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Report

Potential oil product leakages from World War II shipwrecks

Assessment of possible environmental risk

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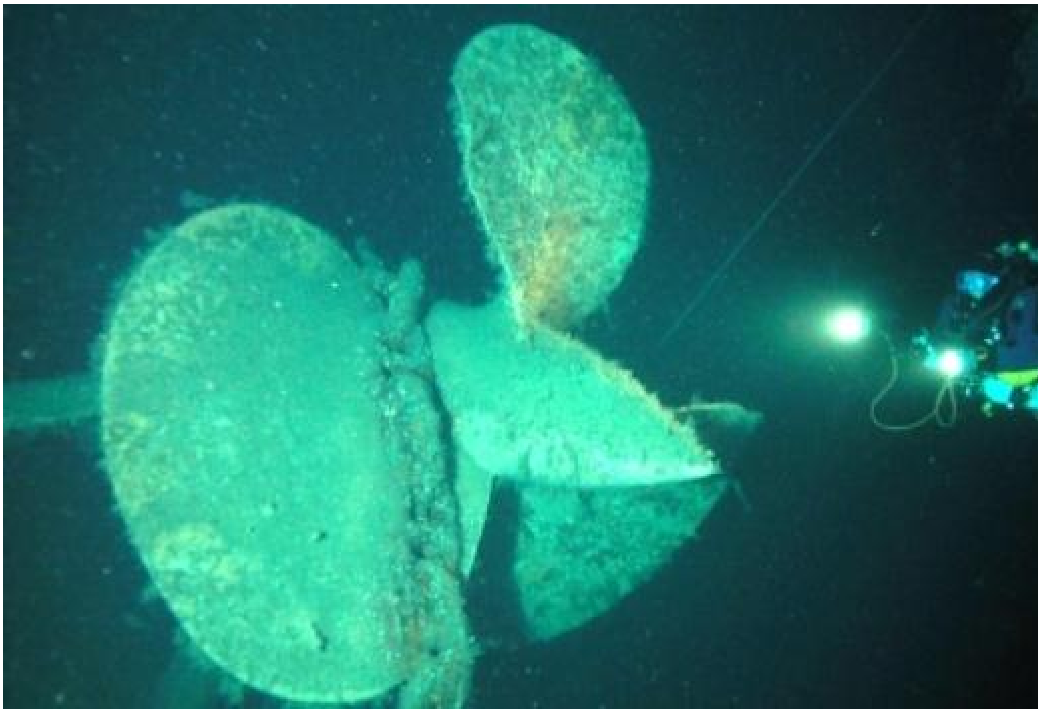

SINTEF Materials and Chemistry
Environmental Technology
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ABSTRACT

The water accommodated fractions (WAFs) of oils from the British sloop HMS "Bittern", the British carrier tanker RFA "Boardale", the German destroyer "Erich Giese", and the German cargo ship MS "Nordvard" have been studied with special emphasis on chemistry and toxicity. A limited study of the weathering properties of three of these oils (not "Nordvard") was also performed to predict the behaviour of oil at sea in order to optimize the effectiveness of potential response operations.

The results from toxicity studies show that the more "synthetic" oils from German WWII shipwrecks "Erich Giese" and "Nordvard" seem to have higher toxicity to marine organisms than the "mineral" oils from the British shipwrecks "Bittern" and Boardale".

There will be no risk for fire hazard during a response operation (flash points >60°C for all oils). Solidification on the sea surface is not expected for any of the oils. A use of weir skimmer could be an option for oil spill recovery for "Erich Giese" and "Boardale", but reduced efficiency is expected for "Bittern" under certain winter conditions. Boom leakage is expected for "Erich Giese" due to low emulsion viscosities. There is a potential for use of dispersants for all three oils in a spill operation.

This has become the basic methodology for assessment on of the potential environmental risk of oil leakage from shipwrecks, and has given valuable input to the decision maker's recommendations of how to deal with the shipwrecks. It has resulted in an altering of the priority list for future oil recovery from WWII wrecks due to the potential for higher impact on the marine environment of coal based oils.

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1 Introduction

In the 1990s, Norwegian Authorities registered more than 2000 shipwrecks along the Norwegian coast, and about 80% of these were classified as likely to pose no environmental risk (Idaas, 1995). However, about 30 wrecks, all of them from the World War II (WWII) era, were classified to have considerable pollution risk (Figure 1.1). The potential environmental risk posed by a wreck depends on where the vessel sits, the types and amount of fuel on board, and the local environment. Priorities for emptying the wrecks for fuel was established, and the oil has now been removed from eight of the wrecks, see Figure 1.1.

Figure 1.1 *Location of shipwrecks that were classified to have considerable pollution risk to the environment. The oil has been removed from the wrecks marked with a red circle. Map from NCA.*

The water accommodated fractions (WAFs) of oils from four of the WWII shipwrecks have been studied with special emphasis on chemistry and biological effects (algal growth (*Skeletonema costatum*) and copepod mortality (*Calanus finmarchicus*)). WAF is of special interest because components dissolved from an oil slick or from rising oil droplets in the water column are known to be bioavailable to marine organisms and therefore have a potential for causing toxic acute effects.

The oils studied were from the British sloop HMS "Bittern", the British carrier tanker RFA "Boardale", the German destroyer "Erich Giese", and the German cargo ship MS "Nordvard". The oils from the British shipwrecks seem to be bunker oils (IFO 20-30), the oil from "Nordvard" was probably a blend of synthetic and natural diesel, while "Erich Giese" carried lignite oil (possibly produced through coal hydrogenation). Pictures of the ships are shown in Figure 1.2. In addition, chemical analyses of the oils from the German cargo ship MS "Welheim", the German heavy cruiser "Blücher", and the German submarine "U-864", were performed.

Completion of recovery of oils from three of the wrecks were performed in 2011-2012; all of them sank during April, 1940: HMS "Bittern" after a German air strike near Namsos, RFA "Boardale" grounded and sank outside Vesterålen, and "Erich Giese" during strike with British forces outside Narvik. The recoveries from these three shipwrecks are documented in Framo (2012). In 2007 the oil was removed from M/S "Nordvard", which sank after a British air strike in December in 1944 in the Oslo fjord, and MS "Welheim", which was sunken by a Norwegian MTB outside Florø in 1944. The oil from "U-864" was removed in March 2013, but it still contains 67 tons of metallic mercury. "U864" was detected and sunk by a British submarine in February 1945 outside Fedje. The cruiser "Blücher" was hit by land based batteries, caught fire, and sank in the Oslo Fjord in April 1940. Most of the oil was removed in 1994.

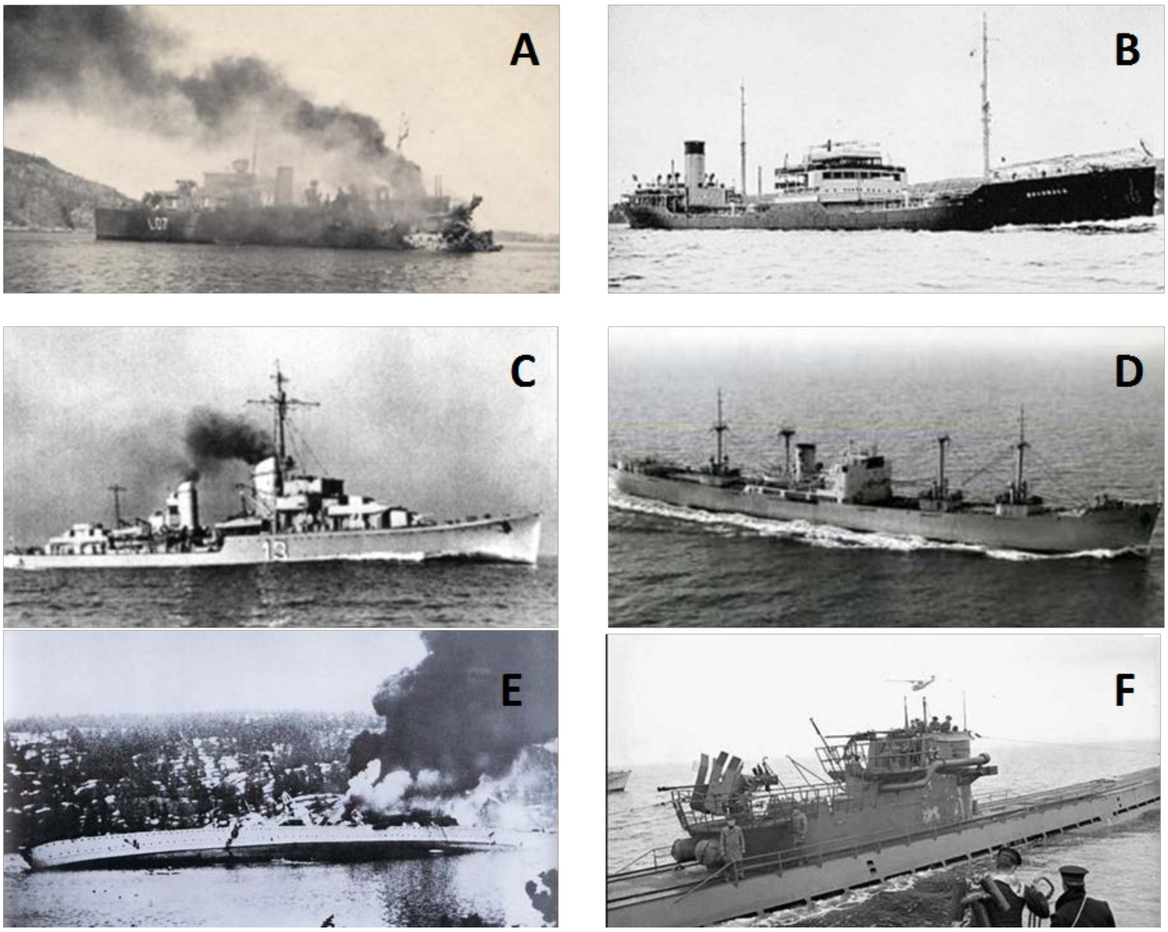

Figure 1.2 *The ships studied: HMS "Bittern" (A), RFA "Boardale" (B), "Erich Giese" (C), m/s Nordvard (D), Blücher (E), and the submarine "U-864). Photos from NCA (no photos of "Welheim" available).*

A limited study of the weathering properties and spreading of the oils is also performed. The data from this laboratory study has been used to as input to the SINTEF Oil Weathering Model to predict the behaviour of the oils at sea at different weathering conditions, and to optimize the effectiveness of potential response operations/countermeasures.

The project will give valuable input to the decision maker's recommendations of how to deal with old shipwrecks containing oil, and it may form a basic "standardized" methodology for assessment of the potential environmental risk of oil leakage from shipwrecks.

Methodology and results have been presented at three international conferences and are published in the Marine Pollution Bulletin. Abstracts and papers are given in Attachment G.

2 Materials and methods

2.1 Oils received

The oils studied were from the British sloop HMS "Bittern", the British carrier tanker RFA "Boardale", the German destroyer "Erich Giese", the German cargo ships MS "Nordvard" and "Welheim" (just chemistry), the German submarine "U-864" (just chemistry), and the German heavy cruiser "Blücher". The oils from the British shipwrecks seem to be classic bunker oils (in the categorization of IFO 20-30), the oils from "Nordvard", "Welheim", and "U-864" were probably a blend of synthetic and natural diesel, while "Erich Giese" and "Blücher" carried lignite oil (possibly produced through coal hydrogenation). More information about German WWII oils can be found in US Naval Technical Reports (1945a and 1945b). Sample description and SINTEF ID are given in Table 2.1.

Table 2.1 Sample description and SINTEF ID (Ger: German; UK: British)

SINTEF ID	Shipwreck	Oil recovered*	Oil received	Comments
2012-0337	Erich Giese (Ger)	189 tons oil and water, and 200 tons emulsion	Approx 20 L mixture of oil and water, but mostly water	Approx 3 L heavy fuel and diesel (brown coal oil)
2012-0338	HMS Bittern (UK)	89 tons oil	3 L oil and water	Approx 2.6 L heavy fuel oil
2012-0339	RFA Boardale (UK)	201 tons oil and water	Approx 20 L mixture of oil and water	Approx 10 L medium bunker oil
2013-0525	U-864 (Ger)	1 ton oil and 4 tons water	Water with oil (3 x 100 mL)	Mostly water, only oil to chemical characterization
2013-0553	Nordvard (Ger)	434 tons oil and 53 tons water	Three small bottles (approx. 100 mL each)	Stored at room temperature since sampling
2013-0719	Blücher (Ger)	1000 tons of oil and 600 tons of contaminated water	Three small bottles (approx. 100 mL each)	Probably stored at room temperature since sampling
2013-0720	Welheim (Ger)	96 tons of oil and 41 tons water	Three small bottles (approx. 100 mL each)	Probably stored at room temperature since sampling

**Information from the Norwegian Coastal Administration*

2.2 WAF preparation

Preparation of low energy WAF (LE-WAF) has been performed under controlled conditions following the guidelines established by the Chemical Response to Oil Spills: Ecological Research Forum (CROSERF). These guidelines were developed to standardize WAF preparation, laboratory exposures to aquatic organisms, and analytical chemistry measurements used to determine the acute toxicity of the water soluble components in the oil (Aurand and Coelho, 1996). LE-WAF can be defined as a water solution of dissolved oil components prepared in closed vessels, as shown in Figure 2.1, with calm mixing of oil and water without the formation of any vortex. LE-WAFs were chosen in order to avoid generation of oil droplets.

The WAFs were prepared with the oil-to-water loadings of 1 to 40 (25 g oil/L water) and 1 to 10000 (100 mg oil/L water), and are described in Table 2.2 and shown in Figure 2.2. These different WAFs illustrate "snapshots" in the dynamic process of dissolution occurring during a spill situation. The oil-to-water ratio of 1:40 is assumed to be "saturated" and therefore represents a "conservative" estimate of the concentrations foreseeable during an oil spill. An oil-to-water ratio of 1 to 10000 is considered to be a more realistic concentration found in the upper surface layer a short time after treatment with chemical dispersants. The WAFs were generated with a contact time between water and oil for four days before the water was collected for chemical characterization and toxicity tests. Samples for analyses of organic compounds were sampled in glass bottles, and sampling for metal analysis in special prepared plastic vials.

Table 2.2 WAF systems with exposure temperatures, oil-to-water ratio, and analyses.

	Temp (°C)	Oil-to-water	Chemistry	*C. finmarchicus*	*S. costatum*
Bittern	13	1:40	X	X	X
Bittern	13	1:10 000	X	X	X
Boardale	13	1:40	X	X	X
Boardale	13	1:10 000	X	X	X
Erich Giese	13	1:40	X	X	X
Erich Giese	13	1:10 000	X	X	X
Nordvard	13	1:40	X	X	X
Nordvard	13	1:10 000	X	X	X

In the WAFs prepared with oil from "Erich Giese", the water phase turned pinkish after a few hours (see Figure 2.1). This oil has characteristics of a lignite oil, most likely prepared from brown coal. However, the chemical analysis indicated that there were no visible oil droplets in the water, so it was assumed that the pinkish colour resulted from other water soluble components in the oil.

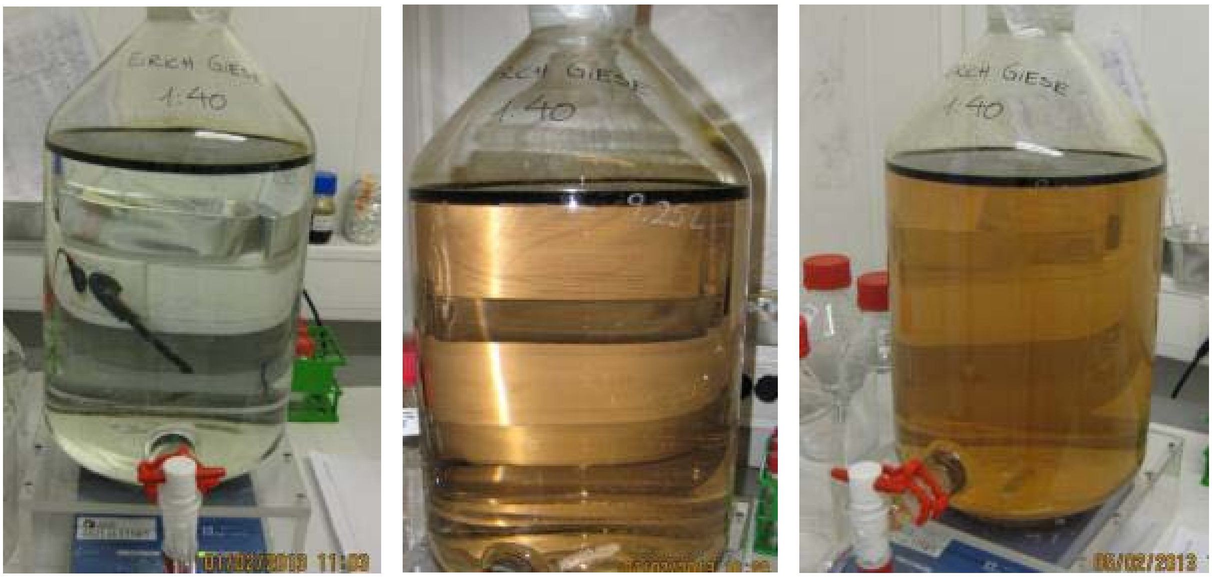

Figure 2.1 WAF of Erich Giese, oil to water ratio of 1 to 40: Immediately after oil application (left photo), after 5.5 hours (middle photo), and after 4 days,

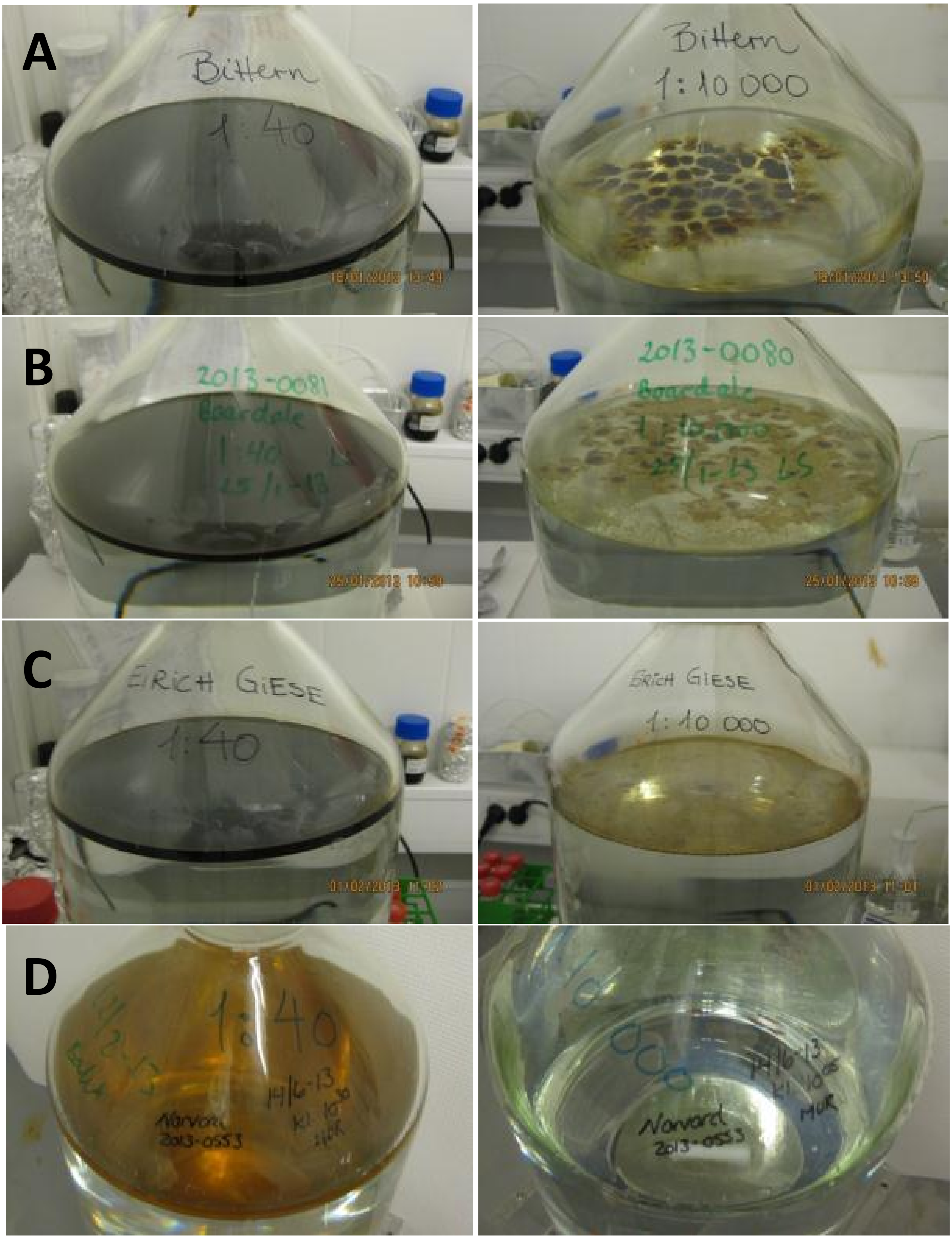

Figure 2.2 *WAF systems with an oil-to-water ratio of 1:40 (left photo) and 1:10000 (right photo): Bittern (A), Boardale (B), Erich Giese (C), and Nordvard (D).*

2.3 Sample preparation

2.3.1 Organic compounds

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

For analyses of semi-volatile organic compounds (SVOC) and total petroleum hydrocarbons (TPH), the water samples were spiked with the appropriate surrogate internal standards and serially extracted with dichloromethane (DCM), thereby following a modification of EPA method 3510C (US EPA, 1996). The combined extracts were dried with sodium sulphate 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. The components quantified are given in Appendix C (Table C 1).

2.3.2 Chemical elements

The oils (approximately 200 mg) were added 50% v/v HNO_3 (6 mL). Digestion of the samples was performed using a high-pressure microwave system according to a temperature profile which increased from room temperature up to 250 °C within one hour. After cooling to room temperature, the digested samples were diluted with ultrapure water to 60 mL to archive a final HNO_3 concentration of 0.6 M. The water samples were diluted 10x and acidified with HNO_3 (0.1 M) prior to analyses.

2.4 Chemical analyses, organic compounds

The samples were analyzed for SVOC (decalins, PAHs and phenols) using GC/MS, for TPH using GC/FID, and for volatile organic compounds (VOC, C_5-C_9), including BTEX (benzene, toluene, ethylbenzene, and xylenes), by use of P&T GC/MS (Purge and Trap Gas Chromatography Mass Spectrometry). A list of all target analytes is shown in Appendix C (Table C 1). This list includes the recommended analytes given by Singer et al. (2000), and is a typical standard list for the target compounds used during post-oil spill damage assessments.

The GC/FID analyses were performed according to a modification of EPA Method 8015D (US EPA, 2003). 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.

The semi-volatiles were quantified by modifications of EPA Method 8270D (US EPA, 2007). The mass spectrometer was operated in the selective ion monitoring mode to achieve 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 total of 35 target volatile analytes in the C_5 to C_{10} range were determined by P&T GC/MS 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 RFs of the individual compounds relative to the internal standards. All standards and samples were analysed in a full scan mode.

2.5 Analysis of metals

All samples were analysed on a high resolution inductivity coupled plasma mass spectrometry (HR-ICP-MS). Each individual sample was scanned three times, and an average value with relative standard deviation was calculated. The instrument was calibrated using a five level solution of multi-element standards in HNO_3. The samples were not added internal standards, but quantified toward the external calibration standards. A list of the selected elements is given in Appendix C (Table C2).

2.6 Acute toxicity of the WAFs

Crude oil is a complex, highly variable mixture of hydrocarbons and other trace components. Exposure may cause a variety of adverse effects, including narcosis, slowed growth, reduced reproduction, and death in marine organisms. Toxicity is the "inherent potential or capacity of a material (e.g. oil) to cause adverse effects in living organisms" (US EPA, 2002). In order to be toxic, oil components must be bio-available to the organisms being exposed. Many of the components in oil are considered toxic to marine organisms, but have limited bio-availability in the environment due to their low solubility. Toxic effects depend on the duration of exposure and the concentration of the chemicals involved. Toxic effects can be lethal (causing death) and sub-lethal (e.g. disorientation, reduced growth and reproduction). Toxic effects can also be acute (caused by short-term exposure, such as following an acute oil spill) or chronic (caused by long-term exposure, such as release of produced water). The toxicity of a chemical is normally quantified as an LC50 or EC50 value, defined as the concentration causing 50% of the organisms in a test population to die or to show a significant negative effect when they are exposed to a fixed concentration of the chemical for a defined time period (Rand et al., 1995).

2.6.1 Growth inhibition to the algae *Skeletonema costatum*

A fixed dilution scheme with a spacing factor of 1.6 between concentrations, from undiluted WAF (100%) to 3% WAF in seawater, was used. A re-test of Erich Giese (1:40) was performed, using a dilution from 5.04% WAF to 0.15% WAF. Furthermore, the experimental design included eight different concentrations in seawater with six parallel tubes in each concentration.

Before onset of exposure, the necessary volume of inoculums of exponentially growing *S. costatum* was determined by adding a 20 µL suspension of algae to a culture tube filled with seawater and then reading the in vivo fluorescence in a Turner TD700 fluorometer (Turner Systems, Sunnyvale, CA, USA). As a final step in the preparation of the exposure solutions, all tubes were inoculated with the algae/nutrient mix and filled to a headspace of 0.5 mL. As a control, 12 tubes in each bioassay were filled with autoclaved seawater and inoculated with the algae/nutrient mix in the same manner. In vivo fluorescence was measured after preparation and then the tubes were placed horizontally on a rocking shaker. The shaker was set to an appropriate speed to ensure the air bubbles in the tubes travelled horizontally from top to bottom before the shaker returned to avoid any stratification and gradient in the nutrient supply to the algae. The shaker was placed in a temperature controlled room at nominally 20±2°C under a mixture of white (Philips TLD 965 18W) and pale yellow (Philips TL20W/33RS) fluorescent tubes.

During the test period of 72 hours, in vivo fluorescence was measured daily by inserting the individual tubes into the fluorometer after gently mixing to ensure a homogenous solution. At the end of exposure, pH was measured in a pooled sample from three control series tubes as well as from the exposure series.

Please note that the calculated values are normalized by setting the response in the control series to 100% for both growth rate and biomass production and then calculating the effect within the span 0 to 100%. The constrainment of the concentration-effect curve to 100 and 0 is eliminating any stimulatory effects of the exposure in calculation of the EC-values.

2.6.2 Acute toxicity to *Calanus finmarchicus*

Potential effects on primary consumers were assessed with the marine copepod *Calanus finmarchicus*.

The acute toxicity testing of *C. finmarchicus* was performed according to ISO 14669:1999 (ISO, 1999), with modifications described in Hansen et al. (2011). Briefly, the WAF samples were diluted in a series of seven concentrations, covering the range from undiluted to 4% WAF in seawater. A re-test of Erich Giese (1:40) was performed using dilutions from 15.1% WAF to 0.62% WAF. Glass bottles (0.5 L) with Teflon lined screw caps were used as the exposure vessels. Each exposure concentration was done in triplicate, and six groups were used as controls containing seawater only. The exposure vessels were filled close to the rim to keep evaporative loss to a minimum during exposure, and each vessel was stocked with seven copepodites V of *C. finmarchicus*. Mortality was monitored at 24, 48, 72, and 96 hours. The temperature was monitored throughout the exposure, and the saturation of oxygen and pH in each dilution was measured at the end of the exposure. The test animals were not fed during exposure.

Please note that the calculated values are not corrected for any mortality in the control series and the effect is calculated within the span 0-100% effect by constraining the top and bottom of the concentration-effect curve to 100 and 0.

2.6.3 Predicted toxicity using toxic units

In the WAFs from petrogenic products, the compounds of concern for toxicity assessment are typically limited to the VOCs and SVOCs, which are structurally classified as Type I narcotics. The target lipid model of narcotic toxicity demonstrates that the acute toxicities of these chemicals vary and are correlated with the octanol-water partition coefficient (K_{ow}) such that LC50 decreases with increasing K_{ow} (DiToro et al., 2007). A toxic unit (TU) for the individual compounds is computed by dividing the measured concentration in the WAF by the compound's water effect concentration using regression models. It appears to be a linear negative relation between log LC50 of the marine organisms and log Kow of the components that may cause toxic effects (McCarty et al. (1992; 1993) and Di Toro et al. (2007)):

$$\log LC50 = m \log (K_{ow}) + b \qquad (1)$$

The slope (m), log K_{ow}, and the intercept (b) for different component groups (e.g MAH, PAH and phenols) are given in McCarty (1993) and Neff et al. (2000). The LC50 (mg/L) is calculated for each component by use of equation (1).

In the WAFs, the TUs of the individual components are summed to compute the total TUs of the WAF. If the sum of the TUs is less than 1 (TU<1), observed effects should be lower than as defined by the water effect concentration (e.g. 50% lethality if using the LC50). If the sum of the TUs in the WAF is greater than 1 (TU>1), adverse effects could potentially be observed.

2.7 Limited study of the weathering properties and oil spreading test

A limited study of the weathering properties was conducted for the 3 shipwreck oils. The standardized weathering procedure for artificial evaporation of oils into their corresponding residues (150°C +, 200°C+, 250°C+) was not possible due to the high level of water in the oils. Therefore, the physical and chemical parameters, and some limited weathering parameters were conducted on the fresh oils only.

2.7.1 Physical and chemical analysis

The physical properties (viscosity, density, pour point and flash point) were determined on the fresh oil. The analytical methods used are given in Table 2.3. The chemical properties were determined using the analytical methods given in Table 2.4.

Table 2.3 Analytical methods used to determine the physical properties

Physical property	Analytical method	Instrument
Viscosity	McDonagh and Hokstad, 1995	Physica MCR 300
Density	ASTM method D4052-81	Anton Paar, DMA 4500
Pour point	ASTM method D97	-
Flash point	ASTM D 56-82	Pensky-Martens, PMP1, SUR
Water content	Titration method	Karl Fisher

Table 2.4 Analytical methods used to determine the chemical properties

Chemical property	Analytical method
Wax content	Bridiè *et al.*, 1980
"Hard" asphaltene	IP 143/90
Gas Chromatography (GC) Hydrocarbon distribution nC_{10}-nC_{40}	GC with Flame Ionization Detector (FID) and fused silica capillary column (30 m × 0.32 mm ID × 0.25 µm film thickness).

2.7.2 Emulsification testing

The w/o-emulsification testing of the shipwreck oils was performed by the rotating cylinders method, developed by Mackay and Zagorski, 1982. The method is described in detail by Hokstad *et al.*, 1993. The principle of the rotating cylinder is illustrated in Figure 2.3. Oil (30 mL) and seawater (300 mL) are rotated (30 rpm.) in separating cylinders (0.5 L). The emulsification kinetics was mapped by measuring the water content at fixed rotation times. The maximum water content was determined after 24 hours rotation. Testing of the emulsifying properties was conducted at 13°C.

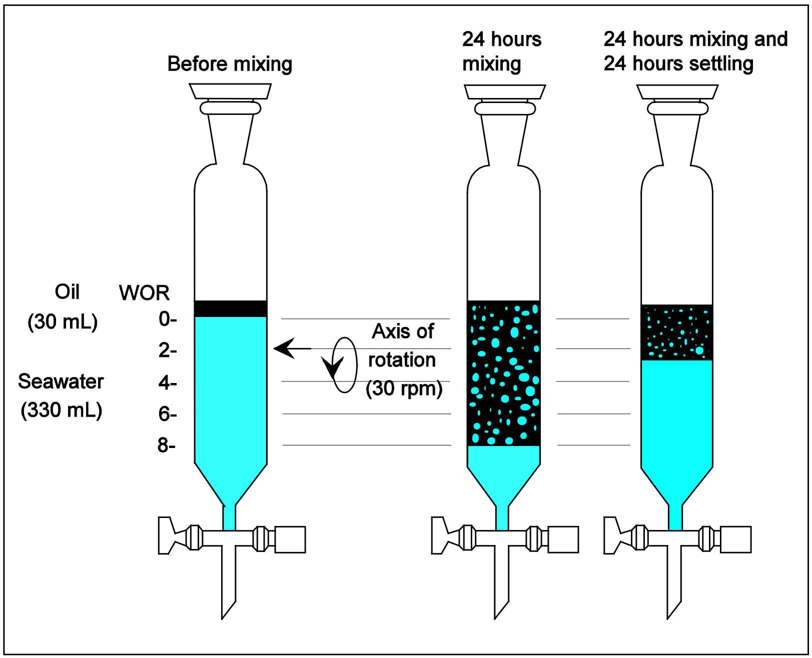

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Figure 2.3: Principle of the rotating cylinder method.

2.7.3 FET - Field Efficacy Test

The 3 shipwreck oils were analysed for their dispersibility by use of a simple Field Efficacy Test (FET). Approximately 1.5 ml of the oil was added carefully to a cylinder (100 ml) pre-filled with 80 ml sea water. The dispersant agent (Corexit 9500) was added drop-wise onto the oil surface. After a contact time between the oil and dispersant of 1 minute, the cylinder was turned up side down for 1 minute with a rotation time corresponding to 30 rpm. A cylinder with sea water and oil with no added dispersant was used as a reference for each test, and the oils dispersibility were visually evaluated.

The following criteria were used for the evaluation of dispersibility:

1. **Good dispersibility:** Formation of brownish dispersion (small oil droplets). A slowly settling of small oil droplets to the surface.
2. **Reduced dispersibility:** Formation of dark /blackish larger oil droplets. Amore rapid settling of oil droplets toward the surface compared with criteria of good dispersibility.
3. **Not dispersible:** No or minor difference compared with the untreated oil (reference). Very rapid settling of large oil droplet to the surface.

2.7.4 Oil spreading test

The oil spreading test simulates the spreading properties on the surface for small leakage of oil. The oil spreading test was conducted at 13°C for the 3 shipwreck oils to simulate both a surface and subsurface leakage.

Experimental setup

A glass vessel was filled with 15 liters of sea water (13°C). A camera (contour) was placed on the top side and in front of the vessel to record the tests. Figure 2.4 illustrates the experimental setup for a subsurface release. The oil droplets were released from an applicator system toward the surface. The applicator system consists of a 2 mm syringe tip (5 mm D) connected to a tube. The applicator system was weighted before and after adding the oil to the system. The tube and the syringe was filled with oil and placed on the bottom of the vessel as shown in Figure 2.4. The oil was released from the syringe in controlled droplets, and the amount of oil droplets was counted and the droplet diameter was estimated.

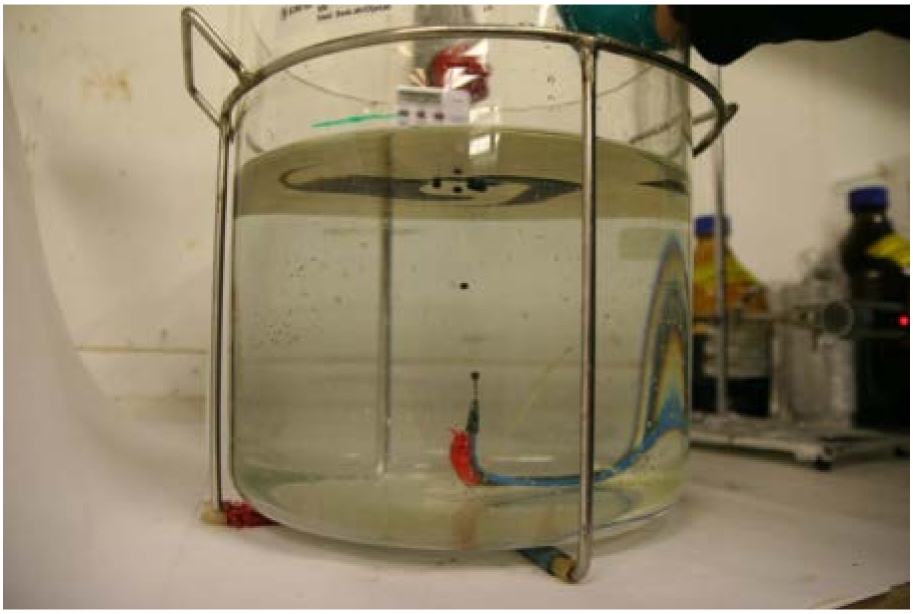

Figure 2.4 Example of experimental setup of oil leakage (subsurface release)

Dimensions of the vessel:
Upper diameter: 28.8 cm
Lower diameter: 26.4 cm
Diameter surface: 28 cm
Water height: 19.5 cm

Calculation of oil film thickness:
Oil film thickness = Volume (cm^3) */ Area* (cm^2)

Volume = weight of oil / density (g/cm^3)
Area of the total slick was calculated based on the video observation and the data program tool (ImageJ).

3 Results and discussions

3.1 Chemical composition of the oils and the WAFs

Seven oils from WW2 shipwrecks have been studied, and the chemistry and toxicity of the water accommodated fraction for four of them have been characterized. Note that a new batch of oil from "Erich Giese" was analyzed in accordance with re-testing of the toxicity of one of the WAFs. Chemical composition of both oils and WAFs are given in the Attachment, while only the results from the re-testing are given here.

3.1.1 Organic compounds

The chemical composition of the oils and their corresponding WAFs are shown in Figure 3.1 and Figure 3.2, respectively. A summary of the chemical composition in oils and all WAF systems are given in Appendix A; oils in Table A 1, and the WAFs in Table A 2. GC chromatograms of all oils are shown in Figure A 1 to Figure A 7 and the WAFs in Figure A 8 to Figure A 17. There are no indications of the presence of dispersed oil droplets in any of WAFs according to the GC chromatograms; solely the water soluble fraction is detected. In addition, the results from the metal and element analysis are given in Table A 3 for the oils and in Table A 4 for the WAFs.

Figure 3.1 summarizes the composition of the main groups of the aromatics in all analyzed oils. The chemical composition of the seven analyzed oils is quite different. The naphthalenes and 2-3 ring PAHs seem to be the dominating groups in Bittern, Erich Giese, Blücher, and U-864, while the content of decalins are quite high in Nordvard. Boardale contains more volatiles than the other oils. There was a relatively high concentration of phenols in the oils from Erich Giese and Blücher. Alkylated phenols are usually not visible in oil analysis, due to excessive interference from other oil components in that boiling point area.

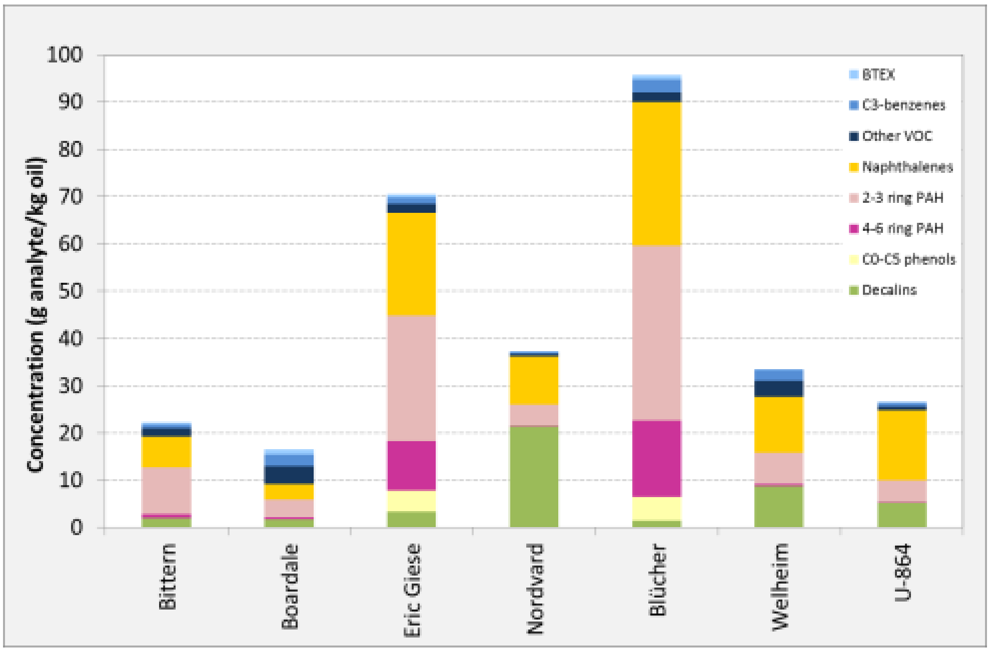

Figure 3.1 Chemical composition of selected components groups from the oils from "Bittern", "Boardale", "Erich Giese", "Nordvard", "Blucher", "Welheim", and "U-864.

The "chemical profile" of a WAF is unlike that of its parent oil due to the different water solubilities of the various compounds. Figure 3.2 shows the concentrations of the water soluble components of the WAFs prepared, including unresolved complex materials (UCM). The UCM is calculated by subtracting the SVOC concentration from the TPH concentration. The total WAF concentrations are based on the sum of TPH and volatiles (C5-C9, including BTEX). The VOCs (especially BTEX and C3-benzenes) constitute a major part of the WAF from fresh oils, and the naphthalens are generally the dominating SVOC components, as they have a relatively high solubility in water. However, in the WAF from Erich Giese (1:40), the phenols contributed to more then 95% of the SVOC and nearly 50% of the total WAF concentration. Also in the WAFs from Boardale and Nordvard, the phenols were the main contributor to the SVOCs (approximately 70%), while the naphthalenes dominated the SVOCs from Bittern. In the WAFs with the oil loading of 1 to 10 000, the naphthalenes were the major contributor to the SVOCs. The remaining components consist mainly of UCM.

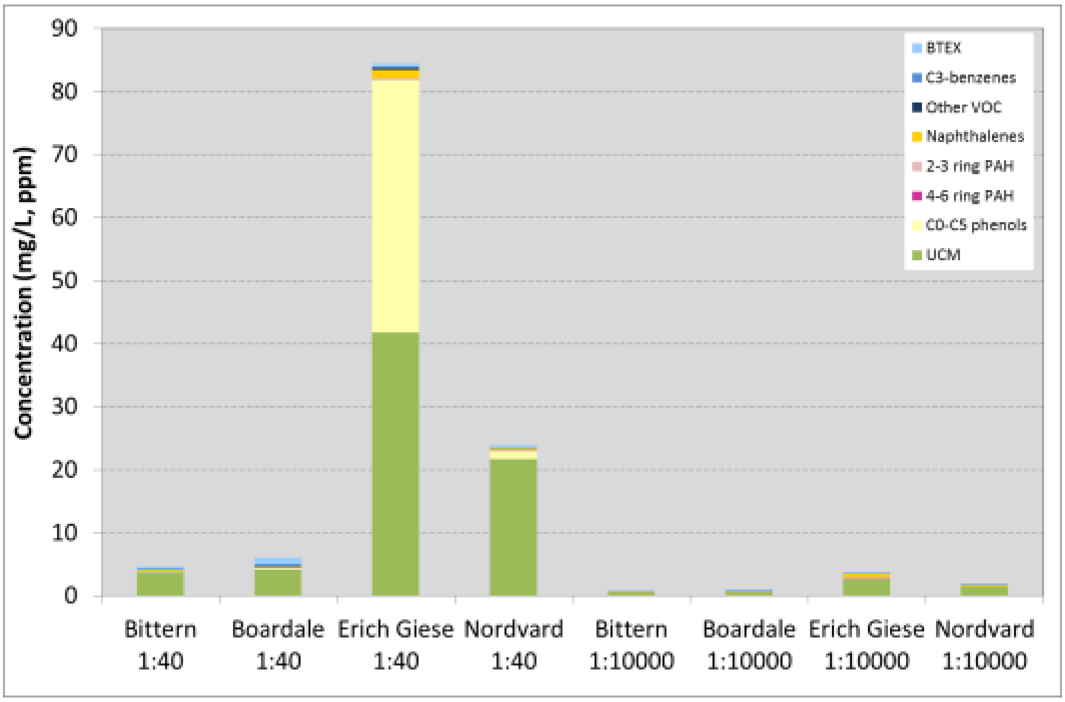

Figure 3.2 Chemical composition of the WAF systems

The WAFs from the shipwrecks with an oil-to-water loading of 1 to 40 are compared with WAFs from North Sea crudes in Figure 3.3. WAF prepared using the lignite oil from Erich Giese had approximately the same total WAF concentration as the condensates from Sleipner and Snøhvit, but the chemical composition was very different. The volatiles dominated the WAFs from the condensates, while UCM and phenols dominated the WAF with oil from German shipwrecks Erich Giese and Nordvard. The WAFs from the British shipwrecks Boardale and Bittern had the chemical composition as expected for light bunker oils.

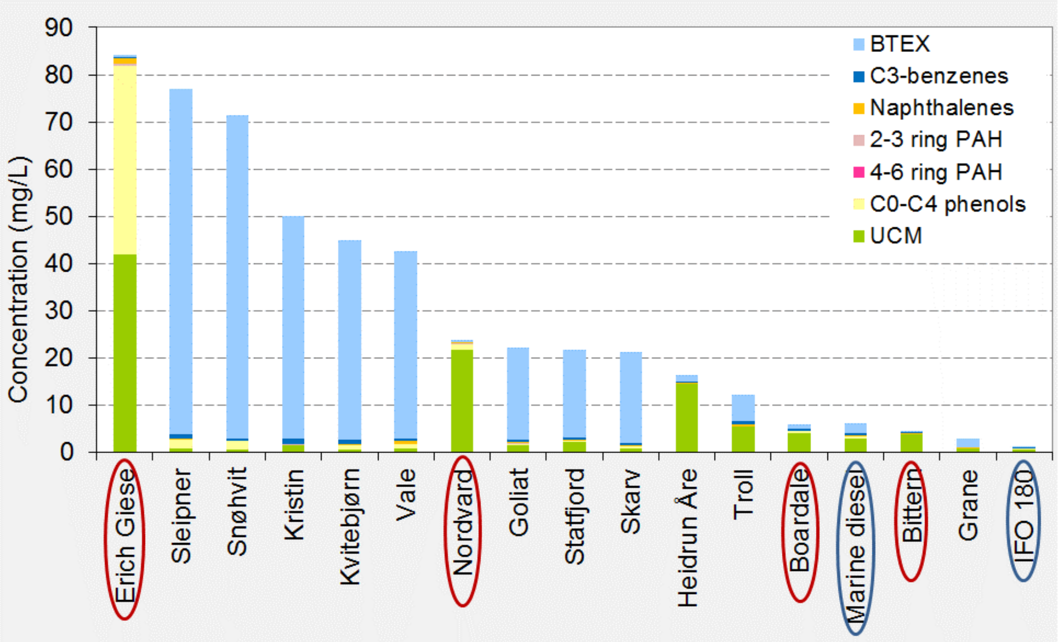

Figure 3.3 *WAF composition of shipwreck oils (red circle) and North Sea oils. Oil-to-water loading of 1 to 40 in all systems.*

3.1.2 Metals and elements

In the oils and the WAF samples 17 metals and elements were quantified, shown in Figure 3.4 and Figure 3.5, respectively. More detailed results are given in Appendix A (Table A 3 and Table A 4). No metal analysis was performed in the oils from Blücher and Welheim.

The results indicate that the WW2 oils contained high concentrations of sulphur, but also iron, magnesium (especially Boardale), vanadium and zinc (Figure 3.4). The WAFs are prepared in seawater, which contains relatively high concentration of several of the elements analyzed (Table A 4). The background levels of the elements in seawater are subtracted from the measured concentrations in the WAFs, and the corrected concentrations are shown in Figure 3.5. However, no clear trend can be seen from the WAF samples, as there seems to be limited correlation between the measured concentrations and the oil to water ratio (several elements with higher concentration in the WAF with oil to water loading of 1 to 10000 than in the 1 to 40 WAF).

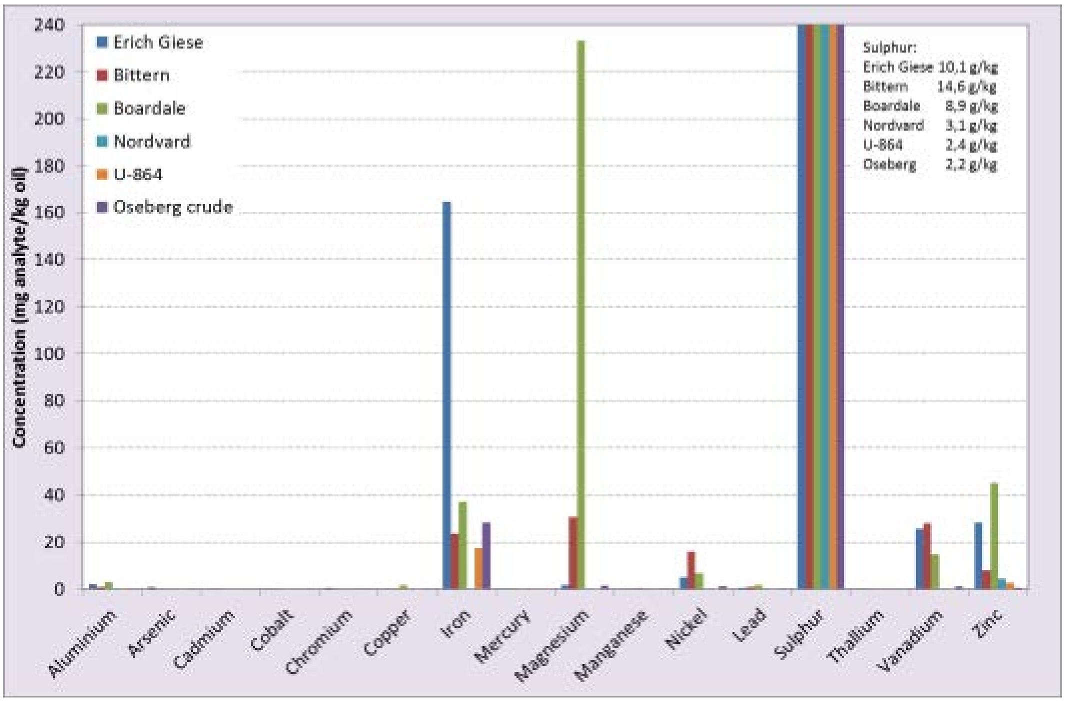

Figure 3.4 *Elements and heavy metals in the oils, given in mg analyte/kg oil. The Norwegian crude Oseberg is shown for comparison.*

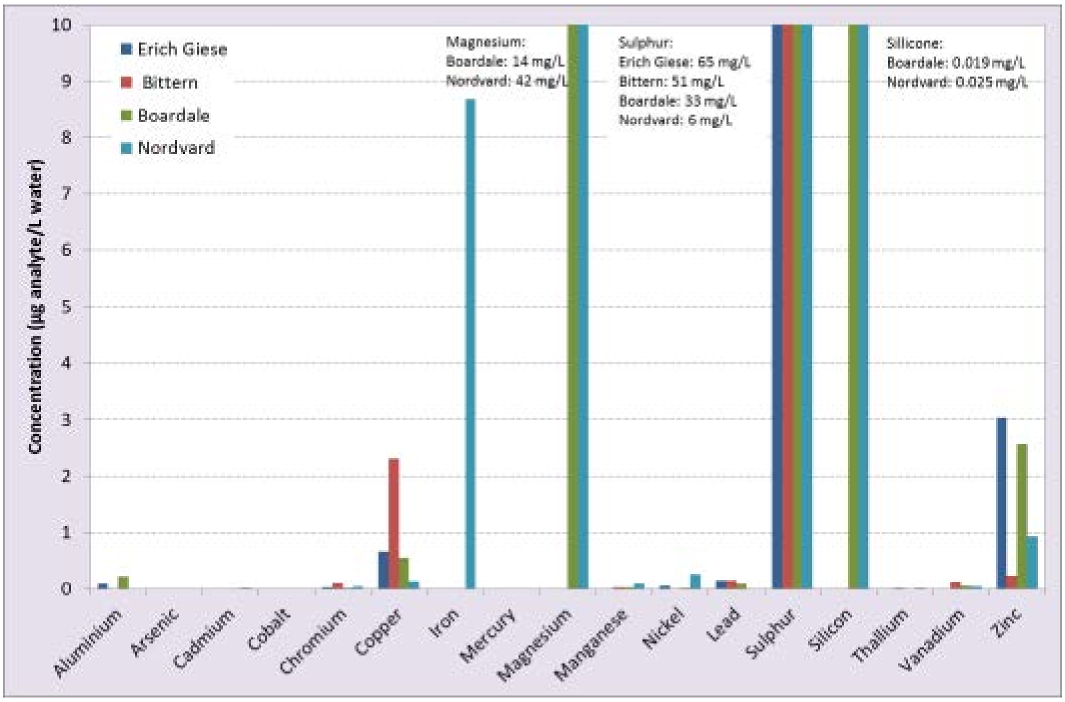

Figure 3.5 *Elements and metals in the WAF with oil-to-water loading of 1 to 10000, given in µg/L water (corrected for background level in the seawater).*

3.2 Acute toxicity

There are several ways to present the toxicity results. The toxicity of a chemical is normally quantified as an EC50 or LC50 value, defined as the concentration causing 50% of the organisms in a test population to die or to show a significant negative effect when they are exposed to a fixed concentration of the chemical for a defined time period (Rand et al., 1995). EC10 and LC10 values reflect the concentration causing 10% of the organisms to die or to show a significant negative effect.

The EC50 and LC50 can be given in percentage dilution of the undiluted WAF (relative toxicity, EC or LC50 (%)), or as normalized to the total WAF concentration (specific toxicity, EC or LC50 (mg/L or ppm)). Low EC50 value indicates a high toxicity, while a high EC50 exhibit a low toxicity. A summary of the toxicity results are given in Table 3.1, and more detailed results can be found in Appendix B (including EC10 and LC10).

Toxicity can also be expressed as percentage effect on the organisms at test endpoint in 100% WAF. This means toxicity results are expressed as percentage reduction in growth rate for *S. costatum* and percentage mortality for *C. finmarchicus* (Figure 3.9).

Following the standard protocol, even in the most diluted WAF (3% (algae) and 4 % (copepods) of total WAF concentration) from Erich Giese (1 to 40) all copepods and algae died immediately (observed by Dag Altin). A re-test of this WAF (including chemistry and toxicity) has been performed using another dilution scheme (from 0.15 % WAF for algae and from 0.62% WAF for copepods). The results from the re-testing of Eric Giese prepared with the oil to water loading of 1 to 40 are presented here.

Table 3.1 Summary of toxicity results of the WAFs. Acute specific toxicities are given both as LC50 and LC10 and are normalized to total WAF concentration.

Oil	Bittern	Bittern	Boardale	Boardale	Erich Giese	Erich Giese	Nordvard	Nordvard
Oil to water loading	1:40	1:10000	1:40	1:10000	1:40	1:10000	1:40	1:10000
Total WAF conc (ppm)	**4,604**	**0,750**	**6,049**	**0,928**	**84,5**	**3,697**	**23,9**	**1,789**
S. costatum EC50 (%) (growth rate)	45,3	64,6	39,1	97,0	1,90	7,98	8,97	63,3
S. costatum EC50 (%) (biomass prod)	27,0	46,7	36,1	36,2	1,40	5,62	**	38,6
C. finmarchicus LC50 (%)	54,6	>100*	50,7	> 100*	2,70	29,0	14,7	40,9
S. costatum EC50 (ppm) (growth rate)	2,09	0,48	2,37	0,90	1,61	0,30	2,14	1,13
S. costatum EC50 (ppm) (biomass prod)	1,24	0,35	2,19	0,34	1,18	0,21	**	0,69
C. finmarchicus LC50 (ppm)	2,51	> 0,75	3,07	>0,93	2,28	1,07	3,51	0,73

**No mortality observed in the non-diluted WAF, not possible to calculate LC50.*
***Biomass production could not be calculated due to the performance of the bioassay*

Acute toxicity expressed as percentage mortality on *C. finmarchicus* in non-diluted WAF (100%) after 24, 48, 72, and 96 hours (test endpoint) is given in Figure 3.6. It was observed 100% mortality already at first monitoring (24 hours) in the WAFs of German oils. At endpoint, there was a mortality of 100% for *C.*

finmarchicus in all WAFs with oil-to-water loading of 1 to 40, and also in Erich Giese 1 to 10000. It was observed 100% growth inhibition for *S. costatum* in all systems at endpoint (72 hrs), except Boardale 1 to 10000 (50% growth inhibition). These data are not shown, but are given in Table B 2.

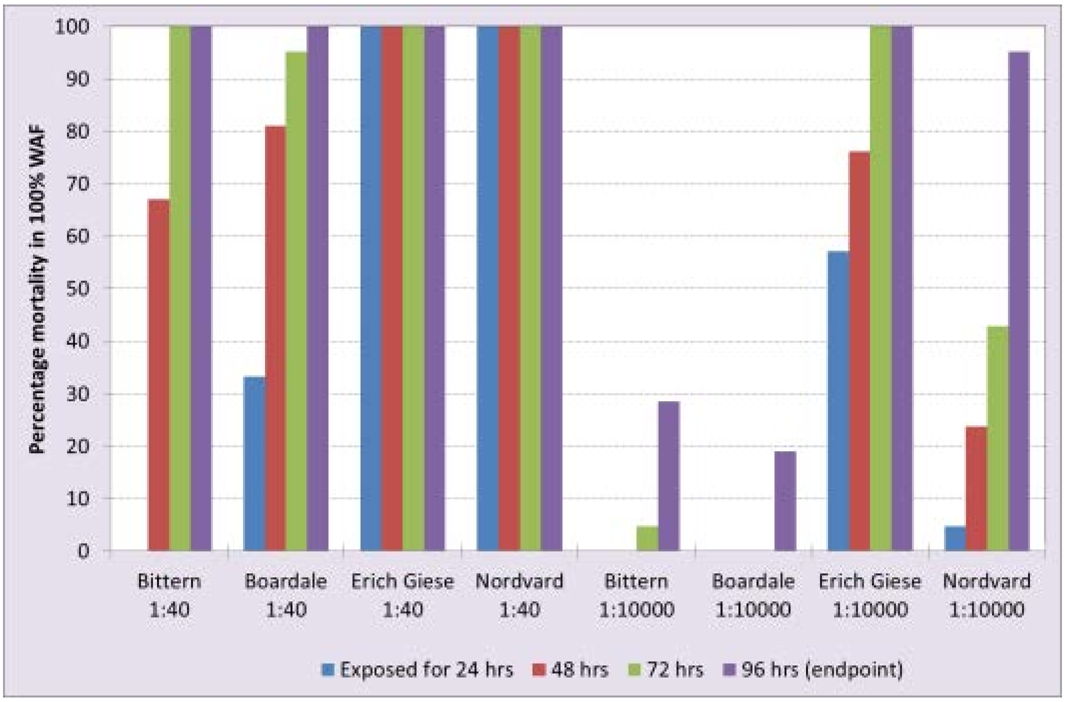

Figure 3.6 Acute toxicity expressed as percentage effect on the organisms in non-diluted WAF (100%): Percentage mortality for C. finmarchicus at 24, 48, 72, and at test endpoint (96 hrs). No bars indicate absence of observed effect on the test organisms.

The relative toxicity in the WAFs is given in Figure 3.7. The results are shown as EC50 and LC50 given as percentage dilution of WAF, and indicate that oil from the German shipwrecks Erich Giese and Nordvard are more toxic to the tested organisms than the oils from the British wrecks Bittern and Boardale. No effect on the copepods was observed in the WAFs from British oils with an oil to water loading of 1 to 10000.

The specific toxicity, normalized to total WAF concentration, is shown in Figure 3.8. Specific toxicity has been the traditional approach for expressing toxicity, but the mass based analysis neglects the fact that the composition of the WAFs varies. Based on the mass based approach, Erich Giese seems to be the most toxic of the WAFs with oil-to-water loading of 1 to 40 to both test organisms. Among the WAFs with oil-to-water loading of 1 to 10000, Erich Giese is most toxic to the algae, Nordvard is slightly more toxic to the copepods.

