55 24 PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated 4-5+ rings) 0.35 25 C25+ (total) 44.2

Table F1Input to OSCAR: Composition of Troll B fresh (2009-0702)



Appendix G: Initial OSCAR simulations

The Oil Spill Contingency and Response (OSCAR) model, which has been developed at SINTEF, is a tool for quantifying the drift and spreading of an oil slick, the environmental consequences of oil spills and the effectiveness of various response methods. OSCAR includes an oil weathering model, an oil spill combat model, and a three-dimensional oil trajectory and chemical fates model (Reed et al., 1995 and 2001).

The OSCAR simulations are a part of WP5 in the Petromaks project and will be presented in a separate report by the end of 2010. Initial OSCAR simulations have been performed using the MetOcean data from the field experiment as input as well as the crude oil composition given in Appendix F. Some of the preliminary predictions, both with ice and open water, are shown in Figure G 1 to G 6.

The input parameters to the OSCAR model are given in Table G 1. The current and wind field used were measured during the field work by the RDCP current profiler and by the Lance, respectively. It has been assumed that both the current and wind are uniform in the model area.

Input parameter	Input
Release position	77.928° N, 30.960° E
Start of simulation	2009-05-15 08:00 (NST)
Simulation time	5 days
Release start	2009-05-15 08:30 (NST)
Oil type	Troll B Crude
Released amount	7 m^3
Current	Profile measured by the RDCP
Wind	Measured by Lance
Wind drift rate	3.0 %
Ice cover	80-90 %

Table G 1Input parameter to the OSCAR model

The simulation with 80 - 90% ice coverage shows that the oil slick stayed together during the entire simulation period, (see Figure G 1 and G 3). Figure G 1 also shows that the oil slick spread somewhat during this period, which is in agreement with the observations made during the field experiment. When comparing the drift of the oil slick with the ice drift shown in Figure 3.5, it can be seen that there is a good resemblance between the simulation and the observations. The path of the oil slick in the simulation is similar to the ice drift from the GPS data, although the direction in the simulation is skewed approximately 15° left of the observed path. The oil slick changed direction at approximately the same time as the observed ice drift.

The simulation with no ice cover shows that when the wind started to increase in the evening of May 16, the oil slick broke apart and spread over a large area (Figure G 2). Much of the oil was then mixed down into the water column (Figure G 4). This is also illustrated by Figure G 5 and G 6, which show the mass balance of the oil during the simulation period for 80 - 90% ice cover and no ice, respectively. It can be seen from Figure G 5 that nearly all the oil remains on the surface when there is an 80 - 90% ice cover.





Figure G 1 Preliminary predictions of surface oil spreading in 80 – 90% ice coverage, given as overall maximum surface oil thickness





Figure G 2 Preliminary predictions of surface oil spreading in open water (no ice), given as overall maximum surface oil thickness





Figure G 3 Preliminary predictions of oil concentration in water in 80 – 90% ice coverage, given as maximum total concentration





Figure G 4 Preliminary predictions of oil concentrations in open water (no ice present), given as overall maximum total concentration




Figure G 5 Preliminary mass balance of oil in 80 – 90% ice coverage



Figure G 6 Preliminary mass balance of oil without ice cover