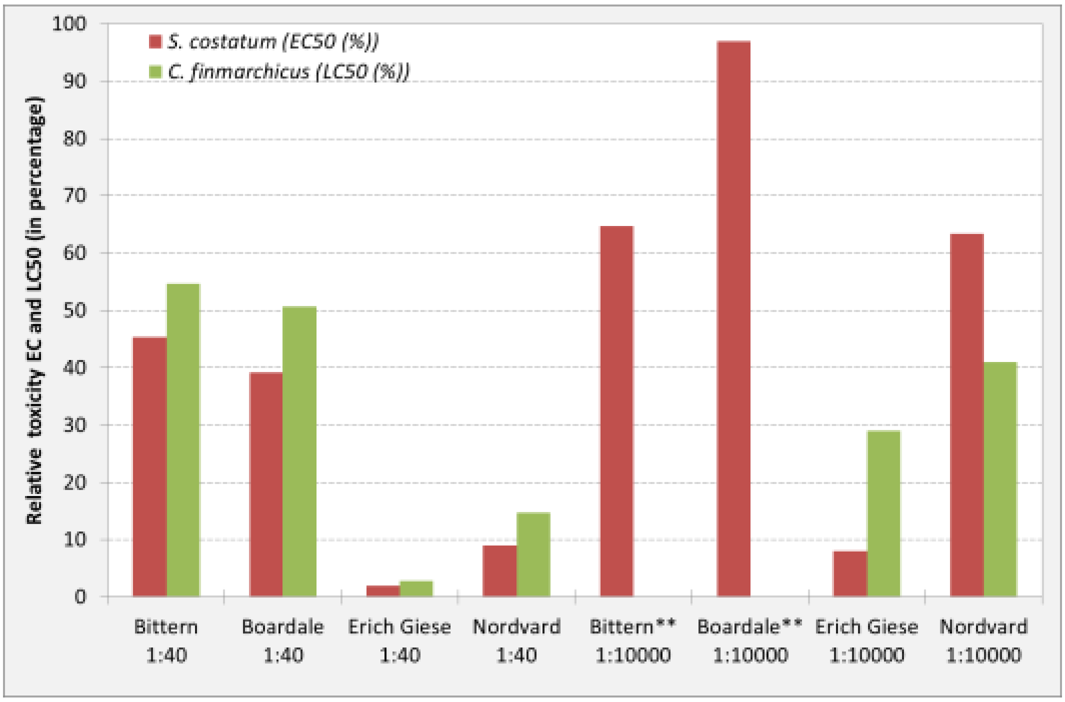

Figure 3.7 *Relative toxicity in the WAFs shown as EC50 and LC50 given in percentage dilution of the non-diluted WAF. No bars indicate absence of an observed effect on the test organisms (*).*

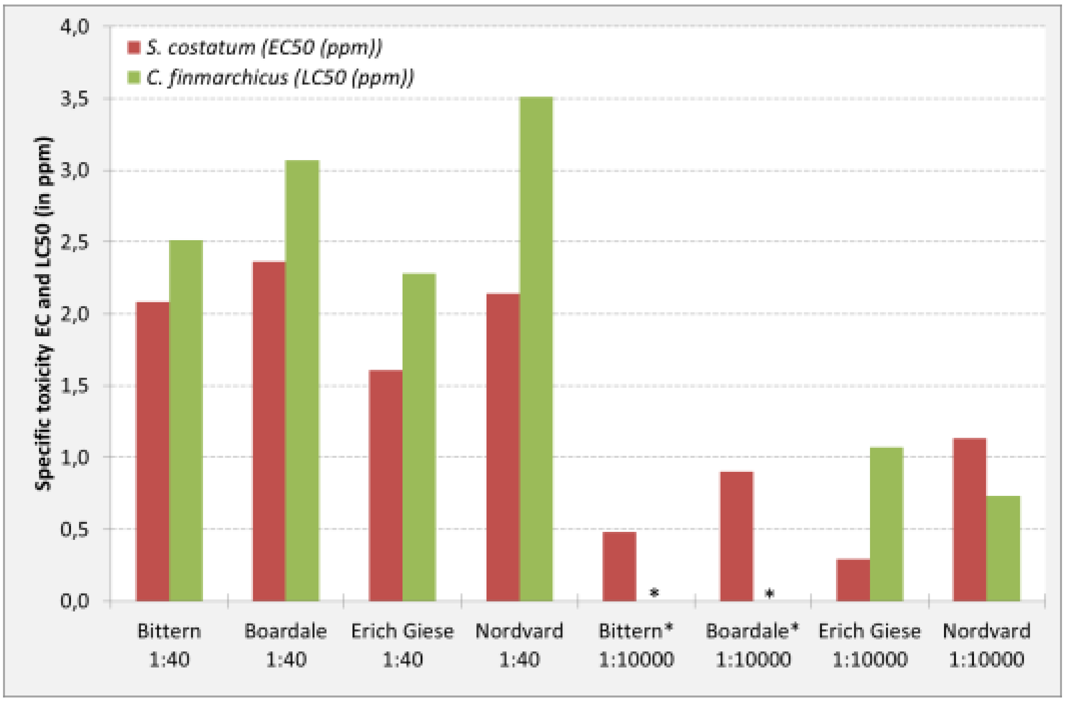

Figure 3.8 *Specific toxicity of the WAFs given as EC50 and LC50 normalized to total WAF concentration. No bars indicate absence of an observed effect on the test organisms (*).*

The acute toxicity can be predicted based on the chemical composition of the WAFs and the K_{ow} for the individual components. The toxicity will then be expressed as Toxic Units (TU). TU for the WAFs are calculated and are compared with other oils in Figure 3.9. A TU>1 for the total WAF implies that it is expected to cause 50% mortality in the test organisms. Although the UCM is not included in the calculated TU, the results indicate that the German oils are more toxic than the British oil, and especially Erich Giese, where the phenols seems to contribute nearly 80% of the TU. This is in accordance with the results presented in Figure 3.6 and Figure 3.7, and reflects that the chemical composition of a WAF is an important factor when observed toxicity should be evaluated.

Based on the chemical composition of the oils that have not been tested for toxicity, one can assume that the oil from Blücher most likely is at least as toxic as the oil from Eric Giese, as both probably are lignite oils. The oils from Welheim and U-864 are probably a blend of synthetic and natural diesel, as Nordvard. Their chemical composition, and that both are from German shipwrecks, could indicate that they possibly are more toxic than Bittern and Boardale. However, as this is just assumptions, studies of the water accommodated fractions of these oils should be performed if more reliable toxicity data are required.

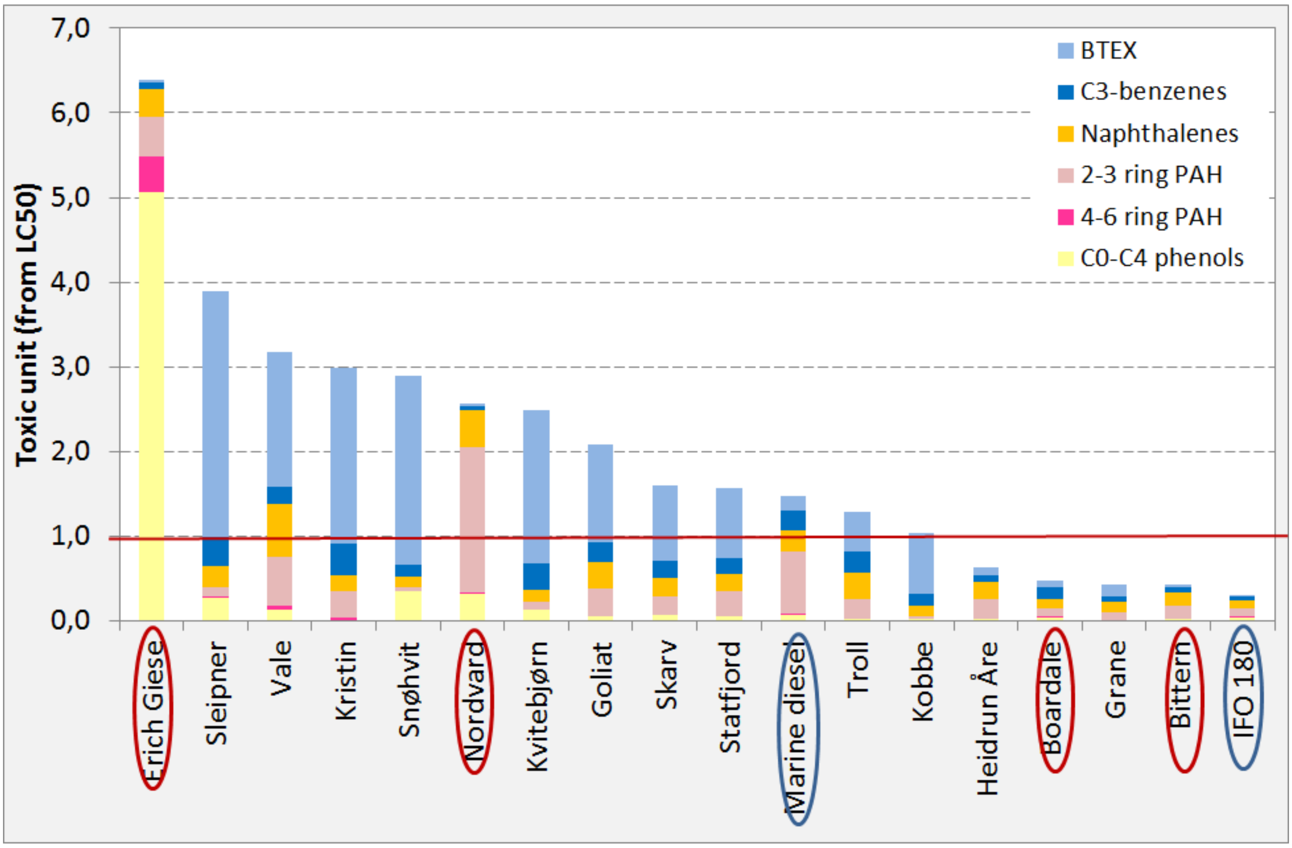

Figure 3.9 *Predicted acute toxicity expressed as toxic unit (TU) for WAFs with an oil-to-water loading of 1 to 40. WAFs from the shipwrecks are marked with a red circle. A TU>1 indicates a 50% mortality for 50% of the tested organisms.*

3.3 Limited weathering study and oil spreading test

The shipwreck oils of from the HMS "Bittern", RFA "Boardale", and "Erich Giese were analysed for their oil properties. A limited oil weathering study was performed on the shipwrecks oil due to the high water content of the oils, and it was therefore not possible to conduct the distillation/topping of the oils into their corresponding residues, due to HSE aspects in the laboratory. The input parameters to the SINTEF OWM for prediction of weathering properties were therefore a combination of experimental data and limited weathering data of the fresh shipwreck oils, and estimated and extrapolated values to make the most reliable predictions as possible, based on the limited weathering study.

3.3.1 Gas chromatographic (GC/FID) characterization

The chemical composition of RFA "Boardale", HMS "Bittern" and "Erich Giese", as characterized by gas chromatography (GC/FID), is shown in Figures A1, A2 and A3 (Appendix A). The gas chromatograms show *n*-alkanes as systematic narrow peaks. The first peaks in the chromatogram represent components with the lowest boiling points. Some of the more complex components, such as resins and naphthenes, shown as a broad and poorly defined bump below the sharp peaks, are often described as "Unresolved Complex Mixture” (UCM).

Based on the GC/FID analysis, both RFA "Boardale" and HMS "Bittern" has a high degree *n*-alkanes from nC_{10}-nC_{36}, which also reflects the medium wax content (see Table 3.3), and exhibits paraffinic characteristics. The oil from the German destroyer "Erich Giese" has a minor content of paraffins (*n*-alkanes) and exhibits more naphthenic/biodegraded features.

3.3.2 Chemical and physical properties

The chemical and physical properties of the oils are listed in Table 3.2 and
Table 3.*3*.

Table 3.2 Physical properties of the 3 shipwreck oils

Oil name	**Water-content***	**Density (g/ml)**	**Flash point (°C)**	**Pour point (°C)**	**Viscosity (mPas) 13°C (10 s^{-1})**	**Viscosity (mPas) 13°C (100 s^{-1})**	**Viscosity (mPas) 13°C (1000 s^{-1})**
"Erich Giese"	8.5	0.937	74	-9	77	76	75
HMS "Bittern"	2.7	0.925	146	-3	397	312	210
RFA "Boardale"	30	0.936	104	-3	280	259	202

**Water content in the fresh oil*

Table 3.3 Asphaltene (“hard”) and wax content of the 3 shipwreck oils

Oil name	**Asphaltene "hard" wt.% ***	**Wax content (wt. %)***
"Erich Giese"	2.4	1.0
HMS "Bittern"	1.3	4.3
RFA "Boardale	0.86	3.0

**The results were corrected for the water content*

The viscosities of the oils from HMS "Bittern" and RFA "Boardale" indicate that the oils are so-called "non-Newtonian" fluid, where the viscosity depends on its shear rate, and the viscosity decreases with increasing shear rate. This is due to the wax lattice structure is being broken or disturbed when influenced by mechanical stress. The viscosity of oil from the German destroyer "Erich Giese" is lower and has an insignificant degree of shear thinning properties.

The shipwrecks oils have high densities (> 0.92 g/ml) which are a typical density range for bunker fuel oils, and the oils have a medium to low wax contents. "Erich Giese" and HMS "Bittern" exhibit high content of asphaltenes, whilst "Boardale" exhibits low content of asphaltenes. HMS "Bittern" and RFA "Boardale" have a medium content of wax, whilst Erich Giese has a low content of wax. In cases when high viscosity of the oil/emulsion is not a limiting factor, high pour point may cause solidification (elastic properties) when oil is spilled on the sea surface, and solidification typically arises at 10-15°C above the sea temperature. The pour points of the shipwreck oils are low, and due to expected low evaporation loss, the pour points will possible not increase and cause solidification of the oils on the sea surface.

The distillation curve, which is obtained by measuring the vapour temperature as a function of the amount of oil distilled, shows the relative distribution of volatile and heavier components in the oil. Figure 3.10 shows the True Boling Point curve (TBP) of vol. % distilled as cumulative fraction of the 3 shipwreck oils in comparison with a marine diesel, IFO-30 and two IFO-180 bunker fuels oils.

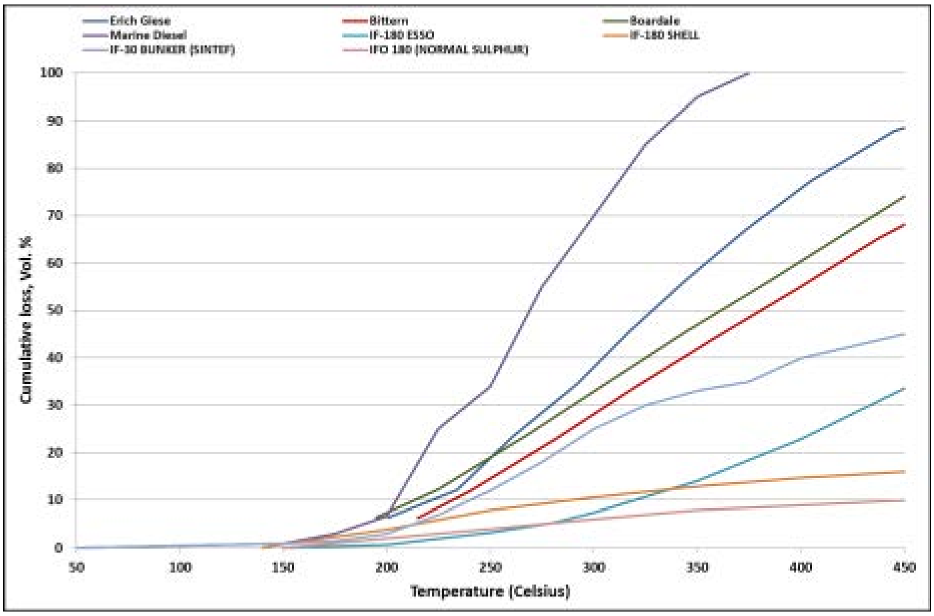

Figure 3.10 *Distillation curves for "Erich Giese", HMS "Bittern" and RFA "Boardale" in comparison with a marine diesel, IFO-30 and two IFO-180s.*

3.3.3 Emulsifying properties

The water uptake rate and maximum water uptake the emulsions were studied in rotating cylinders (Hokstad *et al*., 1993). The emulsion water content as a function of time is shown in Table 3.4. $T_{1/2}$, which is derived from the tabulated data, is defined as the consumed time (hours) needed to incorporate half the maximum water uptake. Figure 3.11 shows the formation of emulsions after 24 hours rotating time.

Figure 3.11 *The maximum water uptake emulsions formed after 24 hours at 13°C of "Erich Giese "(left), HMS "Bittern" (middle) and RFA "Boardale" (right).*

Table 3.4 Water-uptake of the 3 shipwreck oil in rotating cylinders at 13°C.

Mixing time	**Water uptake at 13 °C**		
	Erich Giese (Vol. % water)	**Bittern (Vol. % water)**	**Boardale (Vol. % water)**
Start	0	0	0
5 min	41	30	25
10 min	51	37	33
15 min	57	43	39
30 min	63	51	46
1 hour	68	57	54
2 hours	72	63	58
4 hours	91	68	60
6 hours	91	70	60
24 hours (max. water)	91	78	60
($t_{1/2}$)	0.18	0.24	0.16

Table 3.5 shows the measured viscosities of after emulsification of the fresh oils at 13°C with maximum water content. The oils from HMS "Bittern" and RFA "Boardale" formed stable w/o-emulsions with higher viscosities than the fresh oils. However, the oil from "Erich Giese" did not form typical stable w/o-emulsion based on its emulsification properties. The oil formed very loose emulsion with large water droplets when mixed with water, and the emulsion was easily broken when mechanical stress was applied when measuring the viscosity. The viscosity of the emulsion was therefore lower than the fresh oil due to this water-lubricating phenomenon ("vannsmøring").

Table 3.5 Viscosities of the w/o-emulsions of the shipwreck oils

Oil name	**Water content (vol. %)**	**Viscosity (mPas)**	
		10 s^{-1}	**100 s^{-1}**
"Erich Giese"	91*	7**	4
MS "Bittern"	78	6208	1181
HMS "Boardale"	60	2440	1034

** Super-saturation of the maximum water in the rotating cylinders methodology in the laboratory – all water has been emulsified. A maximum water of 91 vol. % is not likely to happen on the sea surface.*
***Unstable /loose emulsion*

3.3.4 Dispersibility testing -FET (Field Efficacy Test)

The dispersibility testing of the 3 shipwreck oils were conducted by the "FET - Field Efficacy Test", described in chapter 2.7.3. The dispersant Corexit 9500 was used in these tests at 13°C. The results are illustrated in Figure 3.12. The results from the dispersibility testing indicates that the 3 shipwreck oils ("Erich Giese", HMS "Bittern" and RFA "Boardale") are good dispersible, and are expected to have a potential for use of dispersants in case of a spill operation.

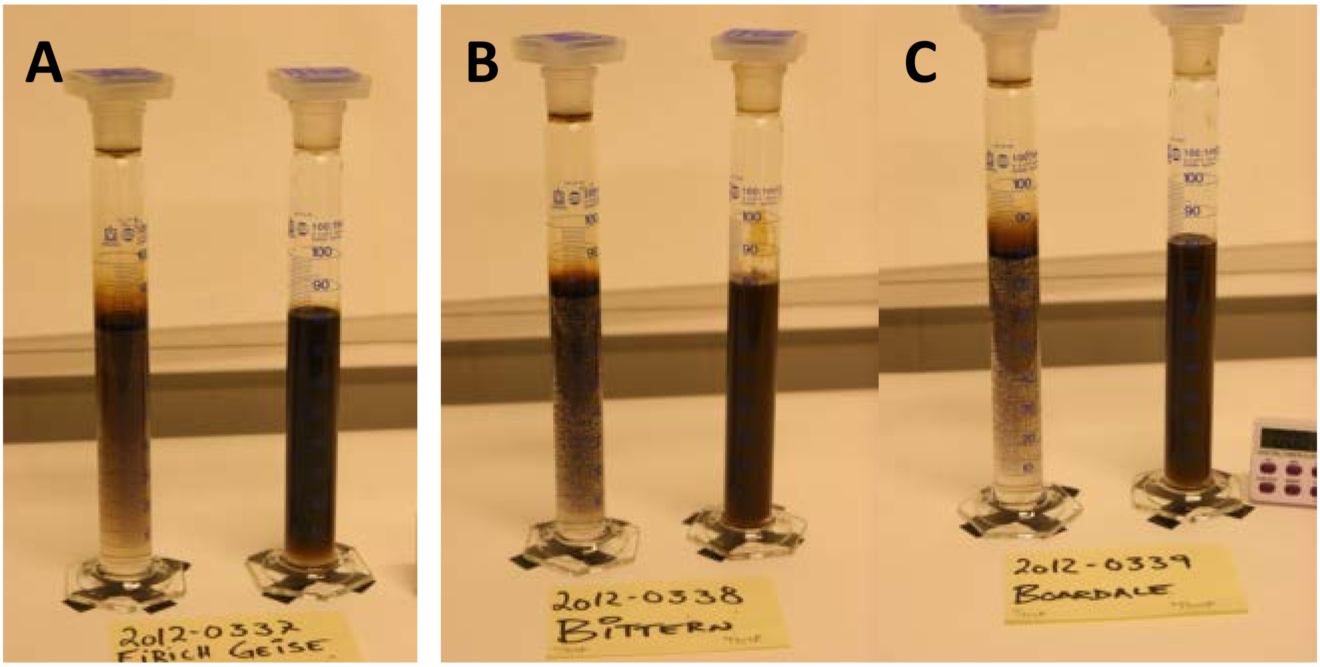

Figure 3.12 Field efficiency test: "Erich Giese" (A), Bittern (B), and Boardale (C). The left cylinders are the references (no dispersant added), and the right cylinders were added Corexit 9500. The dispersibility was good for all oils.

Oil spreading properties

The results from the spreading test of the 3 shipwreck oils are given below. The first application (release 1) indicates the first10 droplets of released oil, and the second application (release 2) indicates the total amount of droplets (a total of 50 droplets) for both a surface and subsurface release. Figure 3.13 to Figure 3.15 show the oil spreading tests for surface release, and Figure 3.16 to Figure 3.18 show the oil spreading test for subsurface release of the three shipwreck oils.

Figure 3.13 to Figure 3.15 show the oil spreading tests for surface release, and Figure 3.16 to Figure 3.18 show the oil spreading test for subsurface release of the 3 shipwreck oils.

Table 3.6 shows the amount of applied oil in the first test (release 1) and the total amount of oil from the second test (release 2); including the corresponding calculated volumes from the surface and subsurface release.

Table 3.7 shows the calculated oil slick area (cm^2) for release 1 and release 2 from the surface and subsurface release.

Table 3.8 shows the calculated oil film thickness (mm) of the first application (release 1) and second application (release 2) for the surface and subsurface release.

Table 3.9 shows the estimated oil droplets for the first and second application from the surface and subsurface release.

Figure 3.13 to Figure 3.15 show the oil spreading tests for surface release, and Figure 3.16 to Figure 3.18 show the oil spreading test for subsurface release of the 3 shipwreck oils.

Table 3.6 *Amount of oil applied in the first test (release 1) and the total amount of oil from the second test (release 2); including the corresponding calculated oil volumes.*

Oil name	**Amount applied oil, g Surface release, (1)**	**Amount applied oil, g Surface release, (2)**	**Amount applied oil, g Subsurf. release, (1)**	**Amount applied oil, g Subsurf. release, (2)**	**Volume of oil, cm^3 Surface release, (1)**	**Volume of oil, cm^3 Surface release, (2)**	**Volume of oil, cm^3 Subsurf. release, (1)**	**Volume of oil, cm^3 Subsurf. release, (2)**
"Erich Giese"	0.08	0.58	1.2	3.46	0.085	0.620	1.28	3.69
RFA "Boardale"	0.09	0.57	1.8	5.51	0.096	0.609	1.92	5.88
HMS "Bittern"	0.11	0.66	1.5	5.15	0.119	0.713	1.62	5.57

Table 3.7 *Oil slick areas calculated for release 1 and release 2*

Oil name	**Oil slick area, cm^2 Surface release, (1)**	**Oil slick area, cm^2 Surface release, (2)**	**Oil slick area, cm^2 Subsurf. release, (1)**	**Oil slick area, cm^2 Subsurf. release, (2)**
"Erich Giese"	49*	615	46	129
RFA "Boardale"	1.8	7.5	30	75
HMS "Bittern"	17	26	50	98

**Total spreading of the first 10 droplets*

Table 3.8 *Calculated oil film thickness for the first and second application for a surface and subsurface release of the 3 wreck oils.*

Oil name	**Oil film thickness Surface release, mm (1)**	**Oil film thickness Surface release, mm (2)**	**Oil film thickness Subsurface release, mm (1)**	**Oil film thickness Subsurface release, mm (2)**
"Erich Giese"	-	0.126	0.276	0.286
RFA "Boardale"	0.527	0.814	0.651	0.787
HMS "Bittern"	0.069	0.270	0.325	0.567

-: not calculated due to a total spreading of the first 10 droplets

Table 3.9 *Estimated oil droplets size for the first and second application for a surface and subsurface release of the 3 wreck oils.*

Oil name	**Oil droplets Surface release, mm (1)**	**Oil droplets Surface release, mm (2)**	**Oil droplets Subsurface release, mm (1)**	**Oil droplets Subsurface release, mm (2)**
"Erich Giese"	-	-	4.3	3.2
RFA "Boardale"	-	-	5.0	4.1
HMS "Bittern"	-	-	5.8	4.5

-: Oil droplets not possible to estimate due to immediately spreading on the surface

Surface release

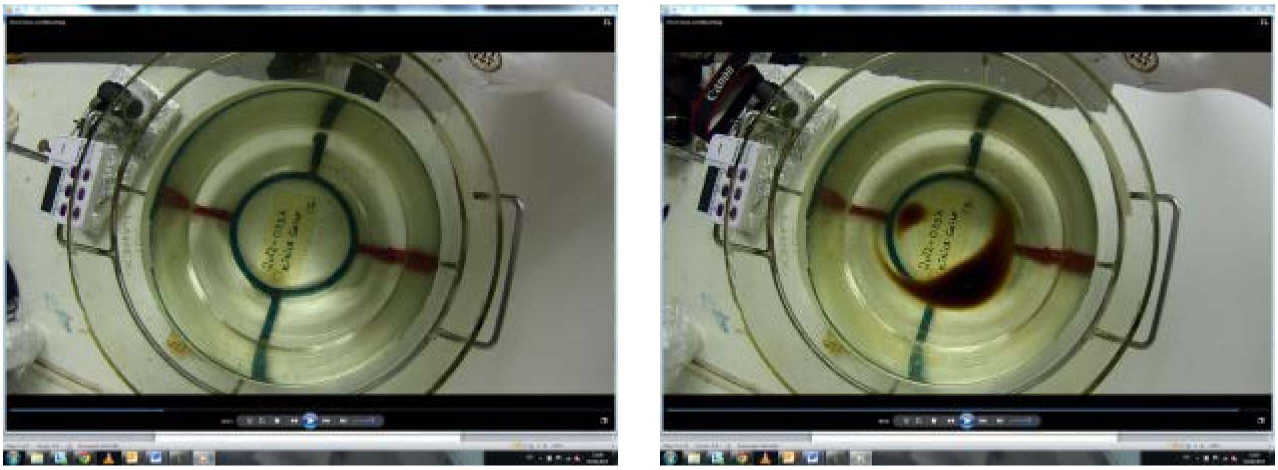

Figure 3.13 Erich Giese; surface release. First application (left) 10 oil droplets and second application (right) with a total of 50 oil droplets

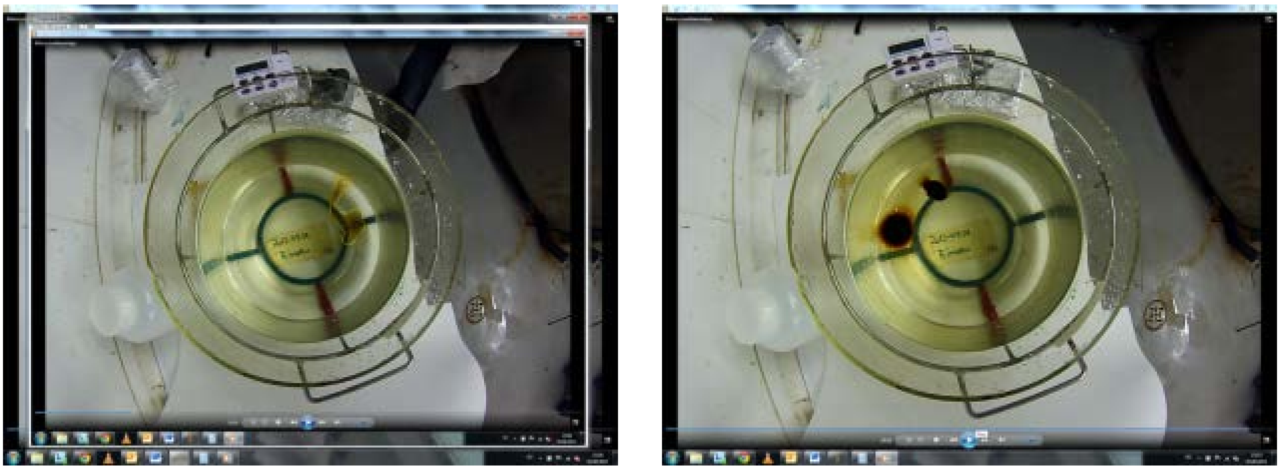

Figure 3.14 HMS Bittern; surface release. First application (left) 10 oil droplets and second application (right) with a total of 50 oil droplets.

Figure 3.15 RFA Boardale; surface release. First application (left) 10 oil droplets and second application (right) with a total of 50 oil droplets.

Subsurface release

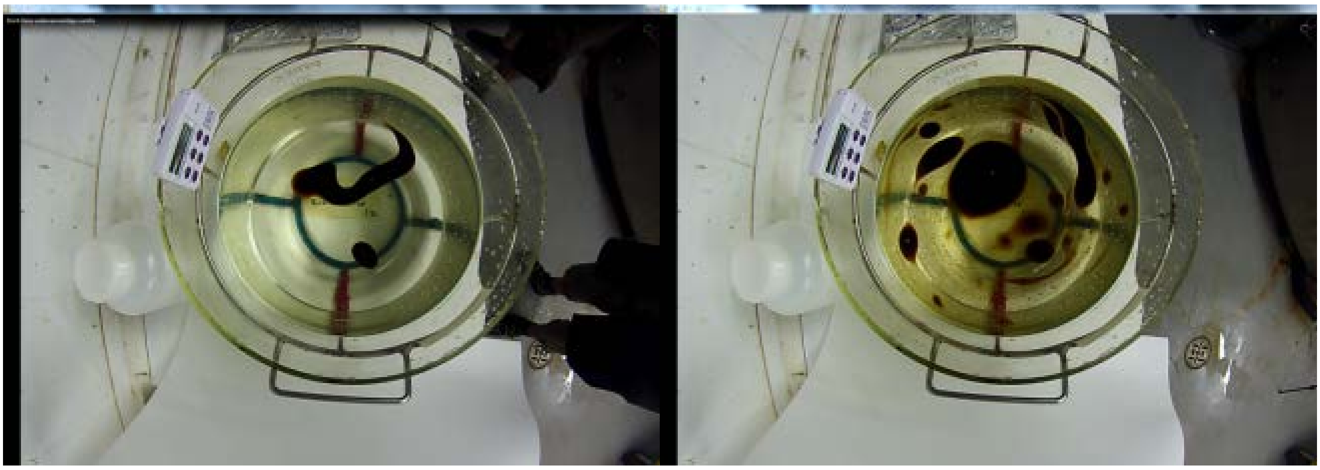

Figure 3.16 Erich Giese; subsurface release. First application (left) 10 oil droplets and second application (right) with a total of 50 oil droplets.

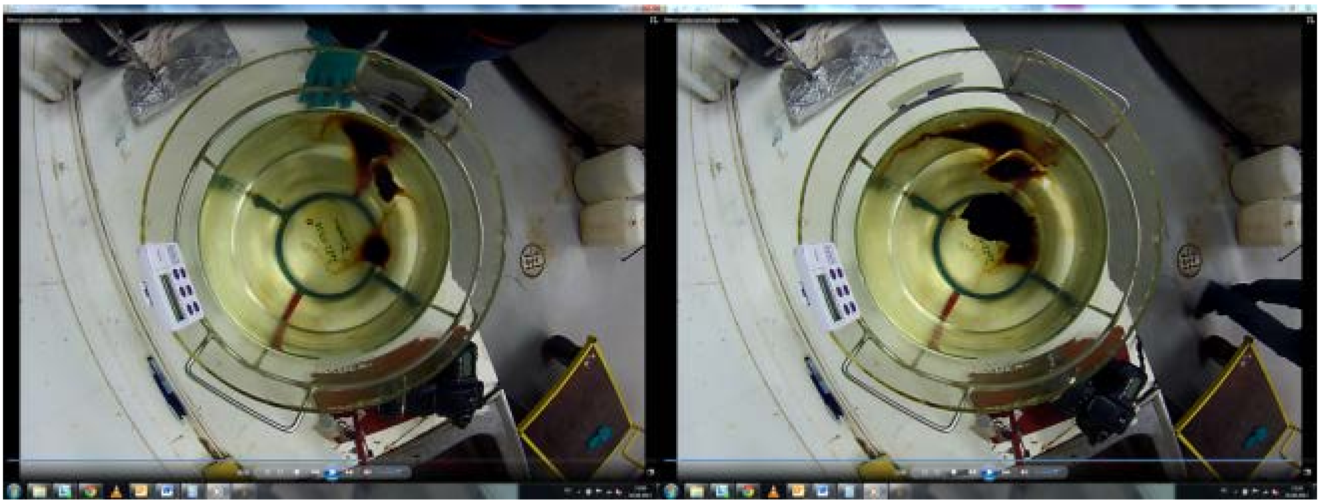

Figure 3.17 HMS Bittern; subsurface release. First application (left) 10 oil droplets and second application (right) with a total of 50 oil droplets.

Figure 3.18 RFA Boardale; subsurface release. First application (left) 10 oil droplets and second application (right) with a total of 50 oil droplets.

3.3.5 Predictions with SINTEF Oil Weathering Model (OWM)

The SINTEF OWM relates oil properties to a chosen set of conditions (oil/emulsion film thickness, sea state and sea temperature) and predicts the change rate of the oil's properties and behaviour on the sea surface. The SINTEF OWM is described in more detail in Johansen (1991), and schematically shown in Figure 3.19.

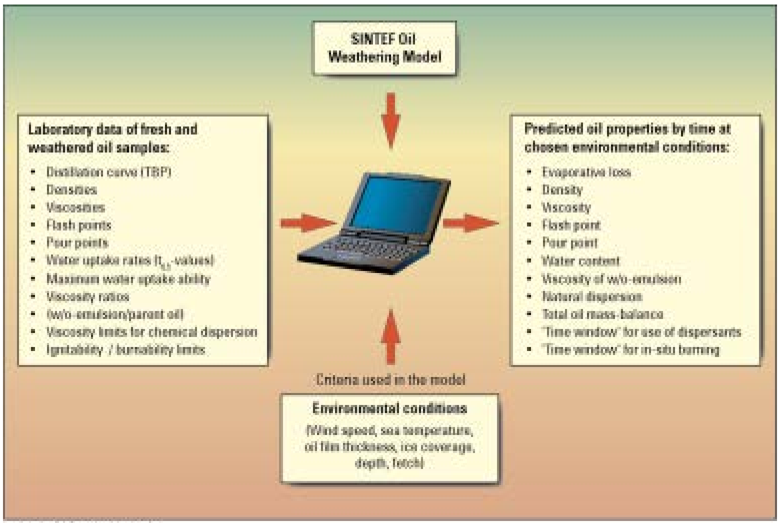

Figure 3.19 Schematic input data to the SINTEF OWM and the predicted output oil properties

Analytical parameters

The analytical parameters were used as input to the SINTEF OWM (version 4.0 beta). A full weathering data matrix as input to the model was not possible to obtain due to the limited weathering study of the shipwreck oils. The analytical parameters of the shipwreck oils were also outside the range to utilize the "crude assay" module in OWM for reliable prediction of the weathering properties. Therefore, it was decided to develop a "synthetic" weathering data matrix that was assumed to give more reliable weathering predictions, based on a combination of experimental data obtained in this project, and extrapolated weathering parameters of a IFO-30 and marine diesel.The weathering data used as input to the SINTEF OWM predictions for the German destroyer "Erich Giese", HMS "Bittern" and RFA "Boardale" are given in Appendix D.

Spill scenario

In this project, a surface release at a standard rate of 1.33 metric tonnes per minute was chosen as the spill scenarios. Predictions of a corresponding subsurface release were also conducted for the shipwreck oils, and these predictions are shown in Appendix E. The water depths for "Erich Giese", HMS Bittern and RFA "Boardale" were 65 m, 165 m and 67 m, respectively, and the gas-to-oil ration (GOR) was set to 10 (estimated fixed value) for the subsurface predictions.

Oil film thickness

In the SINTEF OWM, the oils are categorized into condensate, emulsifying crude, low emulsifying crude, heavy bunker fuel or refined distillate. The terminal film thickness varies among these categories based on experimental field experience. In this project, the terminal oil film thickness was determined by the spreading properties of the shipwreck oil, and the maximum oil film thickness from these studies (given in Table 3.8) were used as input to the OWM predictions (oil film thickness "Erich Giese" 0.3 mm; "Bittern" 0.6 mm; "Boardale" 0.8 mm).

Sea temperature

The prevailing weather conditions may influence the weathering rate of oil on the sea surface. Two sets of predictions are given in this report, one for average summer temperature and one for average winter temperature (5 °C and 15 °C).

Wind speed

The relationship between the wind speed and significant wave heights used in the prediction charts obtained from the SINTEF OWM are shown Table 3.10.

Table 3.10 Relationship between wind speed and significant wave height used in the SINTEF OWM

Wind speed [m/s]	**Beaufort wind**	**Wind type**	**Wave height [m]**
2	2	Light breeze	0.1 - 0.3
5	3	Gentle to moderate breeze	0.5 - 0.8
10	5	Fresh breeze	1.5 - 2.5
15	6 - 7	Strong breeze	3 - 4

Predictions charts of "Erich Giese", HMS "Bittern" and RFA "Boardale" oil weathering properties of a surface release are shown in the figures in Attachment F.

3.4 Comparison of oils

The weathering predictions of Erich Giese, Bittern and Boardale are compared with Marine Diesel, IFO-30, IFO-180 Shell, and IFO-180 Normal Sulphur from Esso Slagen. The predictions are shown at 15 °C and 10 m/s in the figures below.

Figure 3.20 shows that the predicted 3 shipwreck oils have similarities in their evaporative loss. They have higher evaporative loss compared with the bunker fuels oils (IFO-30, IFO-180), and lower evaporative loss compared with Marine Diesel.

As oil is spilled on the sea surface, the temperature of the oil will be cooled to the ambient water temperature within a short period of time. The fire hazard will be at its greatest as long as the flash point of the oil is below the sea temperature. As shown in Figure 3.21, there is no predicted fire hazard for any of the oils at 15 °C and a wind speed of 10 m/s.

Pour point depends on the oil’s wax content and the amount of light components that are able to keep the waxes dissolved in the oil. In cases when high viscosity of the oil/emulsion is not a limiting factor, high pour point may cause solidification (elastic properties) on the sea surface. Solidification typically arises at 10-15°C above the sea temperature (see dotted line in Figure 3.22). The oils in comparison exhibits low predicted pour points and are not expected to cause solidification on the sea surface at 15°C, 10 m/s wind speed.

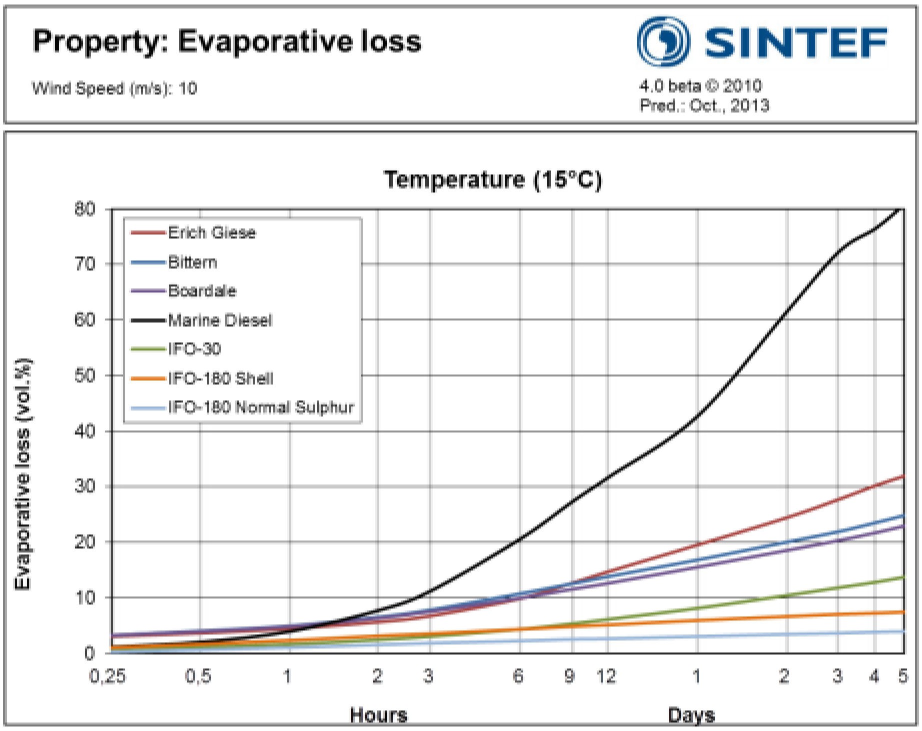

Figure 3.20 *Predicted evaporative loss at 15 °C and 10 m/s for "Erich Giese", HMS "Bittern" and RFA "Boardale" compared with Marine Diesel, IFO-30 and IFO-180 bunker fuel oils.*

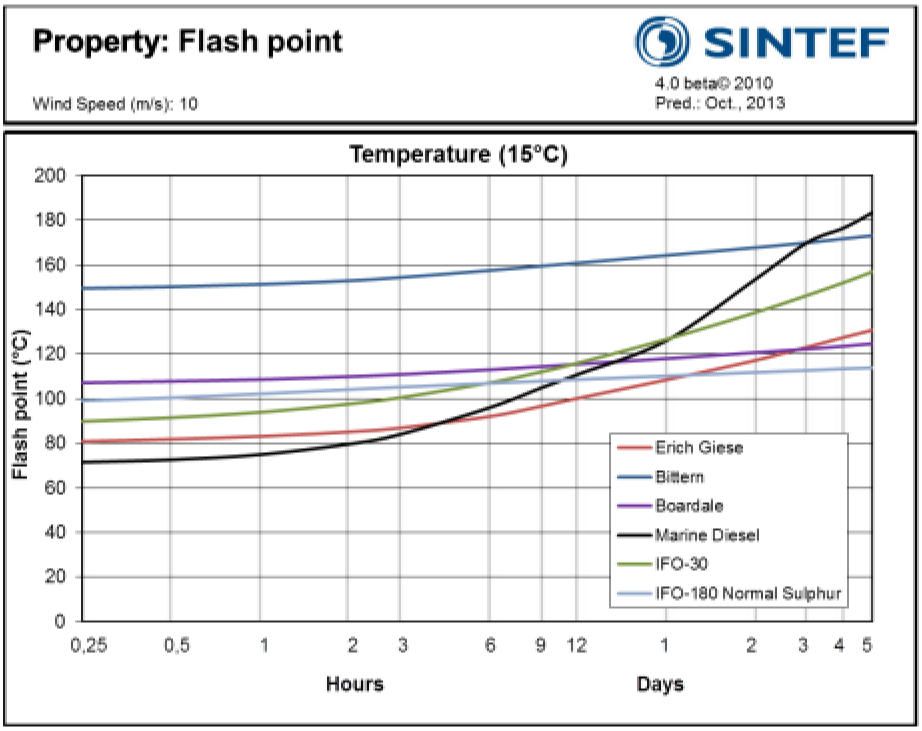

Figure 3.21 *Predicted flash point at 15 °C and 10 m/s for "Erich Giese", HMS "Bittern" and RFA "Boardale" compared with Marine Diesel and IFO-30/ IFO-180 bunker fuel oils.*

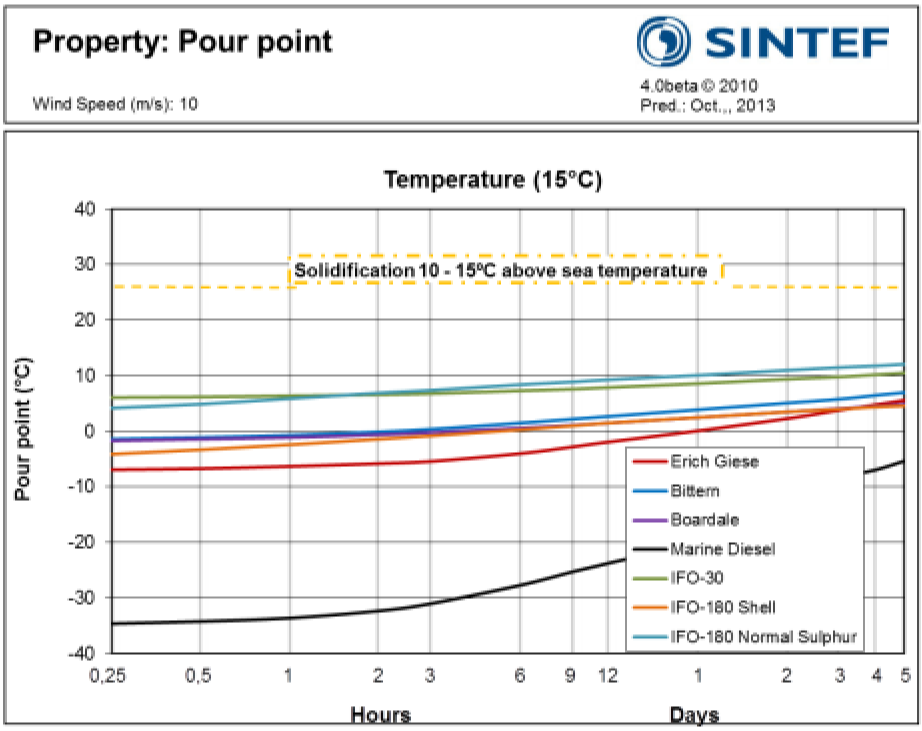

Figure 3.22 Predicted pour point at 15 °C and 10 m/s for "Erich Giese", HMS "Bittern" and RFA "Boardale" compared with Marine Diesel, IFO-30 and IFO-180 bunker fuel oils.

The German destroyer "Erich Giese" and HMS "Bittern" have high predicted water content as shown in Figure 3.23, and reached a predicted maximum water uptake of 80 vol. % after 6 and 24 hours weathering, respectively. RFA "Boardale" has a lower predicted water uptake of approximately 60 vol. % that is lower compared with IFO-30 bunker oil (70 vol. %). However, the two IFO-180 bunker fuel oils have lower water uptake than RFA "Boardale", and the Marine Diesel has no/insignificant predicted water uptake.

Both HMS "Bittern" and RFA "Boardale" form relatively high predicted emulsion viscosities (Figure 3.24), however the viscosities are a bit lower than the emulsion viscosities of the bunker fuel oils (IFO-30 and IFO-180). "Erich Giese" has low predicted emulsion viscosities compared with the tow other shipwreck oils, and is more comparable with the Marine Diesel. The maximum water uptake for Erich Giese is high (80 vol. %), but the stability of the emulsion is low (i.e. easily broken with applied mechanical stress), and has expected low viscosities if spilled on the sea surface.

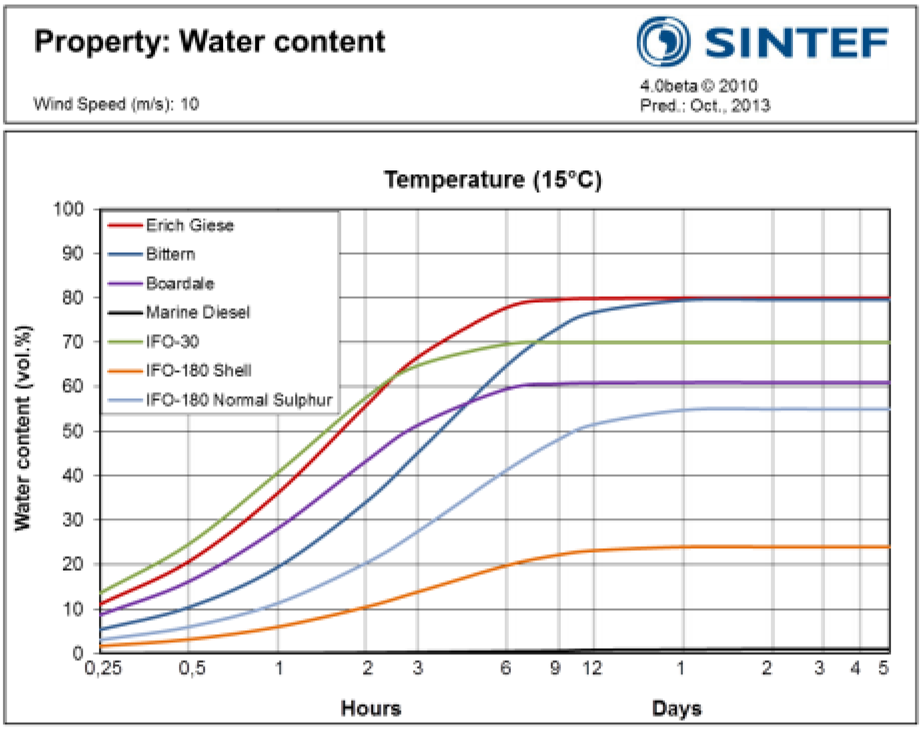

Figure 3.23 *Predicted water content at 15°C and 10 m/s for Erich Giese, Bittern and Boardale compared with Marine Diesel, IFO-30 and IFO-180 bunker fuel oils.*

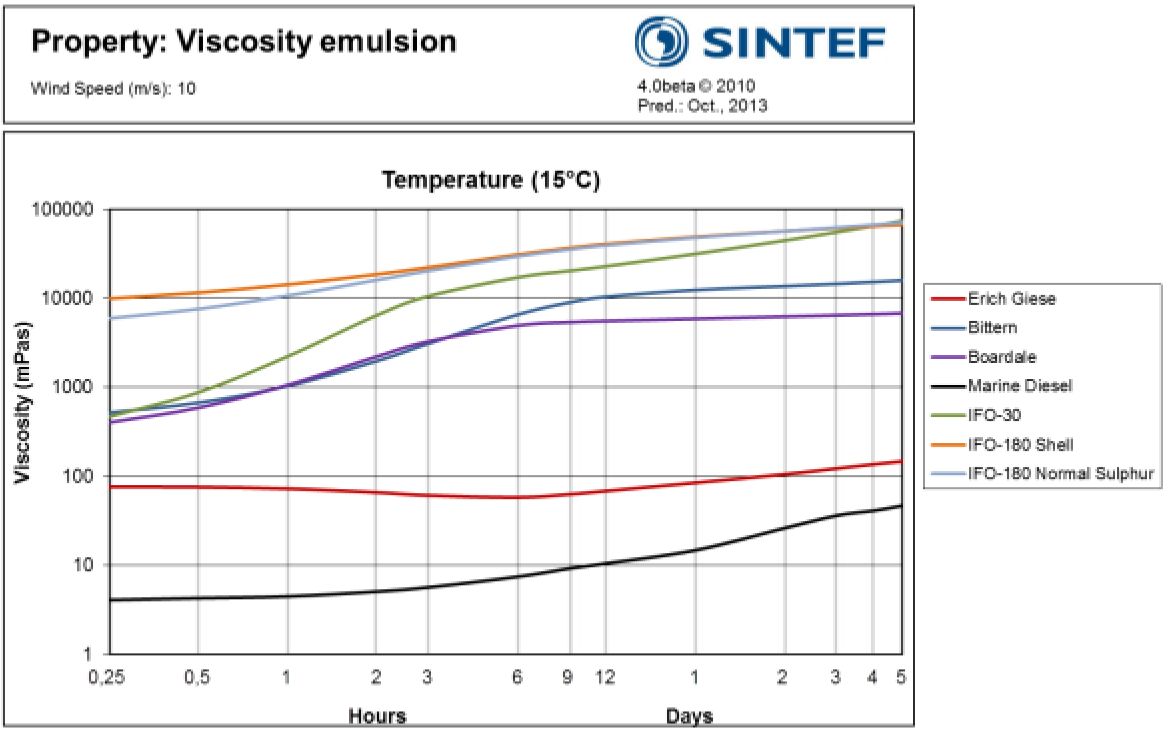

Figure 3.24 *Predicted emulsions at 15°C and 10 m/s for "Erich Giese", HMS "Bittern" and RFA "Boardale" compared with Marine Diesel, IFO-30 and IFO-180 bunker fuel oils.*

The total surface slick of the oils is reduced due to evaporation and natural dispersion during the initial stages of weathering as shown in Figure 3.25. However, the water mixed into the oil may increase the volume, as illustrated in Figure 3.26.

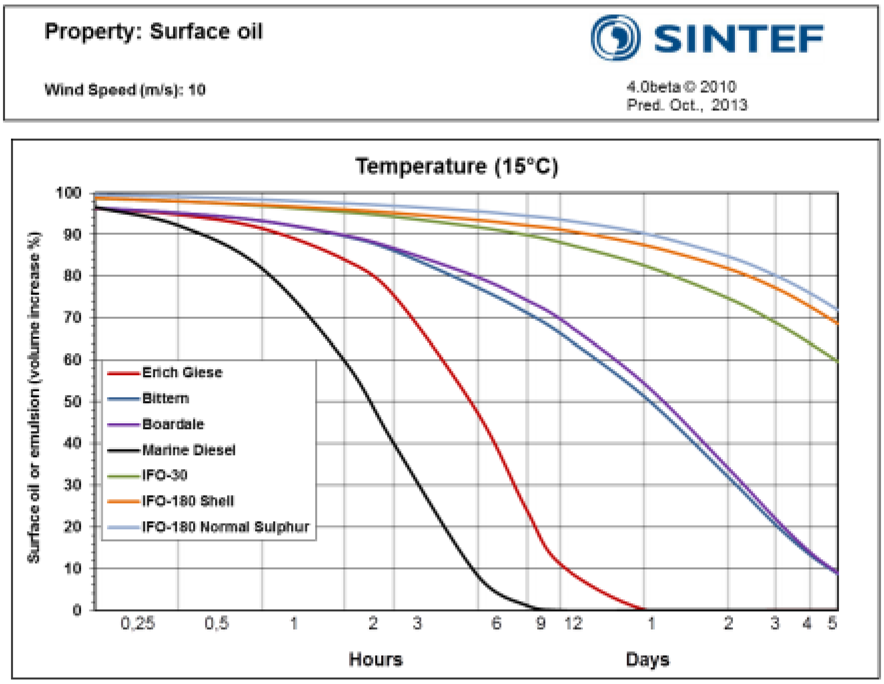

Figure 3.25 Predicted surface oil slick at 15 °C and 10 m/s for "Erich Giese", HMS "Bittern" and RFA "Boardale "compared with Marine Diesel, IFO-30 and IFO-180 bunker fuel oils.

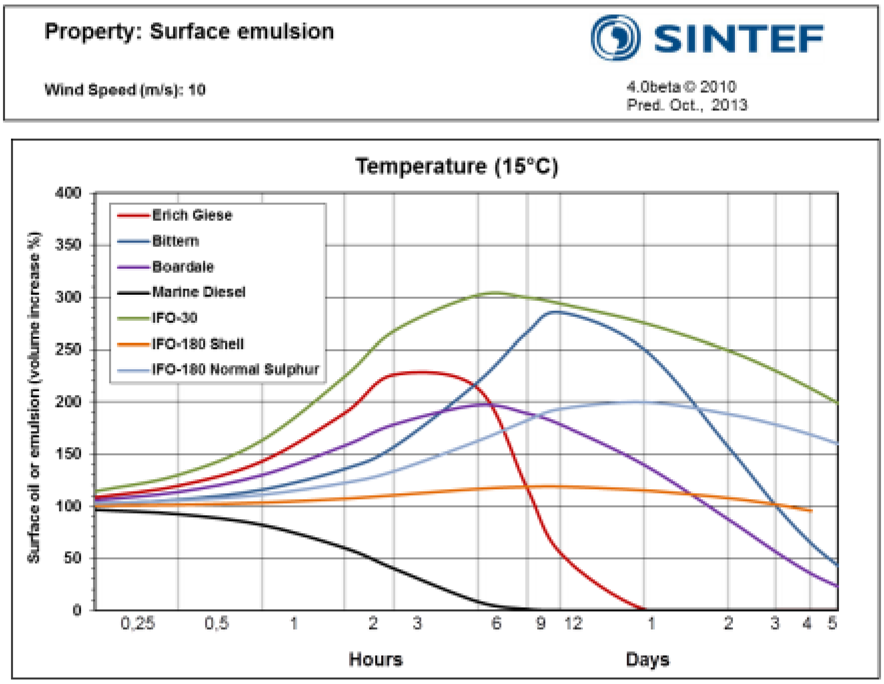

Figure 3.26 Predicted surface emulsions at 15 °C and 10 m/s for "Erich Giese", HMS "Bittern" and RFA "Boardale" compared with Marine Diesel, IFO-30 and IFO-180 bunker fuel oils.

Experiences from Norwegian field trials have demonstrated that the effectiveness of various mechanical recovery operations is reduced due to the high degree of leakage of the confined oil or w/o emulsion from the oil spill boom. This leakage is particularly pronounced if the viscosity of the oil or the w/o emulsion is lower than 1000 mPas (Nordvik *et al*., 1992). The lower viscosity limit for an optimal mechanical clean-up operation has therefore been set at 1000 mPas. However, other factors like towing speed and weather conditions will also influence on the risk of boom leakage, and lower viscosity emulsion is also possible to be to be recovered in very calm conditions. The predictions of the w/o-viscosities for Erich Giese are below 1000 mPas, and a high degree of boom leakage could therefore be expected. The emulsion viscosities for Bittern and Boardale are higher than Erich Giese; however, boom leakage could be expected in summer temperature during the first hours weathering, particularly in calm weather conditions (2-5 m/s).

Studies at SINTEF have shown that weir skimmers may have reduced recovery rate (m^3/t) at viscosities of 15000-20000 mPas (Leirvik *et al*., 2001). Bittern reaches emulsion w/o- viscosities up to approximately 20000 mPas after 12 hours weathering at high wind speeds (10-15 m/s) in winter conditions. Erich Giese and Boardale exhibits lower emulsions viscosities and remains beneath this limit during 5 days weathering, and good flowability towards weir skimmers could therefore be expected.

4 Summary and conclusions

4.1 Chemistry and toxicity of the WAFs

The water accommodated fractions (WAFs) of oils from four WWII shipwrecks have been studied with special emphasis on chemistry and biological effects (algae growth (*Skeletonema costatum*) and copepod mortality (*Calanus finmarchicus*)). The oils were from the British sloop HMS "Bittern", the British carrier tanker RFA "Boardale", the German destroyer "Erich Giese", and the German cargo ship MS "Nordvard". The oils from the British shipwrecks seem to be bunker oils (IFO 20-30), the oil from "Nordvard" was probably a blend of synthetic and natural diesel, while "Erich Giese" carried lignite oil (produced through coal hydrogenation).

The total WAF concentration in the oils from the shipwrecks varied, and the highest concentrations are quantified in the WAFs from "Erich Giese". These WAFs were also the most toxic for both algae and copepods, and it is suggested that the high content of phenols and other polar compounds have impact on the toxicity. WAFs from "Nordvard" were also more toxic than the WAFs from "Bittern" and "Boardale". The results from these studies indicate that the "syntetic" oils from German WWII shipwrecks seem to have higher toxicity to marine organisms than the "mineral" oils from the British shipwrecks studied.

The methodology used here has become the basic standard methodology for characterization of the potential environmental risk of oil leakage from shipwrecks in Norway. The project has given valuable input to the decision maker's recommendations of how to deal with old shipwrecks containing oil, and have also resulted in an altering of the priority list for future oil recovery from WWII wrecks due to the potential for higher impact on the marine environment from coal based oils.

4.2 Properties of the shipwreck oils

A limited study of the weathering properties of the shipwrecks oil from the HMS "Bittern", RFA "Boardale", and "Erich Giese were performed to predict the behaviour of oil at sea in order to optimize the effectiveness of potential response operations. To make the most reliable predictions as possible, the input parameters to the SINTEF OWM were a combination of both experimental data and limited weathering data of the fresh shipwreck oils, and estimated and extrapolated values.

All oils have densities > 0.92 g/ml, which are a typical density range for bunker fuel oils. The measured flash points were well above 60 °C for all oils, so there will be no risk for fire hazard during a response operation. Solidification on the sea surface is not expected for any of the oils as it is assumed that a low evaporative loss will keep their pour point well below ambient water temperature.

The results from the dispersibility testing using the "FET - Field Efficacy Test" indicate that there is a potential for use of dispersants for all three oils in a spill operation. The total surface slicks of the oils will be reduced due to evaporation and natural dispersion during the initial stages of weathering, but the water mixed into the oil may increase the volume.

The results from the predictions using the SINTEF OWM indicate that boom leakage is expected for "Erich Giese" due to low emulsion viscosities (<1000 mPas) in a mechanical response operation. It is expected good flowability toward weir skimmer due to emulsion viscosities < 15000-20000 mPas for "Erich Giese" and "Boardale", where as "Bittern" reaches this limit at high wind speeds (10-15 m/s) in winter conditions after 12 hours weathering.

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Appendix A GC chromatograms of oils and WAFs

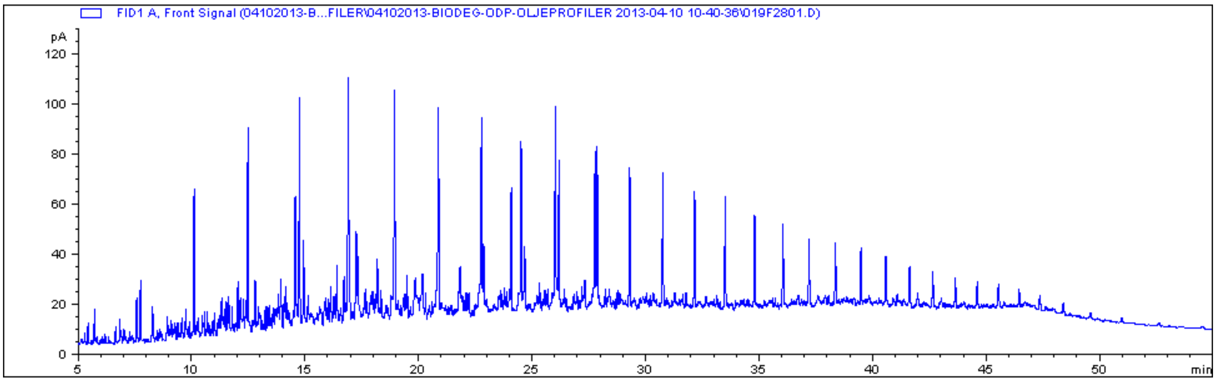

Figure A 1 *GC chromatogram of oil from HMS "Bittern" (SINTEF ID 2012-0338)*

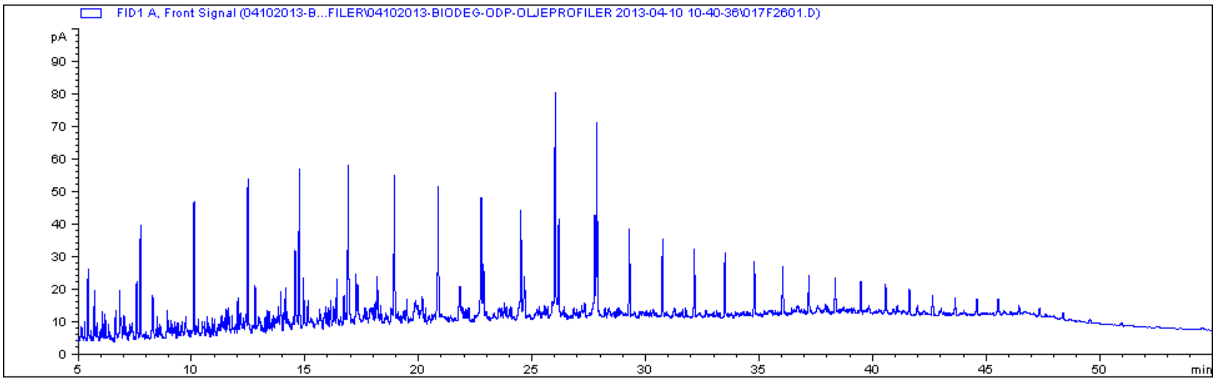

Figure A 2 *GC chromatogram of oil from RFA "Boardale" (SINTEF ID 2012-0339)*

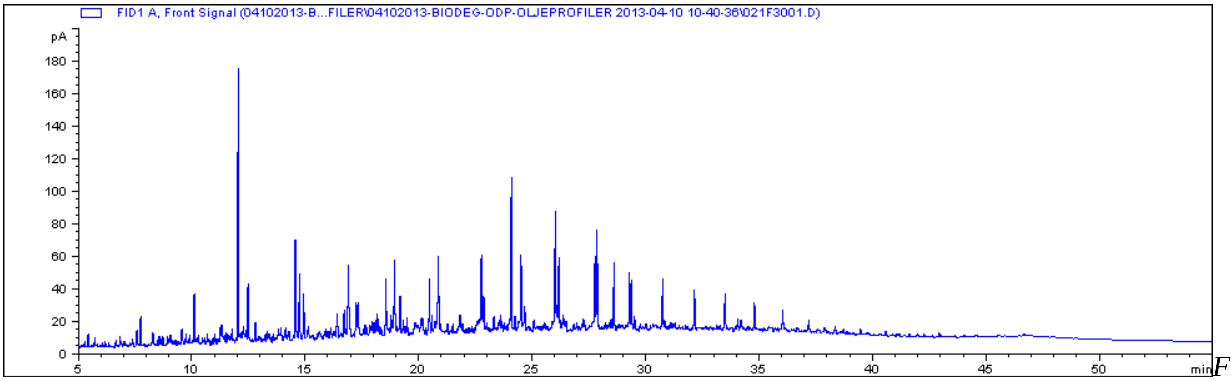

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Figure A 3 *GC chromatogram of oil from "Erich Giese" (SINTEF ID 2012-0337)*

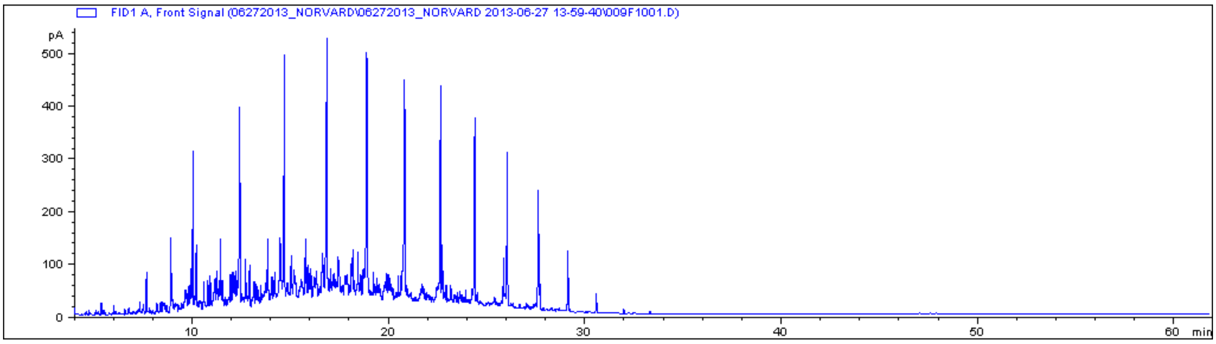


Figure A 4 GC chromatogram of oil from "Nordvard" (SINTEF ID 2012-0551)

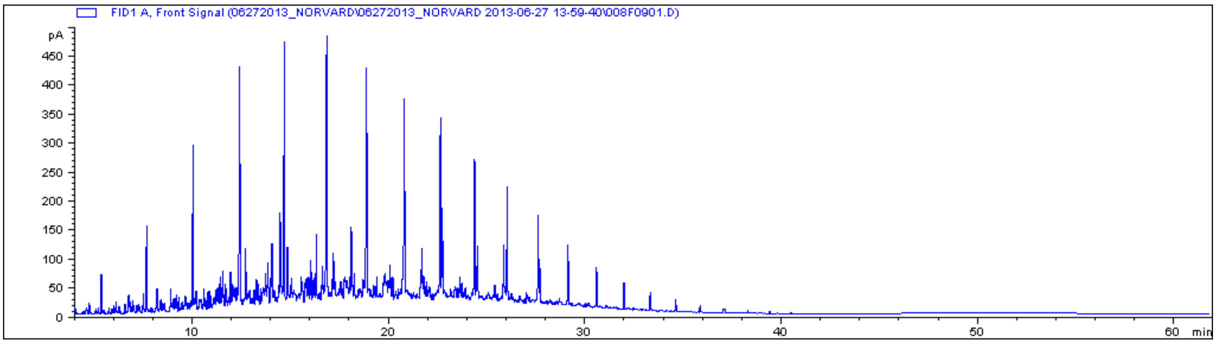


Figure A 5 GC chromatogram of oil from "U-864" (SINTEF ID 2012-0525)

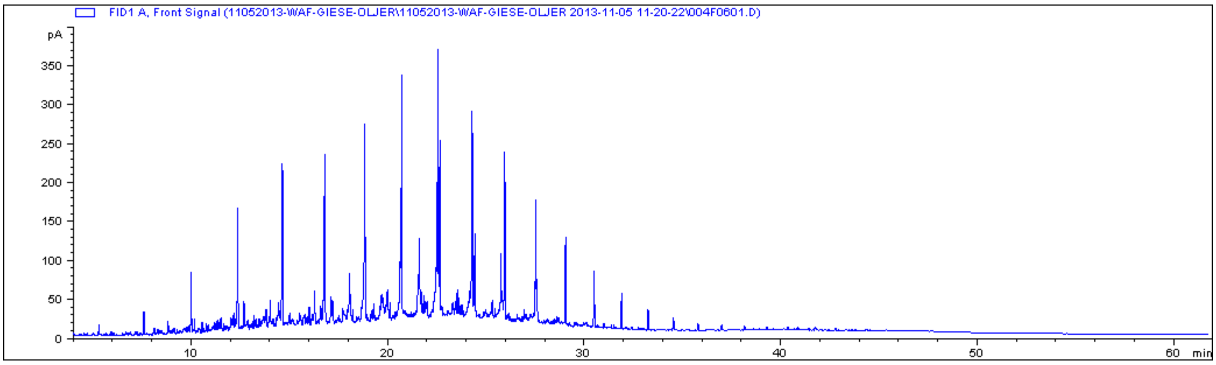


Figure A 6 GC chromatogram of oil from Welheim (SINTEF ID 2013-0720)

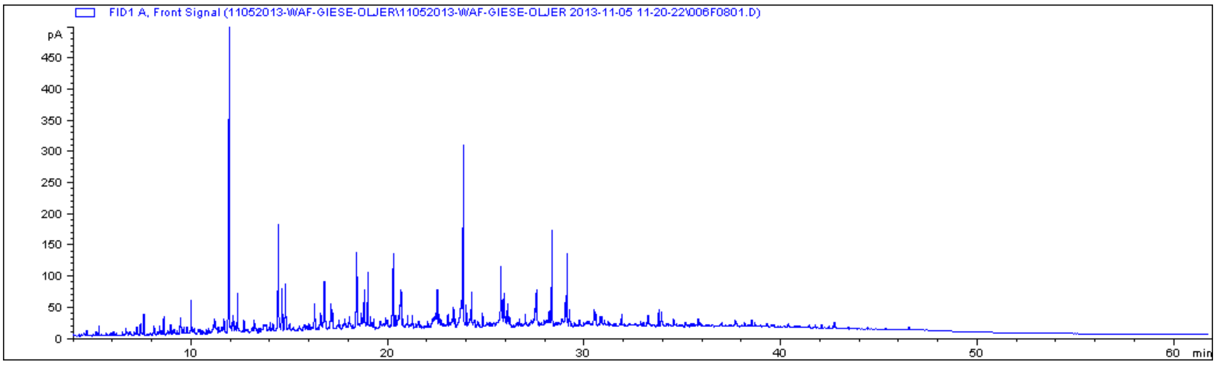


Figure A 7 GC chromatogram of oil from "Blücher" (SINTEF ID 2013-0719)

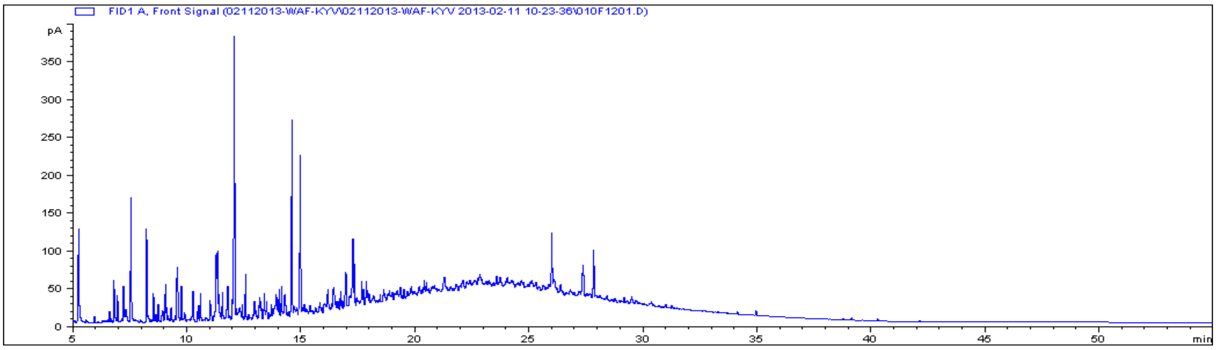


Figure A 8 *GC chromatogram of WAF from "Bittern", oil to water loading of 1 to 40.*

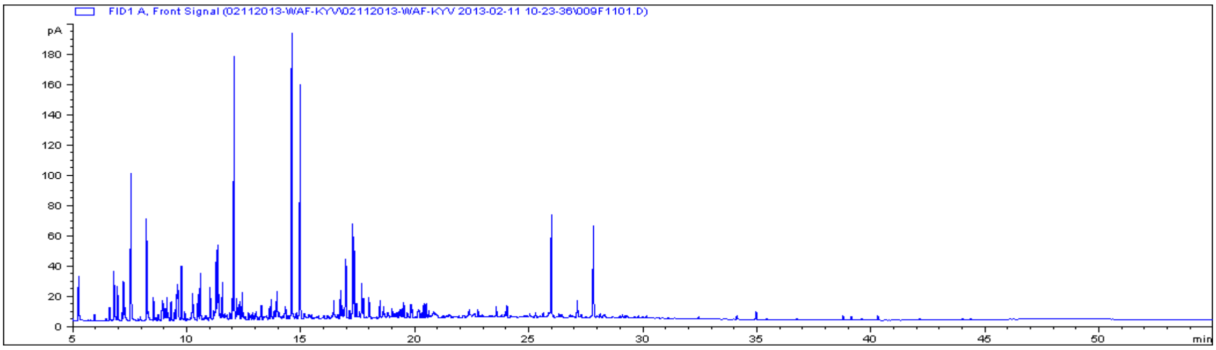


Figure A 9 *GC chromatogram of WAF from "Bittern", oil to water loading of 1 to 10000.*

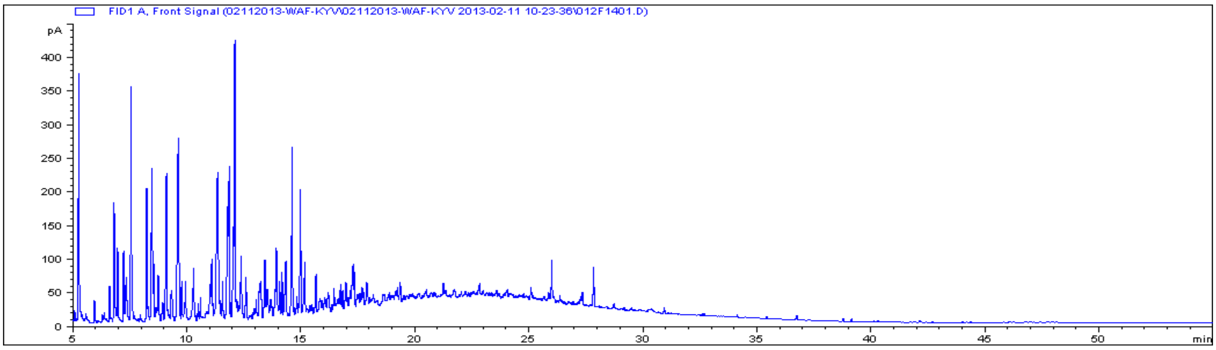


Figure A 10 *GC chromatogram of WAF from "Boardale", oil to water loading of 1 to 40.*

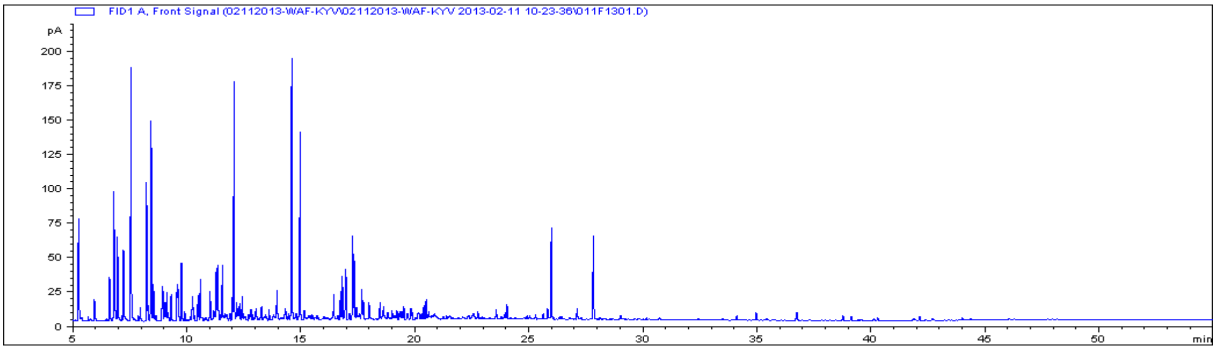


Figure A 11 *GC chromatogram of WAF from "Boardale", oil to water loading of 1 to 10000.*

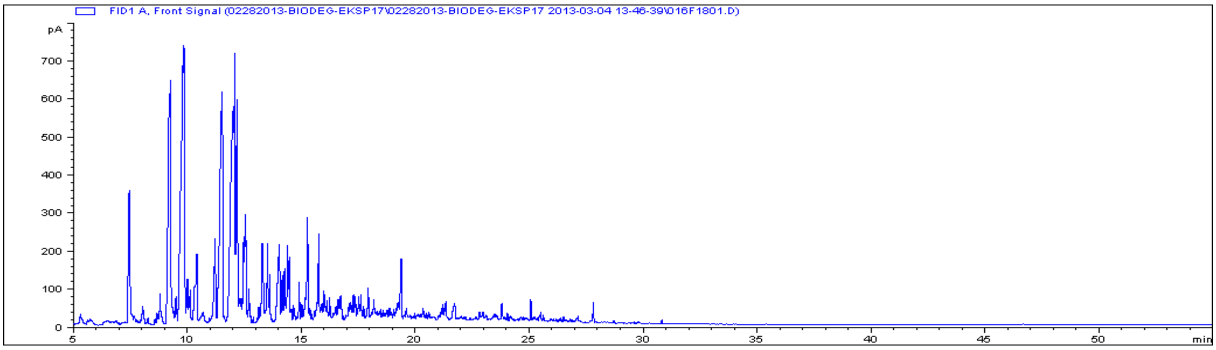


Figure A 12 *GC chromatogram of WAF from "Erich Giese", oil to water loading of 1 to 40. Diluted 10 times, no column clean-up.*

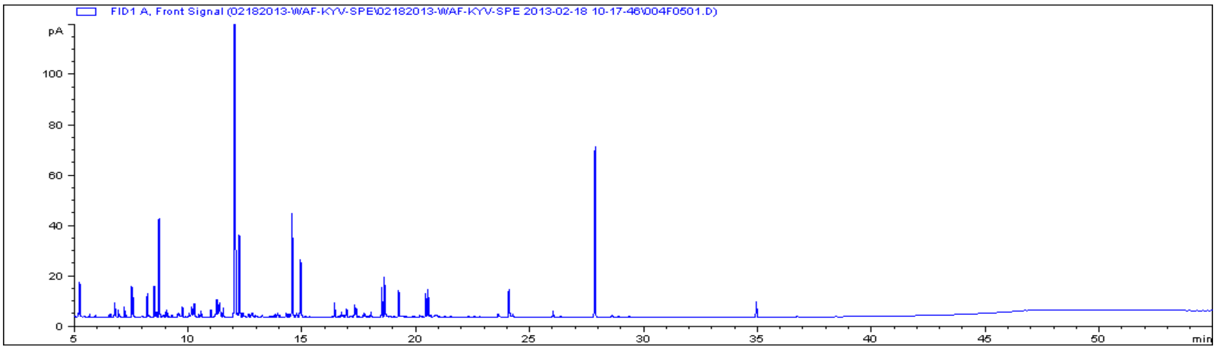


Figure A 13 *GC chromatogram of WAF from "Erich Giese", oil to water loading of 1 to 40. Diluted 10 times and polar compounds removed by extract clean-up.*

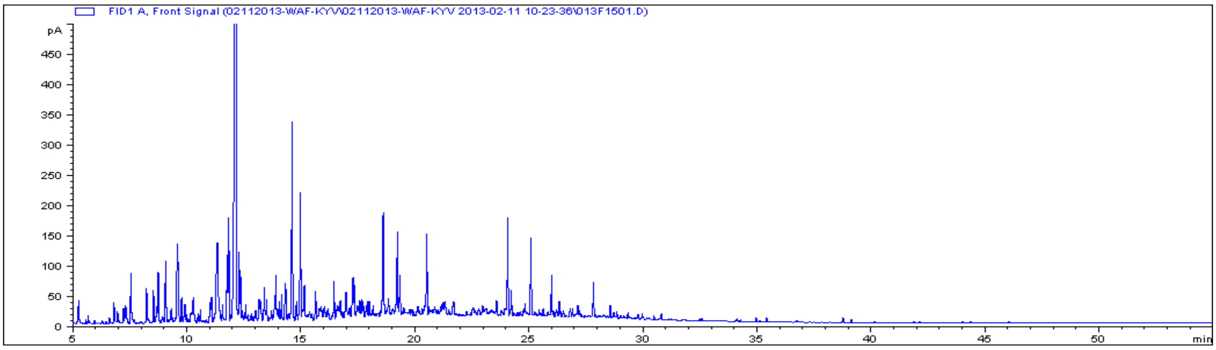


Figure A 14 *GC chromatogram of WAF from "Erich Giese", oil to water loading of 1 to 10000.*

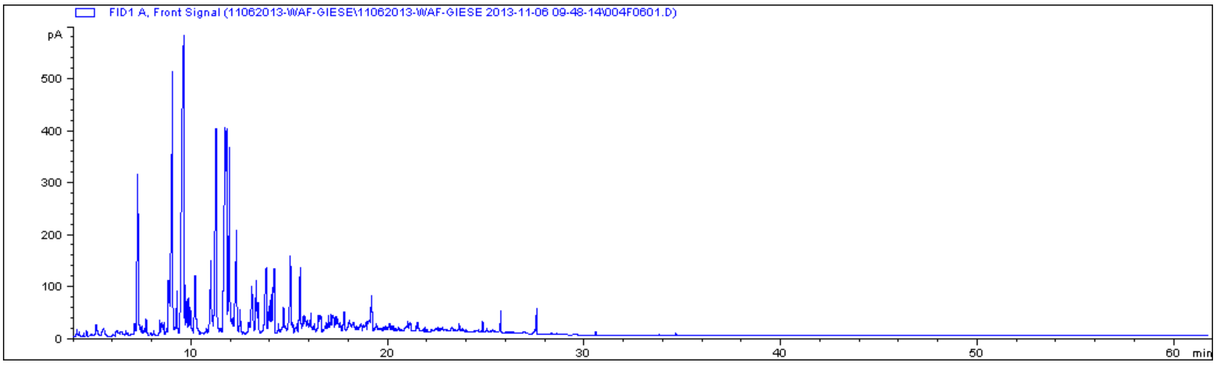


Figure A 15 *GC chromatogram of WAF from "Erich Giese", oil to water loading of 1 to 40. Re-test.*

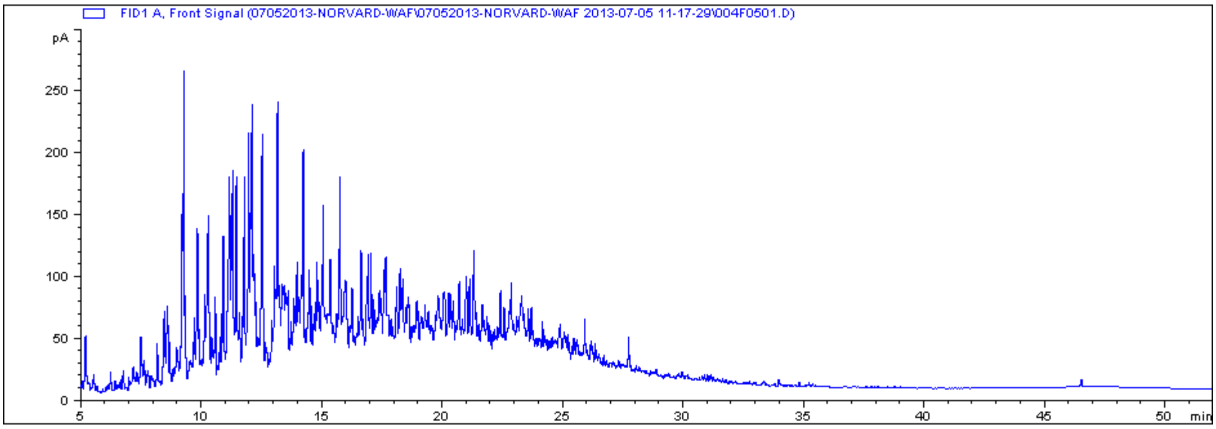


Figure A 16 GC chromatogram of WAF from "Nordvard", oil to water loading of 1 to 40.

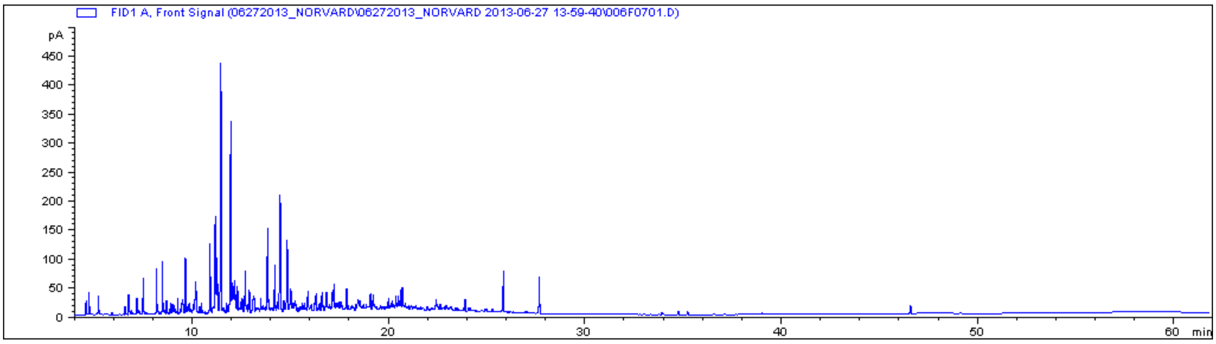


Figure A 17 GC chromatogram of WAF from "Nordvard", oil to water loading of 1 to 10000.

Table A 1 *Summary of the chemical composition of the oils given in g analyte/kg oil (ppm). Total SVOC concentration is the sum of decalins, naphthalenes, 2-6 ring PAH and phenols, total VOC concentration is the sum of BTEX, C3-benzenes, and other volatiles from C5 to C9.*

	Bittern Oil g/kg	Boardale Oil g/kg	Erich Giese Oil g/kg	Nordvard Oil g/kg	Eric Giese Oil re-test* g/kg
Sum SVOC	19,3	9,19	29,9	37,4	66,6
Sum VOC	2,93	7,28	3,04	1,02	3,88
Decalins	1,96	1,66	1,37	21,4	3,39
Naphthalenes	6,61	3,30	9,97	10,2	21,8
2-3 ring PAH	9,80	3,84	13,6	5,59	26,5
4-6 ring PAH	0,89	0,39	5,02	0,22	10,5
C0-C5 phenols	ND	ND	1,60	ND	4,50
BTEX	0,36	1,01	0,38	0,08	0,73
C3-benzenes	0,81	2,49	0,70	0,34	1,32
Other VOC	1,76	3,78	1,96	0,59	1,82

ND: Not detected, NA: Not analyzed

	Blücher Oil g/kg	Welheim Oil g/kg	U-864 Oil g/kg	Boardale water from oil µg/L	Erich Giese water from oil µg/L
Sum SVOC	90,0	27,7	25,3	904	1829
Sum VOC	5,70	5,87	1,83	NA	NA
Decalins	1,39	8,71	5,21	76,1	ND
Naphthalenes	30,4	11,8	14,8	500	1526
2-3 ring PAH	37,0	6,63	5,12	279	285
4-6 ring PAH	16,2	0,54	0,20	49,1	18,0
C0-C5 phenols	5,03	ND	ND	ND	ND
BTEX	1,04	0,25	0,18	NA	NA
C3-benzenes	2,71	2,24	0,76	NA	NA
Other VOC	1,96	3,39	0,90	NA	NA

**Used in re-test of WAF Erich Giese 1:40 (From another bottle than the oil sample used in the first testing, and may contain less water).*

Table A 2 Summary of the chemical composition of the WAFs, given in µg/L (ppb). Total WAF concentration is the sum of TPH and total VOC, total SVOC concentration is the sum of decalins, naphthalenes, 2-6 ring PAH and phenols, total VOC concentration is the sum of BTEX, C3-benzenes, and other volatiles from C5 to C9.

	Bittern	Bittern	Boardale	Boardale	Erich Giese	Erich Giese re-test	Erich Giese	Nordvard	Nordvard
	WAF	WAF	WAF	WAF	WAF	WAF	WAF	WAF	WAF
	1:40	1:10000	1:40	1:10000	1:40	1:40	1:10000	1:40	1:10000
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Tot WAF	4604	750	6049	928	76293	84513	3697	23895	1789
TPH	4057	564	4587	575	75201	83545	3500	23282	1623
Sum SVOC	299	136	448	108	20459	41671	829	1566	216
Sum VOC	547	186	1462	353	1092	969	197	613	166
UCM	3758	428	4139	467	54742	41814	2671	21716	1407
Decalins	0,36	0,23	ND	0,32	ND	ND	0,18	6,19	1,13
Naphthalenes	189	112	123	86,3	1153	1310	521	198	134
2-3 ring PAH	32,6	21,5	25,7	17,3	409	414	162	190	53,3
4-6 ring PAH	0,11	0,22	0,25	0,22	6,233	22,4*	6,47	0,60	0,24
C0-C5 phenols	76,7	2,28	299	3,46	18890	39924	139	1171	27,3
BTEX	347	63,3	933	146	530	531	77,6	432	64,4
C3-benzenes	181	110	390	187	175	152	94,0	100	62,3
Other VOC	20,1	13,5	140	19,7	387	286	25,2	81,1	39,4

**4-6 ring PAH dominated by fluoranthene (17,3 µg/L)*

Table A 3 *Metal and element analysis of the oils (given in mg/kg oil)*

SINTEF ID Oil Isotope	SINTEF ID Oil Element	2012-0337 Erich Giese µg/g	2012-0338 Bittern µg/g	2012-0339 Boardale µg/g	2013-553 Nordvard µg/g	2013-0525 U-864 µg/g
Al27(MR)	Aluminium	2,13	0,80	2,98	0,20	0,30
As75(HR)	Arsenic	0,975	0,110	0,052	0,012	0,058
Cd111(LR)	Cadmium	0,004	0,007	0,021	0,002	0,069
Co59(MR)	Cobalt	0,059	0,340	0,082	0,002	0,002
Cr52(MR)	Chromium	0,461	0,036	0,152	0,010	ND
Cu63(MR)	Copper	0,127	0,311	1,63	0,04	0,21
Fe56(MR)	Iron	165	23,6	37,3	0,17	17,5
Hg202(LR)	Mercury	0,001	0,003	0,008	0,000	0,007
Mg24(MR)	Magnesium	1,89	30,8	233	0,31	0,41
Mn55(MR)	Manganese	0,126	0,363	0,46	0,009	0,037
Ni60(MR)	Nickel	5,01	15,9	6,68	0,05	0,02
Pb208(LR)	Lead	0,559	0,902	1,63	0,027	0,114
S34(MR)	Sulphur	10120	14590	8868	3057	2444
Si28(MR)	Silicon	NA	NA	NA	NA	NA
Tl205(LR)	Thallium	0,0003	0,0002	0,0003	ND	ND
V51(MR)	Vanadium	25,5	27,9	14,8	0,008	0,025
Zn66(MR)	Zinc	28,3	7,9	45,2	4,52	2,70

Table A 4 *Metal and element analysis of WAFs from oils and clean seawater. As WAFs from Nordvard are prepared and analyzed later, new seawater samples were analyzed and used as reference. WAFs were not prepared from U-864.*

Oil Oil to water Element	Erich 1:40 µg/L	Erich 1:10000 µg/L	Bittern 1:40 µg/L	Bittern 1:10000 µg/L	Boardal 1:40 µg/L	Boardal 1:10000 µg/L	*Seawater* *µg/L*	Nordvard 1:40 µg/L	Nordvard 1:10000 µg/L	*Seawater* *µg/L*
Aluminium	2,14	2,82	3,28	2,52	2,56	2,96	*2,74*	15,61	3,18	*3,89*
Arsenic	1,56	1,61	1,51	1,44	1,40	1,48	*1,80*	1,58	1,67	*1,68*
Cadmium	0,181	0,014	0,040	0,039	0,073	0,037	*0,059*	0,053	0,037	*0,03*
Cobalt	0,028	0,006	0,128	0,019	0,018	0,012	*0,019*	0,010	0,013	*0,02*
Chromium	0,186	0,116	0,131	0,196	0,067	0,098	*0,096*	0,260	0,190	*0,15*
Copper	0,51	1,72	2,23	3,37	1,22	1,60	*1,05*	2,90	4,02	*3,89*
Iron	0,168	0,250	0,120	0,279	0,317	0,351	*0,527*	1,320	10,220	*1,53*
Mercury	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	*< 0.02*	<0.01	<0.01	*ND*
Magnesiu	1318078	1206776	131357	128301	1321610	1320438	*130714*	113916	122836	*118634*
Manganes	1,13	0,007	0,424	0,094	0,340	0,104	*0,074*	0,330	0,420	*0,33*
Nickel	0,391	0,359	0,267	0,148	0,315	0,327	*0,315*	0,380	0,510	*0,25*
Lead	0,036	0,158	0,181	0,162	0,284	0,103	*0,015*	0,580	1,160	*1,48*
Sulphur	871762	936767	924656	923319	877140	904558	*871907*	906390	969958	*663740*
Silicon	126	112	144	97,9	161	188	*169*	62	87	*62,3*
Thallium	0,010	0,011	0,007	0,017	0,013	0,010	*0,012*	0,012	0,017	*0,01*
Vanadium	1,37	1,17	1,19	1,47	1,43	1,40	*1,35*	1,23	1,42	*1,38*
Zinc	27,6	3,43	5,050	0,630	7,730	2,960	*0,396*	61,3	3,95	*3,01*

Appendix B Additional results from the toxicity studies

Table B 1 *Preliminary data for total WAF concentration and calculated values for 10 and 50% reduction in algal growth rate and biomass production following 72 hrs exposure to dilutions from WAF systems of the* Skeletonema costatum *bioassay. Data are calculated using a four parameter logistic equation with Sigmoidal curve fitting. For calculation of the EC-values any stimulation of growth is neglected, and the values are calculated within the span of 0 and 100% effect normalized to the control series to make the data comparable between treatments.*

WAF System - Loading	Growth rate - 72h exposure		Biomass production - 72h exposure	
Concentration (mg/L)*	EC$_{10}$ (CI$_{95}$)	EC$_{50}$ (CI$_{95}$)	EC$_{10}$ (CI$_{95}$)	EC$_{50}$ (CI$_{95}$)
HMS Bittern 1:40 4.604 mg/L				
% WAF	29.97 (28.2 – 31.8)	45.29 (43.8 – 46.8)	15.83 (12.9– 19.5)	27.04 (24.5 – 29.9)
mg/L	1.379 (1.30 – 1.47)	2.085 (2.02 – 2.16)	0.729 (0.59 – 0.90)	1.245 (1.13 – 1.38)
HMS Bittern 1:10 000 0.750 mg/L				
% WAF	55.30 (33.2 – 92.1)	64.64 (60.5 – 69.0)	35.63 (28.7 – 44.3)	46.67 (41.3 – 52.7)
mg/L	0.415 (0.25 – 0.69)	0.480 (0.36 – 0.65)	0.267 (0.22 – 0.33)	0.362 (0.32 – 0.41)
RFA Boardale - 1:40 6.049 mg/L				
% WAF	35.70 (very wide)	39.10 (very wide)	33.38 (very wide)	36.14 (very wide)
mg/L	2.161 (very wide)	2.368 (very wide)	2.020 (very wide)	2.188 (very wide)
RFA Boardale 1:10000 0.929 mg/L				
% WAF	34.80 (28.1 – 43.)	96.98 (86.8 – 108)	33.14 (very wide)	36.16 (very wide)
mg/L	0.323 (0.261– 0.40)	0.901 (0.81 – 1.01)	0.308 (very wide)	0.336 (very wide)
Erich Giese - 1:40 76.293 mg/L				
% WAF	< 3.0 (NC)	< 3.0 (NC)	< 3.0 (NC)	< 3.0 (NC)
mg/L	< 2.289 (NC)	< 2.289 (NC)	< 2.289 (NC)	< 2.289 (NC)
Erich Giese - 1:40 84.513 mg/L re-test				
% WAF	1.772 (very wide)	1.935 (very wide)	0.777 (0.72 – 0.84)	1.387 (1.34 – 1.44)
mg/L	1.498 (very wide)	1.635 (very wide)	0.657 (0.60 – 0.70)	1.172 (1.12 – 1.20)
Erich Giese - 1:10 000 3.696 mg/L				
% WAF	5.045 (4.47 – 5.69)	7.981 (7.63 – 8.35)	4.408 (3.78 – 5.14)	5.616 (4.91 – 6.43)
mg/L	0.186 (0.17 – 0.21)	0.295 (0.28 – 0.311)	0.163 (0.14 – 0.19)	0.208 (0.18 – 0.24)
Nordvard – 1;40 23.895 mg/L				
% WAF	7.62 (6.88 – 8.45)	8.97 (7.87 – 10.2)	NC**	NC**
mg/L	1.82 (1.64 – 2.01)	2.14 (1.89 – 2.43)	NC	NC
Nordvard – 1:10000 1.789 mg/L	45.0 (40.0 – 50.8)	63.3 (60.7 – 66.0)	26.4 (21.4 – 32.6)	38.6 (35.6 – 41.9)
% WAF	0.806 (0.72–0.91)	1.13 (1.09 – 1.18)	0.473 (0.381-0.58)	0.69 (0.64 – 0.75)
mg/L	7.62 (6.88 – 8.45)	8.97 (7.87 – 10.2)	NC**	NC**

* Concentration based on analytical data from undiluted WAF;

NC: Not calculated (Due to the performance of the bioassay conclusive data for reduction in biomass production could not be calculated from the results)

Table B 2 *Preliminary data for total WAF concentration and observed effect as % reduction in algal growth rate and biomass production following 72 hrs exposure to undiluted WAF (100 %) of the* Skeletonema costatum *bioassay.*

WAF System - Loading Concentration (mg/L)*	Growth rate - 72h exposure % effect	Biomass production - 72h exposure % effect
HMS Bittern - 1:40 4.604 mg/L	100	100
HMS Bittern 1:10000 0.750 mg/L	100	97.7
RFA Boardale - 1:40 6.049 mg/L	100	100
RFA Boardale - 1:10000 0.929 mg/L	50.4	95.5
Erich Giese - 1:40 76.293 mg/L	100	100
Erich Giese - 1:10 000 3.696 mg/L	100	100
Erich Giese -1:40 84.513 mg/L re-test	100	100
Nordvard – 1:40 23.895 mg/L	100	Not calculated
Nordvard -1:10000 1.789 mg/L	100	95.2

** Concentration based on analytical data from undiluted WAF.*

Table B 3 *Preliminary data for total WAF concentration and calculated values for 10 and 50% lethal immobilization following 24, 48, 72 and 96 hours of exposure to the* Calanus finmarchicus *bioassay of bunker fuel from HMS* ***Bittern.*** *Data are calculated using a four parameter logistic equation with Sigmoidal curve fitting. The data in the exposure series are not corrected for any control mortality and the values are calculated within the span of 0 and 100% effect to make the data comparable between treatments.*

WAF System - Loading Concentration (mg/L)*		24 hours	48 hours	72 hours	96 hours
HMS Bittern - 1:40 4.604 mg/L					
LC_{10}	% WAF ($CI_{95\%}$)	> 100% (NC)	93.24 (very wide)	39.22 (32.3 – 47.6)	31.66 (26.9 – 37.3)
	mg/L ($CI_{95\%}$)	> 4.604(NC)	4.299 (very wide)	1.815 (1.49 – 2.21)	1.459 (1.24 – 1.72)
LC_{50}	% WAF ($CI_{95\%}$)	> 100% (NC)	98.43 (very wide)	61.77 (57.0 – 66.9)	54.62 (50.9 – 58.6)
	mg/L ($CI_{95\%}$)	> 4.604 (NC)	4.530 (very wide)	2.850 (2.61 – 3.09)	2.518 (2.35 – 2.70)
HMS Bittern 1:10000 0.750 mg/L					
LC_{10}	% WAF ($CI_{95\%}$)	> 100% (NC)	> 100% (NC)	> 100% (NC)	61.15 (48.3– 77.5)
	mg/L ($CI_{95\%}$)	> 0.750 (NC)	> 0.750 (NC)	> 0.750 (NC)	0.459 (0.36 – 0.58)
LC_{50}	% WAF ($CI_{95\%}$)	> 100% (NC)	> 100% (NC)	> 100% (NC)	> 100% (NC)
	mg/L ($CI_{95\%}$)	> 0.750 (NC)	> 0.750 (NC)	> 0.750 (NC)	> 0.750 (NC)

* Concentration based on analytical data from undiluted WAF; CI_{95}: 95% Confidence Intervals; NC: Not calculated.

Table B 4 *Preliminary data for total WAF concentration and calculated values for 10 and 50% lethal immobilization following 24, 48, 72 and 96 hours of exposure to the* Calanus finmarchicus *bioassay of bunker fuel from RFA* ***Boardale****. Data are calculated using a four parameter logistic equation with Sigmoidal curve fitting. The data in the exposure series are not corrected for any control mortality and the values are calculated within the span of 0 and 100% effect to make the data comparable between treatments.*

WAF System - Loading Concentration (mg/L)*	24 hours	48 hours	72 hours	96 hours
RFA Boardale - 1:40 6.049 mg/L				
LC$_{10}$ % WAF (CI$_{95\%}$)	96.35 (very wide)	59.21 (51.0 – 68.8)	40.50 (36.1 – 45.5)	38.34 (34.6 – 42.5)
mg/L (CI$_{95\%}$)	5.839 (very wide)	3.584 (3.08 – 4.17)	2.451 (2.18 – 2.75)	2.321 (2.09 – 2.58)
LC$_{50}$ % WAF (CI$_{95\%}$)	> 100% (NC)	81.22 (75.0 – 87.9)	59.68 (57.4 – 62.0)	50.68 (48.6 – 52.9)
mg/L (CI$_{95\%}$)	> 6.049 (NC)	4.917 (4.54 – 5.32)	3.613 (3.48 – 3.76)	3.068 (2.94 – 3.20)
RFA Boardale - 1:10000 0.929 mg/L				
LC$_{10}$ % WAF (CI$_{95\%}$)	> 100% (NC)	> 100% (NC)	> 100% NC)	94.74(very wide)
mg/L (CI$_{95\%}$)	> 0.750 (NC)	> 0.750 (NC)	> 0.750 (NC)	0.880 (very wide)
LC$_{50}$ % WAF (CI$_{95\%}$)	> 100% (NC)	> 100% (NC)	> 100% NC)	> 100% (NC)
mg/L (CI$_{95\%}$)	> 0.929 (NC)	> 0.929 (NC)	> 0.929 (NC)	> 0.929(NC)

* Concentration based on analytical data from undiluted WAF; CI$_{95}$: 95% Confidence Intervals; NC: Not calculated.

Table B 5 *Preliminary data for total WAF concentration and calculated values for 10 and 50% lethal immobilization following 24, 48, 72 and 96 hours of exposure to the* Calanus finmarchicus *bioassay of bunker fuel from* ***Erich Giese****. Data are calculated using a four parameter logistic equation with Sigmoidal curve fitting. The data in the exposure series are not corrected for any control mortality and the values are calculated within the span of 0 and 100% effect to make the data comparable between treatments.*

WAF System - Loading Concentration (mg/L)*	24 hours	48 hours	72 hours	96 hours
Erich Giese - 1:40 76.293 mg/L				
LC$_{10}$ % WAF (CI$_{95\%}$)	6.690 (5.76 – 7.77)	5.553 (4.24 – 7.27)	< 4.20 (NC)	< 4.20 (NC)
mg/L (CI$_{95\%}$)	5.110 (4.40 – 5.93)	4.242 (3.24 – 5.55)	< 3.204 (NC)	< 3.204 (NC)
LC$_{50}$ % WAF (CI$_{95\%}$)	9.226 (8.39 – 10.1)	7.347 (6.89 – 7.83)	4.515 (4.37 – 4.66)	< 4.20 (NC)
mg/L (CI$_{95\%}$)	7.047 (6.44 – 7.75)	5.612 (5.27 – 5.98)	3.449 (3.34 – 3.56)	< 3.204 (NC)
Erich Giese - 1:40 84.513 mg/L re-test				
LC$_{10}$ % WAF (CI$_{95\%}$)	4.689 (4.21 – 5.22)	2.182 (1.70 – 2.80)	1.497 (1.23 – 1.82)	1.254 (1.04 – 1.52)
mg/L (CI$_{95\%}$)	3.963 (3.52 – 4.36)	1.844 (1.42 – 2.34)	1.265 (1.03 – 1.52)	1.060 (0.87 – 1.27)
LC$_{50}$ % WAF (CI$_{95\%}$)	5.855 (5.25 – 6.53)	4.560 (4.07 – 5.11)	3.475 (3.16 – 3.78)	2.667 (2.45 – 2.91)
mg/L (CI$_{95\%}$)	4.948 (4.38 – 5.46)	3.854 (3.40 – 4.27)	2.937 (2.64 – 3.16)	2.254 (2.04 – 2.43)
Erich Giese - 1:10000 3.696 mg/L				
LC$_{10}$ % WAF (CI$_{95\%}$)	59.62 (51.3 – 69.4)	43.92 (34.8– 55.4)	16.12 (12.3 – 21.1)	13.73 (10.8 – 17.4)
mg/L (CI$_{95\%}$)	2.205 (1.90 – 2.57)	1.642 (1.29 – 2.05)	0.595 (0.46 – 0.78)	0.507 (0.40 – 0.64)
LC$_{50}$ % WAF (CI$_{95\%}$)	94.18 (89.4 – 99.2)	74.66 (66.7 – 83.6)	37.70 (33.4 – 42.6)	28.96 (25.9 – 32.3)
mg/L (CI$_{95\%}$)	3.483 (3.31-3.67)	2.761 (2.47 – 3.09)	1.394 (1.23 – 1.57)	1.070 (0.96 – 1.20)

* Concentration based on analytical data from undiluted WAF; CI$_{95}$: 95% Confidence Intervals; NC: Not calculated.

Table B 6 *Preliminary data for total WAF concentration and calculated values for 10 and 50% lethal immobilization following 24, 48, 72 and 96 hours of exposure to the* Calanus finmarchicus *bioassay of bunker fuel from* ***Nordvard****. Data are calculated using a four parameter logistic equation with Sigmoidal curve fitting. The data in the exposure series are not corrected for any control mortality and the values are calculated within the span of 0 and 100% effect to make the data comparable between treatments.*

WAF System - Loading Concentration (mg/L)*	24 hours	48 hours	72 hours	96 hours
Nordvard - 1:40 23.895 mg/L				
LC_{10} % WAF ($CI_{95\%}$)	26.7 (22.7 – 31.3)	13.5 (12.0 – 15.0)	11.6 (9.90 – 13.6)	9.03 (34.6 – 42.5)
mg/L ($CI_{95\%}$)	6.38 (5.43 – 7.48)	3.21 (2.87 – 3.59)	2.77 (2.37 – 3.25)	2.16 (1.99 – 2.34)
LC_{50} % WAF ($CI_{95\%}$)	37.9 (35.2 – 40.8)	23.4 (22.2 – 24.6)	19.7 (18.4 – 21.1)	14.7 (14.1 – 15.3)
mg/L ($CI_{95\%}$)	9.05 (8.41 – 9.75)	5.58 (5.29 – 5.88)	4.71 (4.40 – 5.03)	3.52 (3.38 – 3.66)
Nordvard - 1:10000 1.789 mg/L				
LC_{10} % WAF ($CI_{95\%}$)	> 100% (very wide)	51.3 (38.8 – 67.9)	31.2 (22.4 – 43.6)	22.4 (19.2 – 26.1)
mg/L ($CI_{95\%}$)	> 1.789 (very wide)	0.92 (0.69 – 0.78)	0.56 (0.40 – 0.78)	0.40 (0.34 – 0.47
LC_{50} % WAF ($CI_{95\%}$)	> 100% (very wide)	> 100% (NC)	> 100% (NC)	40.9(38.0 – 43.9)
mg/L ($CI_{95\%}$)	> 1.789 (very wide)	> 1.789 (NC)	> 1.789 (NC)	0.73 (0.68 – 0.79)

* Concentration based on analytical data from undiluted WAF; CI_{95}: 95% Confidence Intervals; NC: Not calculated.

Table B 7 *Preliminary data for total WAF concentration and observed effect as % lethal immobilisation in undiluted WAF (100%) following 24, 48, 72 and 96 hours of exposure to the* Calanus finmarchicus *bioassay of WAF from the bunker fuels.*

WAF System - Loading Concentration (mg/L)*	24 hours % lethal immobilisation	48 hours % lethal immobilisation	72 hours % lethal immobilisation	96 hours % lethal immobilisation
HMS Bittern - 1:40 4.604 mg/L	0	67	100	100
HMS Bittern - 1:10000 0.750 mg/L	0	0	4.8	28.6
RFA Boardale - 1:40 6.049 mg/L	33.3	81	95.2	100
RFA Boardale - 1:10000 0.929 mg/L	0	0	0	19
Erich Giese - 1:40 76.293 mg/L	100	100	100	100
Erich Giese - 1:40 84.513 mg/L (re-test)	100	100	100	100
Erich Giese - 1:10 00 3.696 mg/L	57.1	76.2	100	100
Nordvard – 1:40 23.895 mg/L	100	100	100	100
Nordvard – 1:10000 1.789 mg/L	4.8	23.8	42.9	45.2

* Concentration based on analytical data from undiluted WAF.

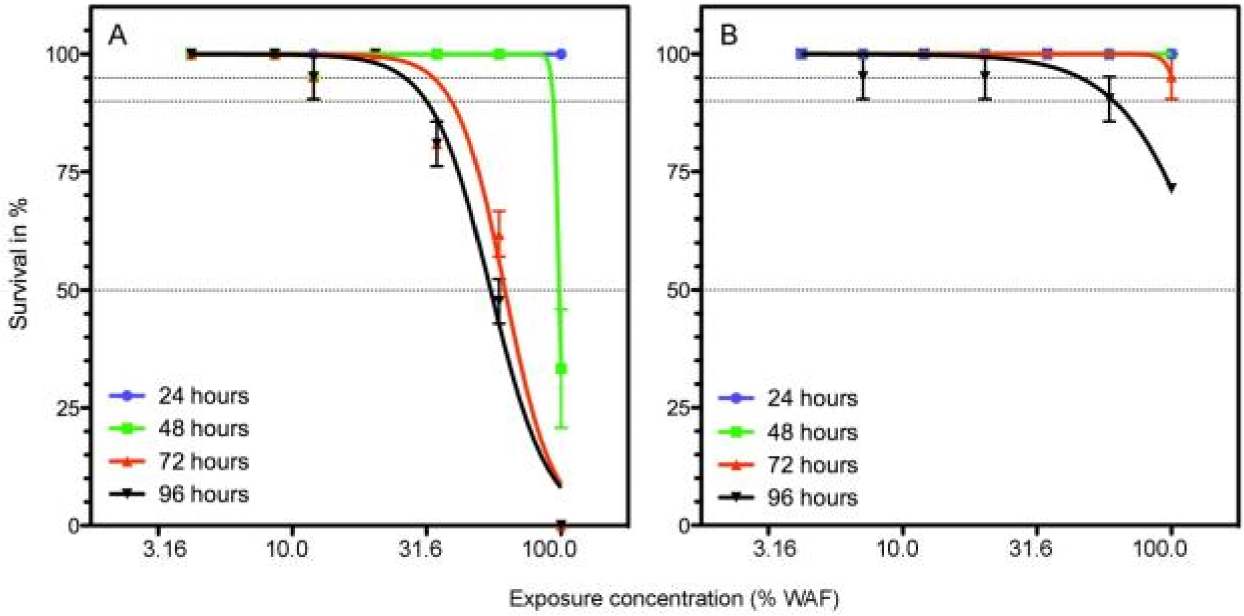


Figure B 1 *WAF from Bittern: Survival of the copepod* Calanus finmarchicus *as a function of WAF concentrations: Oil to water loading 1 to 40(A) and 1 to 10000 (B) for the different time intervals of the test using Sigmoid curve fitting.*

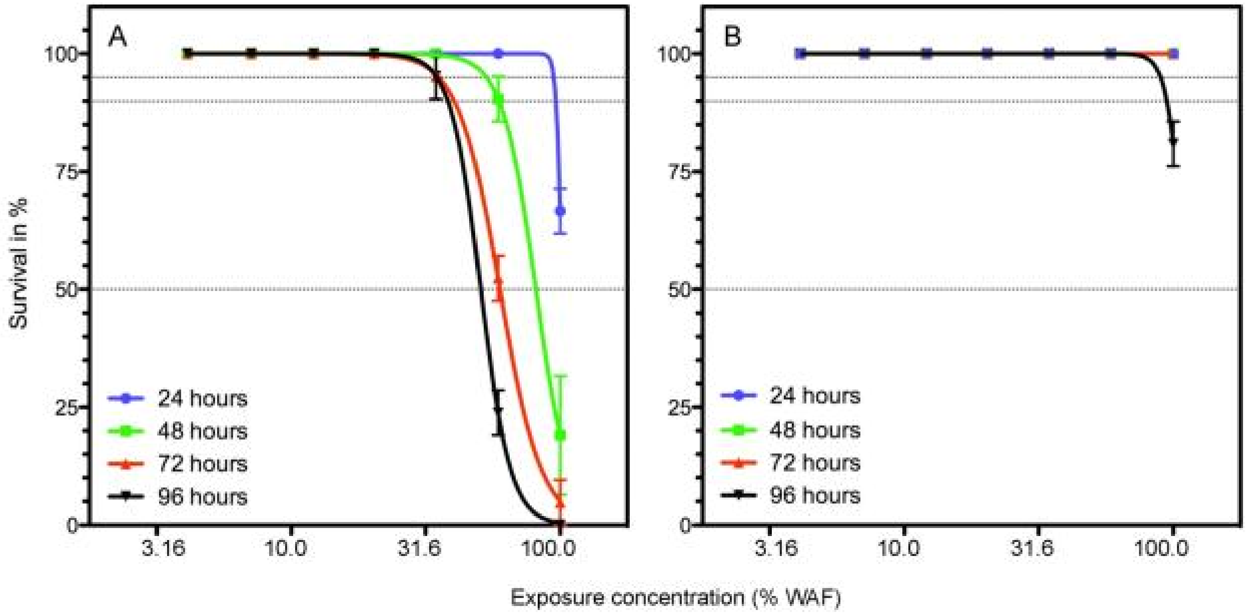


Figure B 2 *WAF from Boardale: Survival of the copepod* Calanus finmarchicus *as a function of WAF concentrations: Oil to water loading 1 to 40(A) and 1 to 10000 (B) for the different time intervals of the test using Sigmoid curve fitting*

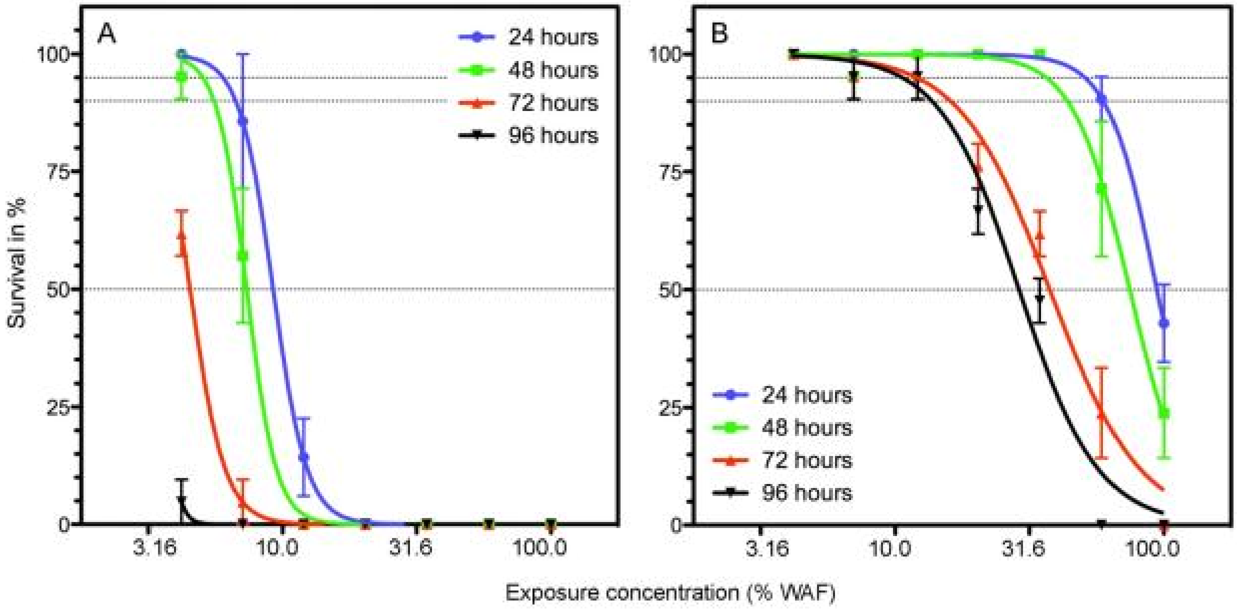


Figure B 3 *WAF from Erich Giese: Survival of the copepod* Calanus finmarchicus *as a function of WAF concentrations: Oil to water loading 1 to 40(A) and 1 to 10000 (B) for the different time intervals of the test using Sigmoid curve fitting*

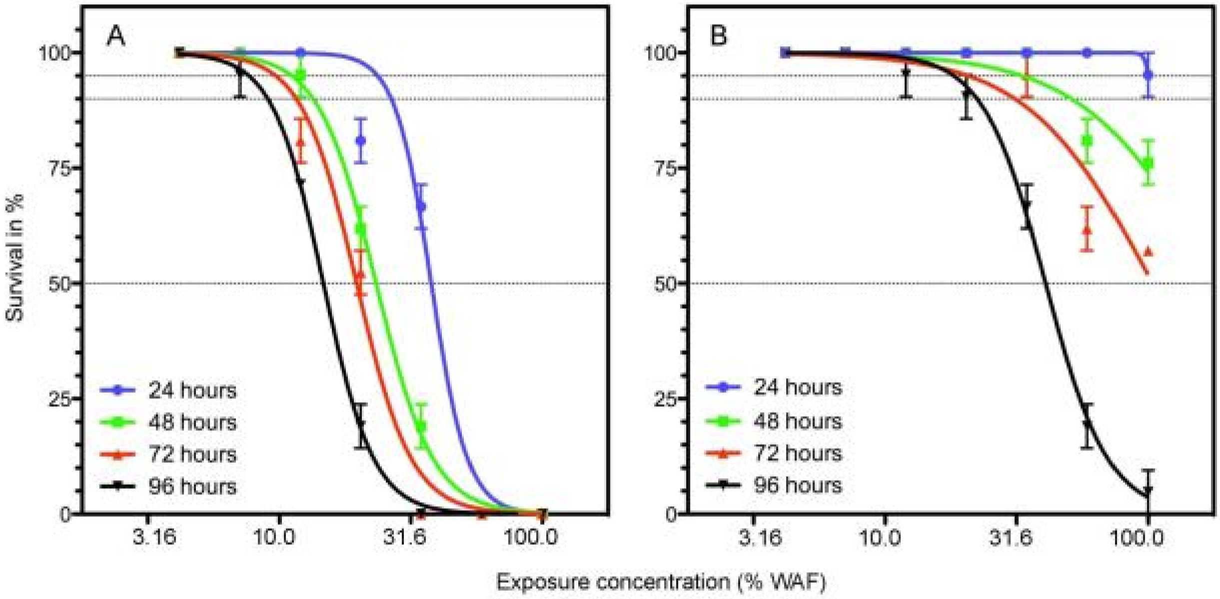


Figure B 4 *WAF from Nordvard: Survival of the copepod* Calanus finmarchicus *as a function of WAF concentrations: Oil to water loading 1 to 40(A) and 1 to 10000 (B) for the different time intervals of the test using Sigmoid curve fitting*

Appendix C Overview of component groups used in tables and figures

Table C 1 Target organic analytes (SVOC: Semi volatile organic compounds, VOC: Volatile organic compounds, TPH: Total petroleum hydrocarbons, UCM. Unresolved organic materials).

	Compound	Abb	Group	Compound	Abb
SVOC	Decalin	DE		Perylene	PE
	C1-decalins	DE1		Indeno[*1,2,3-c,d*]pyrene	IN
	C2-decalins	DE2		Dibenz[*a,h*]anthracene	DBA
	C3-decalins	DE3		Benzo(g,h,i)perylene	BPE
	C4-decalins	DE4	C0-C5 phenols	Phenol	PH
Naphthalenes	Naphthalene	N		C1-phenols	PH1
	C1-naphthalenes	N1		C2-phenols	PH2
	C2-naphthalenes	N2		C3-phenols	PH3
	C3-naphthalenes	N3		C4-phenols	PH4
	C4-naphthalenes	N4		C5-phenols	PH5
2-3 ring PAHs	Benzo(b)thiophene	BT	VOC (incl BTEX and C3-benzenes)	Isopentane	
	C1-benzo(b)thiophene	BT1		n-C5 (Pentane)	
	C2-benzo(b)thiophene	BT2		Cyclopentane	
	C3-benzo(b)thiophene	BT3		2-methylpentane	
	C4-benzo(b)thiophene	BT4		3-methylpentane	
	Biphenyl	B		n-C6 (Hexane)	
	Acenaphthylene	ANY		Methylcyclopentane	
	Acenaphthene	ANA		Cyclohexane	
	Dibenzofuran	DBF		2,3-dimethylpentane	
	Fluorene	F		3-methylhexane	
	C1-fluorenes	F1		n-C7 (Heptane)	
	C2-fluorenes	F2		Methylcyclohexane	
	C3-fluorenes	F3		2,4-dimethylhexane	
	Phenanthrene	P		2-methylheptane	
	Anthracene	A		n-C8 (Octane)	
	C1-phenanthrenes/anthracenes	P1		n-C9 (Nonane)	
	C2-phenanthrenes/anthracenes	P2		n-C10 (Decane)	
	C3-phenanthrenes/anthracenes	P3		n-Butylbenzene	
	C4-phenanthrenes/anthracenes	P4		1,2,4,5-tetramethylbenzene	
	Dibenzothiophene	D		n-pentylbenzene	
	C1-dibenzothiophenes	D1		C4-benzenes	
	C2-dibenzothiophenes	D2		C5-benzenes	
	C3-dibenzothiophenes	D3	BTEX	Benzene	
	C4-dibenzothiophenes	D4		Toluene	
4-6 ring PAHs	Fluoranthene	FL		Ethylbenzene	
	Pyrene	PY		*m*-xylene	
	C1-fluoranthrenes/pyrenes	FL1		*p*-xylene	
	C2-fluoranthenes/pyrenes	FL2		*o*-xylene	
	C3-fluoranthenes/pyrenes	FL3	C3-benzenes	Propylbenzene	
	Benz[*a*]anthracene	BA		1-methyl-3-ethylbenzene	
	Chrysene	C		1-methyl-4-ethylbenzene	
	C1-chrysenes	C1		1,3,5-Trimethylbenzene	
	C2-chrysenes	C2		1-methyl-2-ethylbenzene	
	C3-chrysenes	C3		1,2,4-trimethylbenzene	
	C4-chrysenes	C4		1,2,3-trimethylbenzene	
	Benzo[*b*]fluoranthene	BBF			
	Benzo[*k*]fluoranthene	BKF	TPH	C10-C36	
	Benzo[*e*]pyrene	BEP	WAF	Sum of VOC and TPH	
	Benzo[*a*]pyrene	BAP	UCM	TPH - SVOC	

Table C 2 *Chemical elements analyzed using HR-ICP-MS (LR: Low resolution, MR: Medium resolution, HR: High resolution).*

Element	Isotope
Aluminium	Al27 (MR)
Arsenic	As75 (HR)
Cadmium	Cd111 (LR)
Cobalt	Co59 (MR)
Chromium	Cr52 (MR)
Copper	Cu63 (MR)
Iron	Fe56 (MR)
Mercury	Hg202 (LR)
Magnesium	Mg24 (MR)
Manganese	Mn55 (MR)
Nickel	Ni60 (MR)
Lead	Pb208 (LR)
Sulphur	S34 (MR)
Silicon	Si28 (MR)
Thallium	Tl205 (LR)
Vanadium	V51 (MR)
Zinc	Zn66 (MR)

Appendix D Input data to SINTEF Oil Weathering Model (OWM)

The laboratory data used as input to the SINTEF OWM for Erich Giese, Bittern, and Boardale are given in tables below. The True Boiling Point (TBP) curve for the 3 shipwreck oils were analyzed by High temperature GC/FID at Statoil - Crude Oil and Products (CP) laboratory, 2013.

Table D 1 Physical and chemical properties for the 3 shipwreck oils, used as input in the oil weathering model.

Properties of fresh oil	Erich Giese	Bittern	Boardale
Specific Gravity (60 F/15.5°C)	0.937	0.925	0.936
Pour point (°C)	-9	-3	-3
Reference temperature (°C)	13	13	13
Viscosity at ref. temp. (mPas = cP) *	77	397	280
Asphaltenes (wt.%)	2.4	1.3	0.86
Flash Point (°C)	74	104	146
Wax Content (wt.%)	1.0	4.3	3.0

** Measured at shear rate 10s^{-1}*

Table D 2 True boiling point (TBP) curve for Erich Giese.

Temperature °C	Cumulative loss, Weight %	Cumulative loss, Volume %*
201	5	6
234	10	12
261	20	23
292	30	35
317	40	46
344	50	56
373	60	67
405	70	77
445	80	88
518	90	98

**Calculated values*

Table D 3 True boiling point (TBP) curve for Bittern.

Temperature °C	Cumulative loss, Weight %	Cumulative loss, Volume %*
215	5	6
240	10	12
282	20	23
320	30	34
359	40	44
399	50	55
437	60	65
481	70	75
532	80	85
599	90	98

**Calculated values*

Table D 4 True boiling point (TBP) curve for Boardale

Temperature °C	**Cumulative loss, Weight %**	**Cumulative loss, Volume %***
195	5	6
225	10	12
267	20	24
306	30	35
344	40	45
384	50	56
422	60	66
460	70	77
506	80	87
572	90	97

**Calculated values*

Table D 5 Lab weathering data for Erich Giese, 13 °C. Values marked with "Bold" are analytical data; the other data are estimated (fresh oil are similar with the 150 °C+ residue).

Property	**Fresh**	**150°C+**	**200°C+**	**250°C+**
Vol. topped (%)	0	1	8	22
Weight Residue (wt.%)	100	100	93	79
Specific Gravity (g/ml)	**0.937**	**0.937**	0.94	0.95
Pour point (°C)	**-9**	**-9**	-3	0
Flash Point (°C)	**74**	**74**	90	110
*Viscosity of water-free residue (mPas =cP),	**77**	**77**	100	200
*Viscosity of 50% emulsion (mPas = cP)	-	700	1000	2000
*Viscosity of 75% emulsion (mPas = cP)	-	-	-	-
*Viscosity of max water (mPas = cP)	-	**7**	20	50
Max. water cont. (vol.%)	-	**91**	91	91
($T_{1/2}$) Halftime for water uptake (hrs)	-	**0.18**	0.2	0.2
Stability ratio**	-	**0.97**	0.97	0.97

** Measured at shear rate 10 s^{-1}*

*** The emulsion was highly unstable when mechanical stress was applied*

\- *No data*

Table D 6 Lab weathering data for Bittern, 13 °C. Values marked with "Bold" are analytical data; the other data are estimated (fresh oil are similar with the 150 °C+ residue).

Property	**Fresh**	**150°C+**	**200°C+**	**250°C+**
Vol. topped (%)	0	0	5	15
Weight Residue (wt.%)	100	100	96	87
Specific Gravity (g/ml)	**0.925**	**0.925**	0.93	0.94
Pour point (°C)	**-3**	**-3**	0	2
Flash Point (°C)	**146**	**146**	150	160
*Viscosity of water-free residue (mPas =cP),	**397**	**397**	600	600
*Viscosity of 50% emulsion (mPas = cP)	-	4000	5000	8000
*Viscosity of 75% emulsion (mPas = cP)	-	-	-	-
*Viscosity of max water (mPas = cP)	-	**6208**	8000	12000
Max. water cont. (vol.%)	-	**78**	78	78
($T_{1/2}$) Halftime for water uptake (hrs)	-	**0.24**	0.5	0.5
Stability ratio	-	**0.96**	0.96	0.96

** Measured at shear rate 10 s^{-1}*

- No data

Table D 7 Lab weathering data for Boardale, 13 °C. Values marked with "Bold" are analytical data; the other data are estimated (fresh oil are similar with the 150 °C+ residue).

Property	**Fresh**	**150°C+**	**200°C+**	**250°C+**
Vol. topped (%)	0	1	7	20
Weight Residue (wt.%)	100	100	94	82
Specific Gravity (g/ml)	**0.936**	**0.936**	0.94	0.95
Pour point (°C)	**-3**	**-3**	0	-3
Flash Point (°C)	**104**	**104**	110	120
*Viscosity of water-free residue (mPas =cP),	**280**	**280**	300	400
*Viscosity of 50% emulsion (mPas = cP)	-	2000	4000	8000
*Viscosity of 75% emulsion (mPas = cP)	-	-	-	-
*Viscosity of max water (mPas = cP)	-	**2440**	5000	10000
Max. water cont. (vol.%)	-	**60**	60	60
($T_{1/2}$) Halftime for water uptake (hrs)	-	**0.16**	0.2	0.2
Stability ratio	-	1	1	1

** Measured at shear rate 10 s^{-1}*

- No data

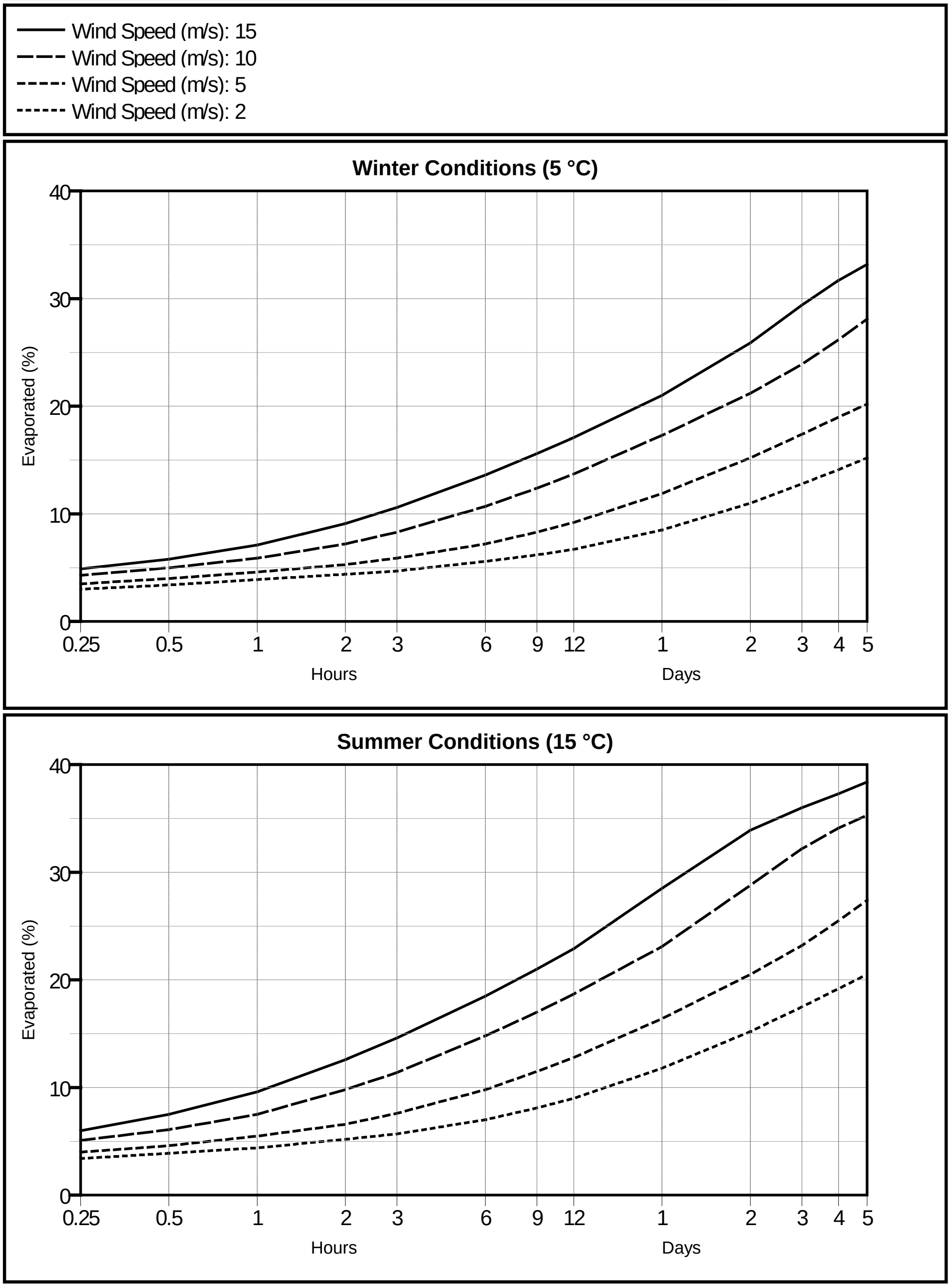
Appendix E Subsurface release predictions by use of SINTEF Oil Weathering Model (OWM)

Property: EVAPORATIVE LOSS
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

OWModel

Release depth/Gas-to-Oil ratio: 65 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013



Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

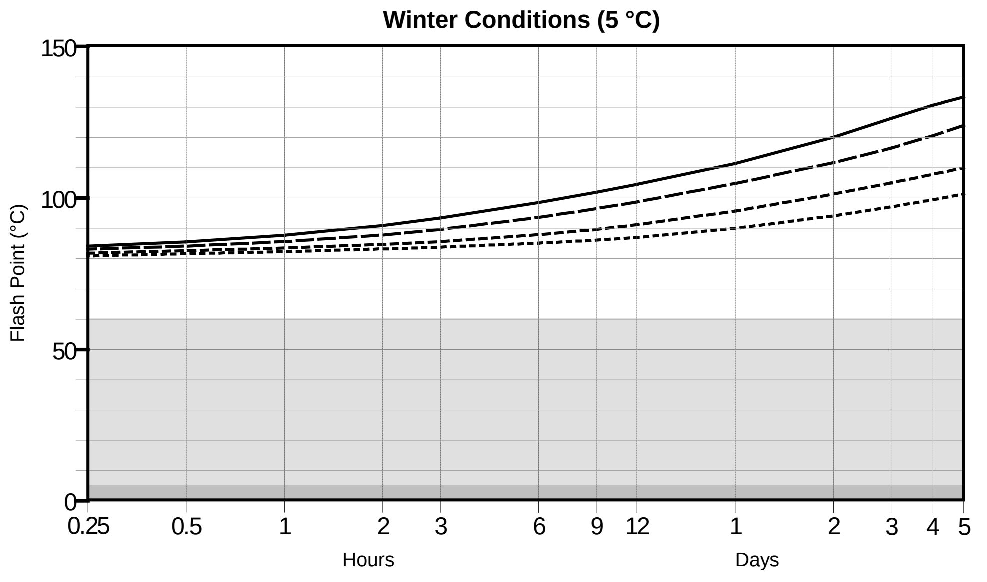
OWModel

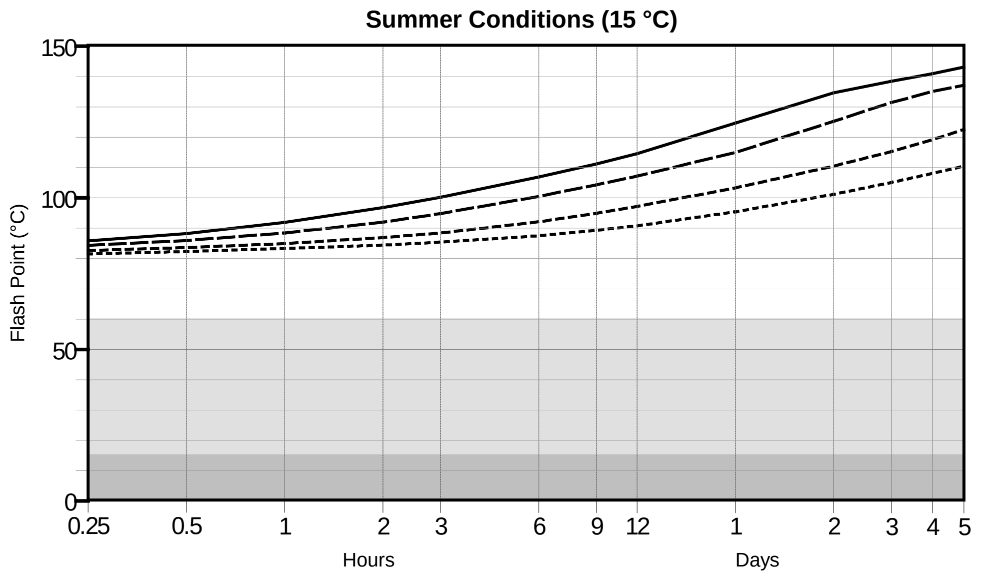
Release depth/Gas-to-Oil ratio: 65 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

—— Wind Speed (m/s): 15
— — — Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
------ Wind Speed (m/s): 2

☐ No fire hazard
▨ Fire hazard in tankage (<60 °C)
■ Fire hazard at sea surface (below sea temperature)





Based on flash point measurements of weathered, water-free oil residues.

Property: POUR POINT FOR WATER-FREE OIL
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

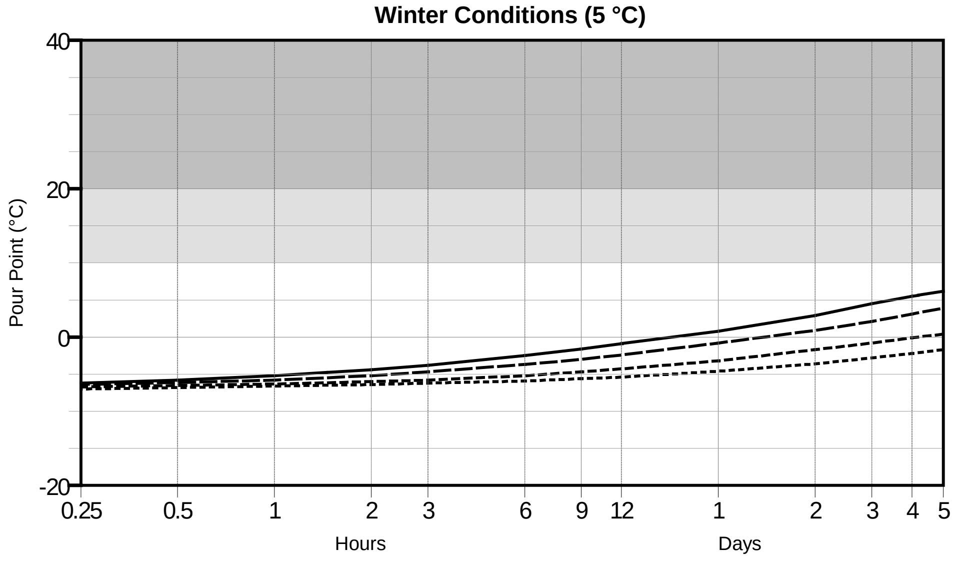
OWModel

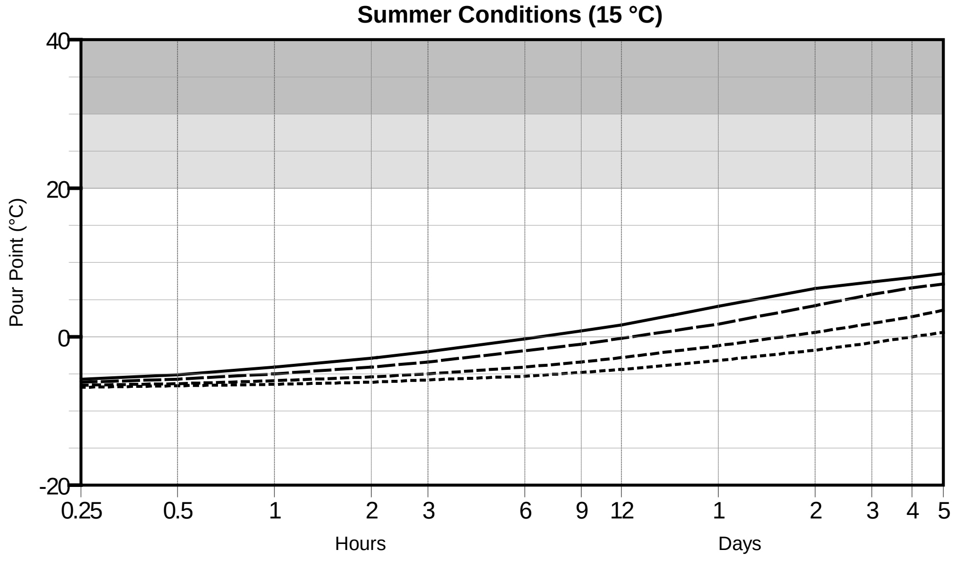
Release depth/Gas-to-Oil ratio: 65 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

—— Wind Speed (m/s): 15
– – – Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
······ Wind Speed (m/s): 2

☐ Chemically dispersible
░ Reduced chemical dispersibility
▒ Poorly / slowly chemically dispersible





Based on pour point measurements of weathered, water-free oil residues.

Property: WATER CONTENT
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

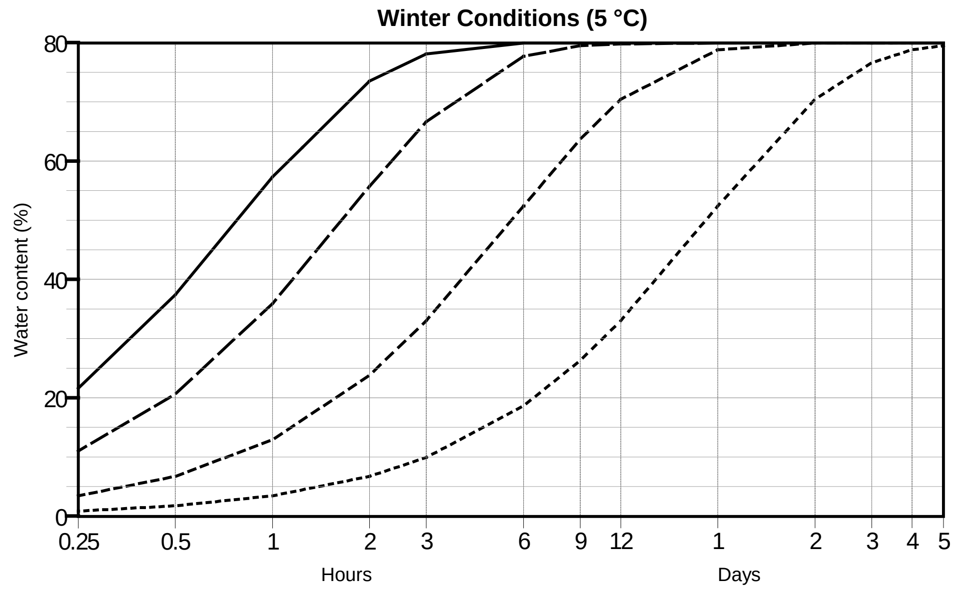
SINTEF

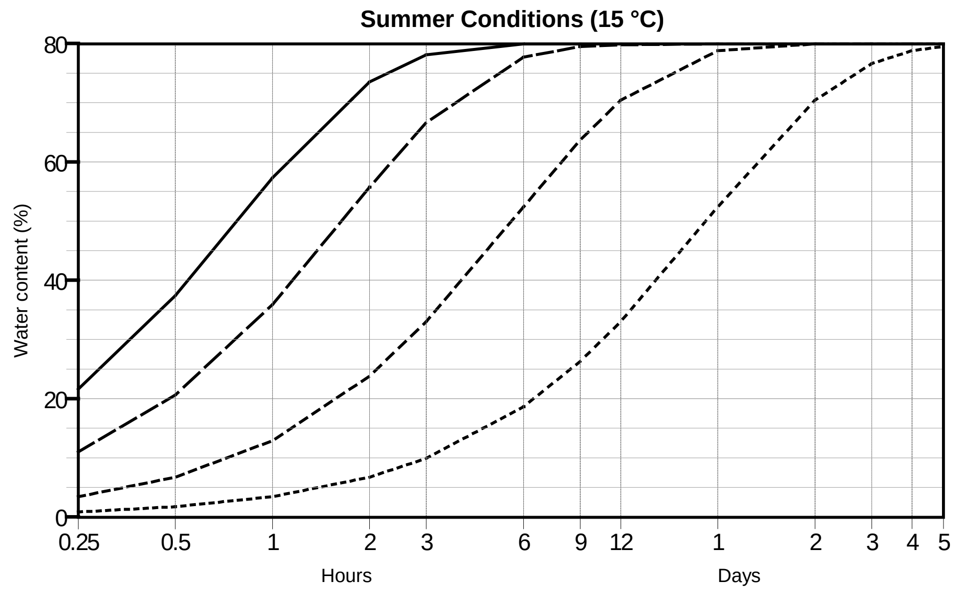
OWModel

Release depth/Gas-to-Oil ratio: 65 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

——— Wind Speed (m/s): 15
— — — Wind Speed (m/s): 10
- - - - - Wind Speed (m/s): 5
------ Wind Speed (m/s): 2





Property: VISCOSITY OF EMULSION
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

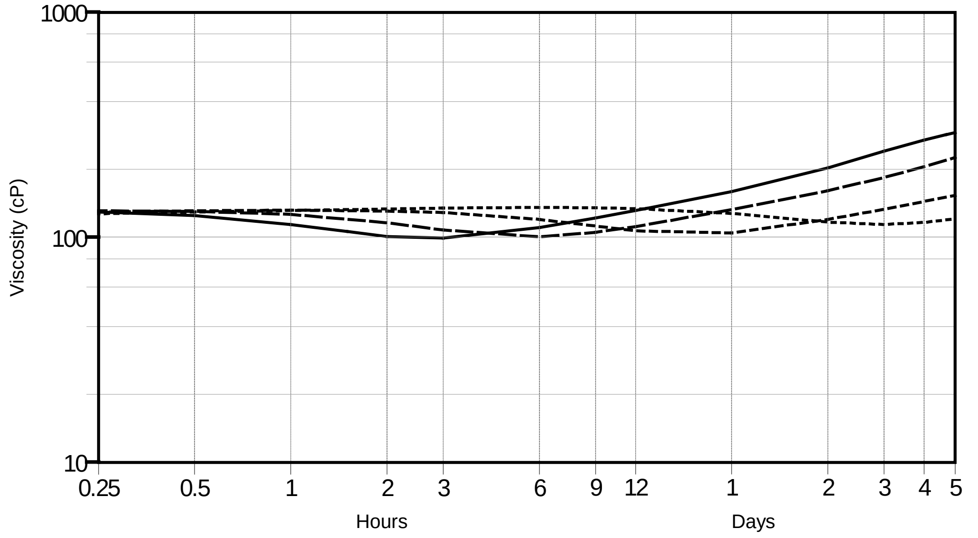
SINTEF

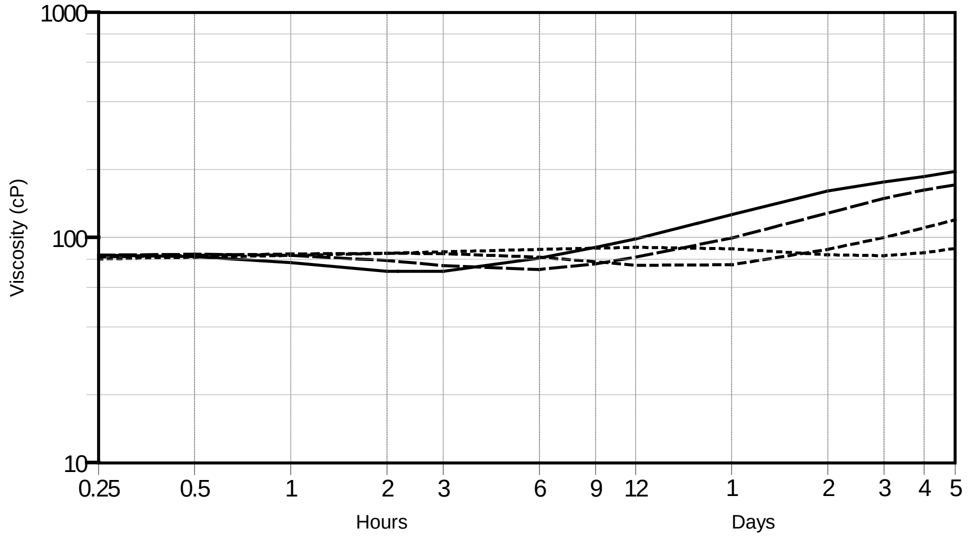
OWModel

Release depth/Gas-to-Oil ratio: 65 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

— Wind Speed (m/s): 15
— — Wind Speed (m/s): 10
- - - Wind Speed (m/s): 5
------ Wind Speed (m/s): 2


Winter Conditions (5 °C)


Summer Conditions (15 °C)

Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Property: MASS BALANCE
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

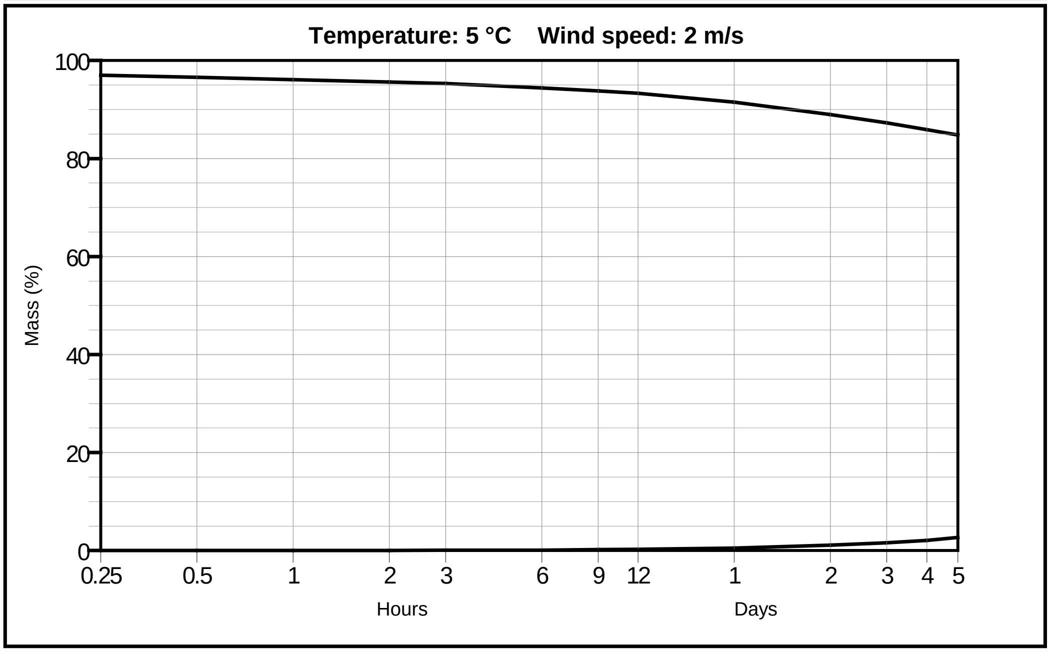
SINTEF

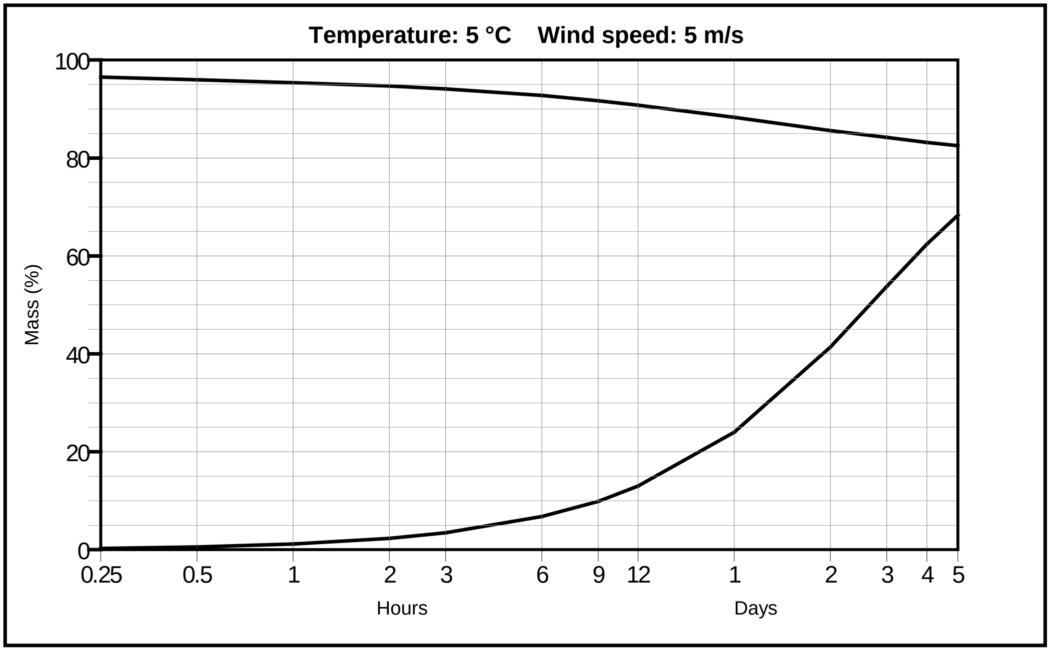
OWModel

Release depth/Gas-to-Oil ratio: 65 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed





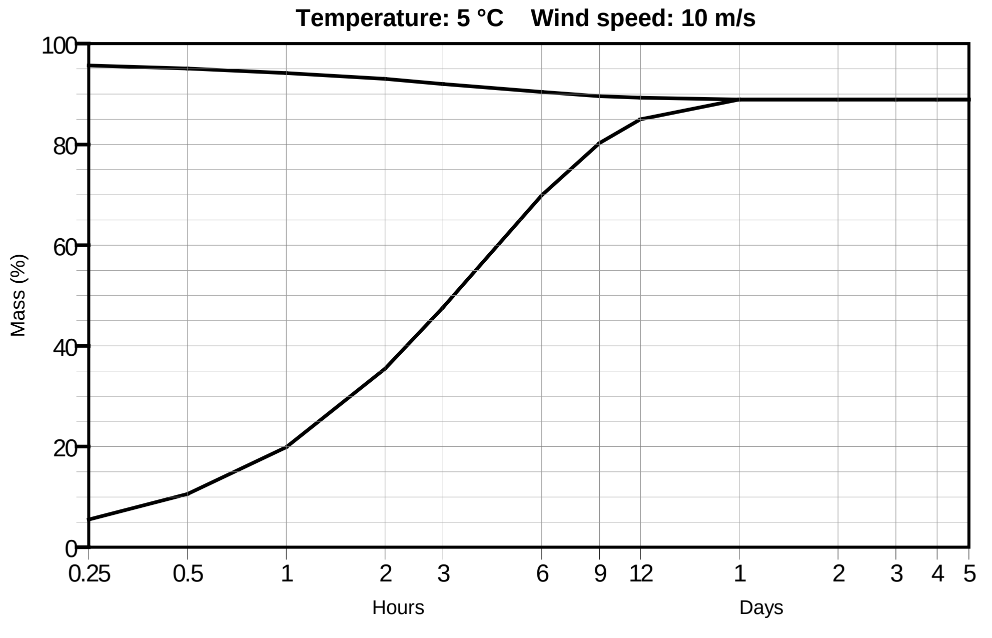
Property: MASS BALANCE
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

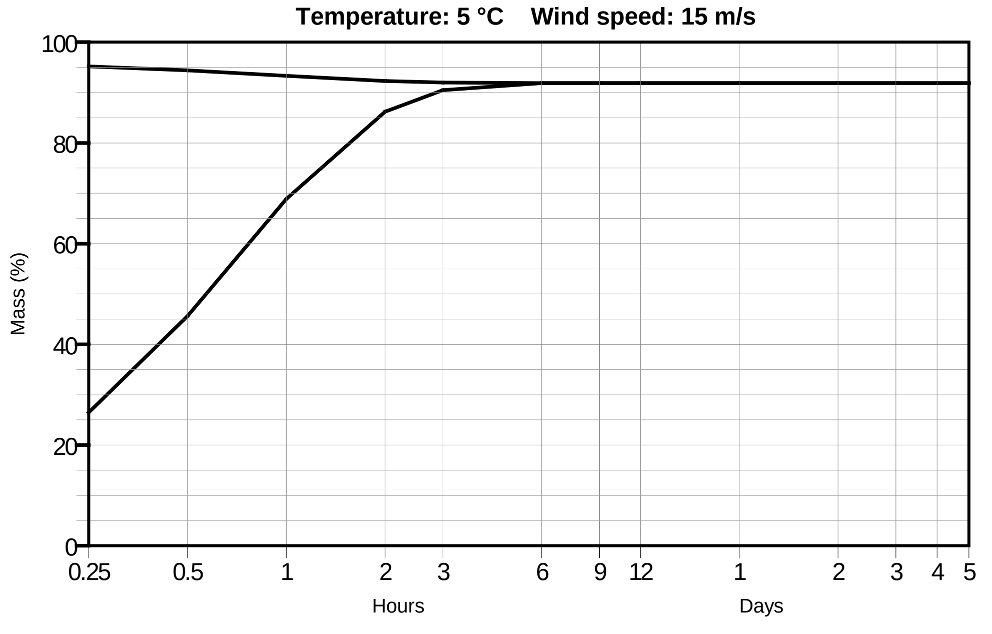
OWModel

Release depth/Gas-to-Oil ratio: 65 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed


Temperature: 5 °C Wind speed: 10 m/s


Temperature: 5 °C Wind speed: 15 m/s

Property: MASS BALANCE
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

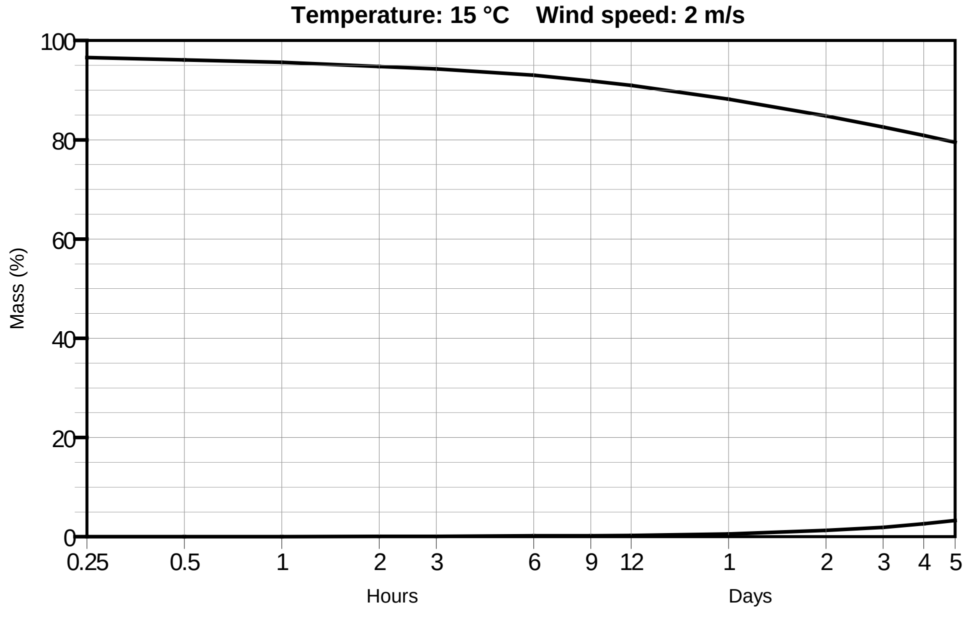
SINTEF

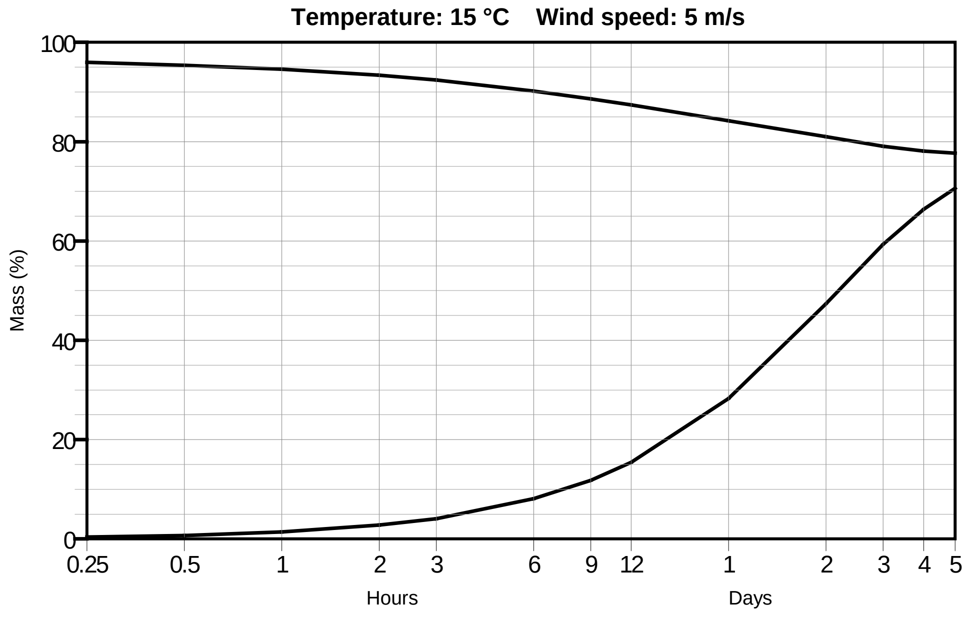
OWModel

Release depth/Gas-to-Oil ratio: 65 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed


Temperature: 15 °C   Wind speed: 2 m/s


Temperature: 15 °C   Wind speed: 5 m/s

Property: MASS BALANCE
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

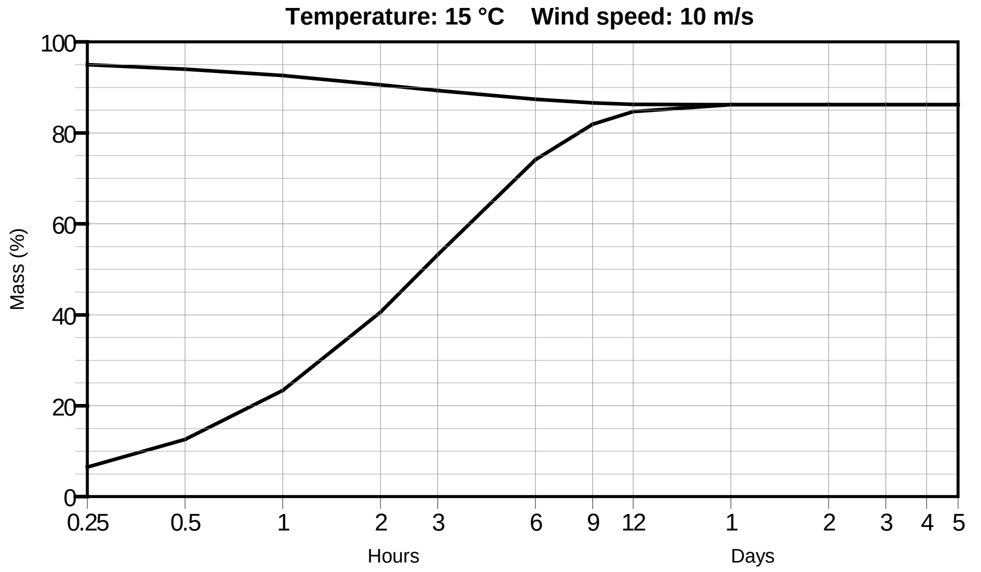
SINTEF

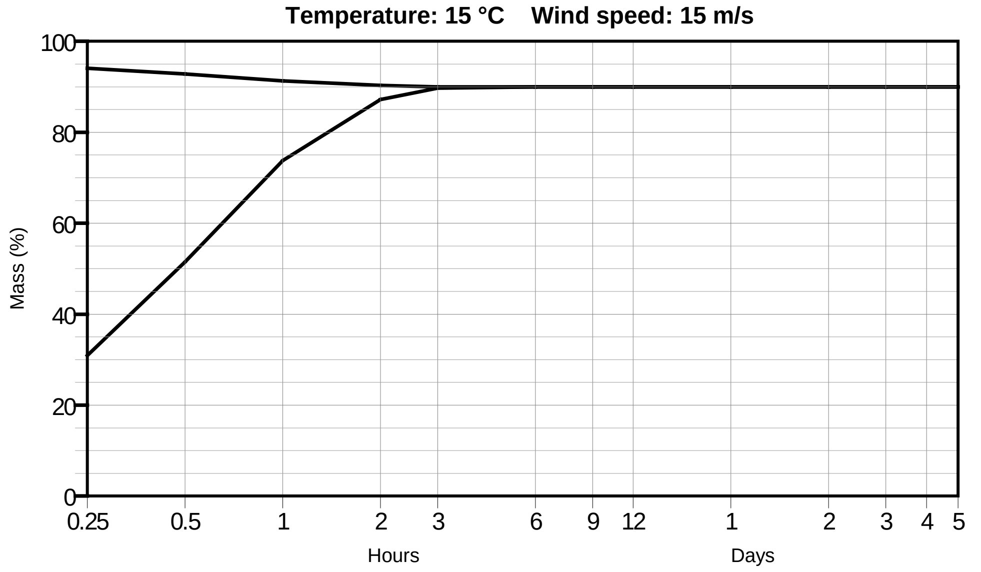
OWModel

Release depth/Gas-to-Oil ratio: 65 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▩ Surface
▨ Naturally dispersed





The algorithm for prediction of natural dispersion is preliminary and is currently under improvement.Model predictions have been field-verified up to 4-5 days.

Property: EVAPORATIVE LOSS
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

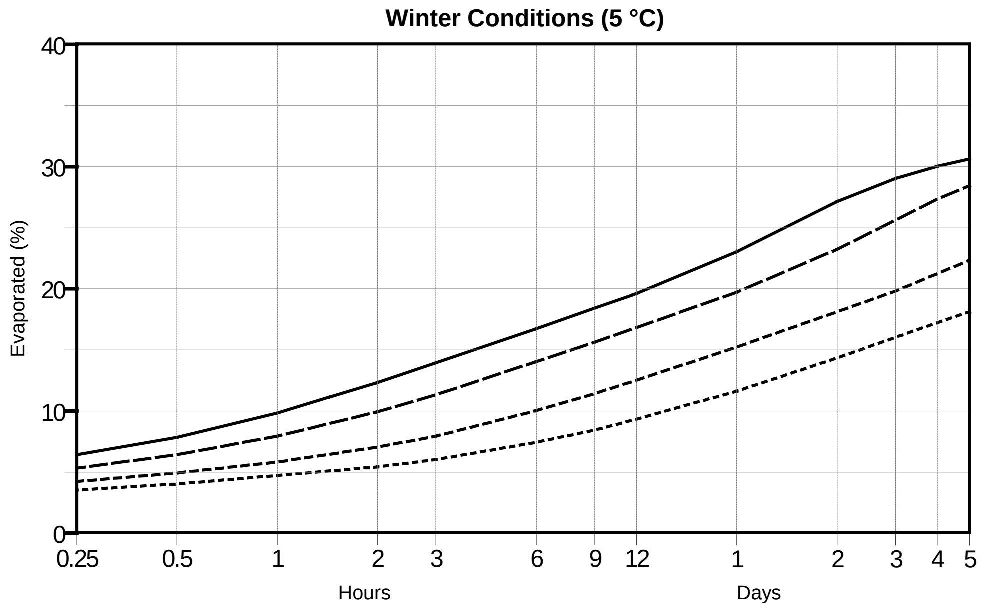
SINTEF

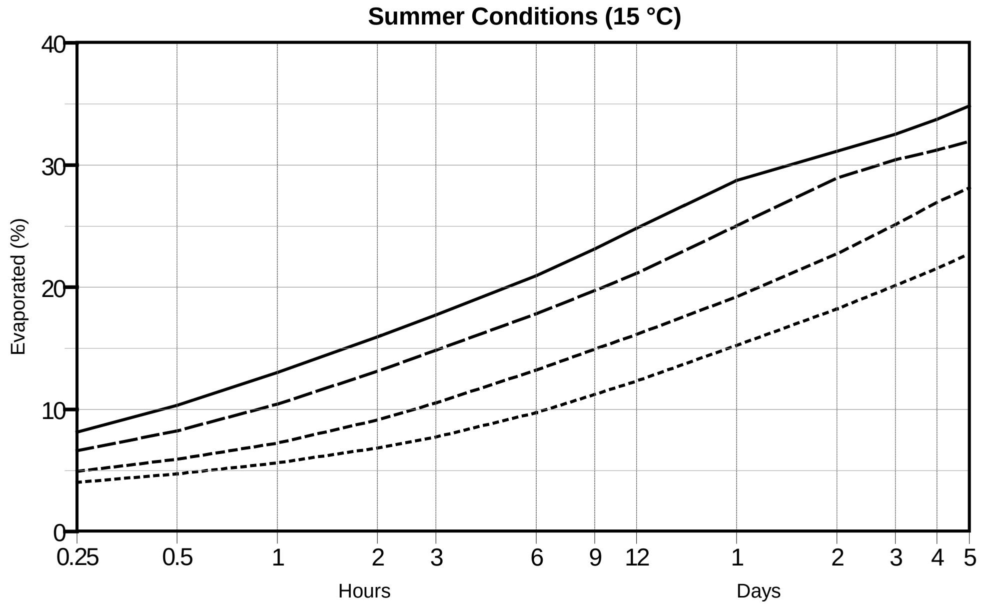
OWModel

Release depth/Gas-to-Oil ratio: 165 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

—— Wind Speed (m/s): 15
— — Wind Speed (m/s): 10
- - - Wind Speed (m/s): 5
······ Wind Speed (m/s): 2





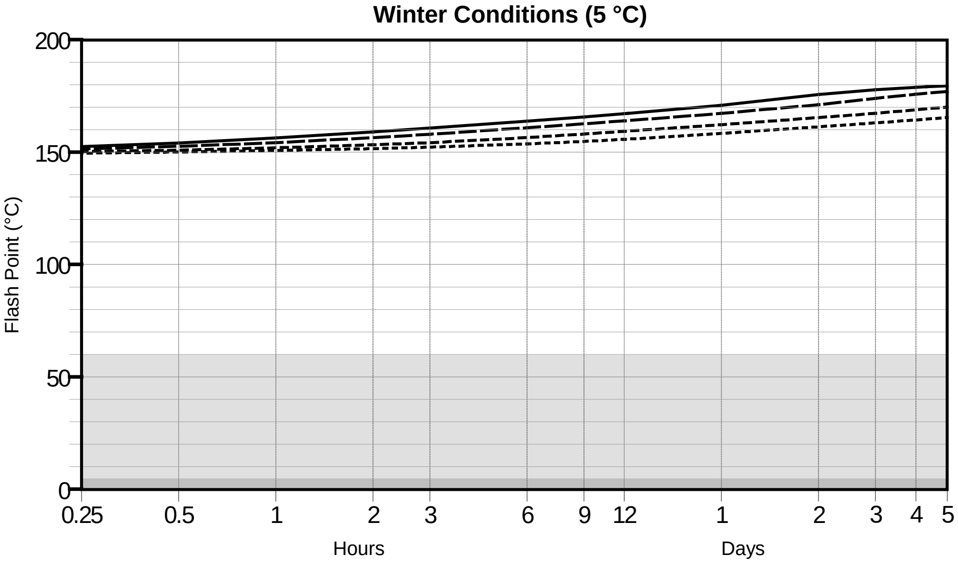
Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

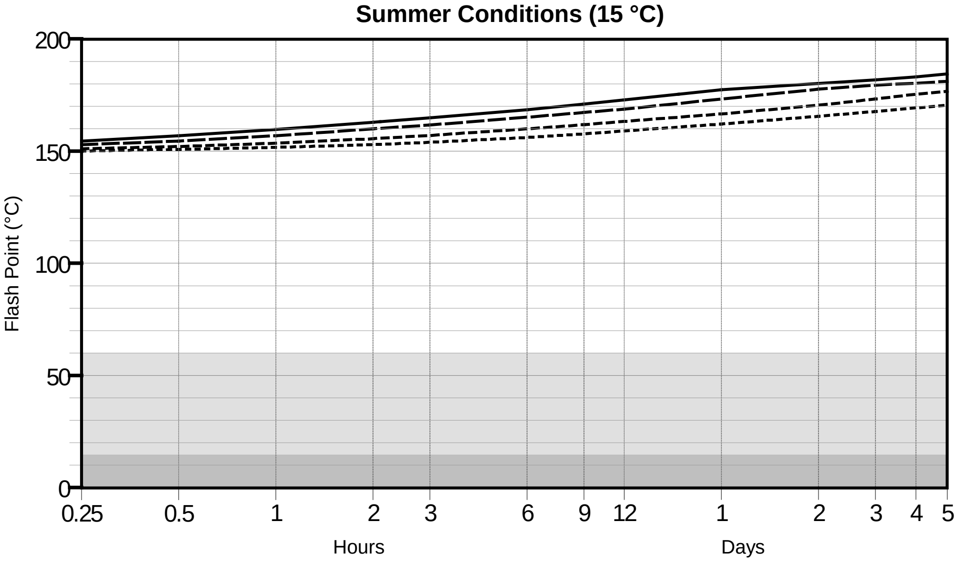
OWModel

Release depth/Gas-to-Oil ratio: 165 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

—— Wind Speed (m/s): 15	☐ No fire hazard
– – – Wind Speed (m/s): 10	▨ Fire hazard in tankage (<60 °C)
- - - - Wind Speed (m/s): 5	■ Fire hazard at sea surface (below sea temperature)
------ Wind Speed (m/s): 2	


Winter Conditions (5 °C)


Summer Conditions (15 °C)

Based on flash point measurements of weathered, water-free oil residues.

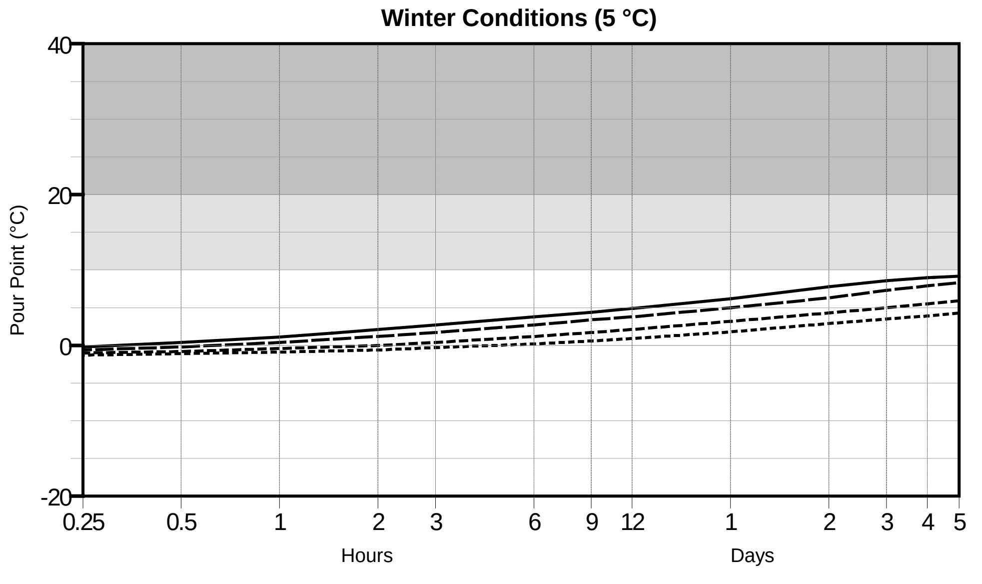
Property: POUR POINT FOR WATER-FREE OIL
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

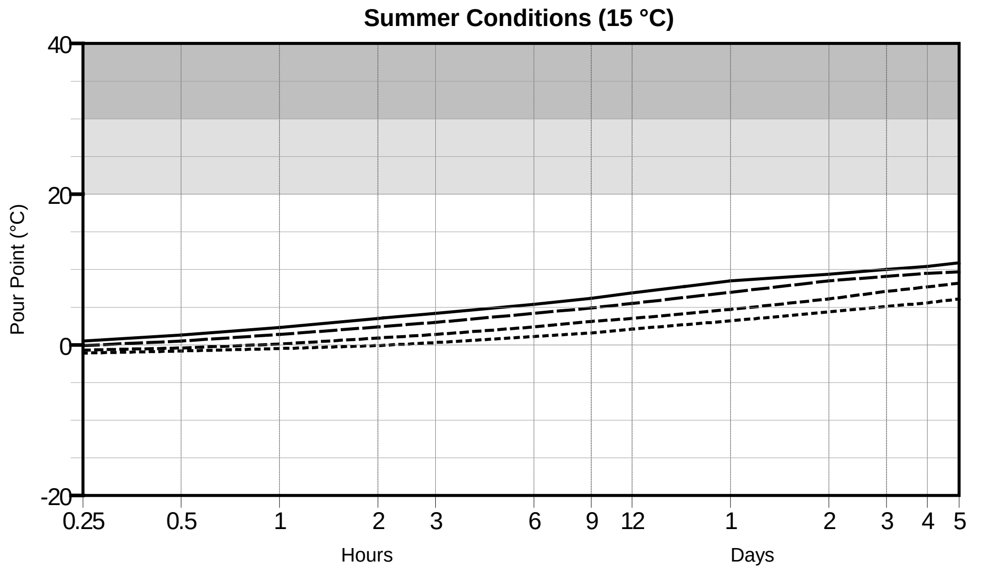
OWModel

Release depth/Gas-to-Oil ratio: 165 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

——	Wind Speed (m/s): 15	☐	Chemically dispersible
— — —	Wind Speed (m/s): 10	▨	Reduced chemical dispersibility
- - - -	Wind Speed (m/s): 5	■	Poorly / slowly chemically dispersible
------	Wind Speed (m/s): 2		


Winter Conditions (5 °C)


Summer Conditions (15 °C)

Based on pour point measurements of weathered, water-free oil residues.

Property: WATER CONTENT
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

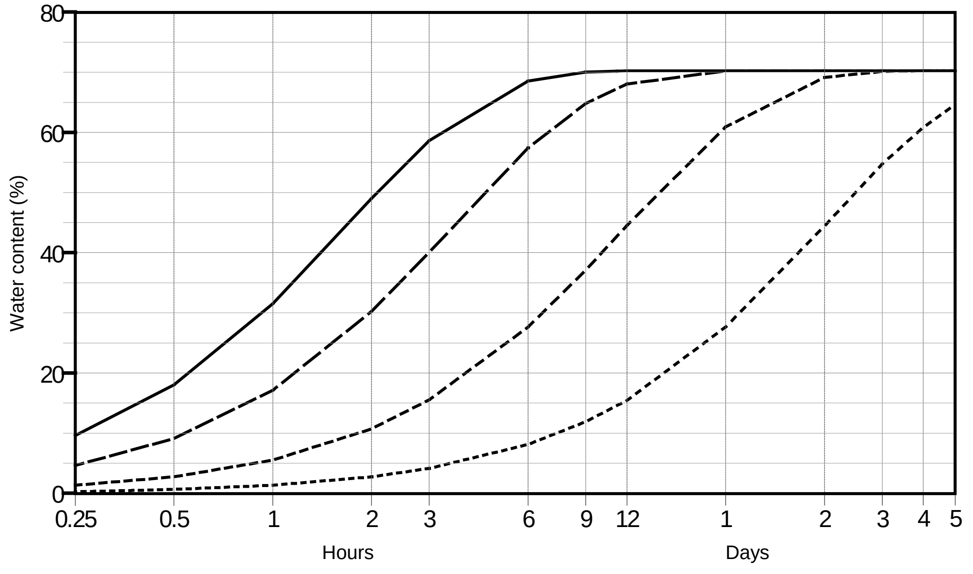
OWModel

Release depth/Gas-to-Oil ratio: 165 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

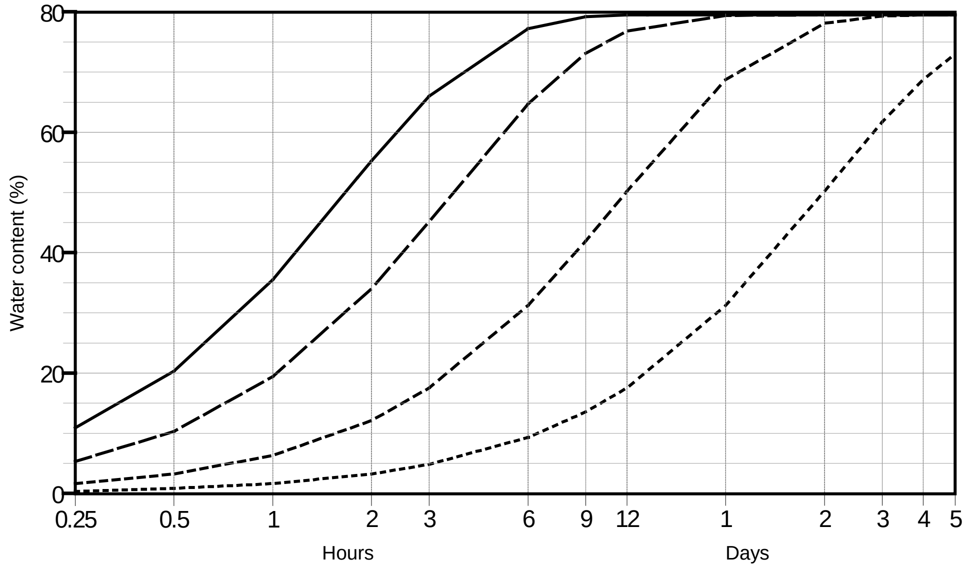
Pred. date: Oct. 24, 2013

—— Wind Speed (m/s): 15
— — Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
------ Wind Speed (m/s): 2

Winter Conditions (5 °C)



Summer Conditions (15 °C)



Property: VISCOSITY OF EMULSION
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

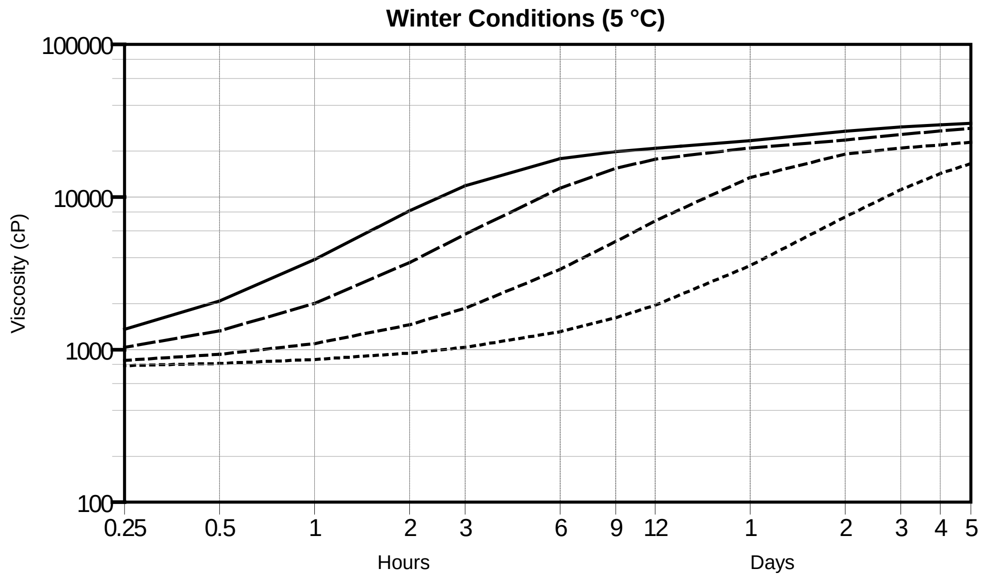
SINTEF

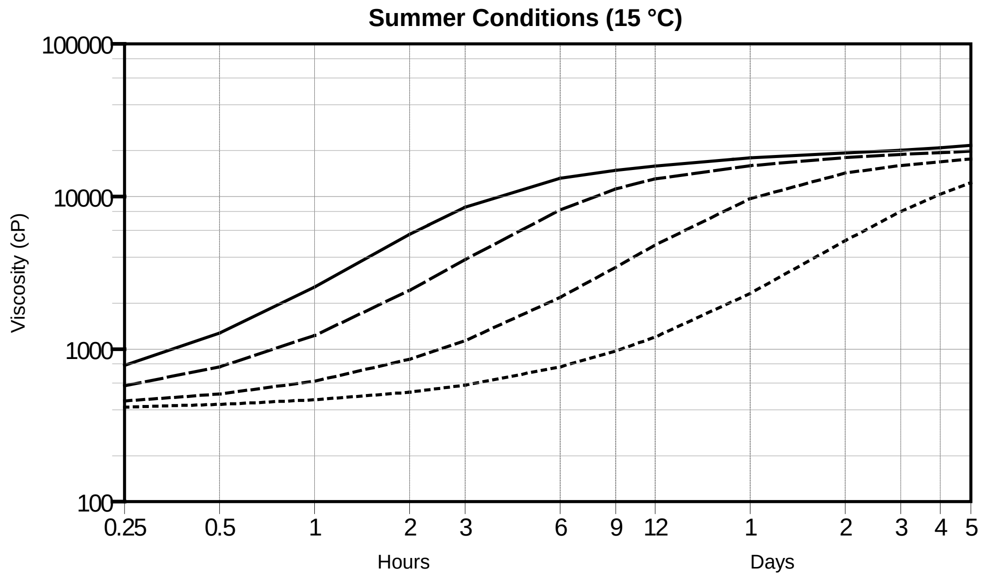
OWModel

Release depth/Gas-to-Oil ratio: 165 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

—— Wind Speed (m/s): 15
— — Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
------ Wind Speed (m/s): 2





Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Property: MASS BALANCE
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

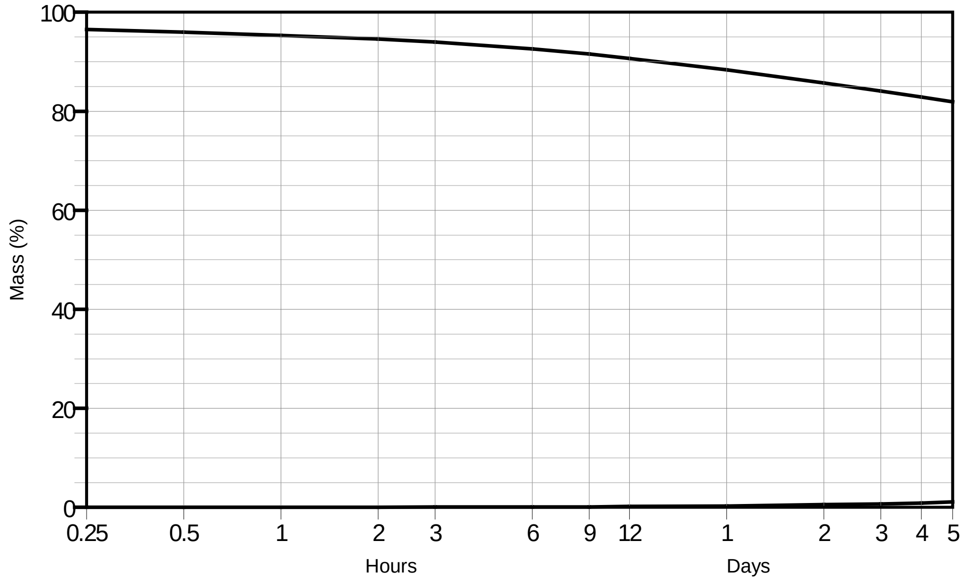
OWModel

Release depth/Gas-to-Oil ratio: 165 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

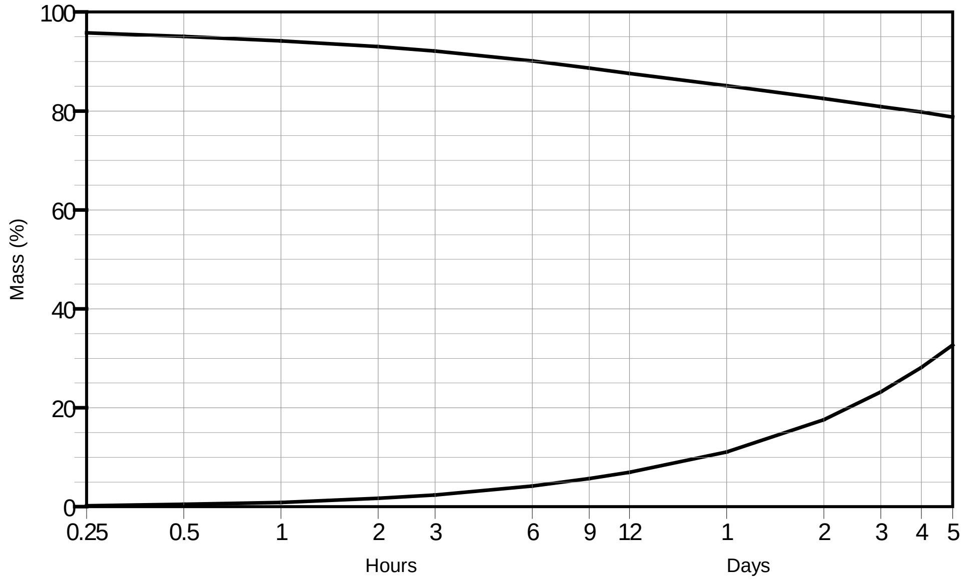
Pred. date: Oct. 24, 2013

▨ Evaporated
▩ Surface
▧ Naturally dispersed

Temperature: 5 °C Wind speed: 2 m/s



Temperature: 5 °C Wind speed: 5 m/s



Property: MASS BALANCE
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

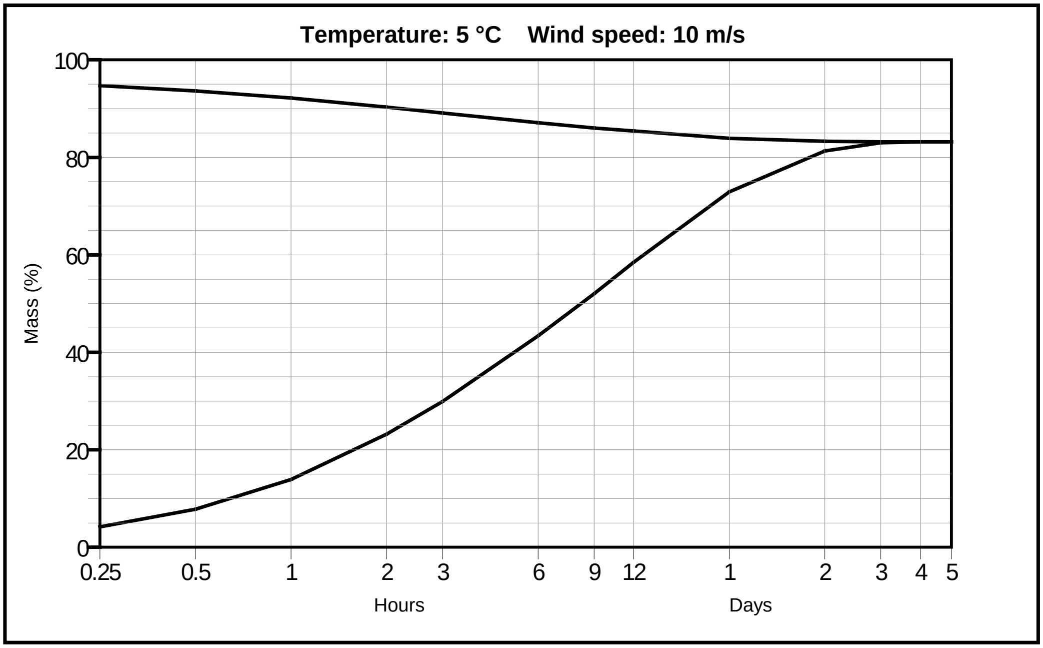
SINTEF

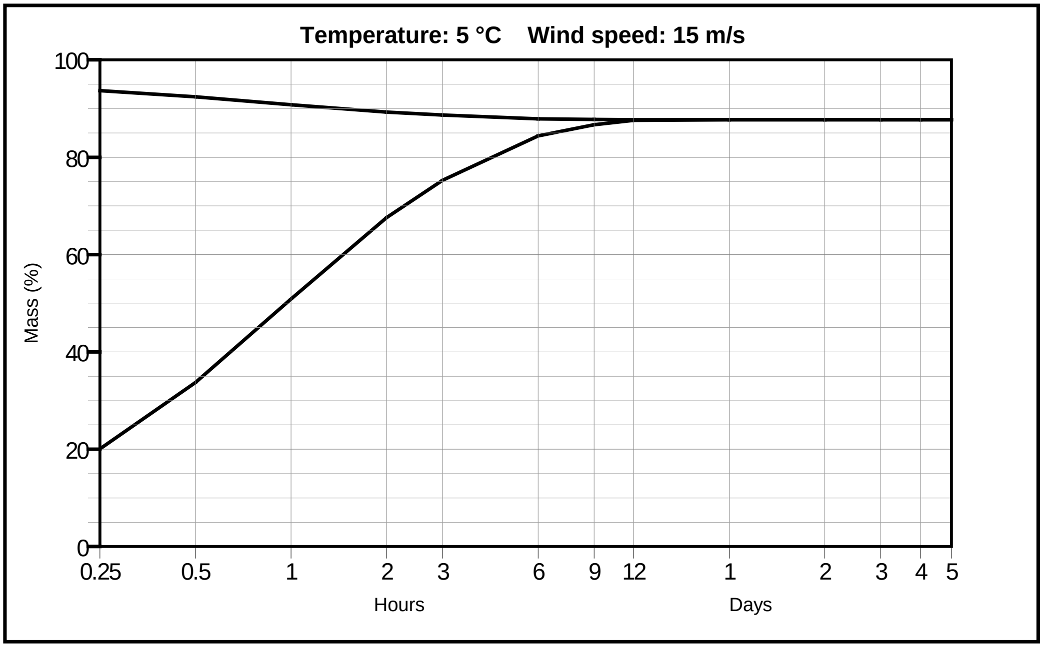
OWModel

Release depth/Gas-to-Oil ratio: 165 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed


Temperature: 5 °C Wind speed: 10 m/s


Temperature: 5 °C Wind speed: 15 m/s

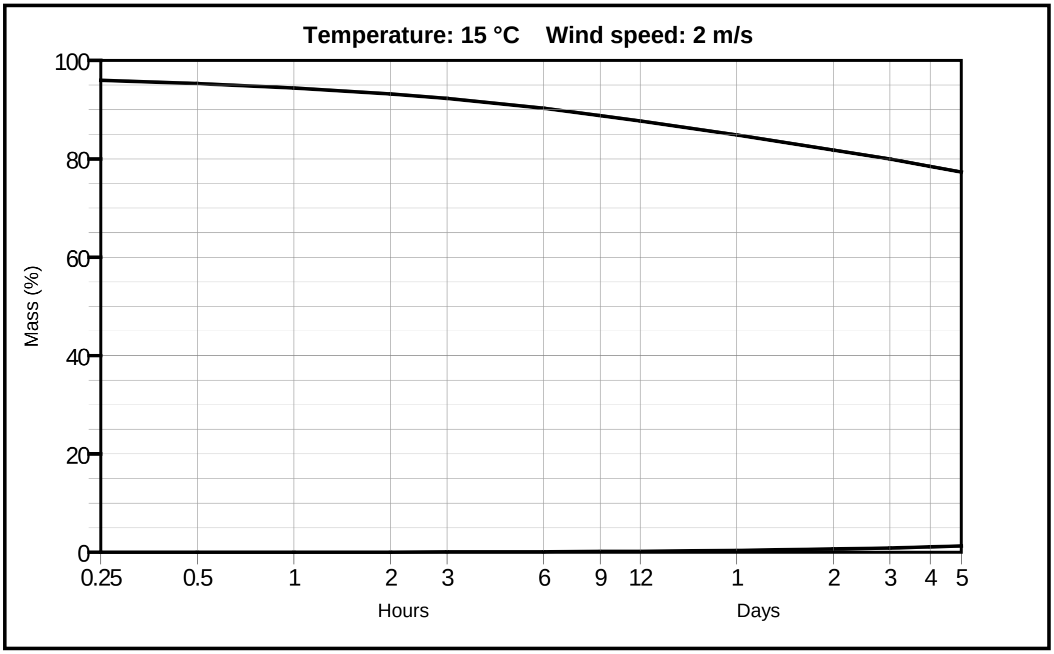
Property: MASS BALANCE
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

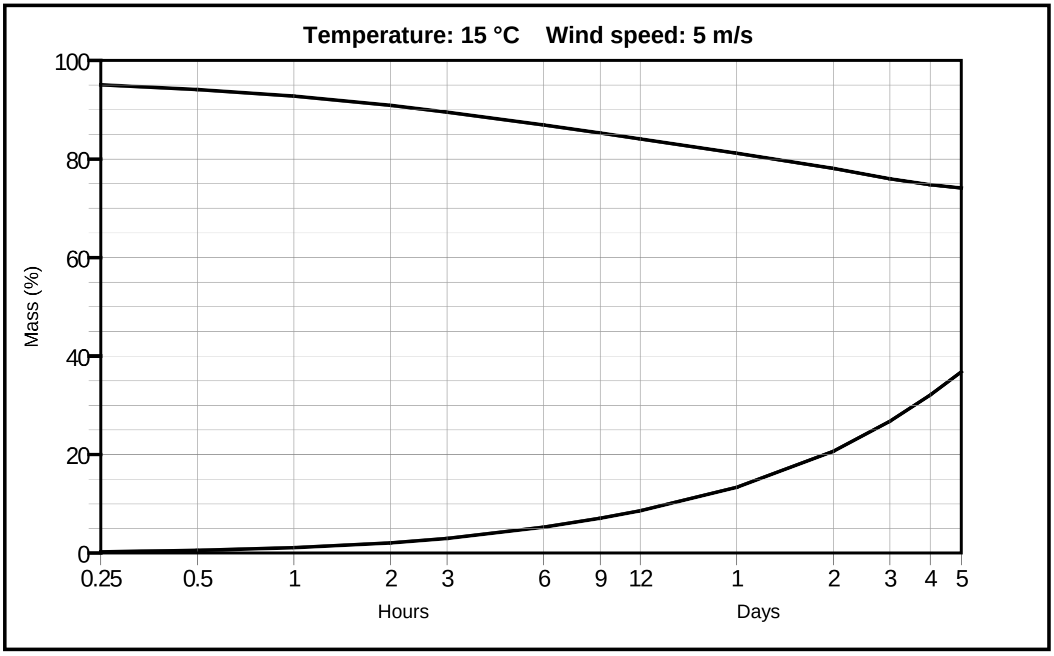
SINTEF
OWModel

Release depth/Gas-to-Oil ratio: 165 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed





Property: MASS BALANCE
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

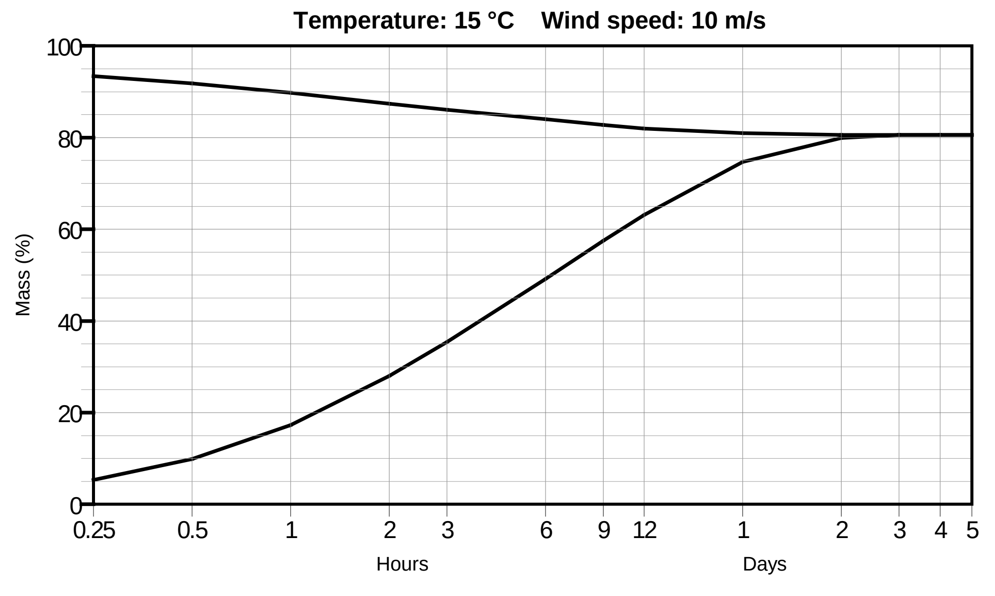
SINTEF

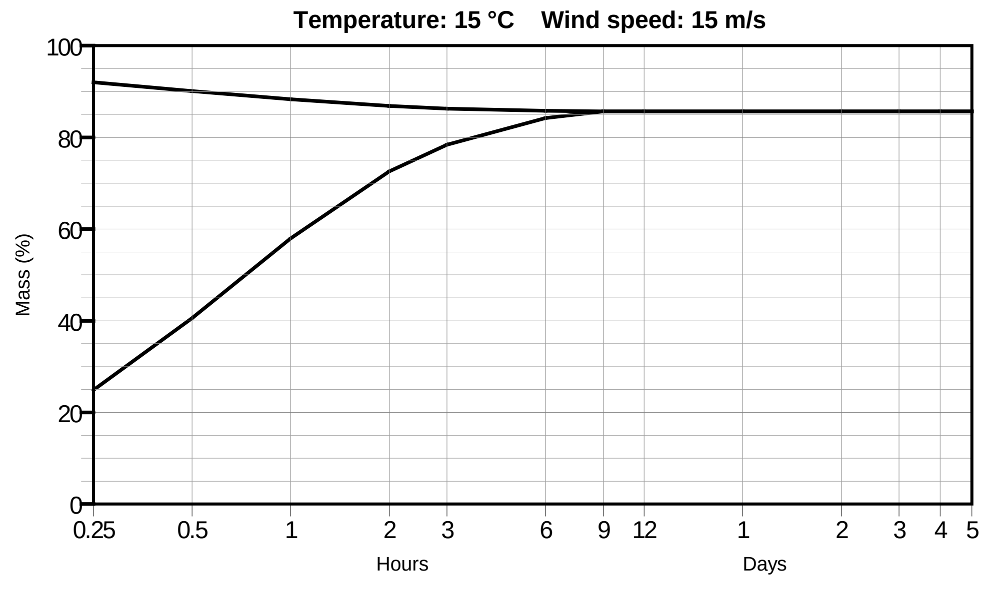
OWModel

Release depth/Gas-to-Oil ratio: 165 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

- ▨ Evaporated
- ▩ Surface
- ▧ Naturally dispersed





The algorithm for prediction of natural dispersion is preliminary and is currently under improvement.Model predictions have been field-verified up to 4-5 days.

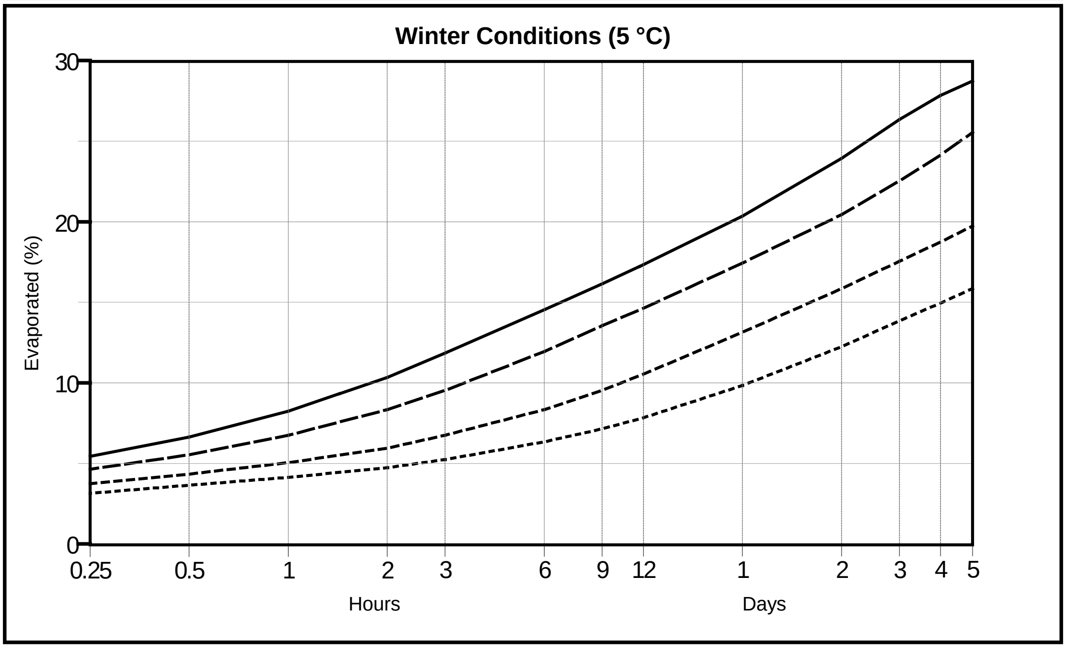
Property: EVAPORATIVE LOSS
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

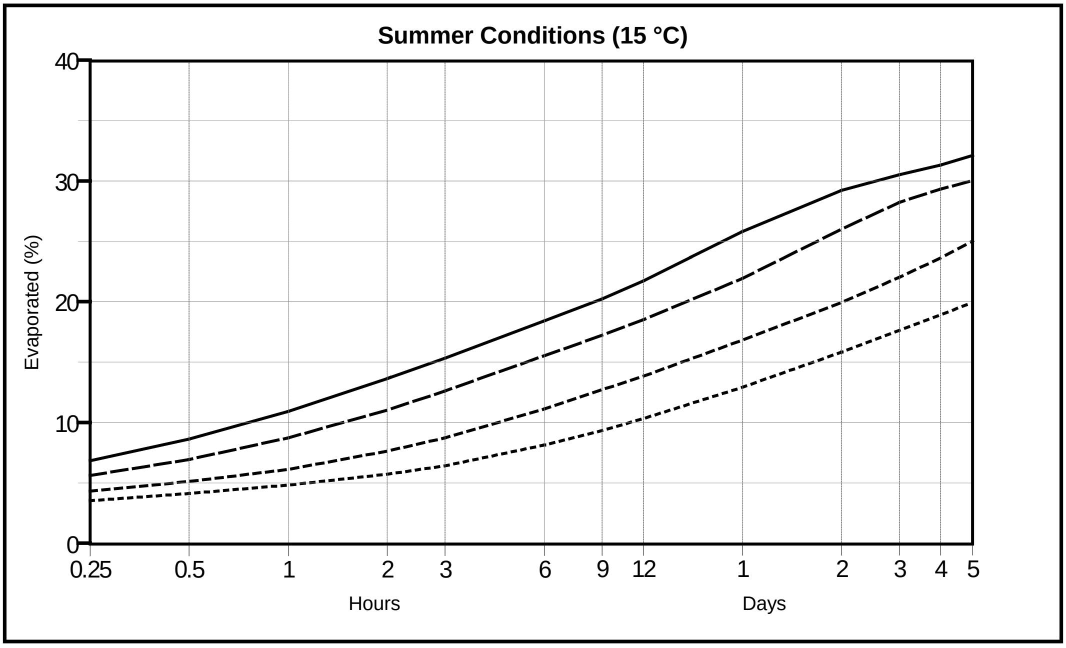
OWModel

Release depth/Gas-to-Oil ratio: 67 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

- Wind Speed (m/s): 15
- Wind Speed (m/s): 10
- Wind Speed (m/s): 5
- Wind Speed (m/s): 2





Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF
OWModel

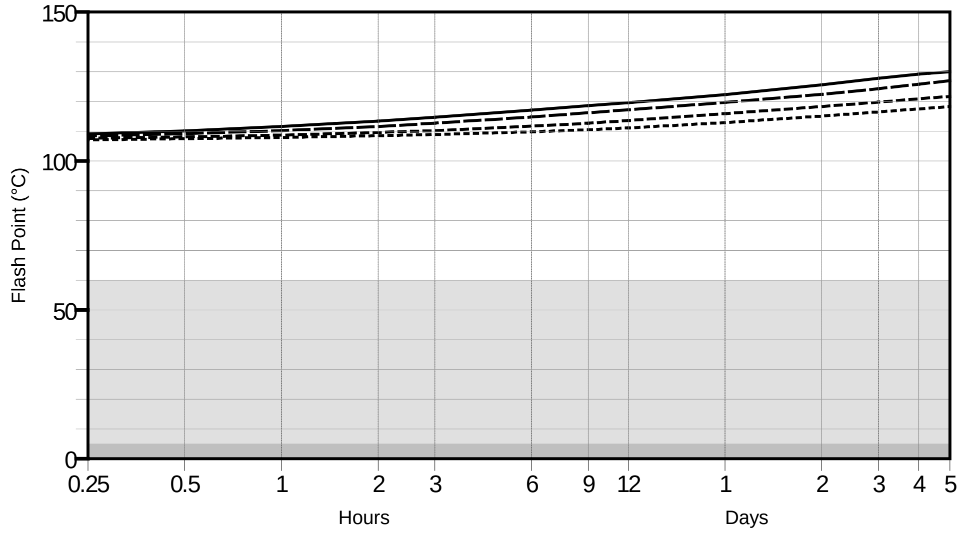
Release depth/Gas-to-Oil ratio: 67 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

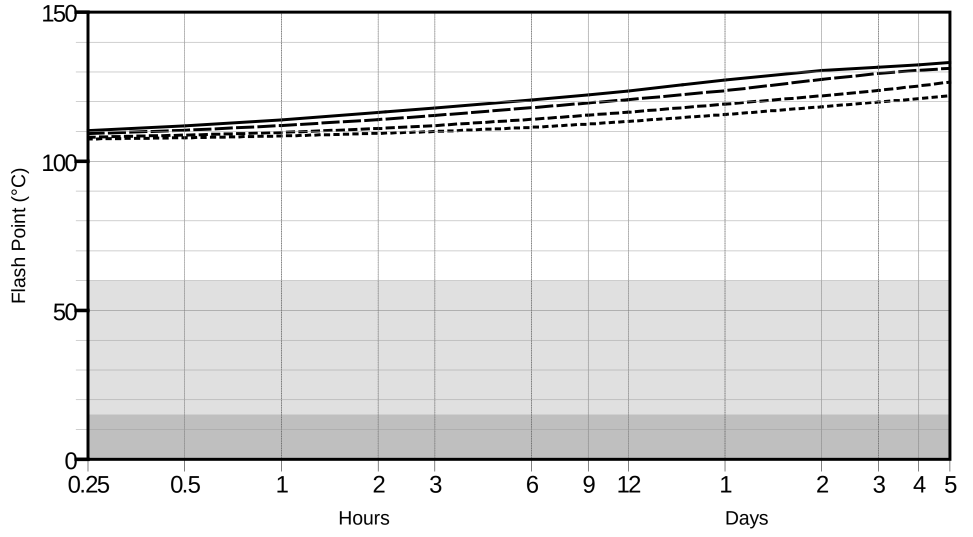
—— Wind Speed (m/s): 15
— — Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
------ Wind Speed (m/s): 2

☐ No fire hazard
▨ Fire hazard in tankage (<60 °C)
■ Fire hazard at sea surface (below sea temperature)

Winter Conditions (5 °C)



Summer Conditions (15 °C)



Based on flash point measurements of weathered, water-free oil residues.

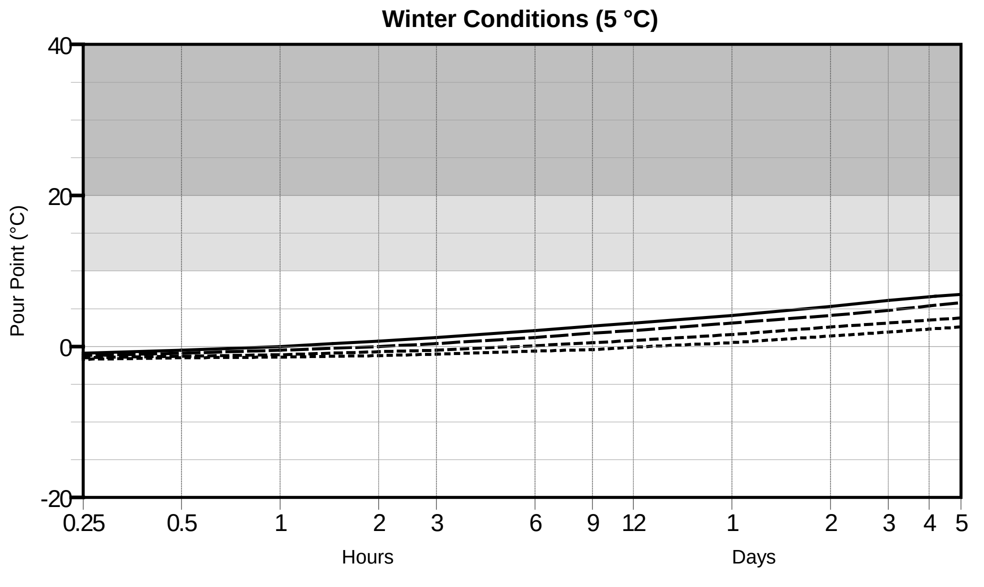
Property: POUR POINT FOR WATER-FREE OIL
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

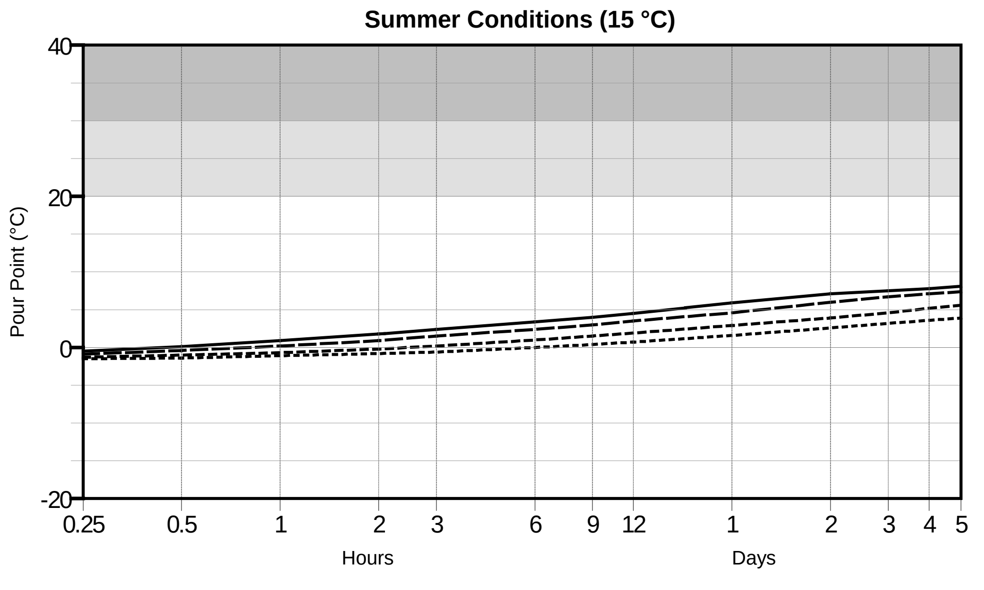
OWModel

Release depth/Gas-to-Oil ratio: 67 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

——	Wind Speed (m/s): 15	□	Chemically dispersible
— — —	Wind Speed (m/s): 10	░	Reduced chemical dispersibility
- - - -	Wind Speed (m/s): 5	▒	Poorly / slowly chemically dispersible
------	Wind Speed (m/s): 2		





Based on pour point measurements of weathered, water-free oil residues.

Property: WATER CONTENT
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

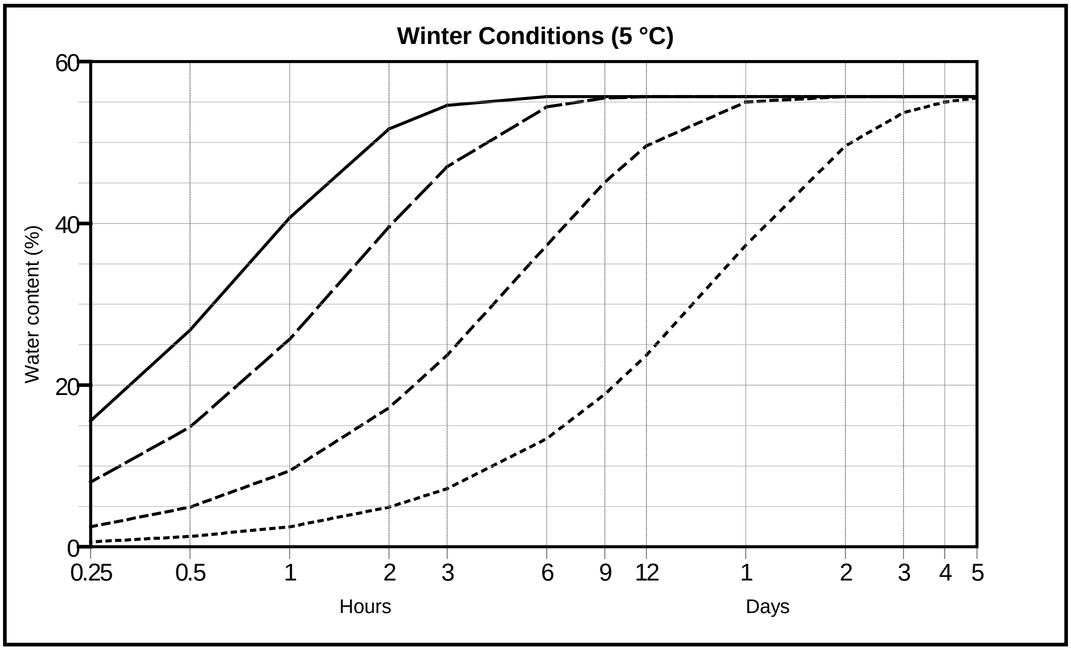
SINTEF

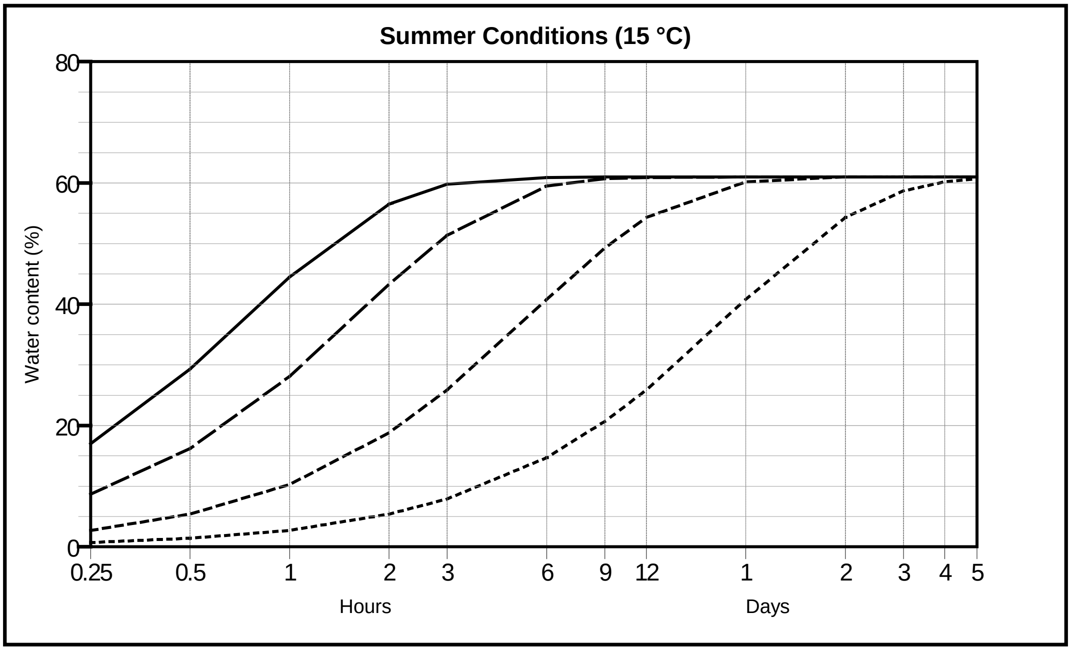
OWModel

Release depth/Gas-to-Oil ratio: 67 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

——— Wind Speed (m/s): 15
— — — Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
------ Wind Speed (m/s): 2





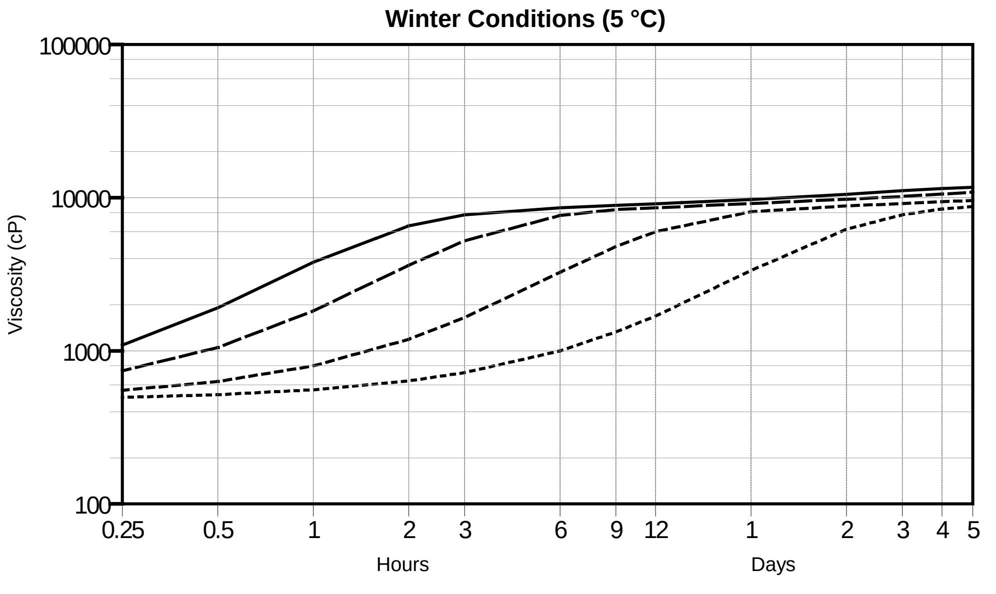
Property: VISCOSITY OF EMULSION
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

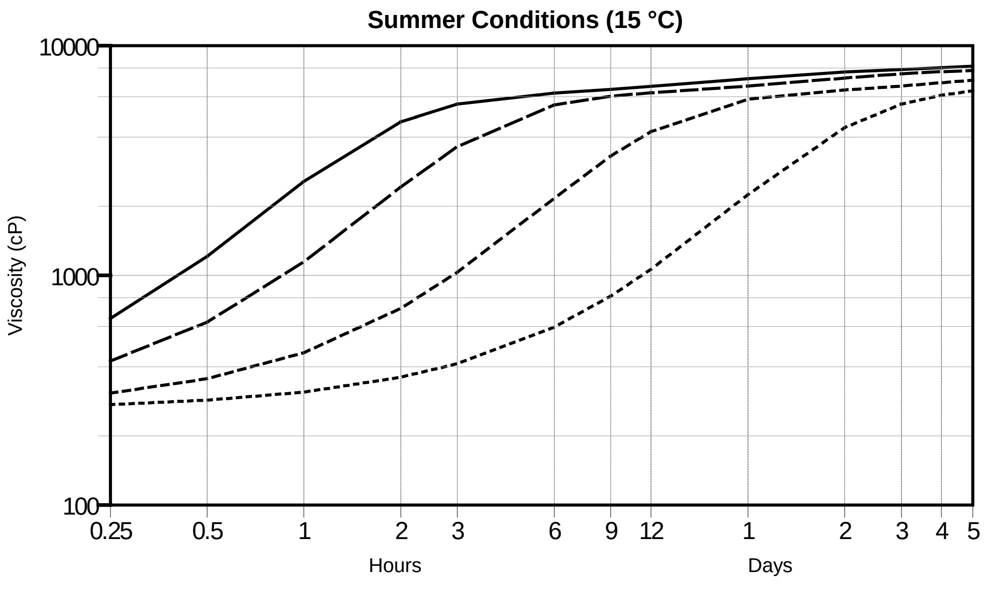
OWModel

Release depth/Gas-to-Oil ratio: 67 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

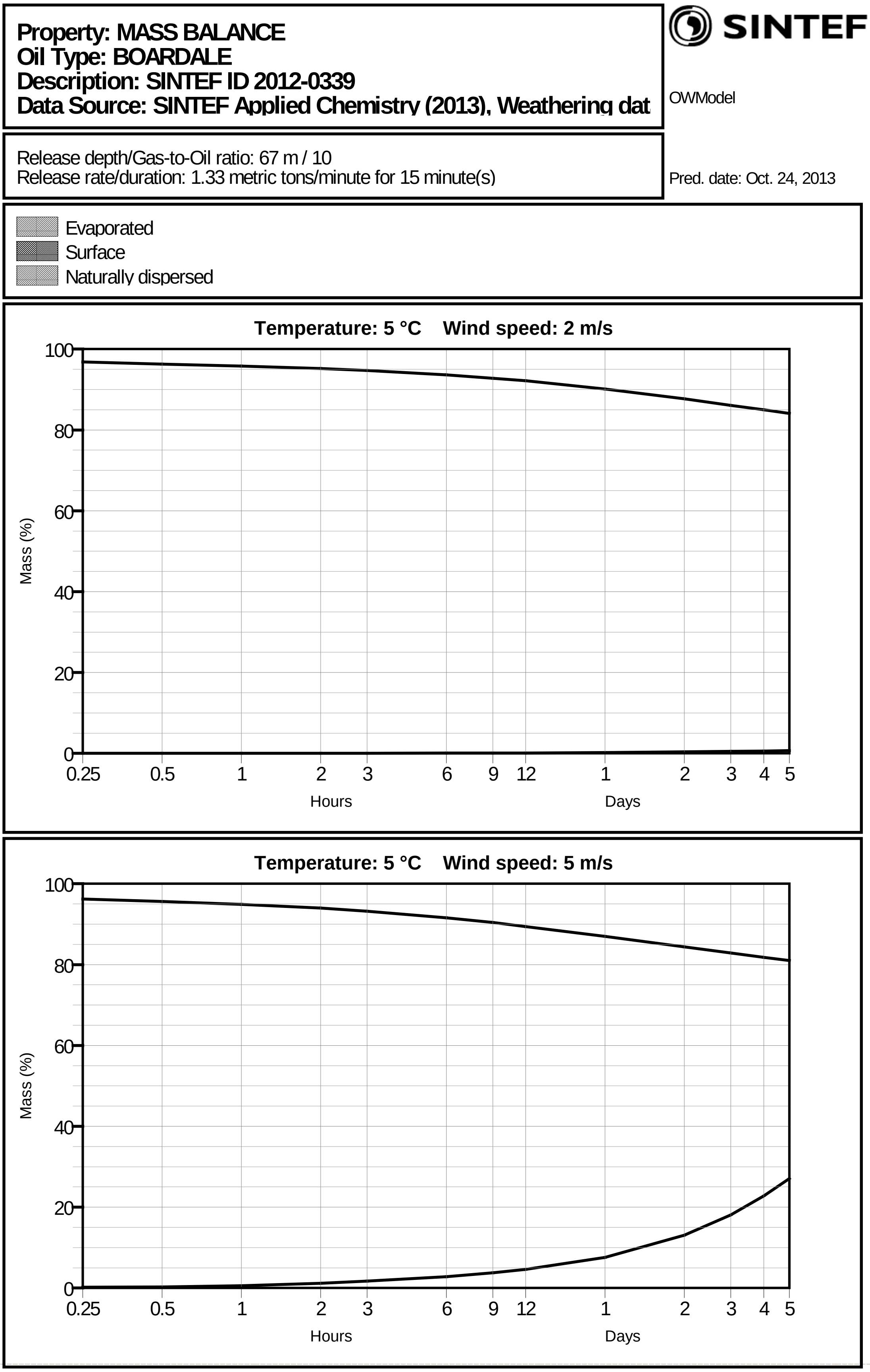
Pred. date: Oct. 24, 2013

——— Wind Speed (m/s): 15
— — — Wind Speed (m/s): 10
- - - - - Wind Speed (m/s): 5
- - - - - - Wind Speed (m/s): 2


Winter Conditions (5 °C)


Summer Conditions (15 °C)

Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.



Property: MASS BALANCE
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

OWModel

Release depth/Gas-to-Oil ratio: 67 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▩ Surface
▨ Naturally dispersed

Property: MASS BALANCE
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

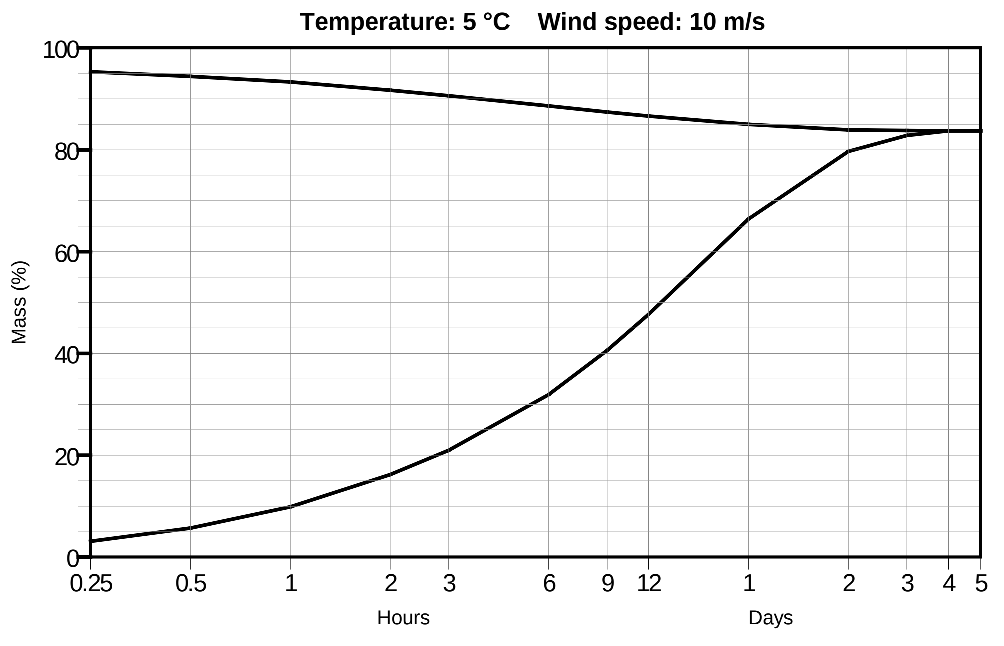
SINTEF

OWModel

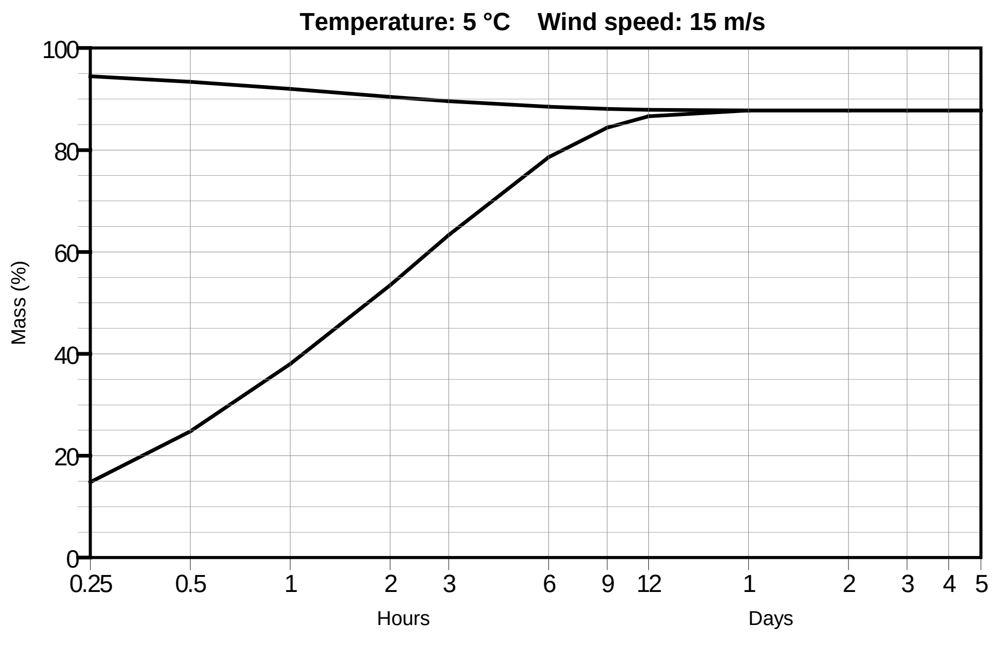
Release depth/Gas-to-Oil ratio: 67 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

- ▨ Evaporated
- ▦ Surface
- ▧ Naturally dispersed



Temperature: 5 °C Wind speed: 10 m/s



Temperature: 5 °C Wind speed: 15 m/s

Property: MASS BALANCE
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

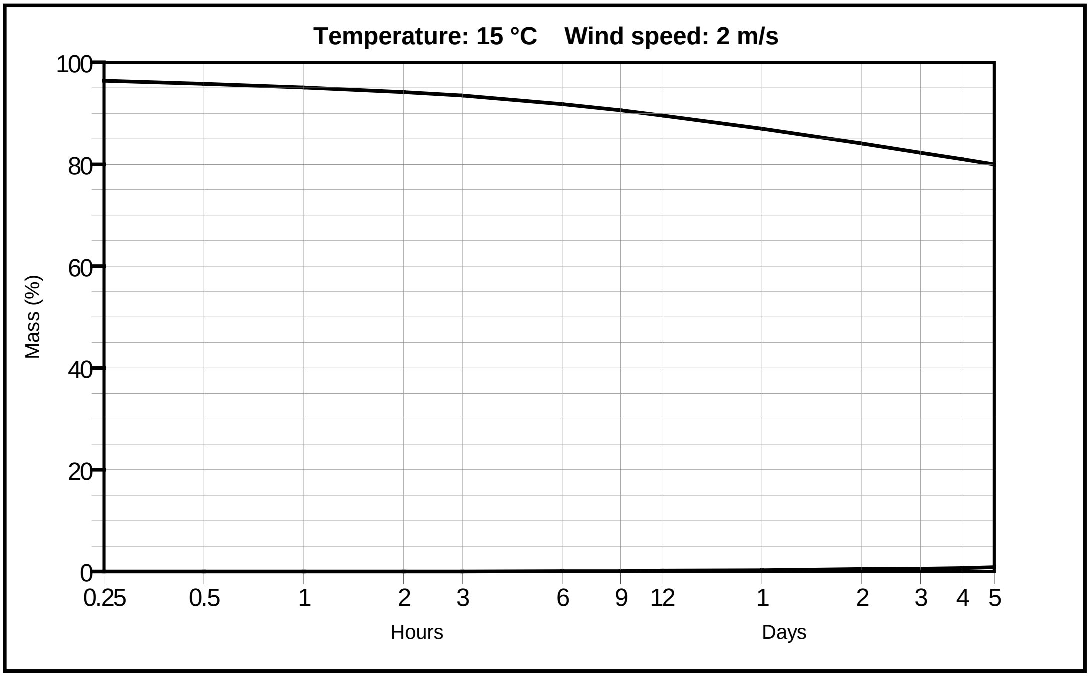
SINTEF

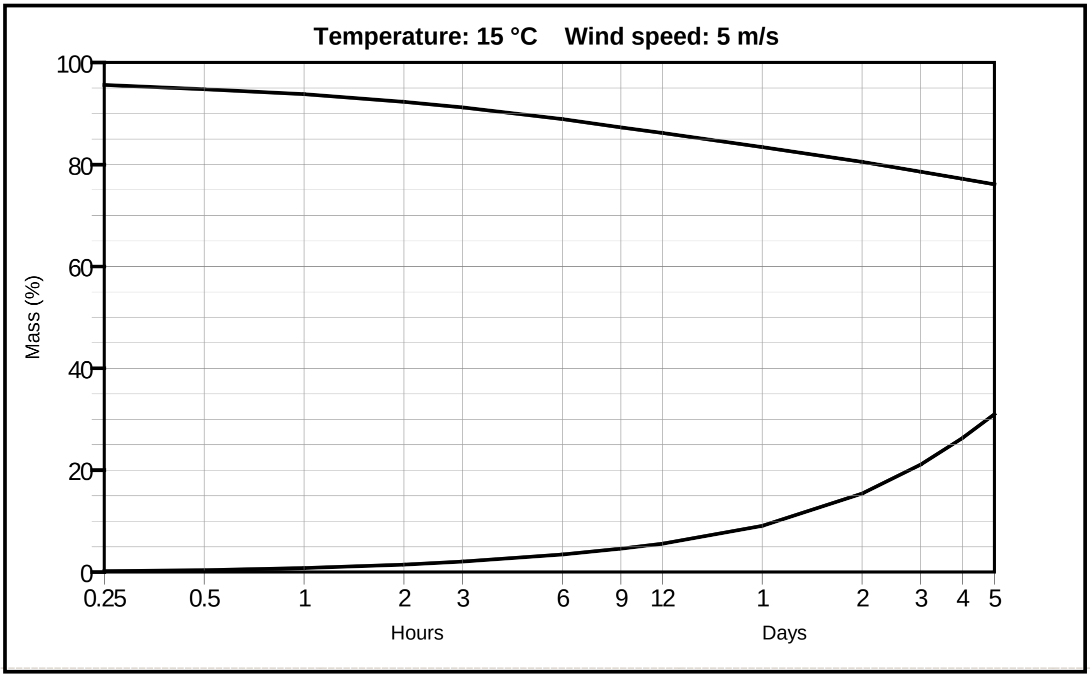
OWModel

Release depth/Gas-to-Oil ratio: 67 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▩ Surface
▧ Naturally dispersed





Property: MASS BALANCE
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

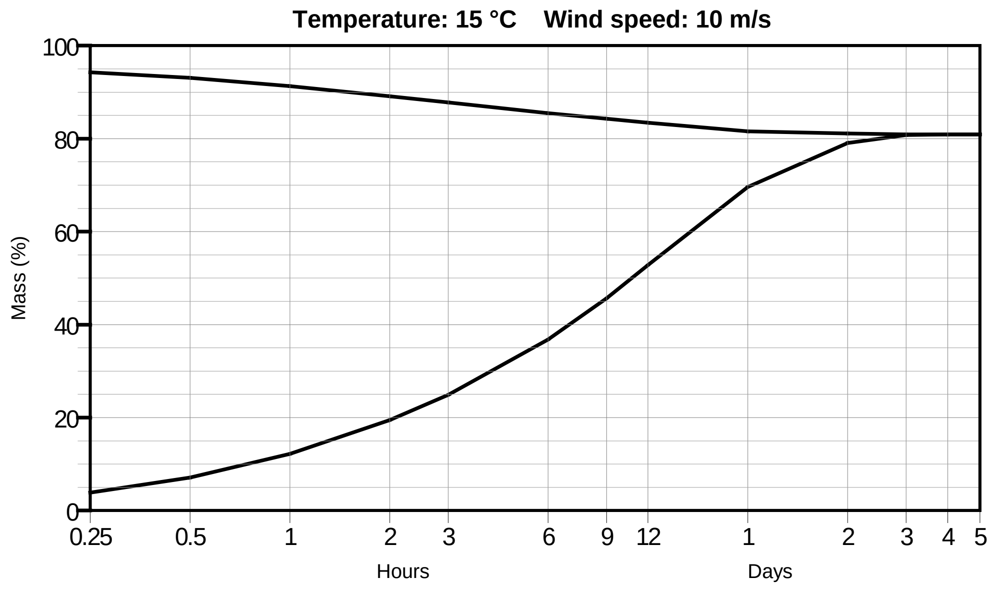
SINTEF

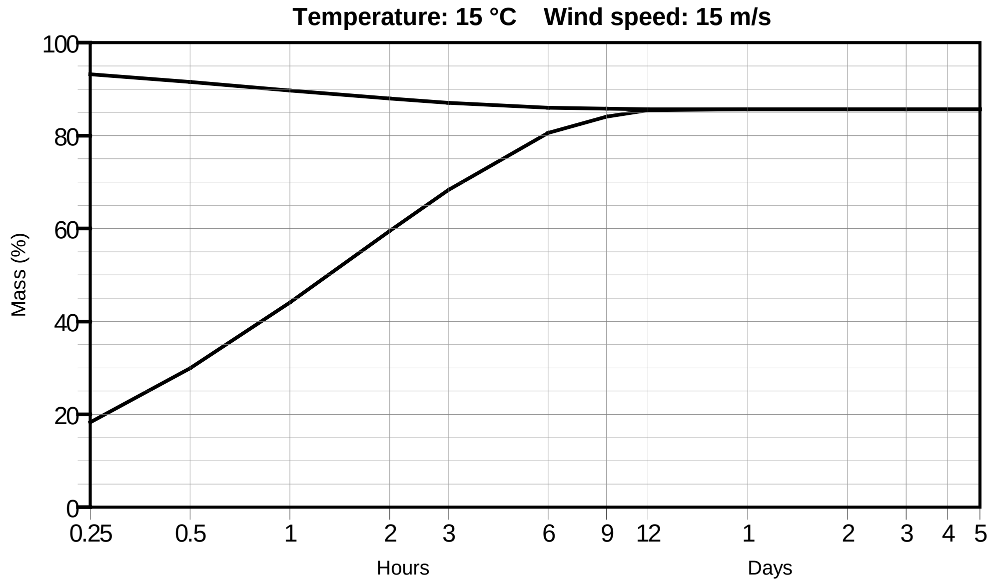
OWModel

Release depth/Gas-to-Oil ratio: 67 m / 10
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▩ Surface
▨ Naturally dispersed


Temperature: 15 °C   Wind speed: 10 m/s


Temperature: 15 °C   Wind speed: 15 m/s

The algorithm for prediction of natural dispersion is preliminary and is currently under improvement.Model predictions have been field-verified up to 4-5 days.

Appendix F Surface release predictions by use of the SINTEF OWM

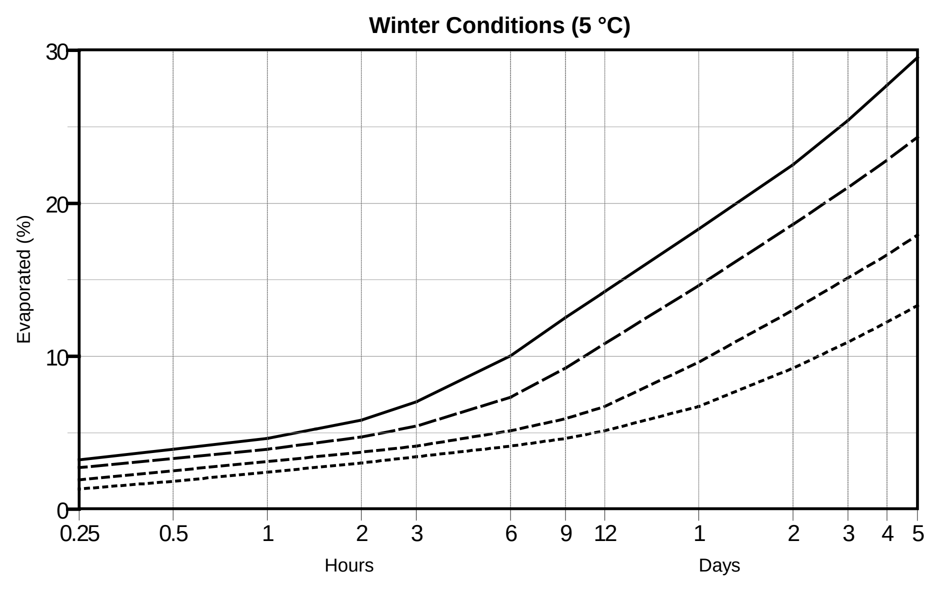
Property: EVAPORATIVE LOSS
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

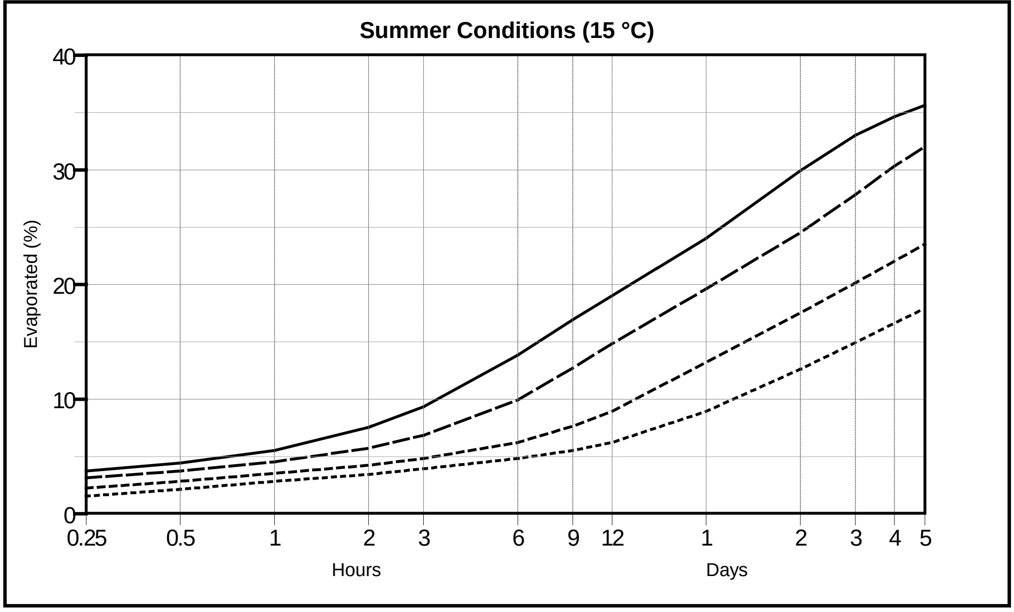
OWModel

Surface release - Terminal Oil film thickness: 0.3 mm
Amount/duration of oil spill: 20 metric tons in 15 minute(s)

Pred. date: Oct. 24, 2013

- ——— Wind Speed (m/s): 15
- — — Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
- ------ Wind Speed (m/s): 2





Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

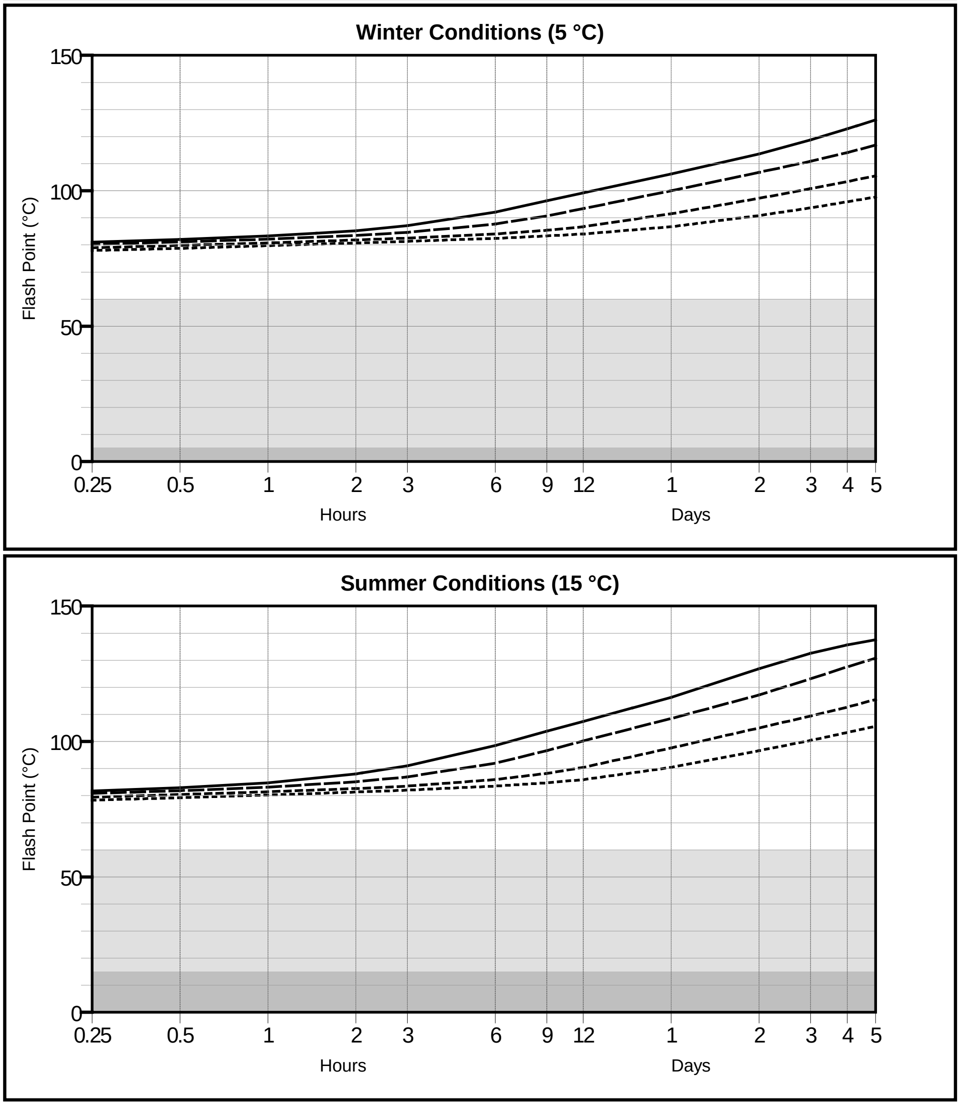
SINTEF

OWModel

Surface release - Terminal Oil film thickness: 0.3 mm
Amount/duration of oil spill: 20 metric tons in 15 minute(s)

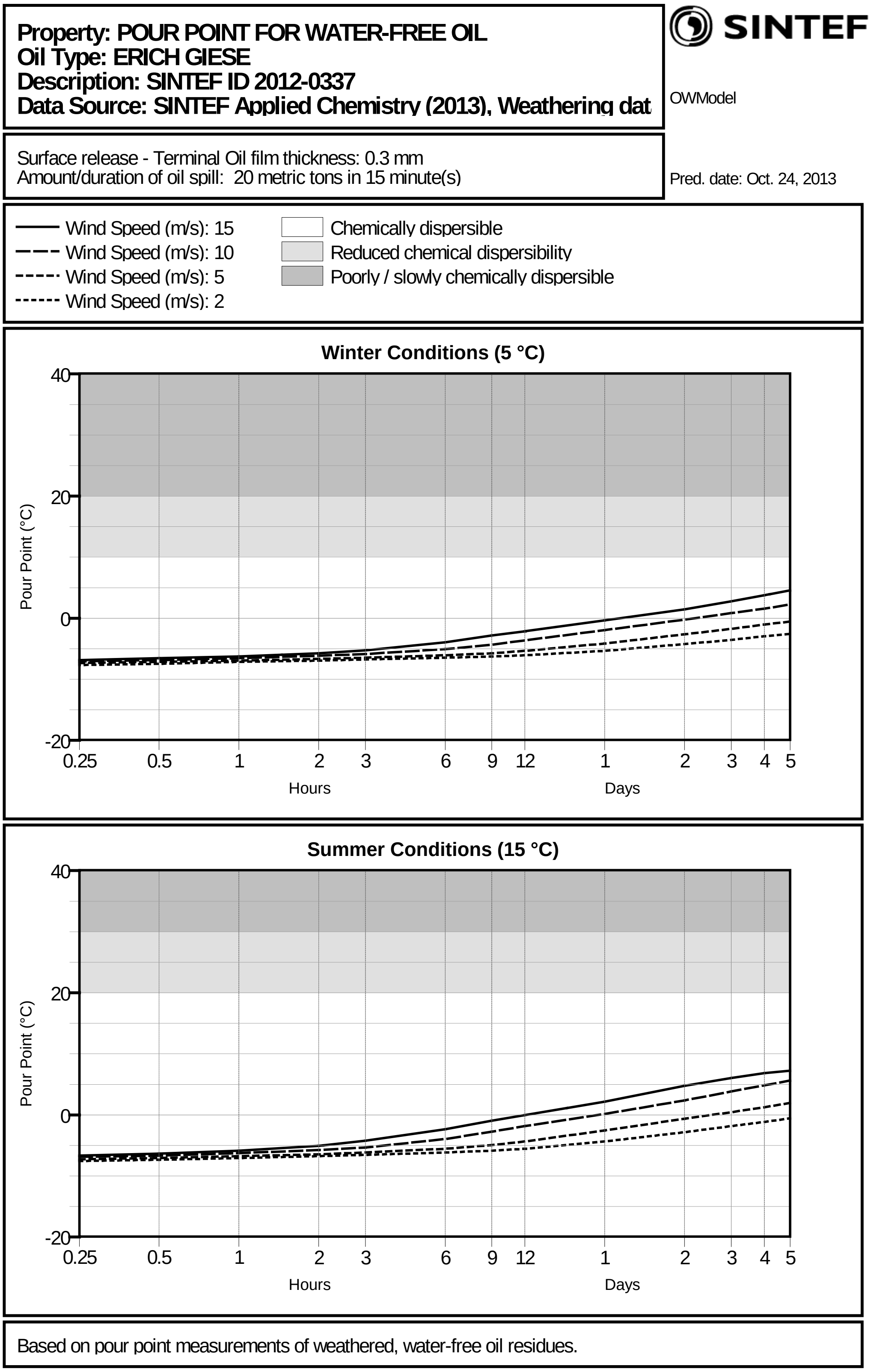
Pred. date: Oct. 24, 2013

—— Wind Speed (m/s): 15	☐ No fire hazard
— — Wind Speed (m/s): 10	▨ Fire hazard in tankage (<60 °C)
- - - - Wind Speed (m/s): 5	■ Fire hazard at sea surface (below sea temperature)
------ Wind Speed (m/s): 2	



Based on flash point measurements of weathered, water-free oil residues.

Flash point of Erich Giese predicted at sea temperatures of 5 °C and 15 °C



Property: POUR POINT FOR WATER-FREE OIL
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

OWModel

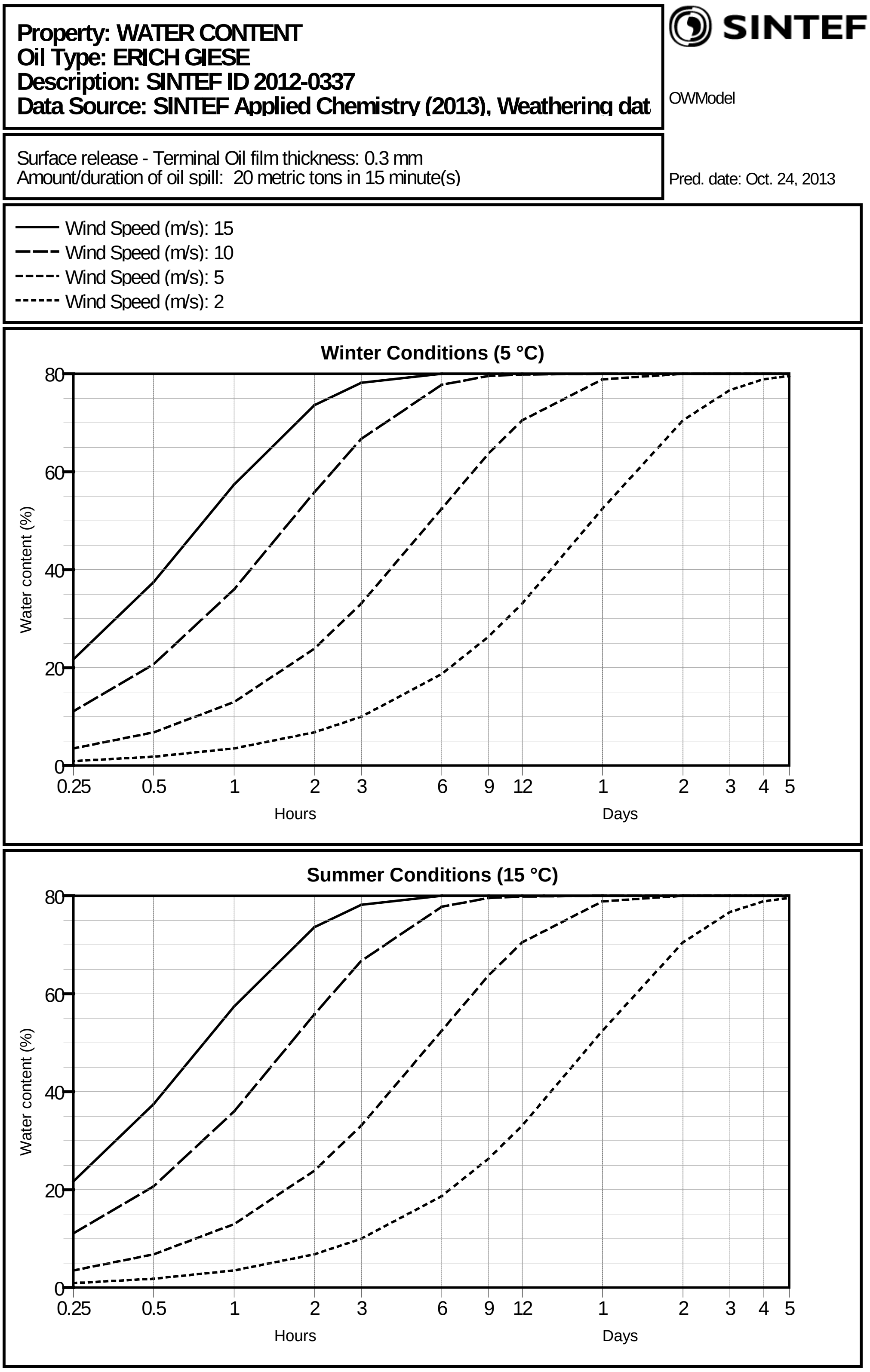
Surface release - Terminal Oil film thickness: 0.3 mm
Amount/duration of oil spill: 20 metric tons in 15 minute(s)

Pred. date: Oct. 24, 2013

—— Wind Speed (m/s): 15	□ Chemically dispersible
— — Wind Speed (m/s): 10	□ Reduced chemical dispersibility
- - - - Wind Speed (m/s): 5	▨ Poorly / slowly chemically dispersible
------ Wind Speed (m/s): 2	

Based on pour point measurements of weathered, water-free oil residues.

Pour point of Erich Giese predicted at sea temperatures of 5 °C and 15 °C



Property: WATER CONTENT
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF
OWModel

Surface release - Terminal Oil film thickness: 0.3 mm
Amount/duration of oil spill: 20 metric tons in 15 minute(s)

Pred. date: Oct. 24, 2013

Water content of Erich Giese predicted at sea temperatures of 5 °C and 15 °C

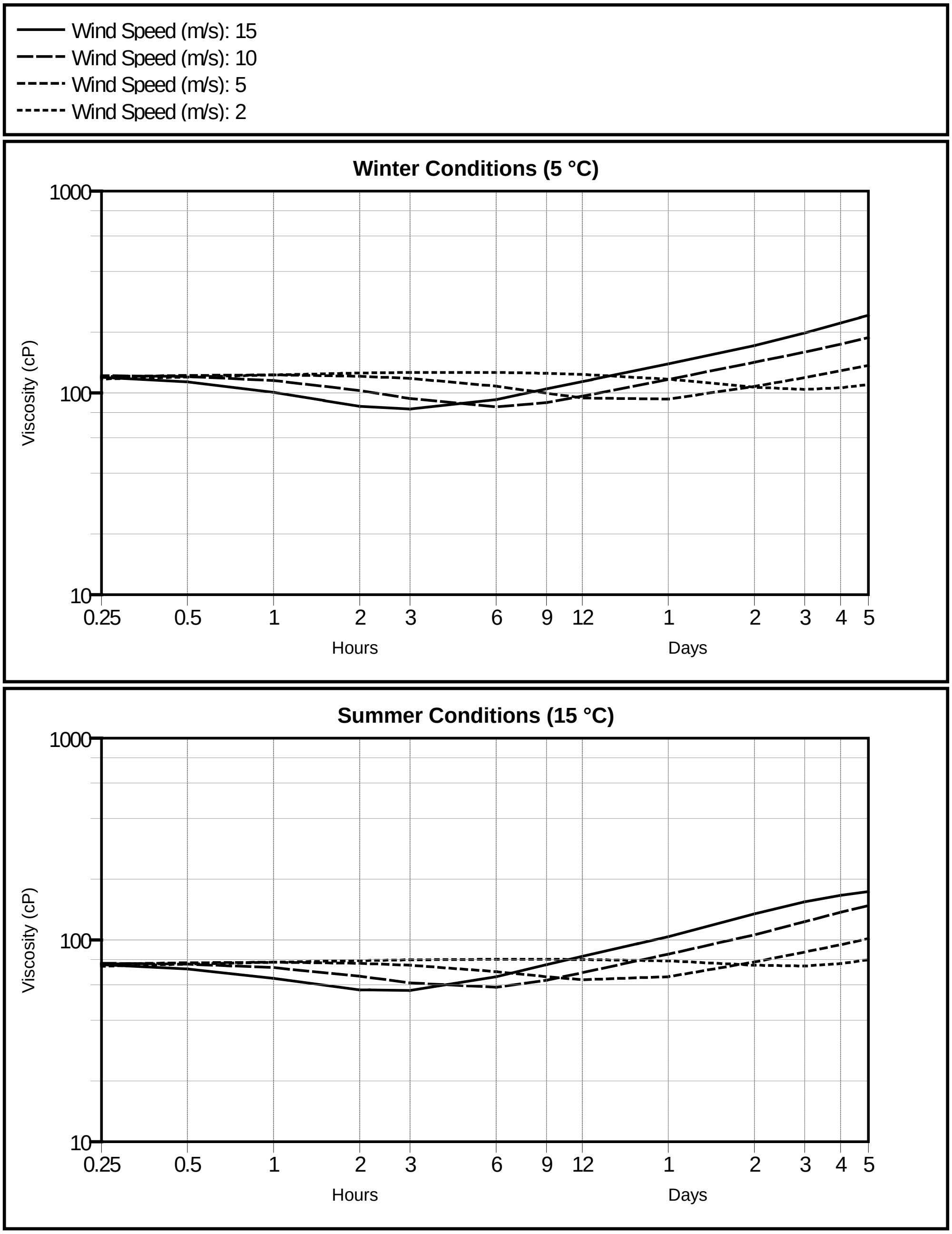
Property: VISCOSITY OF EMULSION
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

OWModel

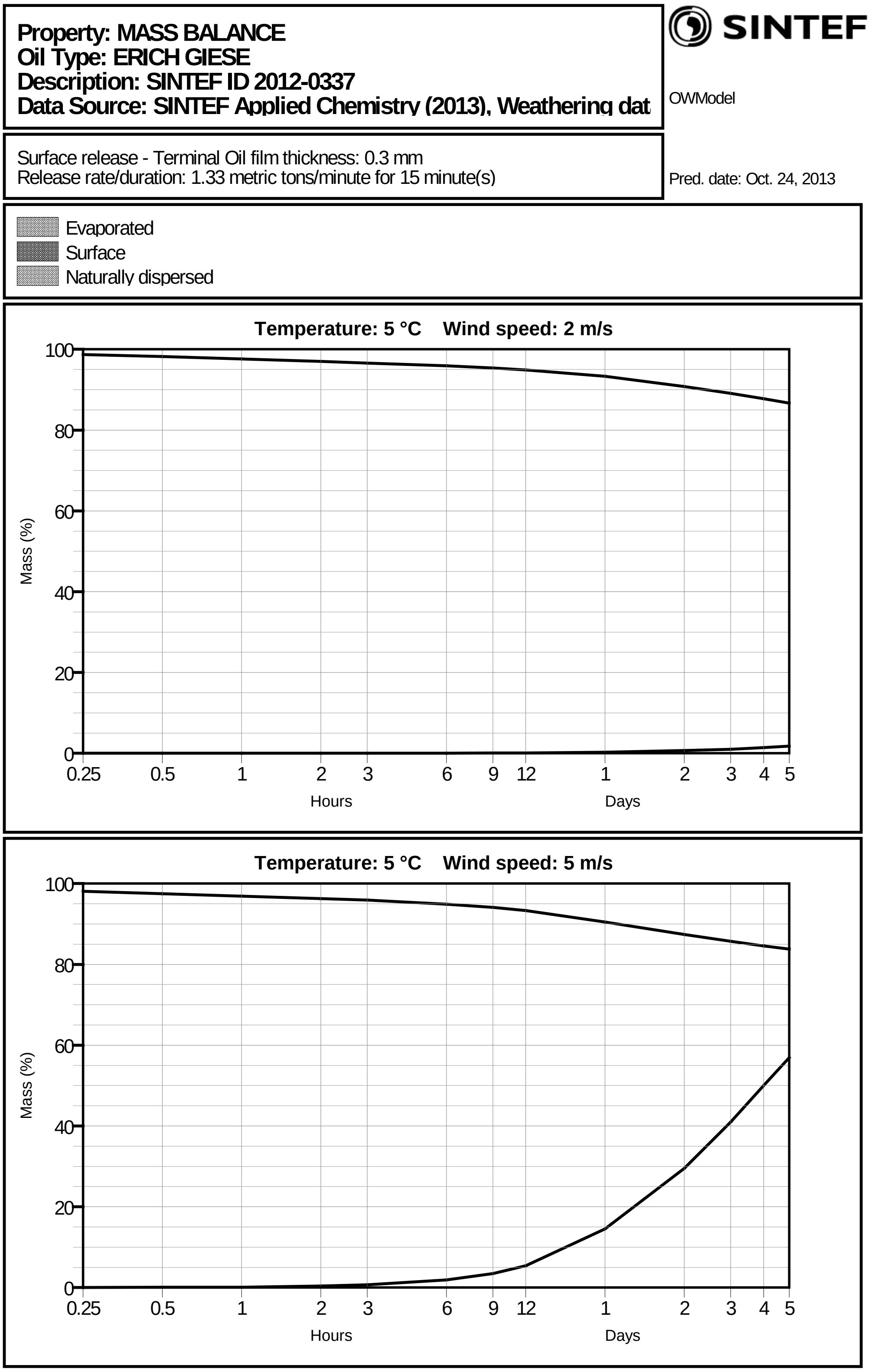
Surface release - Terminal Oil film thickness: 0.3 mm
Amount/duration of oil spill: 20 metric tons in 15 minute(s)

Pred. date: Oct. 24, 2013



Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Viscosity of emulsion of Erich Giese predicted at sea temperatures of 5 °C and 15 °C. Viscosity is predicted based on measurements performed at a shear rate of 10 s^{-1}.



Property: MASS BALANCE
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

OWModel

Surface release - Terminal Oil film thickness: 0.3 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed

Mass balance of Erich Giese predicted at sea temperatures of 5 °C, and wind speeds of 2m/s and 5m/s

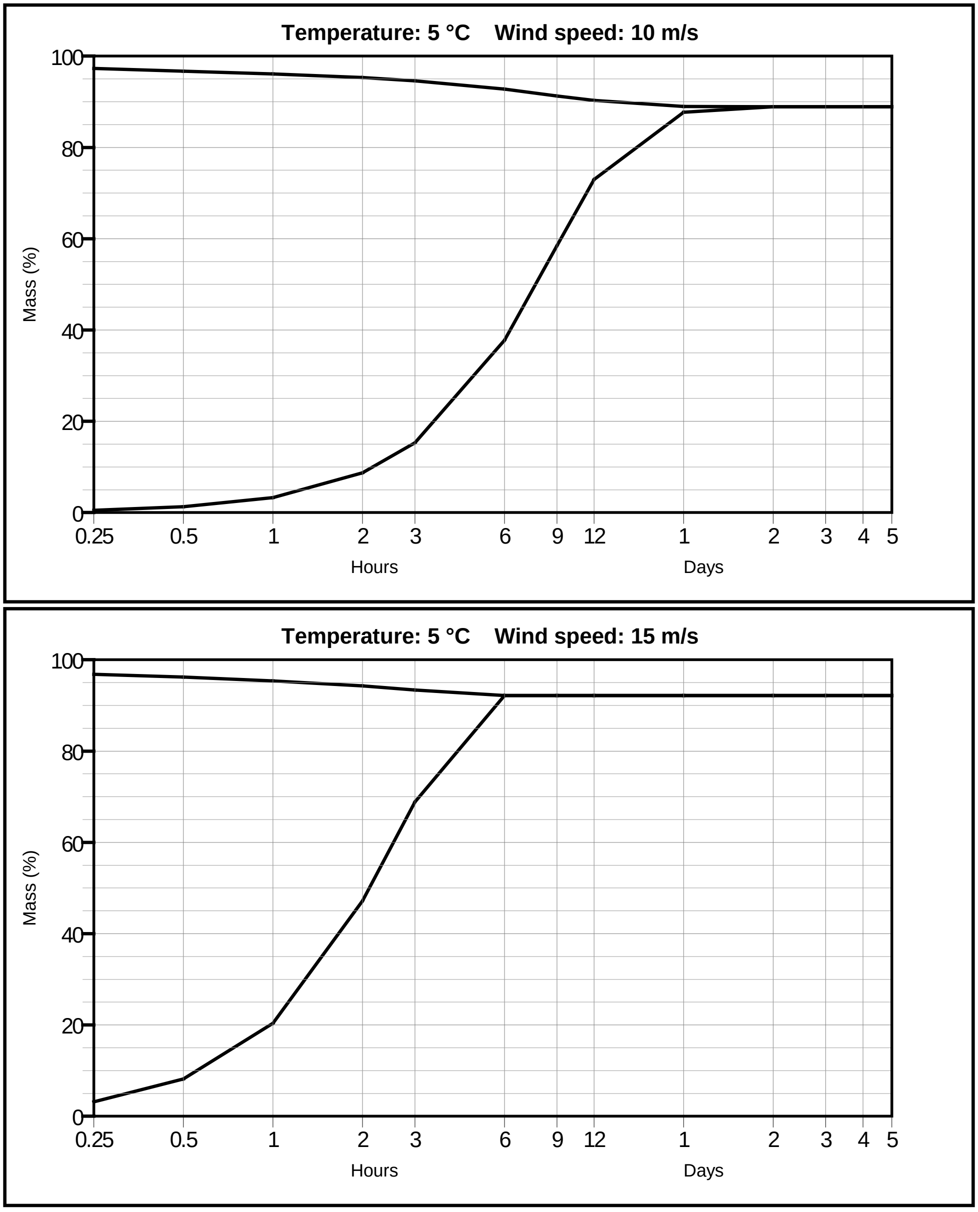
Property: MASS BALANCE
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

OWModel

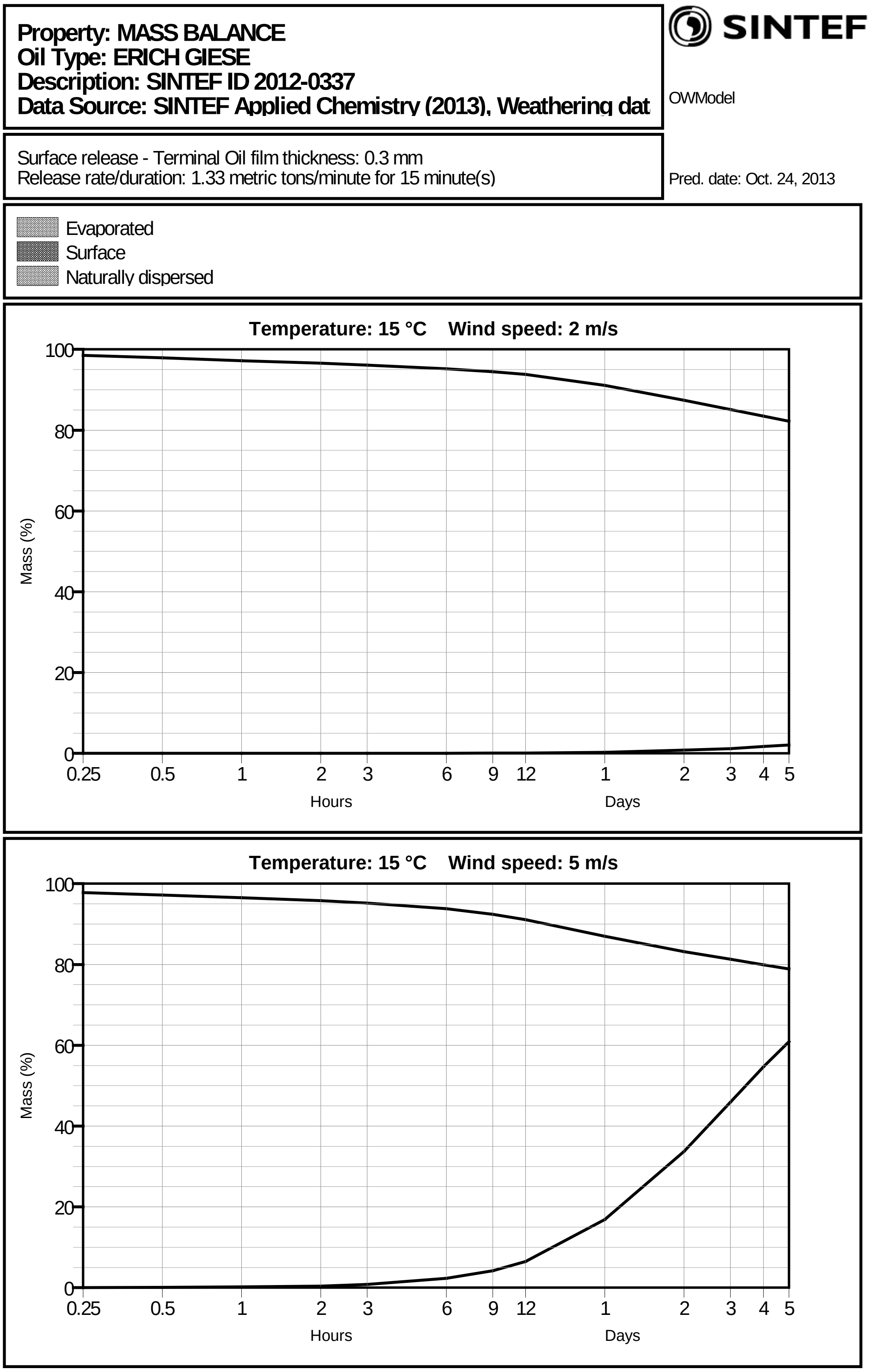
Surface release - Terminal Oil film thickness: 0.3 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▩ Surface
▨ Naturally dispersed



Mass balance of Erich Giese predicted at sea temperatures of 5 °C, and wind speeds of 10m/s and 15m/s



Property: MASS BALANCE
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

OWModel

Surface release - Terminal Oil film thickness: 0.3 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▩ Surface
▨ Naturally dispersed

Mass balance of Erich Giese predicted at sea temperatures of 15°C, and wind speeds of 2m/s and 5m/s

Property: MASS BALANCE
Oil Type: ERICH GIESE
Description: SINTEF ID 2012-0337
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

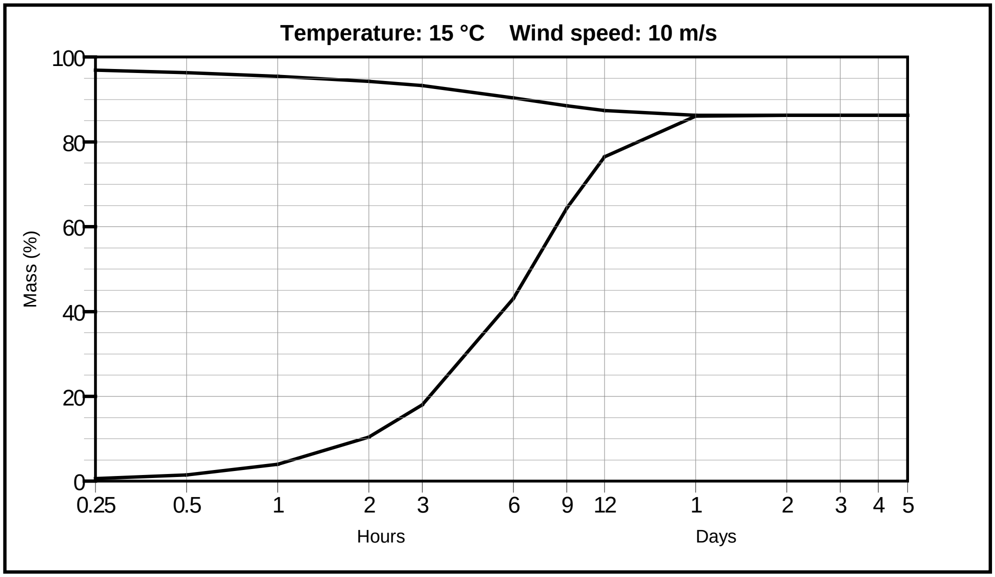
SINTEF

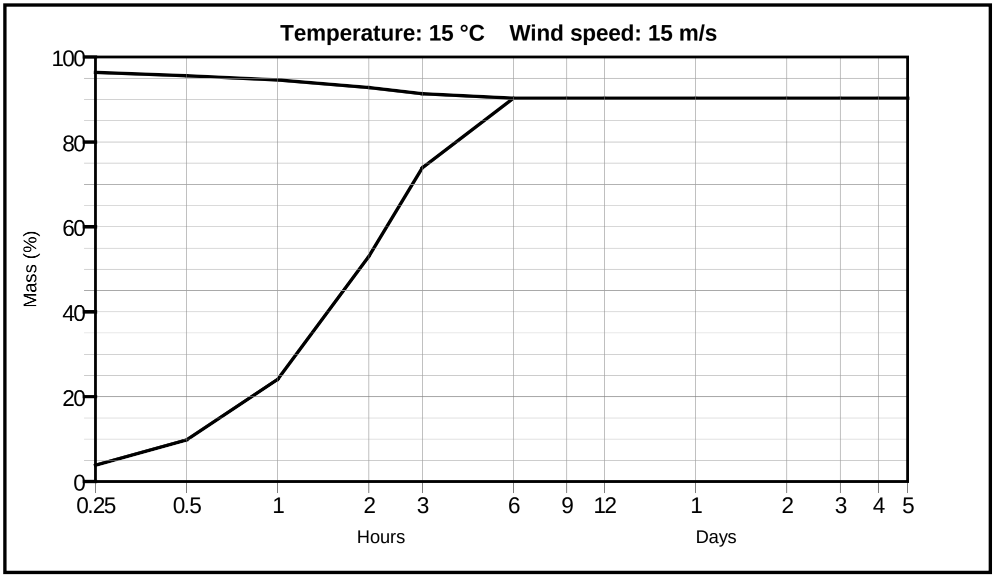
OWModel

Surface release - Terminal Oil film thickness: 0.3 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed





The algorithm for prediction of natural dispersion is preliminary and is currently under improvement.Model predictions have been field-verified up to 4-5 days.

Mass balance of Erich Giese predicted at sea temperatures of 15 °C, and wind speeds of 10m/s and 15m/s

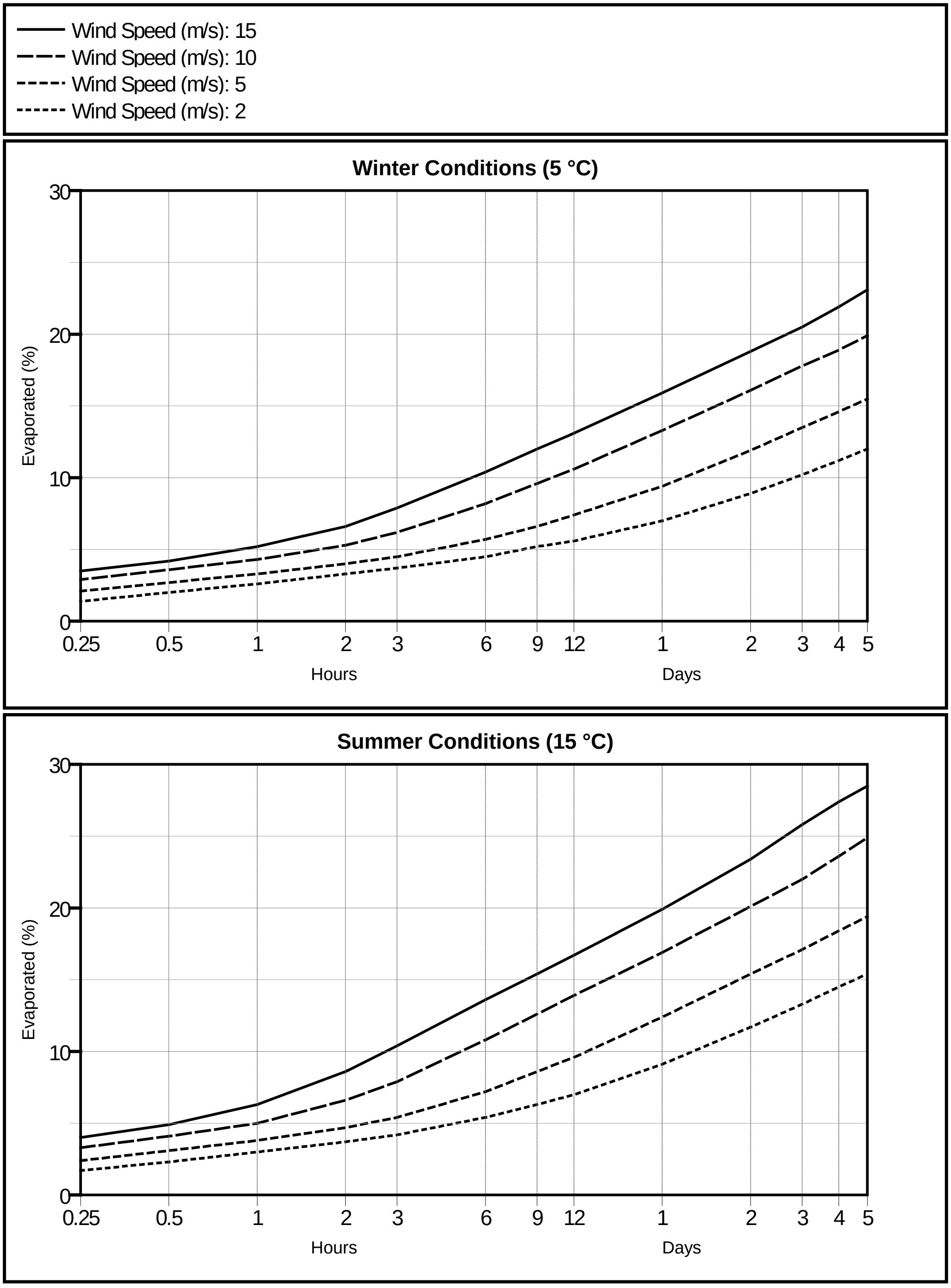
Property: EVAPORATIVE LOSS
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

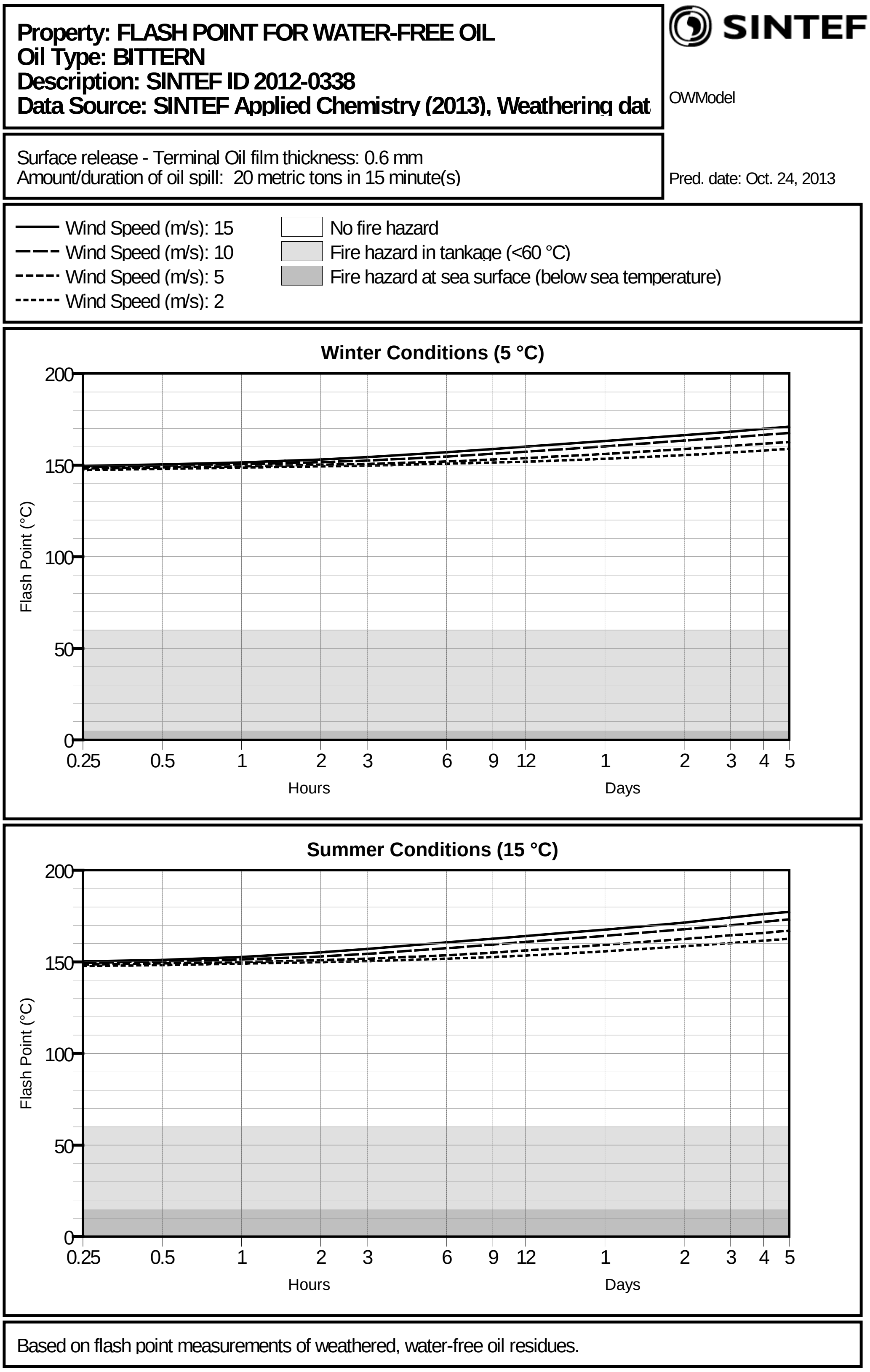
OWModel

Surface release - Terminal Oil film thickness: 0.6 mm
Amount/duration of oil spill: 20 metric tons in 15 minute(s)

Pred. date: Oct. 24, 2013



Evaporative loss of Bittern predicted at sea temperatures of 5 °C and 15 °C



Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

OWModel

Surface release - Terminal Oil film thickness: 0.6 mm
Amount/duration of oil spill: 20 metric tons in 15 minute(s)

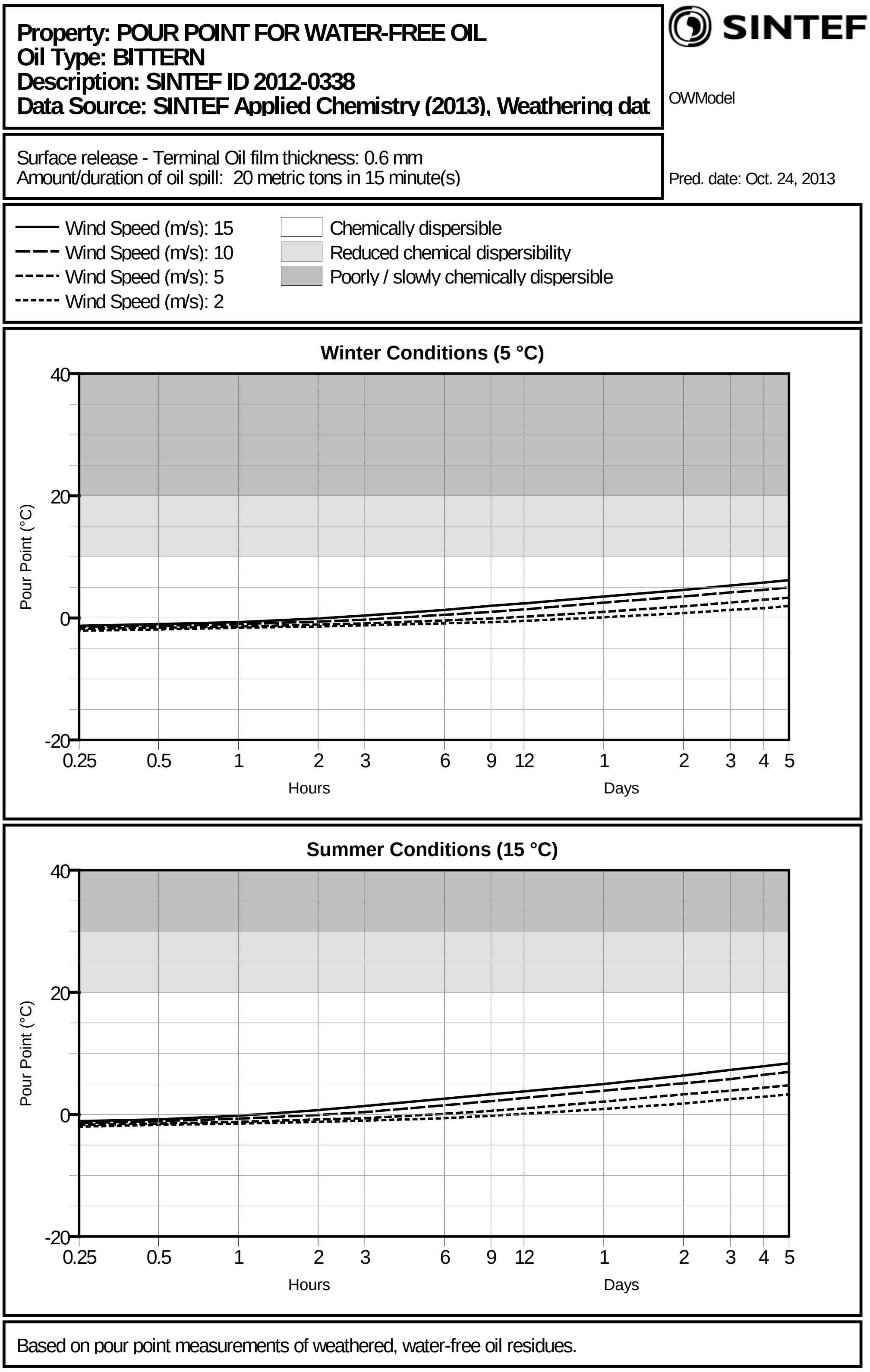
Pred. date: Oct. 24, 2013

—— Wind Speed (m/s): 15
— — — Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
------ Wind Speed (m/s): 2

☐ No fire hazard
▨ Fire hazard in tankage (<60 °C)
▩ Fire hazard at sea surface (below sea temperature)

Based on flash point measurements of weathered, water-free oil residues.

Flash point of Bittern predicted at sea temperatures of 5 °C and 15 °C



Property: POUR POINT FOR WATER-FREE OIL
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF
OWModel

Surface release - Terminal Oil film thickness: 0.6 mm
Amount/duration of oil spill: 20 metric tons in 15 minute(s)

Pred. date: Oct. 24, 2013

—— Wind Speed (m/s): 15
— — Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
------ Wind Speed (m/s): 2

☐ Chemically dispersible
▨ Reduced chemical dispersibility
■ Poorly / slowly chemically dispersible

Based on pour point measurements of weathered, water-free oil residues.

Pour point of Bittern predicted at sea temperatures of 5 °C and 15 °C

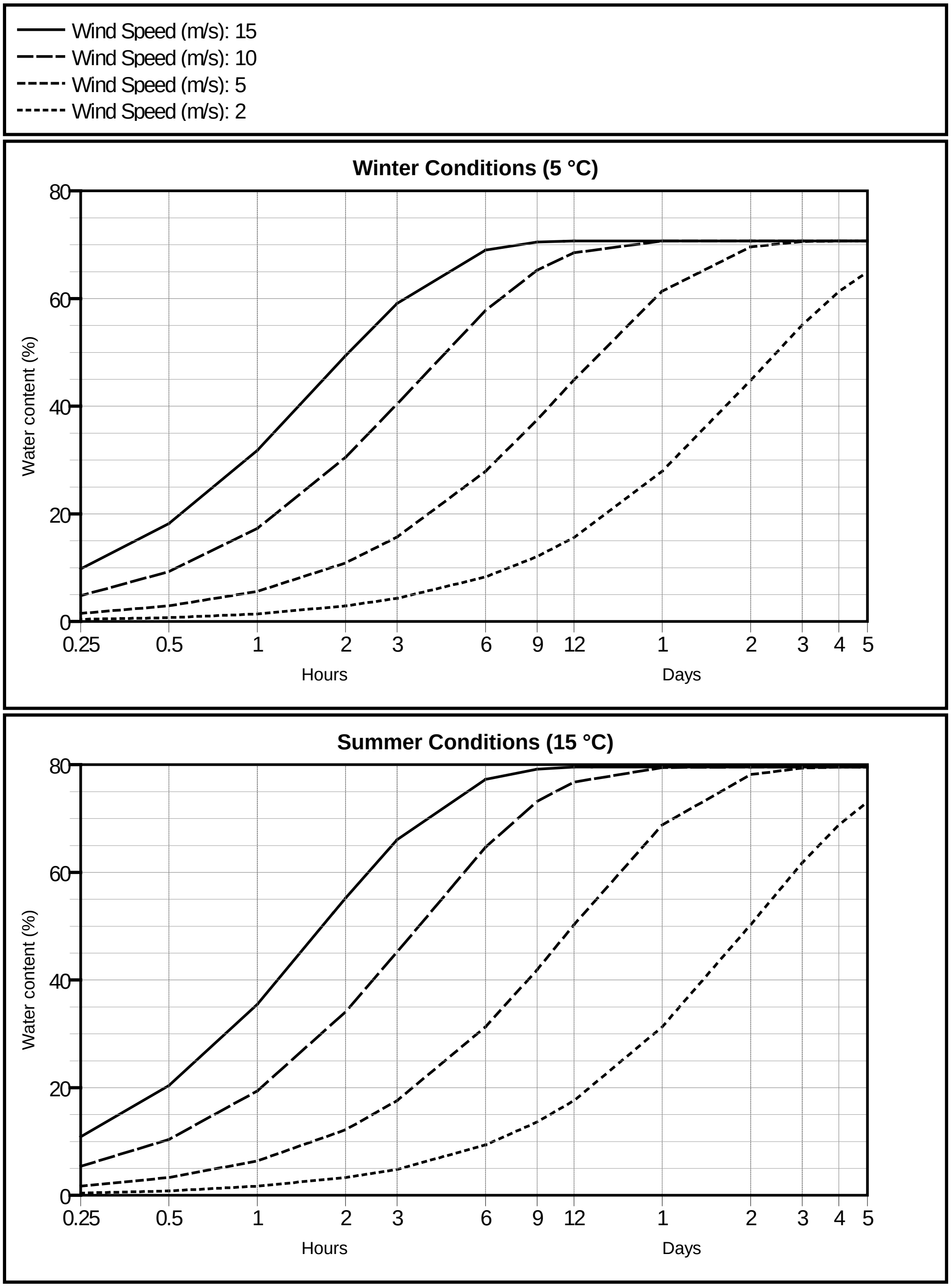
Property: WATER CONTENT
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

OWModel

Surface release - Terminal Oil film thickness: 0.6 mm
Amount/duration of oil spill: 20 metric tons in 15 minute(s)

Pred. date: Oct. 24, 2013



Water content of Bittern predicted at sea temperatures of 5 °C and 15 °C

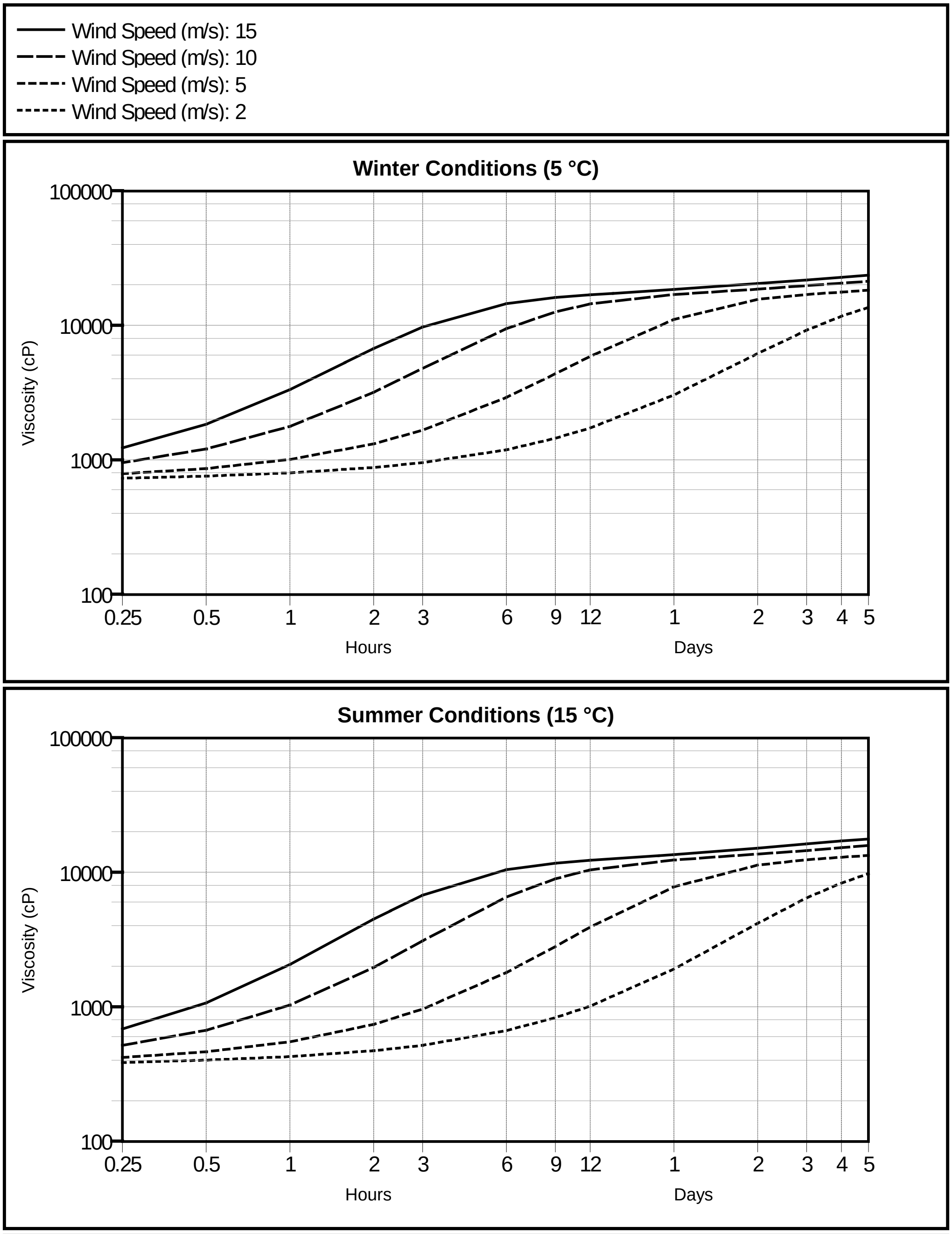
Property: VISCOSITY OF EMULSION
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

OWModel

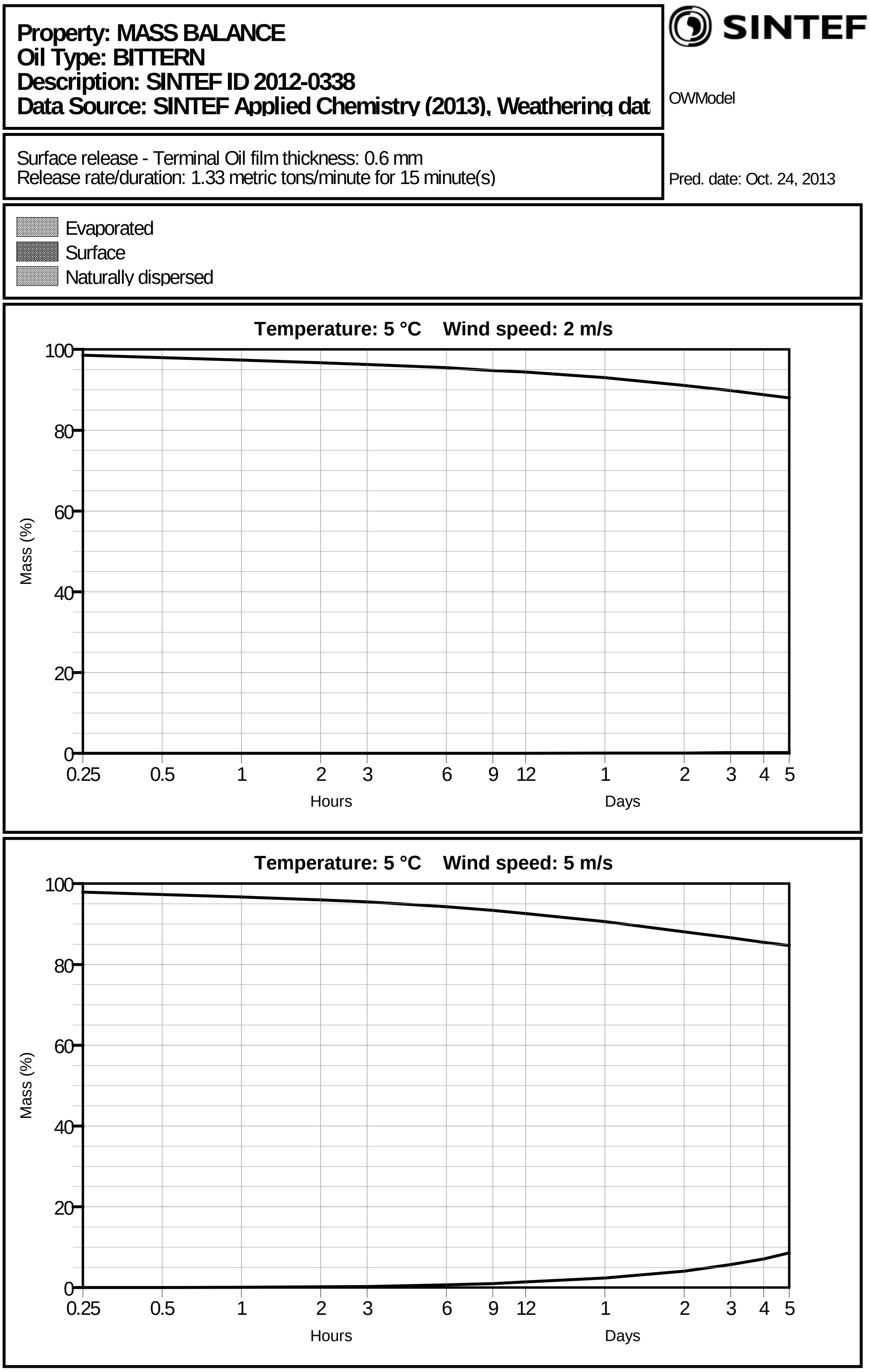
Surface release - Terminal Oil film thickness: 0.6 mm
Amount/duration of oil spill: 20 metric tons in 15 minute(s)

Pred. date: Oct. 24, 2013



Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Viscosity of emulsion of Bittern predicted at sea temperatures of 5 °C and 15 °C. Viscosity is predicted based on measurements performed at a shear rate of 10 s^{-1}.



Property: MASS BALANCE
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

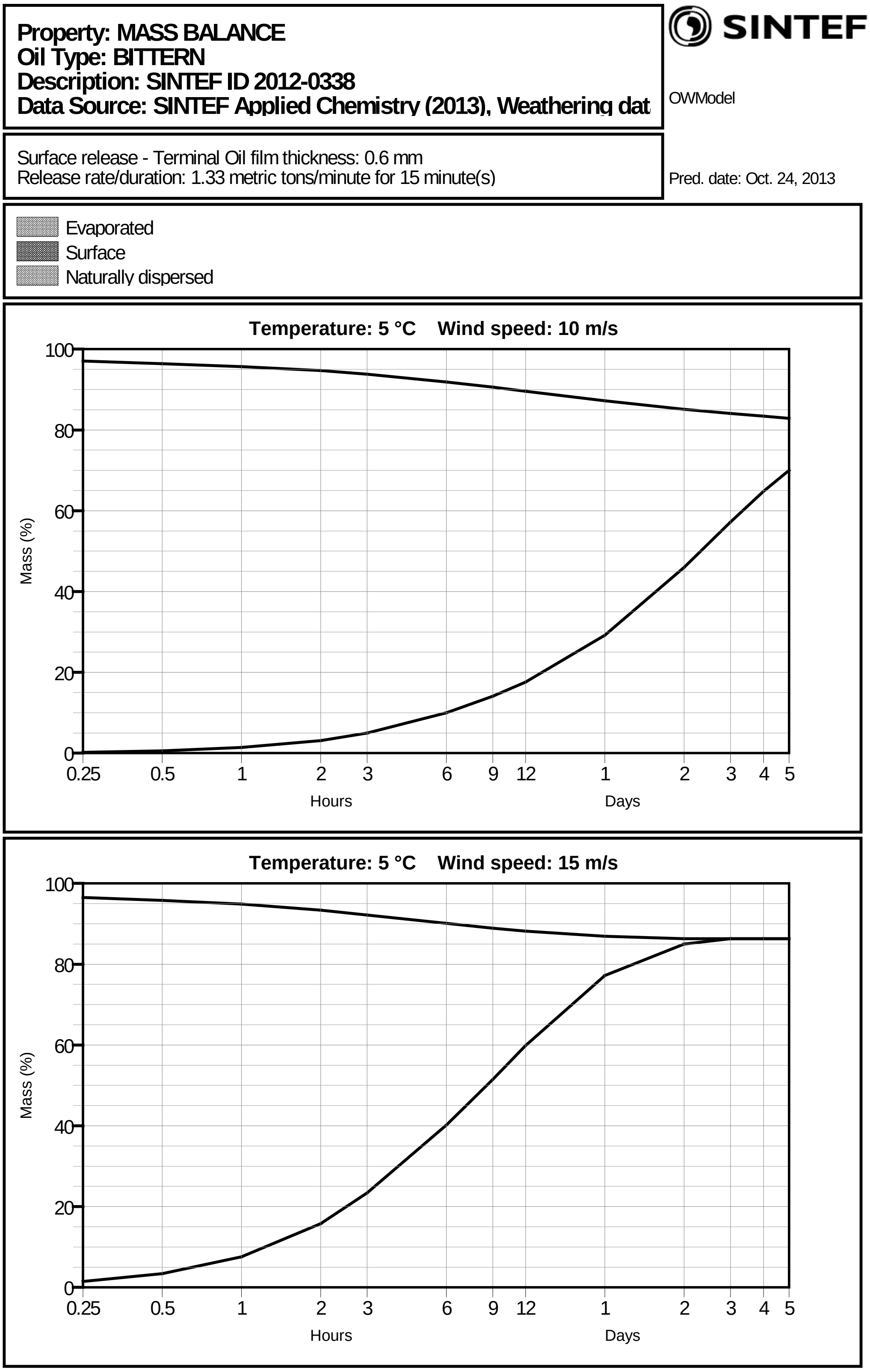
OWModel

Surface release - Terminal Oil film thickness: 0.6 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed

Mass balance of Bittern predicted at sea temperatures of 5 °C, and wind speeds of 2m/s and 5m/s



Property: MASS BALANCE
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

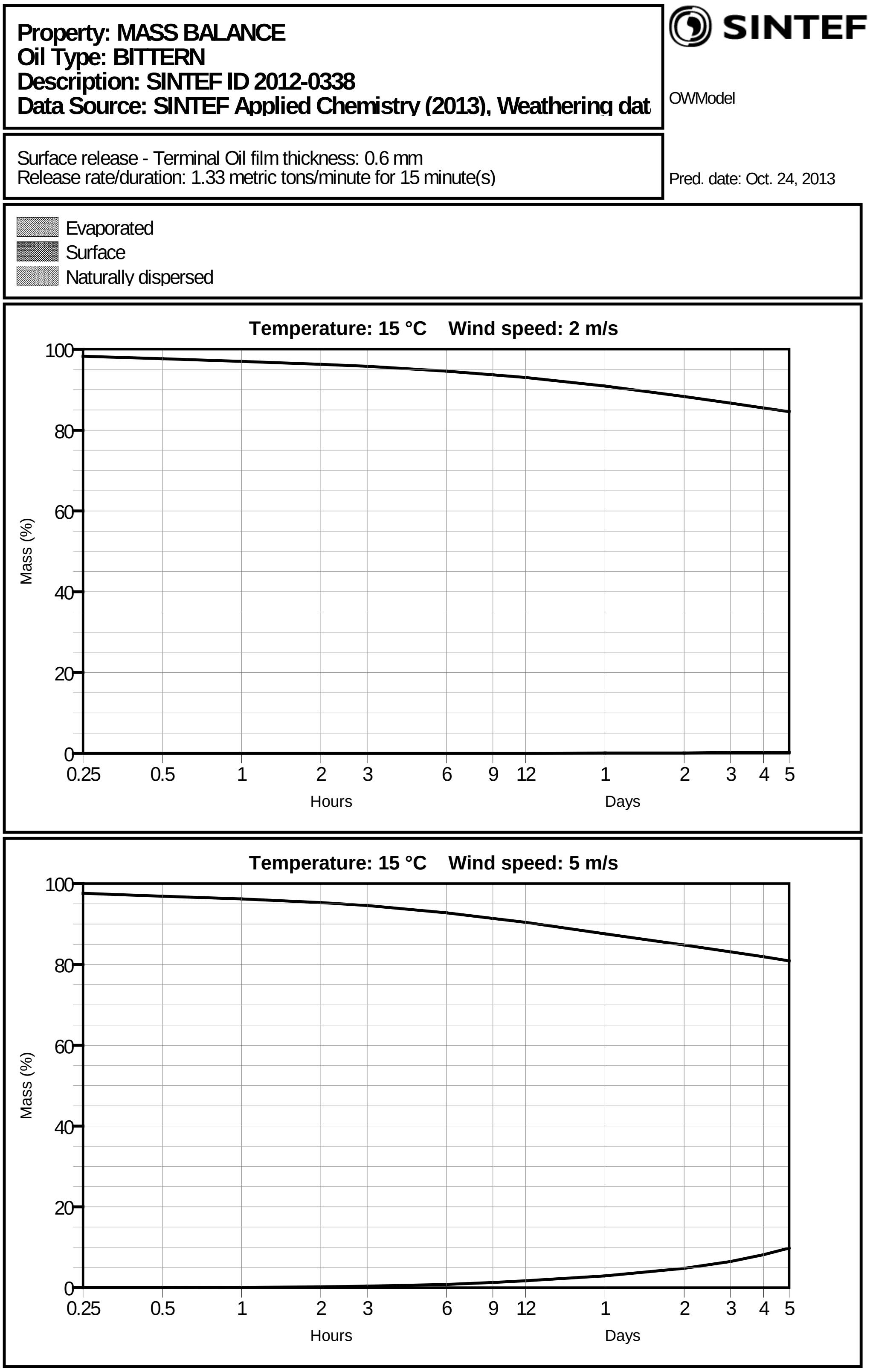
OWModel

Surface release - Terminal Oil film thickness: 0.6 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed

Mass balance of Bittern predicted at sea temperatures of 5 °C, and wind speeds of 10m/s and 15m/s



Property: MASS BALANCE
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

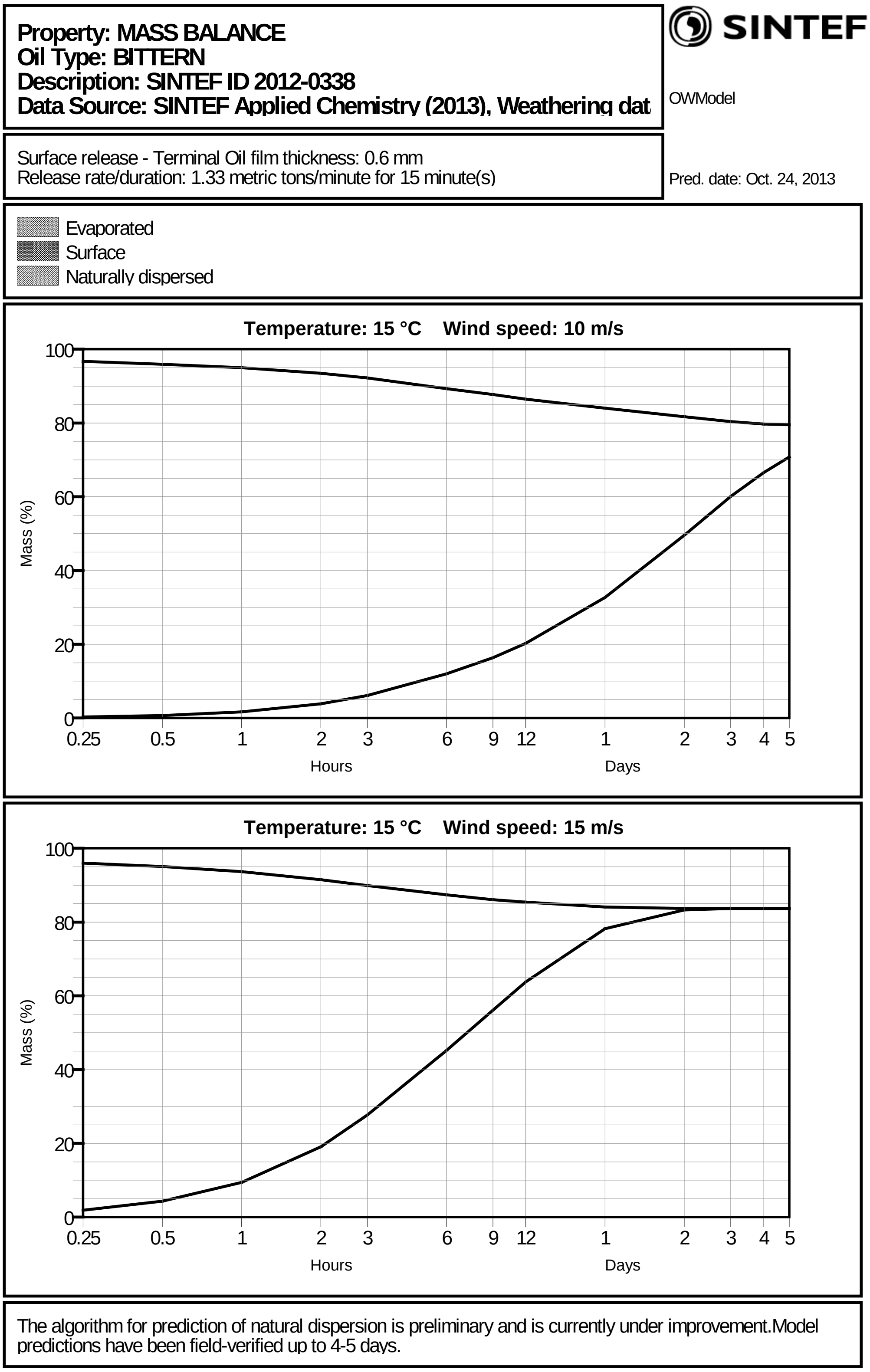
OWModel

Surface release - Terminal Oil film thickness: 0.6 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed

Mass balance of Bittern predicted at sea temperatures of 15 °C, and wind speeds of 2m/s and 5m/s



Property: MASS BALANCE
Oil Type: BITTERN
Description: SINTEF ID 2012-0338
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

OWModel

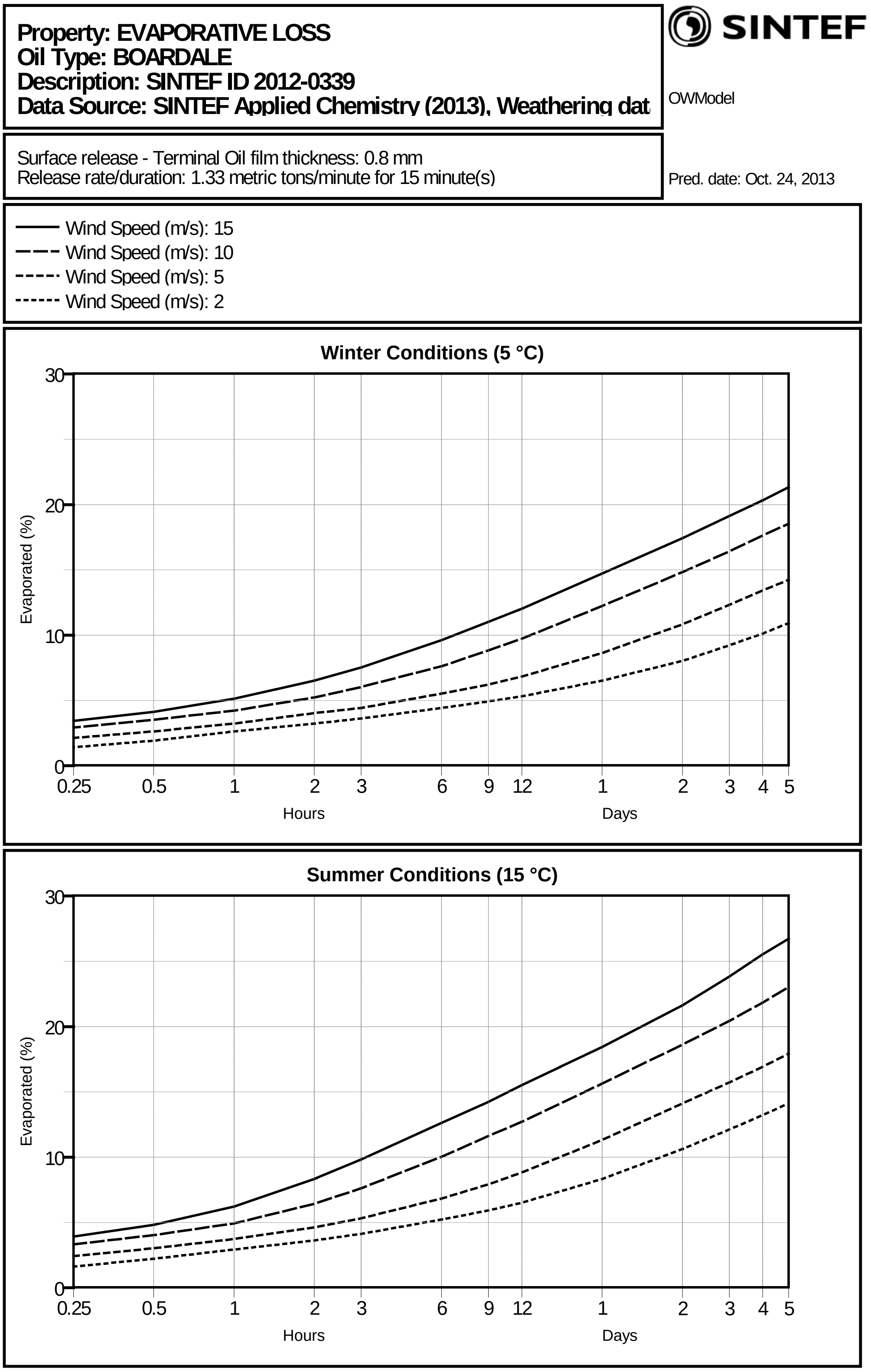
Surface release - Terminal Oil film thickness: 0.6 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed

The algorithm for prediction of natural dispersion is preliminary and is currently under improvement.Model predictions have been field-verified up to 4-5 days.

Mass balance of Bittern predicted at sea temperatures of 15 °C, and wind speeds of 10m/s and 15m/s



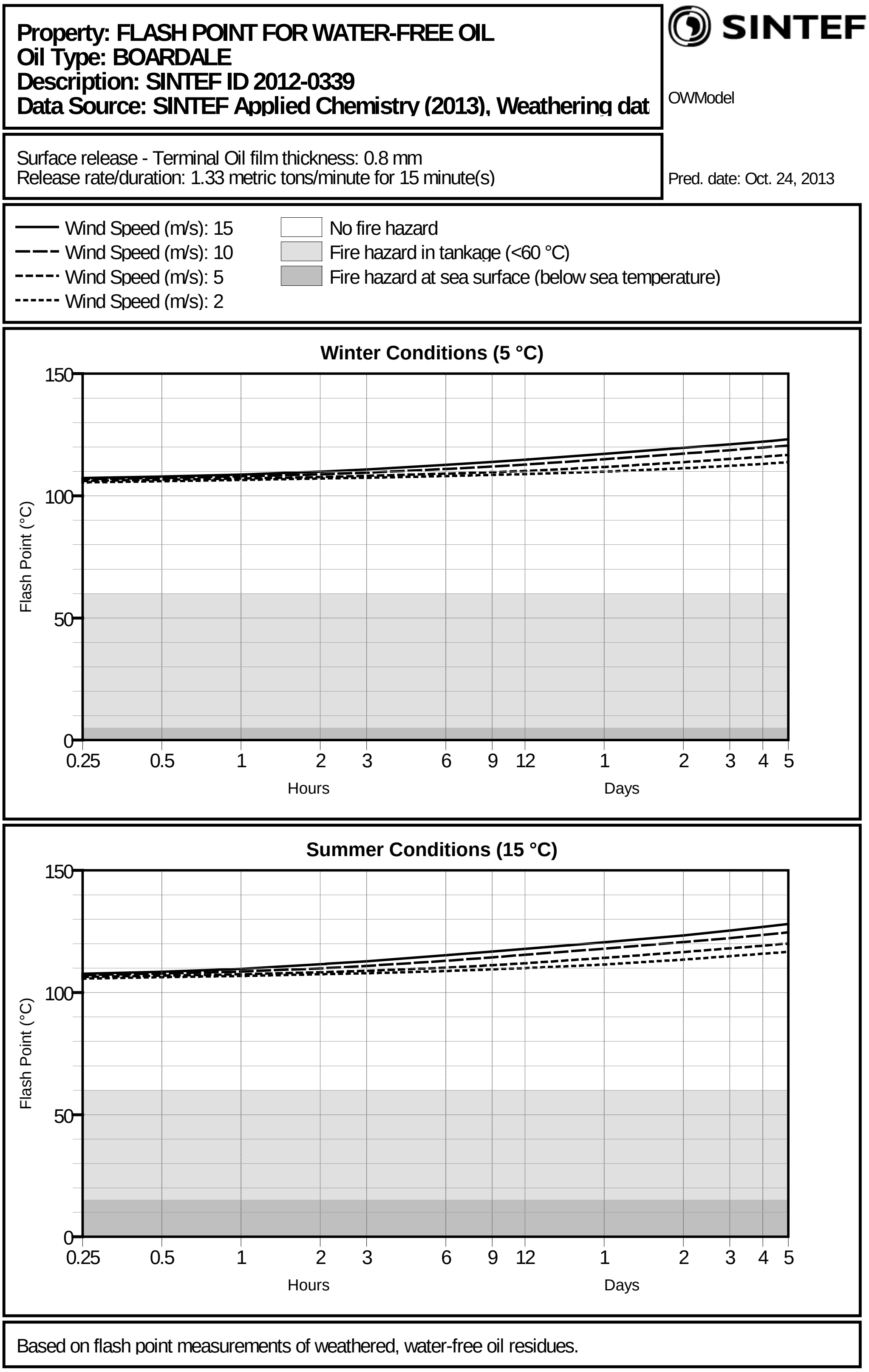
Property: EVAPORATIVE LOSS
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

OWModel

Surface release - Terminal Oil film thickness: 0.8 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

Evaporative loss of Boardale predicted at sea temperatures of 5 °C and 15 °C



Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

OWModel

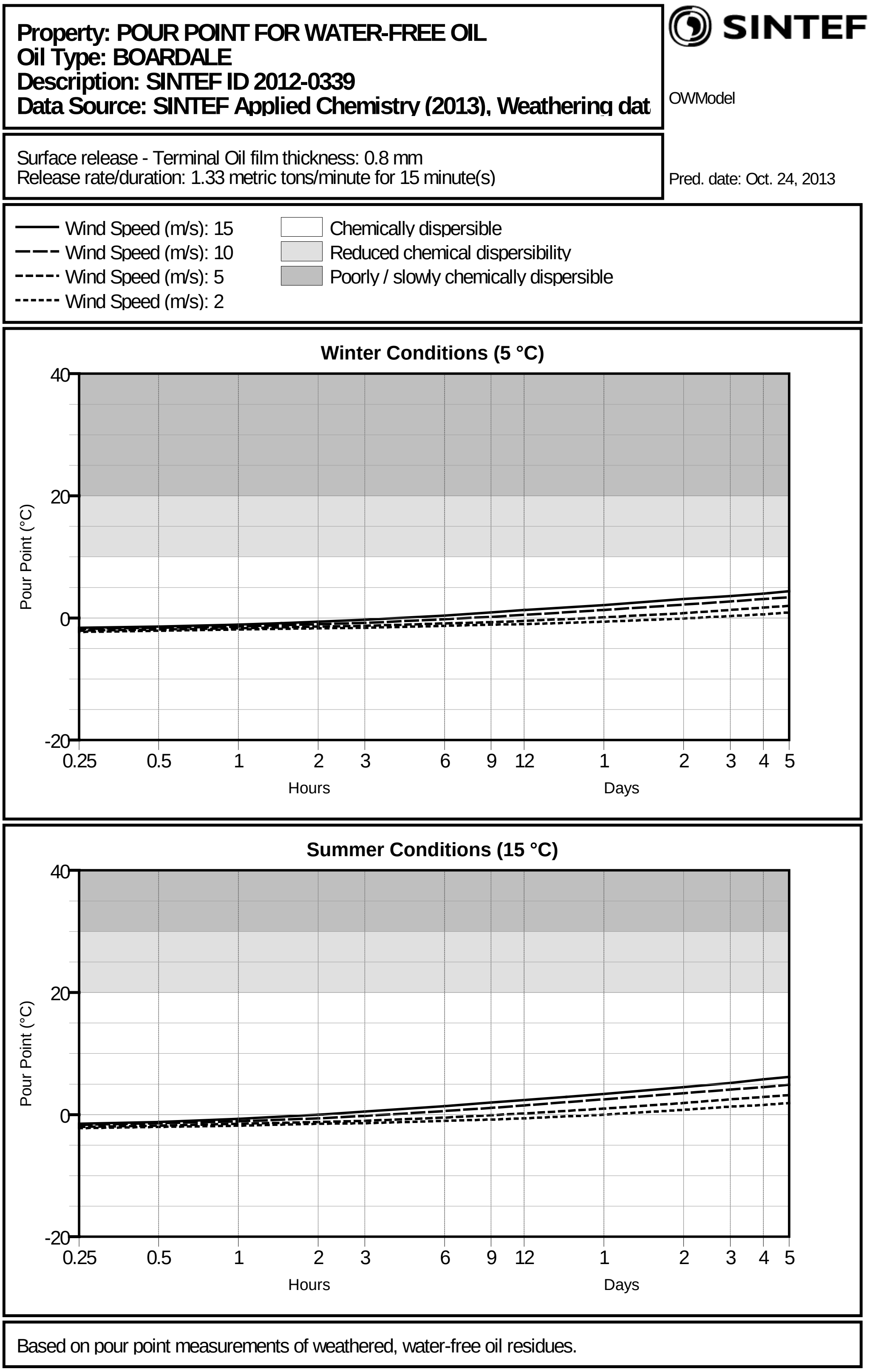
Surface release - Terminal Oil film thickness: 0.8 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

—— Wind Speed (m/s): 15	☐ No fire hazard
– – – Wind Speed (m/s): 10	▨ Fire hazard in tankage (<60 °C)
- - - - Wind Speed (m/s): 5	■ Fire hazard at sea surface (below sea temperature)
------ Wind Speed (m/s): 2	

Based on flash point measurements of weathered, water-free oil residues.

Flash point of Boardale predicted at sea temperatures of 5 °C and 15 °C



Property: POUR POINT FOR WATER-FREE OIL
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

OWModel

Surface release - Terminal Oil film thickness: 0.8 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

—— Wind Speed (m/s): 15
— — Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
------ Wind Speed (m/s): 2

☐ Chemically dispersible
░ Reduced chemical dispersibility
▒ Poorly / slowly chemically dispersible

Winter Conditions (5 °C)

Summer Conditions (15 °C)

Based on pour point measurements of weathered, water-free oil residues.

Pour point of Boardale predicted at sea temperatures of 5 °C and 15 °C

Property: WATER CONTENT
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

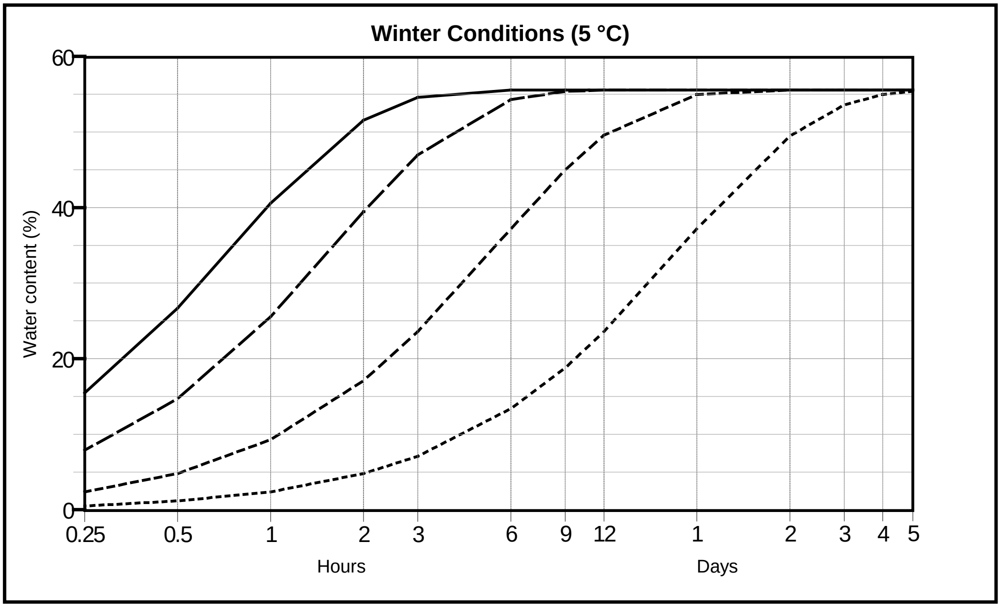
SINTEF

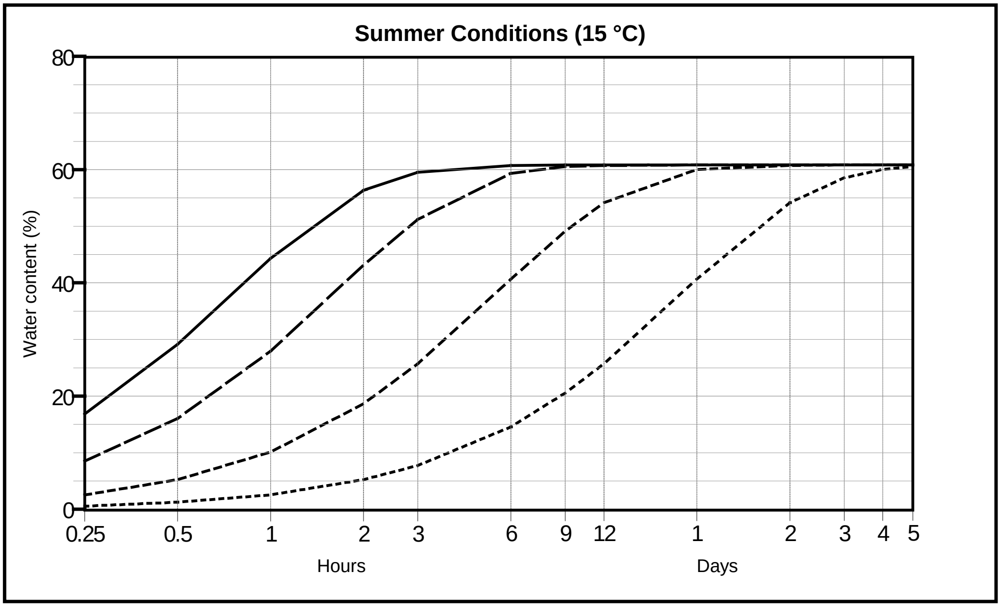
OWModel

Surface release - Terminal Oil film thickness: 0.8 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013

——— Wind Speed (m/s): 15
— — — Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
------ Wind Speed (m/s): 2


Winter Conditions (5 °C)


Summer Conditions (15 °C)

Water content of Boardale predicted at sea temperatures of 5 °C and 15 °C

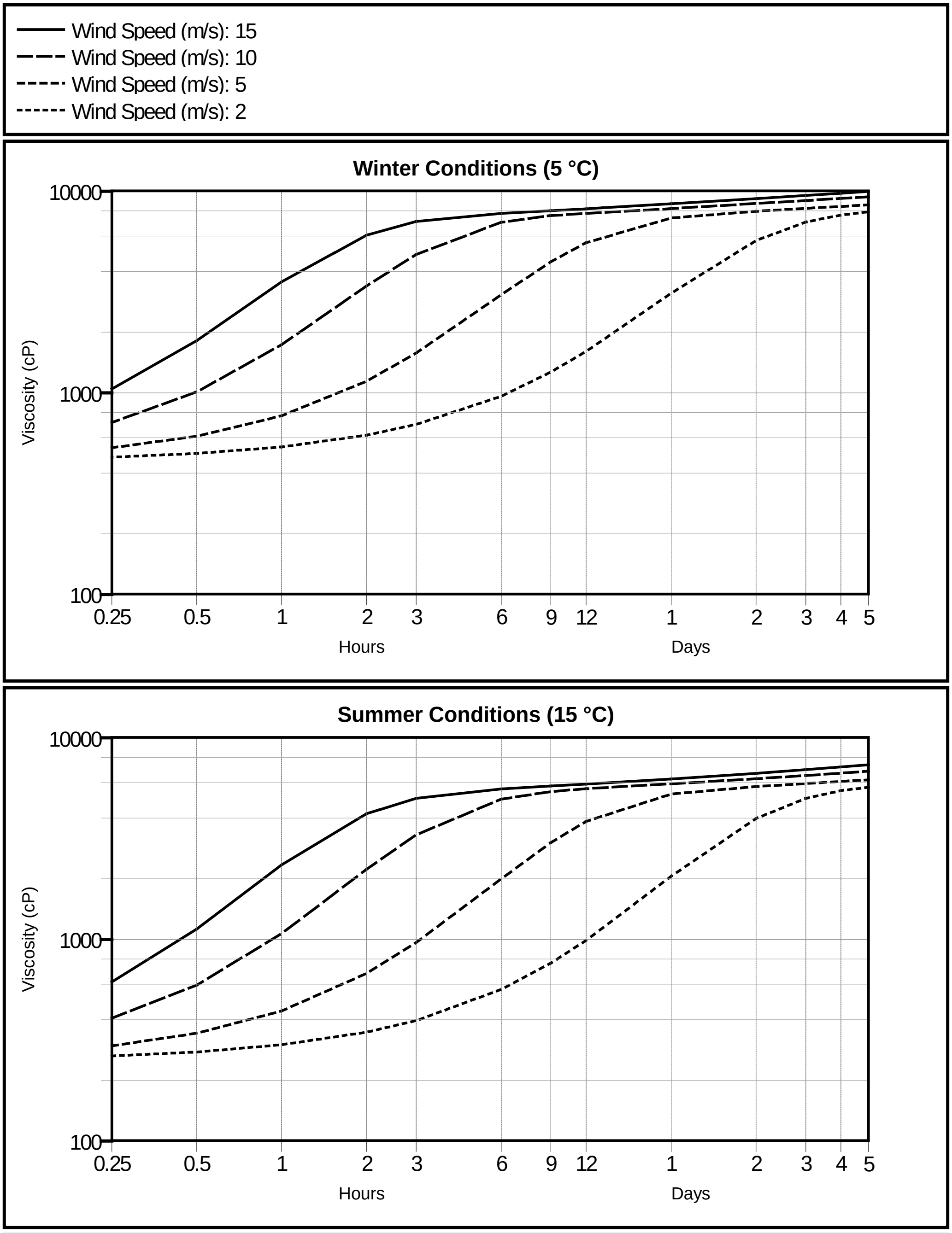
Property: VISCOSITY OF EMULSION
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

SINTEF

OWModel

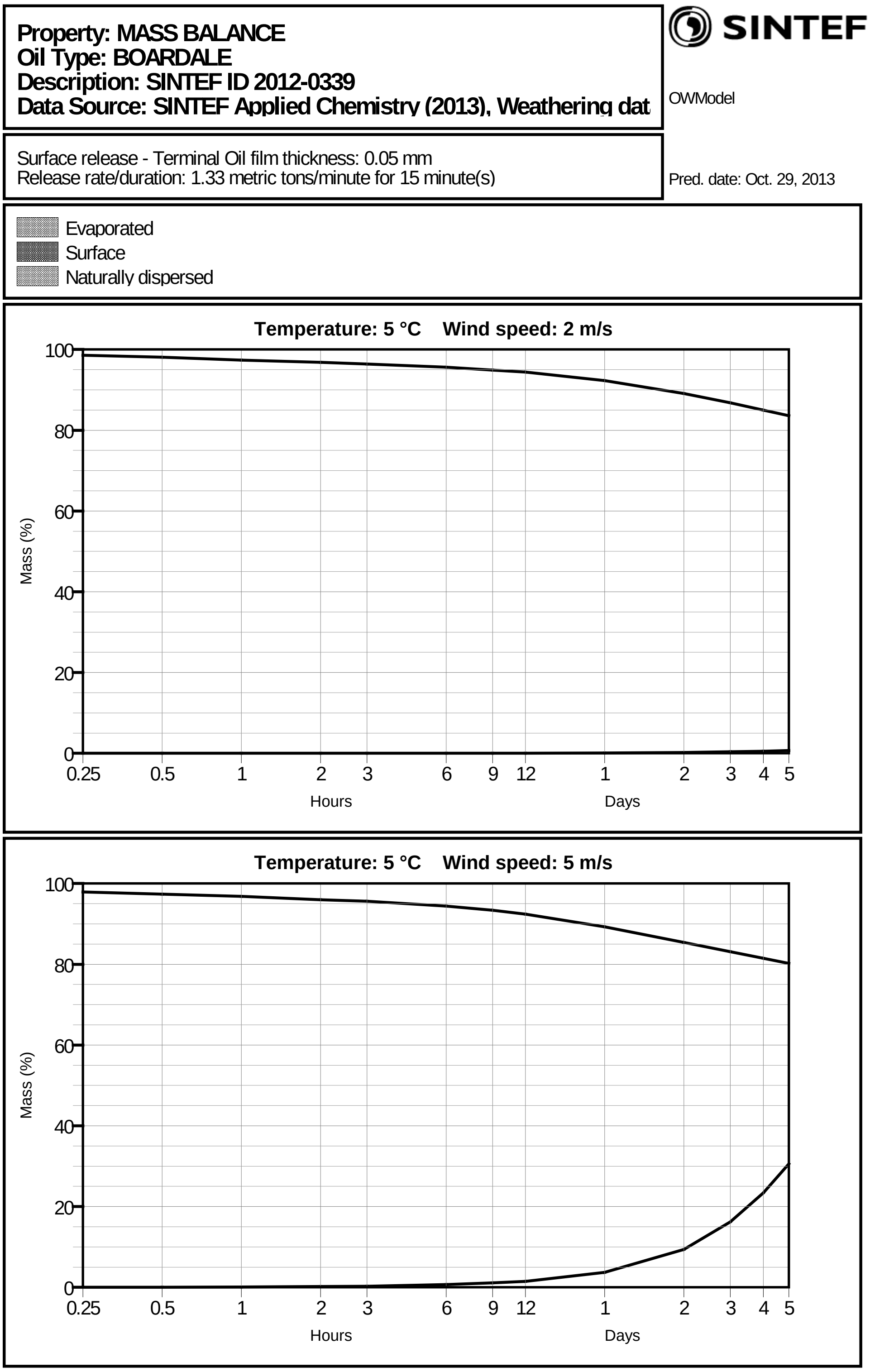
Surface release - Terminal Oil film thickness: 0.8 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 24, 2013



Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Viscosity of emulsion of Boardale predicted at sea temperatures of 5 °C and 15 °C



Property: MASS BALANCE
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

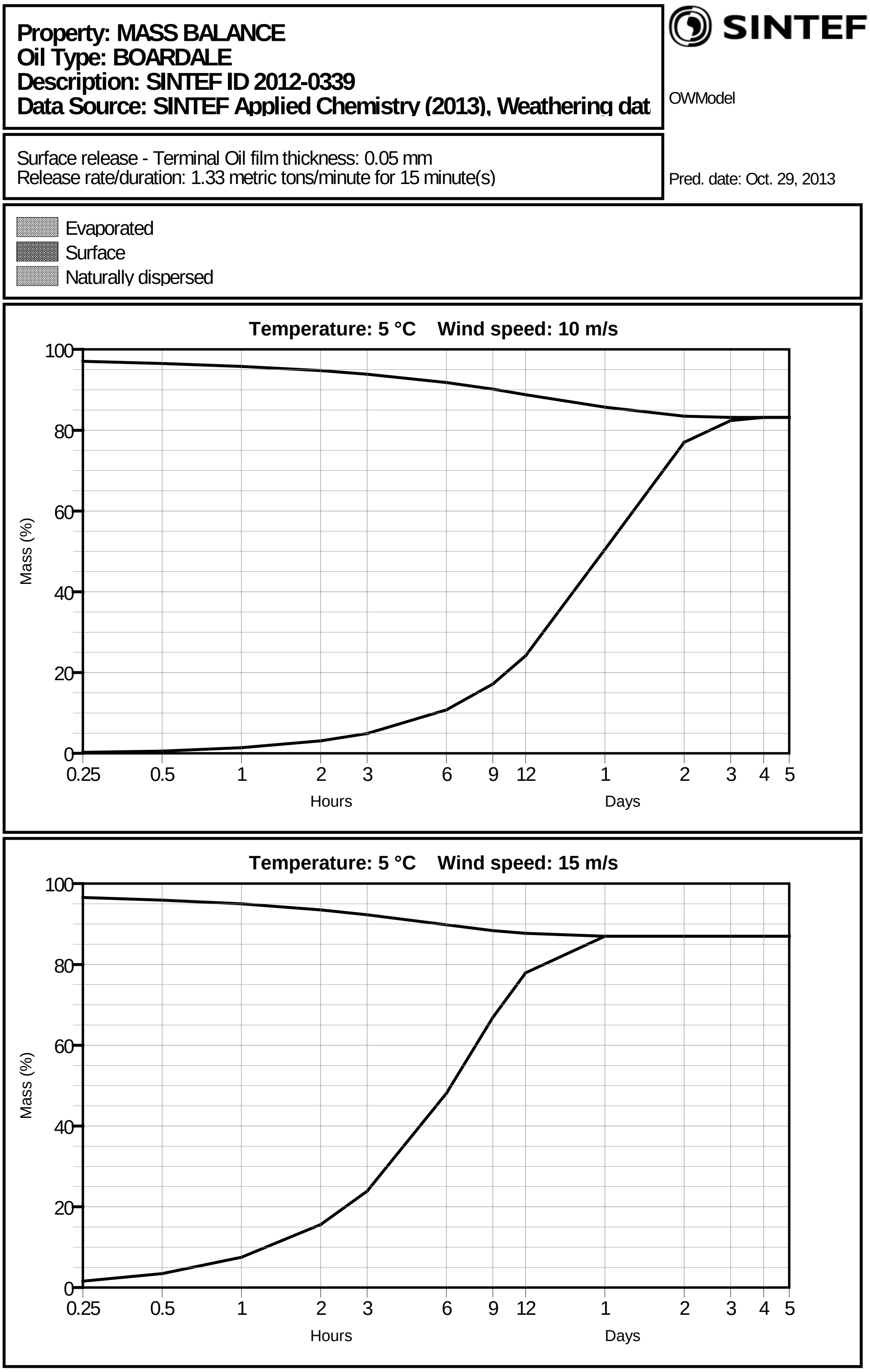
OWModel

Surface release - Terminal Oil film thickness: 0.05 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 29, 2013

▨ Evaporated
▩ Surface
▨ Naturally dispersed

Mass balance of Boardale predicted at sea temperatures of 5 °C, and wind speeds of 2m/s and 5m/s



Property: MASS BALANCE
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

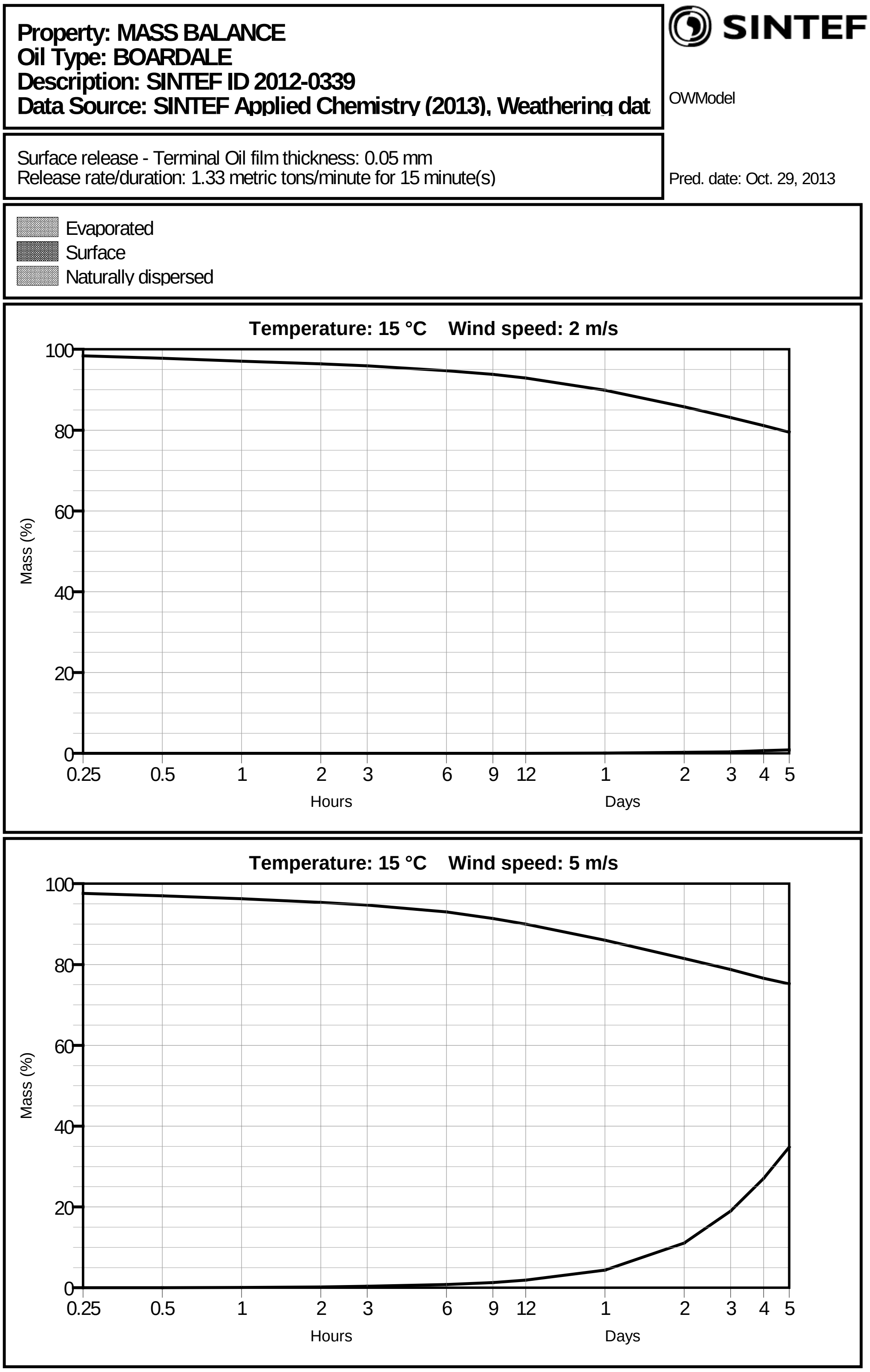
SINTEF
OWModel

Surface release - Terminal Oil film thickness: 0.05 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 29, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed

Mass balance of Boardale predicted at sea temperatures of 5 °C, and wind speeds of 10m/s and 15m/s



Property: MASS BALANCE
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

OWModel

Surface release - Terminal Oil film thickness: 0.05 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 29, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed

Mass balance of Boardale predicted at sea temperatures of 15 °C, and wind speeds of 2m/s and 5m/s

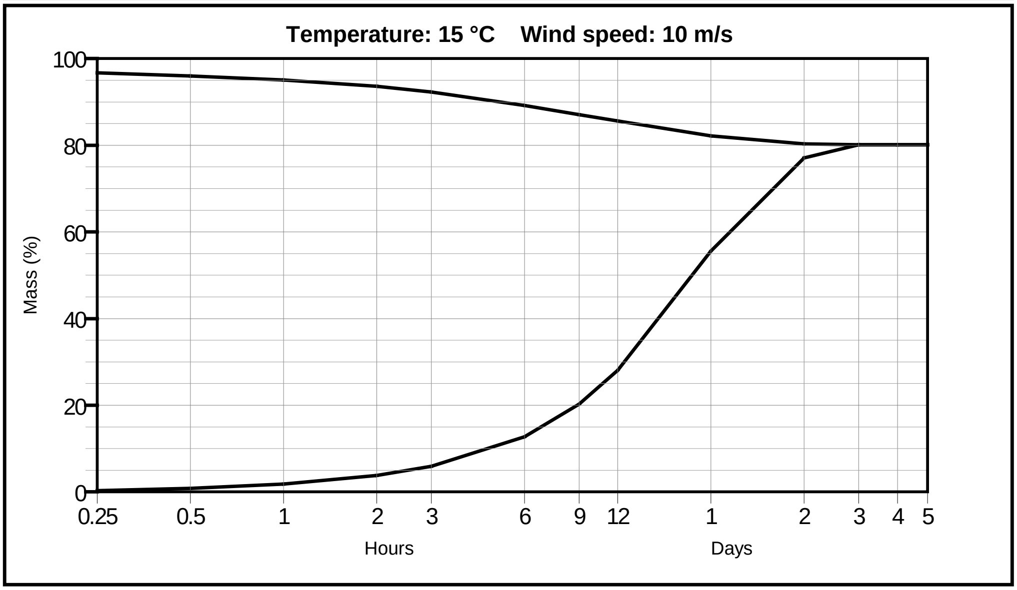
Property: MASS BALANCE
Oil Type: BOARDALE
Description: SINTEF ID 2012-0339
Data Source: SINTEF Applied Chemistry (2013), Weathering dat

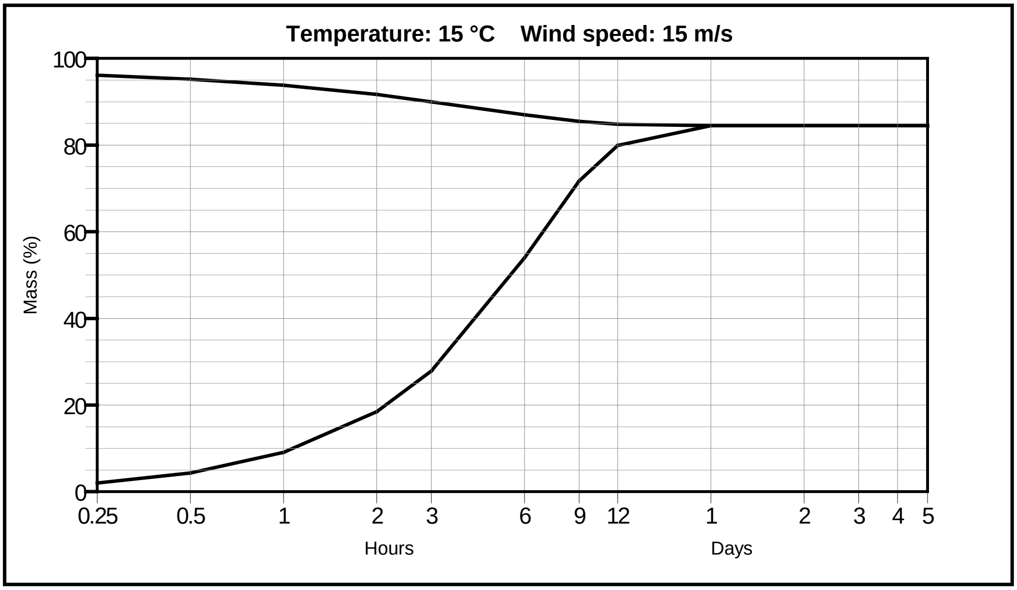
OWModel

Surface release - Terminal Oil film thickness: 0.05 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Oct. 29, 2013

▨ Evaporated
▨ Surface
▨ Naturally dispersed





The algorithm for prediction of natural dispersion is preliminary and is currently under improvement.Model predictions have been field-verified up to 4-5 days.

Mass balance of Boardale predicted at sea temperatures of 15 °C, and wind speeds of 10m/s and 15m/s.

Appendix G Abstracts to international conferences and publications

The methodology and results from the characterization of the oils and their potential toxic effects have been presented at three international conferences, and are published in the Marine Pollution Bulletin. Abstracts and publications are given in this Appendix:

- The 36th AMOP Technical Seminar on Environmental Contamination and Response, June 4-6, 2013, Halifax, Canada. (Abstract and presentation): Faksness, L.G., P. Daling, D. Altin, K.R. Sørheim, and H. Dolva. Leakage of oil products from Word War II shipwrecks – Is there a potential environmental risk?

- The International Oil Spill Conference (IOSC), May 4-8, 2014, Savannah, USA.
  Abstract, paper in the proceedings, and presentation: Faksness, L.G., P. Daling, D. Altin, H. Dolva, B. Fosbæk, and R. Bergstrøm: Potential for environmental impact from leaking World War II shipwrecks due to the relative bioavailability and toxicity of their fuel oils. IOSC Proceedings: May 2014, Vol. 2014, No. 1, pp. 2000-2013. doi: http://dx.doi.org/10.7901/2169-3358-2014.1.2000

- The wreck of the world III: Shipwreck risk assessment, October 12-13, 2015, Gothenburg, Sweden.
  Abstract and presentation: Faksness, L.G., D. Altin, P. Daling, H. Dolva, and R. Bergstrøm. Relative bioavailability and toxicity of fuel oils leaking from World War II shipwrecks.

- Faksness, L.G., P. Daling, D. Altin, H. Dolva, B. Fosbæk, and R. Bergstrøm (2015). Relative bioavailability and toxicity of fuel oils leaking from World War II shipwrecks. Marine Pollution Bulletin 94: 123-130.

Abstract to the 36th AMOP Technical Seminar, June 4-6, 2013, Halifax.

Leakage of oil products from Word War II shipwrecks – Is there a potential environmental risk?

Liv-Guri Faksness[1], Per Daling[1], Dag Altin[2], Kristin Rist Sørheim[1], and Hilde Dolva[3]

[1]*SINTEF Materials and Chemistry, Brattorkaia 17c, NO-7465 Trondheim, Norway*
[2]*Altins BioTrix, NO-7022 Trondheim, Norway*
[3]*Norwegian Coastal Administration, NO-3187 Horten, Norway*

**Corresponding author: livgurif@sintef.no*

In 2006, the Norwegian Coastal Administration was taking an inventory of 30 coastal shipwrecks along the Norwegian coast, all of them sank during Word War II (WWII), and identified those that posed the most significant threat to the surrounding environment. There are often already small oil leaks and growing concern that more oil contained in the ruined vessels will leak into the marine environment. The longer these ships are down there corroding or getting battered by waves, the higher the risk of a spill. Cleanup is laborious, expensive, and can cause its own problems if handled incorrectly, releasing oil or other pollutants into ocean waters. However, the risk posed by a wreck depends on where the vessel sits, the types and amount of fuel on board, and the local environment, as acute contamination from these wrecks might be a potential environmental risk.

Priorities for emptying the wrecks were established, and the oil has recently been removed from three of the wrecks: HMS "Bittern" located on 150 m depth close to Namsos, RFA "Boardale", which grounded and sank outside Vesterålen, and "Eric Giese" located in the inlet to the harbor of Narvik on 65 m depth. SINTEF has received oil samples from these three WWII shipwrecks, and an ongoing project is characterizing toxicity of the water accommodated fraction (WAF) of the oils with special emphasis on chemistry and acute biological effects (algae growth (*Skeletonema costatum*) and copepod mortality (*Calanus finmarchicus*). WAF is of special interest because components dissolved from an oil slick or from rising oil droplets in the water column are known to be bioavailable to marine organisms and therefore have a potential for causing toxic effects. A limited study of the weathering properties of the oils is also performed. The data from this laboratory study will be used to as input to the SINTEF Oil Weathering Model to predict the behavior of the oils at sea at different weathering conditions, and to optimize the effectiveness of potential response operations/countermeasures.

The ongoing project will give valuable input to the decision maker's recommendations of how to deal with old shipwrecks containing oil. It may form a basic "standard" methodology for characterization of the potential environmental risk of oil leakage from shipwrecks.

2014 INTERNATIONAL OIL SPILL CONFERENCE

Potential for environmental impact from leaking World War II shipwrecks due to the relative bioavailability and toxicity of their fuel oils

Liv-Guri Faksness[1], Per Daling[1], Dag Altin[2], Hilde Dolva[3], Bjørn Fosbæk[3], and Rune Bergstrøm[3]

[1]*SINTEF Materials and Chemistry, Brattorkaia 17c, NO-7465 Trondheim, Norway*
[2]*BioTrix, NO-7022 Trondheim, Norway*
[3]*Norwegian Coastal Administration, NO-3187 Horten, Norway*
**Corresponding author: livgurif@sintef.no*

ABSTRACT 299444:

The Norwegian Authorities have classified 30 World War II (WWII) shipwrecks to have a considerable potential for pollution to the local environment, based on the location and condition of the wreck and the types and amount of fuel on board. Oil thus far has been removed from eight of these WWII shipwrecks. The water accommodated fractions (WAFs) of oils from the British sloop HMS "Bittern", the British carrier tanker RFA "Boardale", the German destroyer "Erich Giese", and the German cargo ship MS "Nordvard" have been studied with special emphasis on chemistry and biological effects (algae growth (*Skeletonema costatum*) and copepod mortality (*Calanus finmarchicus*)). WAF is of special interest because components dissolved from an oil slick or from rising oil droplets in the water column are known to be bioavailable to marine organisms and therefore have a potential for causing toxic effects.

The total WAF concentration in the oils from the shipwrecks varied, and the highest concentrations are quantified in the WAFs from "Erich Giese". These WAFs were also the most toxic for both algae and copepods, and it is suggested that the high content of phenols and other polar compounds have impact on the toxicity. WAFs from "Nordvard" were also more toxic than the WAFs from "Bittern" and "Boardale". The results from these studies show that the more "synthetic" oils from German WWII shipwrecks seem to have higher toxicity to marine organisms than the "mineral" oils from the British shipwrecks studied. This observation has resulted in an altering of the priority list for oil recovery from WWII wrecks by the Norwegian Authorities.

INTRODUCTION:

In the 1990s, Norwegian Authorities registered more than 2000 shipwrecks along the Norwegian coast, and about 80% of these were classified as likely to pose no environmental risk (Idaas, 1995). The wrecks were categorized based on the estimated amount of oil products and cargo they contained, and the vulnerability of the marine environment they were situated in. However, about 30 wrecks, all of from the World War II era, were classified to have considerable pollution risk (see Figure 1). Priorities for offloading fuel from the wrecks were established (described in Bergstrøm, 2014) and the oil has now been removed from eight of them.

Norway is a fishing nation and both the commercial fishing waters and the aquaculture industry are crucial for many coastal communities. As a large number of the shipwrecks are located in areas popular for fishing and recreation, seafood safety and bathing restrictions are significant practical considerations. Removal of oil from shipwrecks in spawning season should be avoided, as small oil leaks may occur, exposing fish eggs and larvae to oil components.

Therefore, the objective has been to study the potential for environmental impact from leaking wrecks by preparing WAFs of oils from four WWII shipwrecks to characterize their chemical composition and acute toxicity. Two species representing different tropic levels, the primary producer *Skeletonema costatum* (algae) and the primary consumer *Calanus finmarchicus* (copepod), were used as toxicity test species. WAF is of special interest because components dissolved from an oil slick or from rising oil droplets in the water column are known to be bioavailable to marine organisms and therefore have a potential for causing acute toxic effects (Neff and Stubblefield, 1995).

Oil is a complex, highly variable mixture of hydrocarbons and other trace components. Bunker fuel oils can vary greatly in chemical composition, depending on the type and origin of the oil, the refining process, and the production process. Exposure to hydrocarbons may cause a variety of adverse effects in marine organisms, including narcosis, slowed growth, reduced reproduction, and death. In order to cause an effect, oil components must be bio-available to the organisms being exposed. Many of the components in oil are potentially toxic to marine organisms, but have limited bio-availability in the environment due to their low solubility. Toxic effects depend on the duration of exposure and the concentration of the oil components involved. Toxic effects can be lethal (causing death) and sub-lethal (e.g. disorientation, reduced growth and reproduction). Toxic effects can also be acute (caused by short-term exposure, such as following an acute oil spill) or chronic (caused by long-term exposure, such as release of produced water).

The oils studied were from the British sloop HMS "Bittern", the British carrier tanker RFA "Boardale", the German destroyer "Erich Giese", and the German cargo ship MS "Nordvard". Completion of recovery of oils from three of the wrecks were performed in 2011-2012; all of them sank during April, 1940: HMS "Bittern" after a German air strike near Namsos, RFA "Boardale" grounded and sank outside Vesterålen, and "Erich Giese" during strike with British forces outside Narvik. In 2007, the oil was removed from M/S "Nordvard", which sank after a British air strike in December in 1944 in the Oslo Fjord. More details regarding the recovery operations are given in Bergstrøm (2014).

METHODS:

Oils

The oils studied from the British shipwrecks "Bittern" and "Boardale" seem to be classic mineral bunker oils (in the categorization of IFO 20-30), the oil from the German wreck "Nordvard" was probably a blend of synthetic and natural diesel, while "Erich Giese" carried lignite oil (possibly produced through coal hydrogenation). More information on German WW2 oils can be found in e.g. US Naval Technical reports (1945a and 1945b).

WAF preparation

Preparation of low energy WAF (LE-WAF) has been performed under controlled conditions following the guidelines established by the Chemical Response to Oil Spills:

Ecological Research Forum (CROSERF). These guidelines were developed to standardize WAF preparation, laboratory exposures to aquatic organisms, and analytical chemistry measurements used to determine the acute toxicity of the water soluble components in the oil (Aurand and Coelho, 1996). LE-WAF can be defined as a water solution of dissolved oil components prepared in closed vessels with calm mixing of oil and water without the formation of any vortex. LE-WAFs were chosen in order to avoid generation of oil droplets.

The WAFs were prepared with the oil-to-water loadings of 1 to 40 (25 g oil/L water) and 1 to 10000 (100 mg oil/L water). These different WAFs illustrate "snapshots" in the dynamic process of dissolution occurring during a spill situation. The oil-to-water ratio of 1 to 40 is assumed to be "saturated" and therefore represents a "conservative" estimate of the concentrations foreseeable during an oil spill. An oil-to-water ratio of 1 to 10000 is considered to be a more realistic concentration found in the upper surface layer a short time after treatment with chemical dispersants. The WAFs were generated with a contact time between water and oil for four days before the water was collected for chemical characterization and toxicity tests.

Sample preparation

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

For analyses of semi-volatile organic compounds (SVOC) and total petroleum hydrocarbons (TPH), the water samples were spiked with the appropriate surrogate internal standards and serially extracted with dichloromethane (DCM), thereby 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. The components quantified are given in Table 1.

Chemical analysis

The samples were analyzed for SVOC (decalins, PAHs and phenols) using GC/MS, for TPH using GC/FID, and for volatile organic compounds (VOC, C_5-C_9), including BTEX (benzene, toluene, ethylbenzene, and xylenes), by use of P&T GC/MS (Purge and Trap Gas Chromatography Mass Spectrometry). A list of all target analytes is shown in Table 1. This list includes the recommended analytes given by Singer et al. (2000), and is a typical standard list for the target compounds used during post-oil spill damage assessments.

The GC/FID analyses were performed according to a modification of EPA Method 8015D (US EPA, 2003). 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.

The semi-volatiles were quantified by modifications of EPA Method 8270D (US EPA, 2007). The mass spectrometer was operated in the selective ion monitoring mode to achieve 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 total of 35 target volatile analytes in the C_5 to C_{10} range were determined by P&T GC/MS 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 RFs of the individual compounds relative to the internal standards. All standards and samples were analyzed in a full scan mode.

Acute toxicity of the WAFs

Growth inhibition in the algae *Skeletonema costatum*

The unicellular marine algae *Skeletonema costatum* was chosen as a relevant representative of marine producers. The bioassays were performed as a modification of ISO 10253 (2006a) with growth rate inhibition and biomass production as endpoints (EC50). The original protocol is not designed for testing of solutions containing volatiles, and has been adapted for testing of WAFs by exchanging the recommended semi open Erlenmeyer flasks (250 mL) with closed culture tubes (15 mL) in borosilicate glass following recommendations in ISO 14442 (2006b).

As an experimental design, a fixed dilution scheme with a spacing factor of 1.6 between concentrations (from undiluted 100% WAF to 3% WAF) was used covering a total of eight different dilutions with six replicate tubes in each dilution. All tubes were inoculated with the algae/nutrient mix and filled to a headspace of 0.5 mL. As a control, 12 tubes in each bioassay were filled with autoclaved seawater and inoculated with the algae/nutrient mix in the same manner. In vivo fluorescence was measured after preparation and then the tubes were placed horizontally on a rocking shaker in a temperature controlled room at nominally 20±2°C under a mixture of white (Philips TLD 965 18W) and pale yellow (Philips TL20W/33RS) fluorescent tubes.

During the test period of 72 hours, in vivo fluorescence was measured daily by a Turner TD700 fluorometer (Turner Systems, Sunnyvale, CA, USA). At the end of exposure, pH was measured in a pooled sample from three control series tubes as well as from the exposure series. The calculated values are normalized by setting the response in the control series to 100% for growth rate and then calculating the effect within the span 0 to 100%. The top and bottom of the concentration-effect curve are constrained to 100 and 0, eliminating any stimulatory effects.

Acute toxicity to *Calanus finmarchicus*

Potential effects on primary consumers were assessed with the marine copepod *Calanus finmarchicus*. The acute toxicity testing of was performed according to ISO 14669:1999 (ISO, 1999), with modifications described in Hansen et al. (2011). Briefly, the WAF samples were diluted in a series of seven concentrations with a spacing factor of 1.7 between dilutions in glass bottles (0.5 L) with Teflon lined screw caps. Each exposure concentration was made in triplicate, and six bottles were used as controls containing seawater only. The exposure vessels were filled close to the rim to keep evaporative loss to a minimum during exposure, and each was stocked with seven copepodites V of *C. finmarchicus* at onset exposure. Mortality was monitored at 24, 48, 72 and 96 hours. The test animals were not fed during exposure. The calculated values are not corrected for any mortality in the control series and the effect is calculated within the span 0-100% effect by constraining the top and bottom of the concentration-effect curve to 100 and 0.

Predicted toxicity using toxic units

In the WAFs from petrogenic products, the compounds of concern for toxicity assessment are typically limited to the VOCs and SVOCs, which are structurally classified as Type I narcotics. The target lipid model of narcotic toxicity demonstrates that the acute toxicities of these chemicals vary and are correlated with the octanol-water partition coefficient (K_{ow}) such that LC50 decreases with increasing K_{ow} (DiToro et al., 2007). A toxic unit (TU) for the individual compounds is computed by dividing the measured concentration in the WAF by the compound's water effect concentration using regression models. It appears to be a linear negative relation between log LC50 of the marine organisms and log K_{ow} of the components that may cause toxic effects (McCarty et al. (1993) and Di Toro et al. (2007)):

$$\mathbf{\log LC50 = m \log (K_{ow}) + b}$$

The slope (m), log K_{ow}, and the intercept (b) for different component groups (e.g MAH, PAH and phenols) are given in McCarty (1993) and Neff et al. (2000). The LC50 (mg/L) is calculated for each component by use of the equation above.

In the WAFs, the TUs of the individual components are summed to compute the total TUs of the WAF. If the sum of the TUs is less than 1 (TU<1), observed effects should be lower than as defined by the water effect concentration (e.g. 50% lethality if using the LC50). If the sum of the TUs in the WAF is greater than 1 (TU>1), adverse effects could potentially be observed.

RESULTS AND DISCUSSION:

Chemical composition of the oils and the WAFs

GC chromatograms of the oils and their WAFs are shown in Figure 2. The GC chromatograms of the oils can give information about the oils weathering degree and possibly the oil type. The oils from "Bittern" and "Boardale" seem to be bunker oils (IIFO 20-30), the oil from "Nordvard" a diesel oil, while "Erich Giese" carried lignite oil. The "chemical profile" of a WAF is very unlike that of the parent oil. This is due to different water solubilities of the various oil components, as illustrated by the GC chromatograms of the WAFs.

Figure 3 summarizes the composition of the main groups of the aromatics in the oils. The chemical composition of the four analyzed oils is quite different. The naphthalenes and 2-3 ring PAHs seem to be the dominating groups in "Bittern" and "Erich Giese", while the content of decalins are quite high in "Nordvard". "Boardale" contains more volatiles than the other oils. There was a relatively high concentration of phenols in the oil from "Erich Giese". Alkylated phenols are usually not detected in mineral oil analysis using GC/MS, due excessive interference from other oil components in the same retention time range.

As mentioned above, the "chemical profile" of a WAF is unlike that of its parent oil due to the different water solubilities of the various compounds. Figure 4 shows the concentrations of the water-soluble components of the WAFs prepared, including unresolved complex materials (UCM). The UCM is calculated by subtracting the SVOC concentration from the TPH concentration. The total WAF concentrations are based on the sum of TPH and volatiles (C5-C9, including BTEX). The VOCs (especially BTEX and C3-benzenes) constitute a major part of the WAF prepared from fresh oils, and the naphthalenes are generally the dominating SVOC components, as they have a relatively high solubility in water. However, in the WAF from "Erich Giese" (1:40), the phenols contributed to more then 95% of the SVOC and nearly 50% of the total WAF concentration. Also in the WAFs from "Boardale" and "Nordvard", the phenols were the main contributor to the SVOCs (approximately 70%), while the naphthalenes dominated the SVOCs from "Bittern". In the WAFs with the oil loading of 1 to 10000, the naphthalenes were the major contributor to the SVOCs. The remaining total WAF consists mainly of UCM.

The WAFs from the shipwrecks with an oil-to-water loading of 1 to 40 are compared with WAFs from North Sea crudes in Figure 5. The total WAF concentration in the lignite oil from "Erich Giese" was in the same range as in the condensates from "Sleipner" and "Snøhvit", but the chemical composition was very different. The volatiles dominate the WAFs from the condensates, while UCM and phenols dominated the WAF with oil from German shipwrecks "Erich Giese" and "Nordvard". The WAFs from the British shipwrecks "Boardale" and "Bittern" have the chemical composition as expected for light bunker oils.

Acute toxicity

There are several ways to present the toxicity results. The toxicity of a chemical is normally quantified as an EC50 or LC50 value, defined as the concentration causing 50% of the organisms in a test population to die or to show a significant negative effect when they are exposed to a fixed concentration of the chemical for a defined time period (Rand et al., 1995). The EC50 and LC50 can be given in percentage dilution of the undiluted WAF (relative toxicity, EC or LC50 (%)), or as normalized to the total WAF concentration (specific toxicity, EC or LC50 (mg/L or ppm)). Low EC50 value indicates a high toxicity, while a high EC50 corresponds to a lower toxicity.

A summary of the toxicity results are given in Table 2. Specific toxicity is normalized to the total WAF concentration, and has been the traditional approach for expressing toxicity. However, the mass-based analysis neglects the fact that the composition of the WAFs varies both between oil types and with oil-to-water loading. Based on the mass-based approach, "Erich Giese" seems to be the most toxic of the WAFs with an oil-to-water loading of 1 to 40 to both test organisms. Among the WAFs with oil-to-water loading of 1 to 10000, "Erich Giese" was most toxic to the algae, while "Nordvard" was slightly more toxic to copepods.

The relative toxicity (Figure 6) is presented as EC50 and LC50 given in percentage of the diluted WAF, and show that oil from the German shipwrecks "Erich Giese" and "Nordvard" were more toxic to the tested organisms than the oils from the British wrecks "Bittern" and "Boardale". No mortality was observed in copepods exposed to the WAFs from the British wrecks with the oil to water loading of 1 to 10000.

The acute toxicity, expressed as TU, can be predicted based on the chemical composition of the WAFs and the K_{ow} for the individual components. TU for the WAFs are computed and are compared with other oils in Figure 7. A TU>1 for the total WAF implies that it is expected to cause more than 50% mortality in the test organisms. Although the UCM is not included in the calculated TU, the results indicate that the German oils studied are more toxic than the British oils, and especially "Erich Giese", where the phenols seem to contribute to nearly 80% of the TU. This is in accordance with the results presented in Table 2 and

Figure 6, and reflects that the chemical composition of a WAF is an important factor when observed toxicity should be evaluated.

CONCLUSIONS:

The water accommodated fractions (WAFs) of oils from four WWII shipwrecks have been studied with special emphasis on chemistry and biological effects (algae growth of *Skeletonema costatum)* and copepod mortality *(Calanus finmarchicus)*). The oils were from the British sloop HMS "Bittern", the British carrier tanker RFA "Boardale", the German destroyer "Erich Giese", and the German cargo ship MS "Nordvard". The oils from the British shipwrecks seem to be bunker oils (IFO 20-30), the oil from "Nordvard" was probably a blend of synthetic and natural diesel, while "Erich Giese" carried lignite oil (produced through coal hydrogenation).

The total WAF concentration in the oils from the shipwrecks varied, and the highest concentrations are quantified in the WAFs from "Erich Giese". These WAFs were also the most toxic for both algae and copepods, and it is suggested that the high content of phenols and other polar compounds (in the UCM) have impact on the toxicity. WAFs from "Nordvard" were also more toxic than the WAFs from "Bittern" and "Boardale". The results from these studies indicate that the more "synthetic" oils from German WWII shipwrecks seem to have higher toxicity to marine organisms than the "mineral" oils from the British shipwrecks studied.

The methodology used here has become the basic standard methodology for assessment on of the potential environmental risk of oil leakage from shipwrecks in Norway. The project has given valuable input to the decision maker's recommendations of how to deal with old shipwrecks containing oil, and have also resulted in an altering of the priority list for future oil recovery from WWII wrecks due to the potential for higher impact on the marine environment of coal based oils.

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Table 1. Target organic analytes (SVOC: Semi volatile organic compounds, VOC: Volatile organic compounds, TPH: Total petroleum hydrocarbons, UCM. Unresolved organic materials).

	Compound	Abb	Group	Compound	Abb
SVOC	Decalin	DE		Perylene	PE
	C1-decalins	DE1		Indeno[*1,2,3-c,d*]pyrene	IN
	C2-decalins	DE2		Dibenz[*a,h*]anthracene	DBA
	C3-decalins	DE3		Benzo(g,h,i)perylene	BPE
	C4-decalins	DE4	C0-C5 phenols	Phenol	PH
Naphthalenes	Naphthalene	N		C1-phenols	PH1
	C1-naphthalenes	N1		C2-phenols	PH2
	C2-naphthalenes	N2		C3-phenols	PH3
	C3-naphthalenes	N3		C4-phenols	PH4
	C4-naphthalenes	N4		C5-phenols	PH5
2-3 ring PAHs	Benzo(b)thiophene	BT	VOC	Isopentane	
	C1-benzo(b)thiophene	BT1	(incl BTEX and	n-C5 (Pentane)	
	C2-benzo(b)thiophene	BT2	C3-benzenes)	Cyclopentane	
	C3-benzo(b)thiophene	BT3		2-methylpentane	
	C4-benzo(b)thiophene	BT4		3-methylpentane	
	Biphenyl	B		n-C6 (Hexane)	
	Acenaphthylene	ANY		Methylcyclopentane	
	Acenaphthene	ANA		Cyclohexane	
	Dibenzofuran	DBF		2,3-dimethylpentane	
	Fluorene	F		3-methylhexane	
	C1-fluorenes	F1		n-C7 (Heptane)	
	C2-fluorenes	F2		Methylcyclohexane	
	C3-fluorenes	F3		2,4-dimethylhexane	
	Phenanthrene	P		2-methylheptane	
	Anthracene	A		n-C8 (Octane)	
	C1-phenanthrenes/anthracenes	P1		n-C9 (Nonane)	
	C2-phenanthrenes/anthracenes	P2		n-C10 (Decane)	
	C3-phenanthrenes/anthracenes	P3		n-Butylbenzene	
	C4-phenanthrenes/anthracenes	P4		1,2,4,5-tetramethylbenzene	
	Dibenzothiophene	D		n-pentylbenzene	
	C1-dibenzothiophenes	D1		C4-benzenes	
	C2-dibenzothiophenes	D2		C5-benzenes	
	C3-dibenzothiophenes	D3	BTEX	Benzene	
	C4-dibenzothiophenes	D4		Toluene	
4-6 ring PAHs	Fluoranthene	FL		Ethylbenzene	
	Pyrene	PY		*m*-xylene	
	C1-fluoranthrenes/pyrenes	FL1		*p*-xylene	
	C2-fluoranthenes/pyrenes	FL2		*o*-xylene	
	C3-fluoranthenes/pyrenes	FL3	C3-benzenes	Propylbenzene	
	Benz[*a*]anthracene	BA		1-methyl-3-ethylbenzene	
	Chrysene	C		1-methyl-4-ethylbenzene	
	C1-chrysenes	C1		1,3,5-Trimethylbenzene	
	C2-chrysenes	C2		1-methyl-2-ethylbenzene	
	C3-chrysenes	C3		1,2,4-trimethylbenzene	
	C4-chrysenes	C4		1,2,3-trimethylbenzene	
	Benzo[*b*]fluoranthene	BBF			
	Benzo[*k*]fluoranthene	BKF	TPH	C10-C36	
	Benzo[*e*]pyrene	BEP	WAF	Sum of VOC and TPH	
	Benzo[*a*]pyrene	BAP	UCM	TPH - SVOC	

Table 2. *Summary of toxicity results of the WAFs expressed as reduction in growth rate for* S. costatum *and mortality for* C. finmarchicus. *The acute toxicity is given both as relative toxicity (LC50 (%)) and as specific toxicity (LC50 (ppm)).*

Oil	Bittern	Boardale	Erich Giese	Nordvard	Bittern	Boardale	Erich Giese	Nordvard
Oil to water loading	1:40	1:40	1:40	1:40	1:10000	1:10000	1:10000	1:10000
Total WAF conc (ppm)	4.60	6.05	84.5	23.9	0.750	0.928	3.70	1.79
S. costatum EC50 (%)	45.3	39.1	1.90	8.97	64.6	97.0	7.98	63.3
C. finmarchicus LC50 (%)	54.6	50.7	2.70	14.7	>100*	>100*	29.0	40.9
S. costatum EC50 (ppm)	2.09	2.37	1.61	2.14	0.48	0.90	0.30	1.13
C. finmarchicus LC50 (ppm)	2.51	3.07	2.28	3.51	>0.750*	>0.928*	1.07	0.73

**No mortality observed in the non-diluted WAFs, not possible to calculated LC50.*

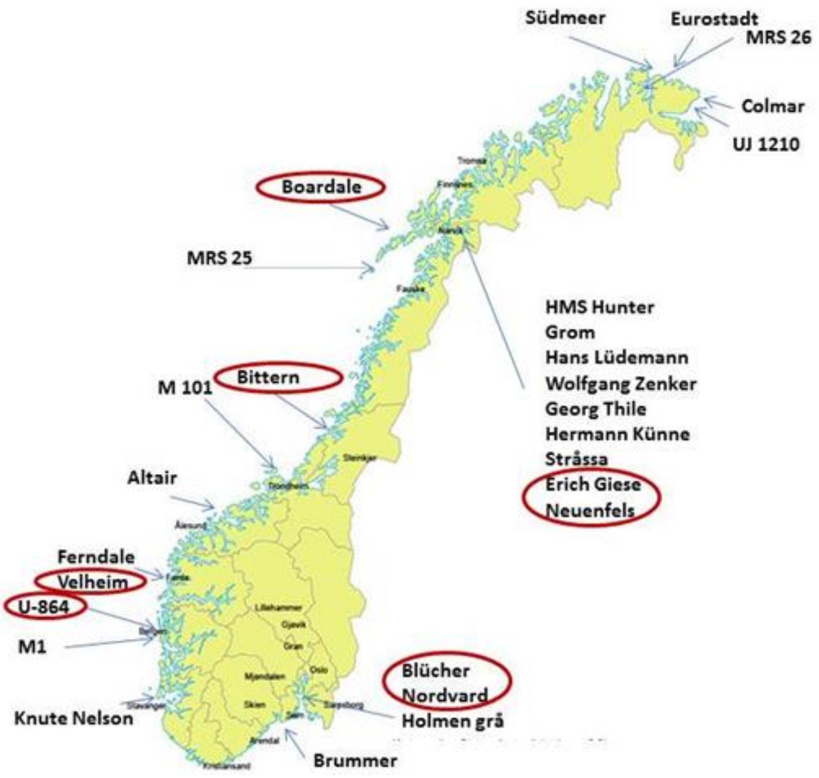

Figure 1. *Location of shipwrecks that were classified to have considerable pollution risk to the environment. The oil has been removed from the wrecks marked with a red circle. Map from the Norwegian Coastal Administration.*

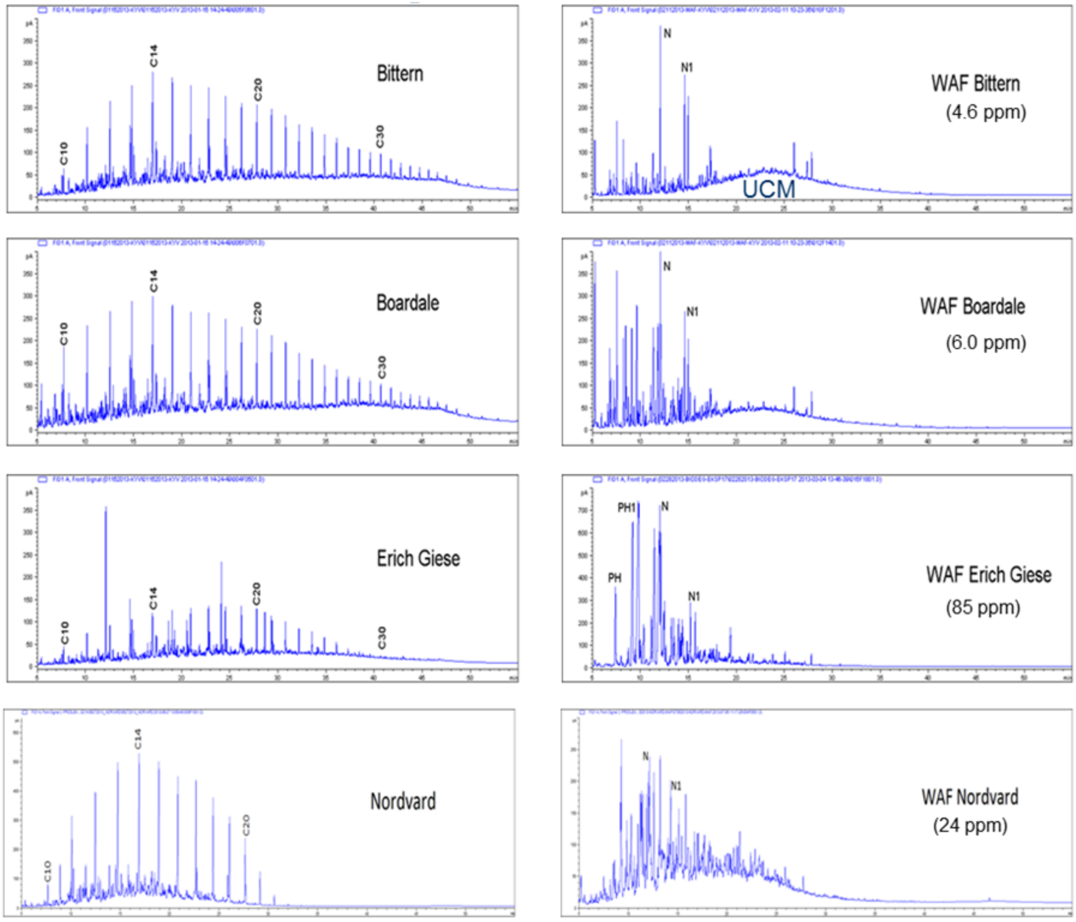

Figure 2. GC chromatograms of the oils and their WAFs (1:40). (N: Naphthalene; N1: C1-naphthalenes; PH: Phenol; PH1: C1-phenols).

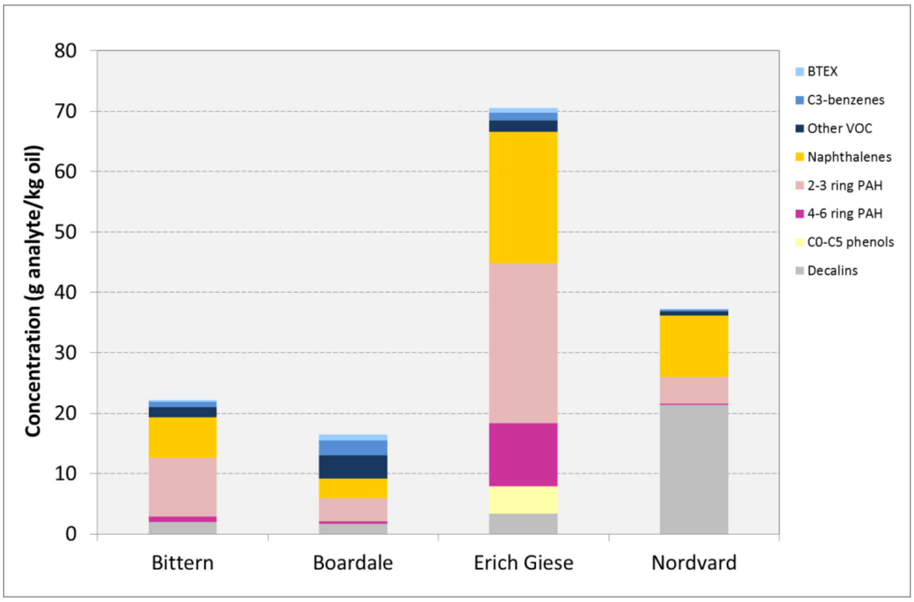

Figure 3. Chemical compositions of selected components groups from the oils from HMS "Bittern", RFA "Boardale", "Erich Giese", and "Nordvard".

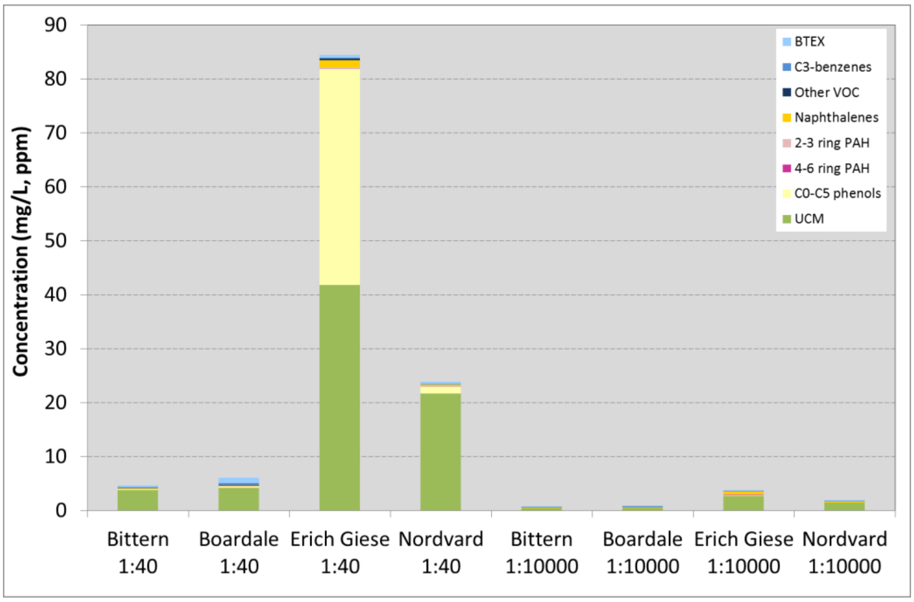

Figure 4. Chemical composition of the WAF systems.

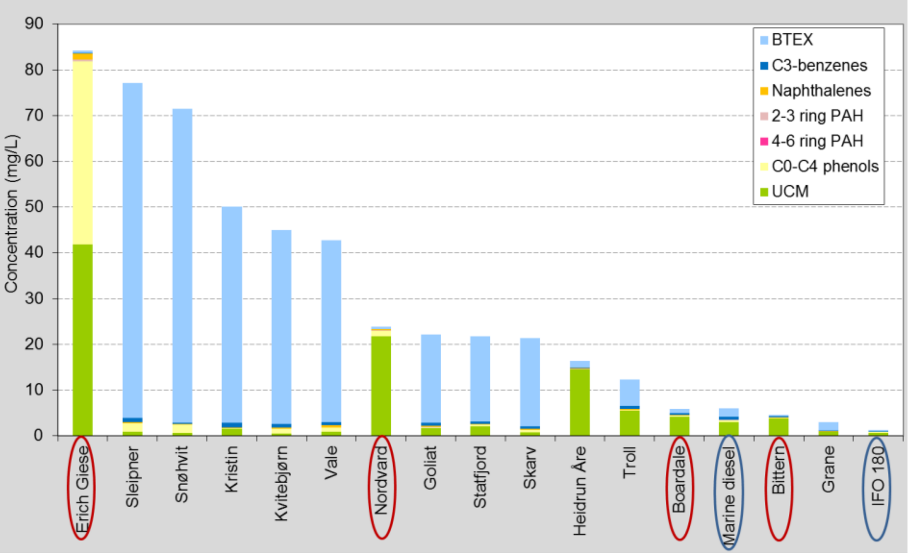

Figure 5. WAF composition of shipwreck oils (red circle), North Sea oils, and the refined products marine diesel and IFO 180 (blue circles). Oil-to-water loading of 1 to 40 in all systems.

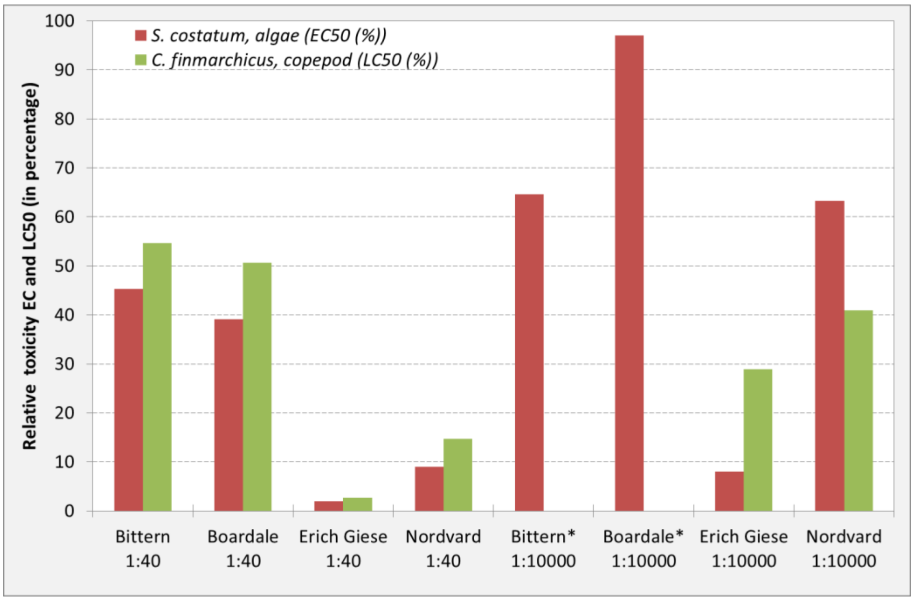

Figure 6. *Relative toxicity of the WAFs given as EC50 and LC50 (in % of the WAF dilution). Lower bars indicate higher toxicity. No bars indicate absence of an observed effect on the test organisms (*). See Table 2.*

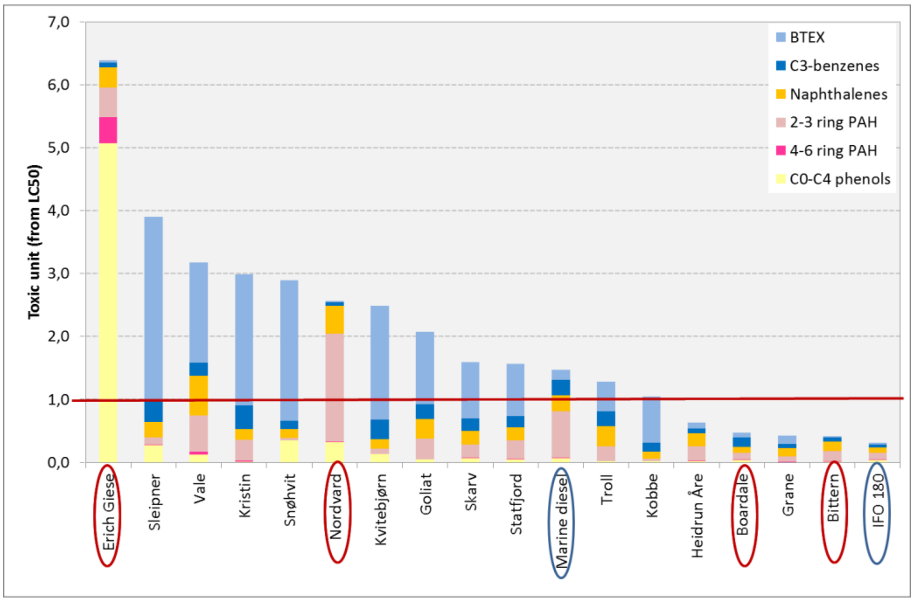

Figure 7. *Predicted acute toxicity expressed as toxic unit (TU) for WAFs with an oil-to-water loading of 1 to 40. WAFs from the shipwrecks are marked with red circles, and the refined products marine diesel and IFO 180 with blue circles. A TU>1 indicates mortality for more than 50% of the tested organisms.*

Abstract to "The wreck of the world III: Shipwreck risk assessment", October 12-13, 2015, Gøteborg.

Relative bioavailability and toxicity of fuel oils leaking from World War II shipwrecks

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ABSTRACT

The Norwegian Authorities have classified 30 World War II (WWII) shipwrecks to have a potential for pollution to the local environment, based on the location and condition of the wreck and the types and amount of fuel on board. Oil thus far has been removed from eight of these wrecks. The water accommodated fractions (WAFs) of oils from the British sloop HMS "Bittern", the British carrier tanker RFA "Boardale", the German destroyer "Erich Giese", and the German cargo ship MS "Nordvard" have been studied with special emphasis on chemistry and biological effects (algae growth (*Skeletonema costatum*) and copepod mortality (*Calanus finmarchicus*)). WAF is of special interest because components dissolved from an oil slick or from rising oil droplets in the water column are known to be bioavailable to marine organisms and therefore have a potential for causing toxic effects. In addition, chemical analyses of the oils from the German cargo ship MS "Welheim", the German heavy cruiser "Blücher", and the German submarine "U-864", have been performed. The oils from the British shipwrecks had characteristics of mineral bunker oils (corresponding to IFO 20-30), the oil from the German wrecks "Nordvard", "Welheim" and "U-864" were probably a blend of synthetic and mineral diesel, while "Erich Giese" and "Blücher" carried lignite oils (possibly produced through coal hydrogenation).

The total WAF concentration in the oils from the shipwrecks varied, and the highest concentrations are quantified in the WAFs from "Erich Giese". These WAFs were also the most toxic for both algae and copepods. WAFs from "Nordvard" were also more toxic than the WAFs from "Bittern" and "Boardale". The results from these studies indicate that the more "synthetic produced" oils from German WWII shipwrecks seem to have higher toxicity to marine organisms than the "mineral" oils from the British shipwrecks. The methodology used here has become the basic standard methodology for assessment on of the potential environmental risk of oil leakage from shipwrecks in Norway. The project has given valuable input to the decision maker's recommendations of how to deal with shipwrecks containing oil, and have resulted in an altering of the priority list for future oil recovery from WWII wrecks due to the potential for higher impact on the marine environment of coal based oils.

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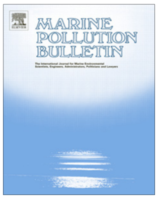

Relative bioavailability and toxicity of fuel oils leaking from World War II shipwrecks

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ABSTRACT

The Norwegian Authorities have classified 30 WWII shipwrecks to have a considerable potential for pollution to the environment, based on the location and condition of the wreck and the types and amount of fuel. Oil thus far has been removed from eight of these shipwrecks. The water accommodated fractions of oils from two British wrecks and two German wrecks have been studied with special emphasis on chemistry and biological effects (algae growth (*Skeletonema costatum*) and copepod mortality (*Calanus finmarchicus*)). Chemical analyses were also performed on three additional German wreck oils. The results from these studies show that the coal based oils from German WWII shipwrecks have higher toxicity to marine organisms than the mineral oils from the British shipwrecks. The potential for higher impact on the marine environment of coal based oils has resulted in an altering of the priority list for oil recovery from WWII wrecks by the authorities.

1. Introduction

There has been increased awareness and concern about the oil-pollution risks posed by sunken wreck, both recent and relic. Especially shipwrecks from World War II (WWII) are becoming a major problem for many nations. In a previous international survey, Michel et al. (2005) identified over 8500 sunken shipwrecks around the world, which posed a significant risk for oil pollution. Efforts have been made to compile data on WWII shipwrecks, such as the South Pacific Regional Environment Programme (SPREP WWII shipwreck database) containing over 3800 vessels lost in the Pacific and East Asia (Monfils et al., 2006), and the Atlantic, Mediterranean and Indian Ocean (AMIO) database, that contains information on the location and ownership of nearly 4000 WWII shipwrecks (Monfils, 2005). The wrecks that date back to WWII have been submerged for approximately 70 years, so there is a growing concern that corrosion will lead to that these wrecks will eventually leak oil to an extent that may cause potential impacts to the environment.

In USA, the National Oceanic and Atmospheric Administration (NOAA) maintains a large database (The Resources and Undersea Treats (RUST)), which includes approximately 20,000 shipwrecks in US waters, most of them unlikely to be of substantial threats to the marine environment. Recently, a list of the most ecologically and economically significant potentially polluting wrecks in U.S. waters have been prepared by NOAA and U.S. Coast Guard (NOAA, 2013). The objective with the NOAA report was to filter an overwhelming list of potentially polluting wrecks, leaving a shorter list of 87 high and medium priority wreck that can realistically be used for regional and area contingency planning. NOAA (2013) concluded that the U.S. coastlines are not littered with “ticking time bombs” containing oil, although there are definitely wrecks of concern that should be further assessed and monitored. The vast majority of potentially polluting shipwrecks lost in U.S. waters can be tracked to a four-year period between 1941 and 1945 when Japanese and German submarines sought to destroy tankers and freighters along the U.S. coasts. WWII resulted in the majority (53 of the 87) of the shipwrecks in the final list.

Norway has a long weather-beaten coastline, and our sea-faring traditions and war history have resulted in a considerable number of shipwrecks along the Norwegian coast. In the 1990s, Norwegian Authorities registered more than 2000 shipwrecks larger than 100 DWT along the coast, and about 80% of these were classified as likely to pose no environmental risk (Idaas, 1995). The wrecks were categorized based on the estimated amount of oil products and cargo they contained, and the vulnerability of the marine environment they were located in. However, about 30 wrecks, all of from the World War II era, were classified to have considerable pollution

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Fig. 1. Location of shipwrecks that were classified to have considerable pollution risk to the environment. The oil has been removed from the wrecks marked with a circle. Map from the Norwegian Coastal Administration.

risk (see Fig. 1). Priorities for offloading fuel from the wrecks were established (described in Bergstrøm, 2014) and the oil has now been removed from eight of them.

Oil is a complex, highly variable mixture of hydrocarbons and other trace components. Bunker fuel oils can vary greatly in chemical composition, depending on the type and origin of the oil, the refining process, and the production process (NRC, 1989). Exposure to hydrocarbons may cause a variety of adverse effects in marine organisms, including narcosis, reduction in growth and reproduction, as well as death (Boyd et al., 2001). In order to cause an effect, oil components must be bio-available to the organisms being exposed. Many of the components in oil are potentially toxic to marine organisms, but have limited bio-availability in the environment due to their low solubility. Toxic effects depend on the duration of exposure and the concentration of the oil components involved and can be lethal (causing death) or sub-lethal, e.g. disorientation, reduced growth and reproduction (Rand et al., 1995). Toxic effects can be classified as acute caused by short-term exposure to a high concentration (such as following an acute oil spill) or chronic caused by long-term exposure to a lower concentration (such as release of produced water).

Norway is a fishing nation and both the commercial fishing waters and the aquaculture industry are crucial for many coastal communities. As a large number of the shipwrecks are located in areas popular for fishing and recreation, seafood safety and bathing restrictions are significant practical considerations. Therefore, the objective has been to study the potential for environmental impact from leaking wrecks by preparing low energy water accommodated fractions (WAFs) of oils from four WWII shipwrecks to characterize their chemical composition and acute toxicity. Two species representing different trophic levels, the primary producer *Skeletonema costatum* (algae) and the primary consumer *Calanus finmarchicus* (copepod) were used as test species for acute toxic effects. The WAF of an oil is of special interest because components dissolved from an oil slick or from rising oil droplets in the water column are known to be bioavailable to marine organisms and therefore have a potential for causing acute toxic effects (Neff and Stubblefield, 1995). Chemical analyses have been performed on three additional German WWII wreck oils, as the oil volumes available of these oils were not sufficient to prepare WAFs.

2. Materials and methods

2.1. The shipwreck oils

The oils studied were from the British sloop HMS "Bittern", the British carrier tanker RFA "Boardale", the German destroyer "Erich Giese", and the German cargo ship MS "Nordvard". In addition, chemical analyses of the oils from the German cargo ship MS "Welheim", the German heavy cruiser "Blücher", and the German submarine "U-864", have been performed. Completion of recovery of oils from three of the wrecks were performed in 2011–2012; all of them sank during April, 1940: HMS "Bittern" after a German air strike near Namsos, RFA "Boardale" grounded and sank outside Vesterålen, and "Erich Giese" during strike with British forces outside Narvik. The recoveries from these three shipwrecks are documented in Framo (2012). In 2007 the oil was removed from M/S "Nordvard", which sank after a British air strike in December in 1944 in the Oslo fjord, and MS "Welheim", which was sunken by a Norwegian MTB outside Florø in 1944. The oil from "U-864" was removed in March 2013, but it still contains 67 tons of metallic mercury. "U864" was detected and sunk by a British submarine in February 1945 outside Fedje. The cruiser "Blücher" was hit by land based batteries, caught fire, and sank in the Oslo Fjord in April 1940. Most of the oil was removed in 1994. More details regarding the recovery operations are given in Bergstrøm (2014).

The oils from the British shipwrecks “Bittern” and “Boardale” seem to be classic mineral bunker oils (in the categorization of IFO 20–30), the oil from the German wrecks “Nordvard”, “Welheim”, and “U-864” were probably a blend of synthetic and mineral diesel, while “Erich Giese” and “Blücher” carried lignite oils (possibly produced through coal hydrogenation). More information on German WWII oils can be found in e.g. US Naval Technical reports (1945a,b).

2.2. Preparation of WAF

Preparation of low energy WAF (LE-WAF) has been performed under controlled conditions following the guidelines established by the Chemical Response to Oil Spills: Ecological Research Forum (CROSERF). These guidelines were developed to standardize WAF preparation, laboratory exposures to aquatic organisms, and analytical chemistry measurements used to determine the acute toxicity of the water soluble components in the oil (Aurand and Coelho, 2005). LE-WAF can be defined as a water solution of dissolved oil components prepared in closed vessels with calm mixing of oil and water without the formation of any vortex. LE-WAFs were chosen in order to avoid generation of oil droplets.

The WAFs were prepared with the oil-to-water loadings of 1:40 (25 g oil/L water) and 1:10,000 (100 mg oil/L water). These different WAFs illustrate “snapshots” in the dynamic process of dissolution occurring during a spill situation. The oil-to-water ratio of 1:40 is assumed to be “saturated” and therefore represents a conservative estimate of the concentrations foreseeable during an oil spill or an underwater release, and hence represents a worst-case scenario. An oil-to-water ratio of 1:10,000 is considered to be a more realistic concentration, e.g. found in the upper surface layer a short time after treatment with chemical dispersants. The WAFs were generated with a contact time between water and oil for four days before the water was collected for chemical characterization and toxicity tests.

2.3. Chemical composition of the oils and the WAFs

2.3.1. Sample preparation

Surrogate internal standards (SIS, *o*-terphenyl, naphthalene-d_8, phenanthrene-d_{10}, chrysene-d_{12}, phenol-d_6, 4-methylphenol-d_8) were added to the water samples prior to processing, and recovery internal standards (RIS, 5α-androstane, fluorene-d_{10}, and acenaphthene-d_{10}) were added prior to analysis on GC/FID (gas chromatography/flame ionization detection) and GC/MS (gas chromatography/mass spectrometry). The oils were dissolved in dichloromethane (DCM) to an appropriate concentration and added the same internal standards as the water samples.

For analyses of semi-volatile organic compounds (SVOC) and total petroleum hydrocarbons (TPH), the water samples were spiked with the appropriate surrogate internal standards and serially extracted with DCM, thereby 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. The components quantified are given in Table 2.

2.3.2. Chemical analyses

The samples were analyzed for SVOC (decalins, PAHs and phenols) using GC/MS, for TPH using GC/FID, and for volatile organic compounds (VOC, C_5–C_9), including BTEX (benzene, toluene, ethylbenzene, and xylenes), by use of P&T GC/MS (Purge and Trap Gas Chromatography Mass Spectrometry). A list of all target analytes is shown in Table 2. This list includes the recommended analytes given by Singer et al. (2000), and is a typical standard list for the target compounds used during post-oil spill damage assessments.

The GC/FID analyses were performed according to a modification of EPA Method 8015D (US EPA, 2003). TPH (resolved plus unresolved petroleum hydrocarbons) was quantified by the method of internal standards using the baseline corrected total area of the chromatogram and the average response factor for the individual C_{10}–C_{36} n-alkanes.

The semi-volatiles were quantified by modifications of EPA Method 8270D (US EPA, 2007). The mass spectrometer was operated in the selective ion monitoring mode to achieve 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 total of 35 target volatile analytes in the C_5–C_{10} range were determined by P&T GC/MS 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 RFs of the individual compounds relative to the internal standards. All standards and samples were analyzed in a full scan mode.

2.4. Acute toxicity of the WAFs

2.4.1. Growth inhibition experiments with S. costatum

The unicellular marine algae *S. costatum* was chosen as a relevant representative of marine producers. The bioassays were performed as a modification of ISO 10253 (2006a) with inhibition of growth rate and biomass production as endpoints (EC_{50}). The original protocol is not designed for testing of solutions containing volatiles, and has been adapted for testing of WAFs by exchanging the recommended semi open Erlenmeyer flasks (250 mL) with closed culture tubes (15 mL) in borosilicate glass following recommendations in ISO 14442 (2006b).

As an experimental design, a fixed dilution scheme with a spacing factor of 1.6 between concentrations (from undiluted 100% WAF to 3% WAF) was used covering a total of eight different dilutions with six replicate tubes in each dilution. All tubes were inoculated with the same volume of exponentially growing *S. costatum* (clone NIVA BAC-1) and nutrient mix. All tubes were filled to a headspace of 0.5 mL to ensure mixing in the tube during incubation. As negative control, 12 tubes in each bioassay were filled with autoclaved seawater and inoculated with the algae/nutrient mix in the same manner. *In vivo* fluorescence was measured by a Turner TD700 fluorometer (Turner Systems, Sunnyvale, CA, USA) after preparation. The tubes were then placed horizontally on a rocking shaker in a temperature controlled room at nominally 20 ± 2 °C under a mixture of white (Philips TLD 965 18 W) and pale yellow (Philips TL20 W/33RS) fluorescent tubes under constant light.

During the test period of 72 h, *in vivo* fluorescence was measured daily by the Turner TD700 fluorometer. At the end of exposure, pH was measured in a pooled sample from three control series tubes as well as from the different dilutions in the exposure series. The calculated values are normalized by setting the response in the control series to 100% for growth rate and then calculating the effect within the span 0–100% relative to the control series. The top and bottom of the concentration-effect curve are constrained to 100 and 0, thus eliminating any stimulatory effects.

2.4.2. Acute toxicity to C. finmarchicus

Potential effects on primary consumers were assessed with the marine copepod *C. finmarchicus*, which is one of the key ecological species in northern temperate oceans. The acute toxicity testing was performed according to a modification of ISO 14669:1999 (ISO, 1999) with lethal immobilization (LC_{50}) as the endpoint. The original ISO protocol is not designed for testing of solutions containing volatiles with *C. finmarchicus*, and was modified by using borosilicate glass bottles (0.5 L) with Teflon lined screw caps to preserve volatiles and to accommodate for the larger body mass of *C. finmarchicus* compared to the listed species in the ISO protocol (ISO, 1999). To ensure that the observed effects were approaching the incipient toxicity level of LC_{50} for the species, the exposure time was increased to 96 h at a set temperature of 10 ± 2 °C. The WAF samples were diluted in a series of seven concentrations with a spacing factor of 1.7 between dilutions with each exposure concentration made in triplicate. Six bottles were used as negative controls containing seawater only. The exposure vessels were filled close to the rim to keep potential evaporative loss to a minimum during exposure, and each vessel was stocked with seven copepodites V of *C. finmarchicus* at onset exposure. Mortality was monitored at 24, 48, 72 and 96 h. The test animals were not fed during exposure. The calculated values are not corrected for any mortality in the control series and the effect is calculated within the span 0-100% effect by constraining the top and bottom of the concentration-effect curve to 100 and 0.

2.5. Predicted toxicity using toxic units

In the WAFs from petrogenic products, the compounds of concern for acute toxicity assessment are typically limited to the VOCs and SVOCs, which are structurally classified as Type I narcotics. The target lipid model of narcotic toxicity demonstrates that the acute toxicities of these chemicals vary and are correlated with the octanol–water partition coefficient (K_{ow}) such that LC_{50} decreases with increasing K_{ow} (Di Toro et al., 2007). A toxic unit (TU) for the individual compounds is computed by dividing the measured concentration in the WAF by the compound's water effect concentration using regression models. It appears to be a linear negative relation between $\log LC_{50}$ of the marine organisms and $\log K_{ow}$ of the components that may cause toxic effects (McCarty et al., 1993; Di Toro et al., 2007):

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

The slope (m), $\log K_{ow}$, and the intercept (b) for different component groups (e.g. MAH, PAH and phenols) are given in McCarty (1993) and Neff (2002). The LC_{50} (mg/L) is calculated for each component by use of the equation above.

In the WAFs, the TUs of the individual components are summed to compute the total TUs of the WAF. If the sum of the TUs is less than 1 ($TU < 1$), observed effects should be lower than as defined by the water effect concentration (e.g. 50% lethality if using the LC_{50}). If the sum of the TUs in the WAF is greater than 1 ($TU > 1$), adverse effects could potentially be observed.

3. Results and discussions

Seven oils from WWII shipwrecks have been studied, and the chemistry and toxicity of the WAF for four of them have been characterized: "Bittern", "Boardale", "Eric Giese", and "Nordvard". As the oil volumes available of the three remaining oils, all German, were not sufficient to prepare WAFs, only chemical characterization of these oils have been performed.

Germany had limited availability to mineral oil products during WWII, but produced substantial amounts of fuel oils, e.g. coal-derived fuels. Several methods were developed and tested, and the Fischer–Tropsch process and the hydrogenation process changed coal directly into liquid. By 1937, Germany had five hydrogenation plants producing 4.8 million barrels of various grades of fuels (Becker, 1981). Some of the synthetic distillates had to be blended with mineral products and were often added chemicals to improve their properties. For example decalins were added to diesel fuel blends to delay their ignitability (US Tech rep no. 187-45).

3.1. Chemical composition of the oils and the WAFs

GC chromatograms of the oils and WAFs are shown in Fig. 2. The GC chromatograms of the oils can give information about the oils weathering degree and possibly the oil type. The oils from "Bittern" and "Boardale" resemble bunker oils (IFO 20–30), the oils from "Nordvard", "Welheim", and "U-864" diesel oils, while "Erich Giese" and "Blücher" most likely are lignite oils. The "chemical profile" of a WAF is very unlike that of the parent oil. This is due to different water solubilities of the various oil components, as illustrated by the GC chromatograms of the WAFs, where water soluble components as phenols and naphthalenes have been identified.

Fig. 3 summarizes the composition of the main groups of the aromatics in the oils. The chemical composition of the seven analyzed oils is quite different. "Boardale" contains more volatiles than the other oils, while the naphthalenes and 2–3 ring PAHs seem to be the dominating groups in "Bittern", "Blücher", and "Erich Giese". There was a relatively high concentration of phenols in the oils from "Erich Giese" and "Blücher", which confirm that they are lignite oils originated from brown coal (USN Tech rep no. 187-45, 1945, Wright and Dauble, 1986). The content of decalins were quite high in "Nordvard", but also higher in the other German oils than the British oils, suggesting that these fuels could be a blend of mineral products and a synthetic distillate, e.g. from the Fischer–Tropsch synthesis known as Kogasin, which ignites to fast (USN Tech rep no. 187-45, 1945).

As mentioned above, the "chemical profile" of a WAF is unlike that of its parent oil due to the different water solubilities of the various compounds. Table 1 shows the concentrations of the water-soluble components of the WAFs prepared, including unresolved complex materials (UCM). The UCM is calculated by subtracting the SVOC concentration from the TPH concentration. The total WAF concentrations are based on the sum of TPH and volatiles (C_5–C_9, including BTEX). The VOCs (especially BTEX and C_3-benzenes) constitute a major part of the WAF prepared from fresh oils, and the naphthalenes are generally the dominating SVOC components, as they have a relatively high solubility in water. However, in the WAF from "Erich Giese" (1:40), the phenols contributed to more then 95% of the SVOC and nearly 50% of the total WAF concentration. Also in the WAFs from "Boardale" and "Nordvard", the phenols were the main contributor to the SVOCs (approximately 70%), while the naphthalenes dominated the SVOCs from "Bittern". In the WAFs with the oil loading of 1:10,000, the naphthalenes were the major contributor to the SVOCs. The remaining total WAF consists mainly of UCM.

Significant coal liquefaction research and development was started up in the early 1970s, particularly in the USA, UK, and Japan in the response to various oil price shocks due to political changes in the major oil-producing regions. Since the 1980s, thought, developments have been largely put on hold due to lower oil prices. Some of the studies investigated the chemistry and toxicity of the water soluble fraction (WSF) from coal liquefaction materials. Dauble et al. (1983) have shown that phenols usually comprised up to 90% of water-soluble chemical components in

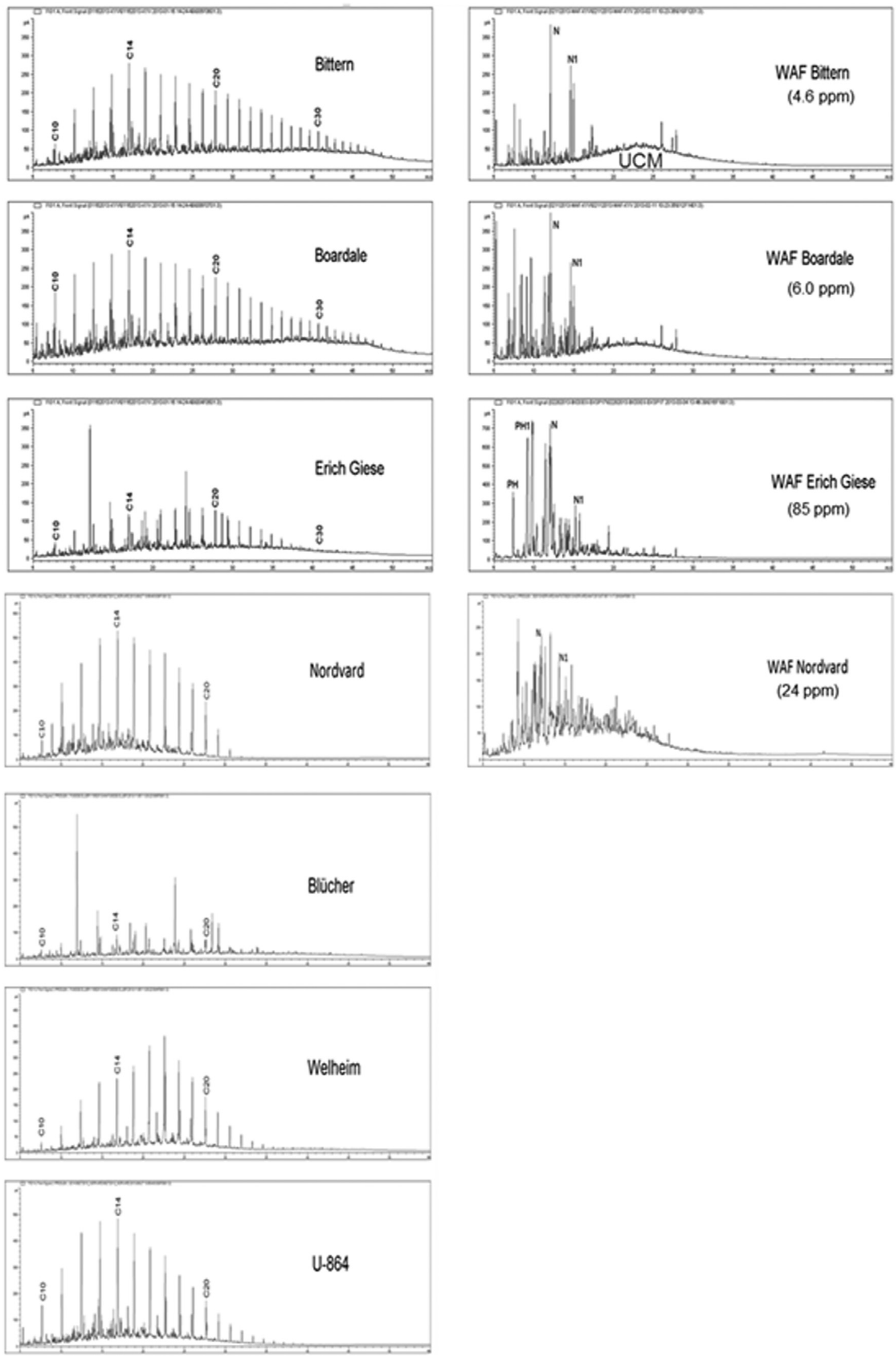

Fig. 2. GC chromatograms of the oils and their WAFs (1:40) (N: naphthalene; N1: C1-naphthalenes; PH: phenol; PH1: C1-phenols), and the three German oils where no WAF studies have been performed.

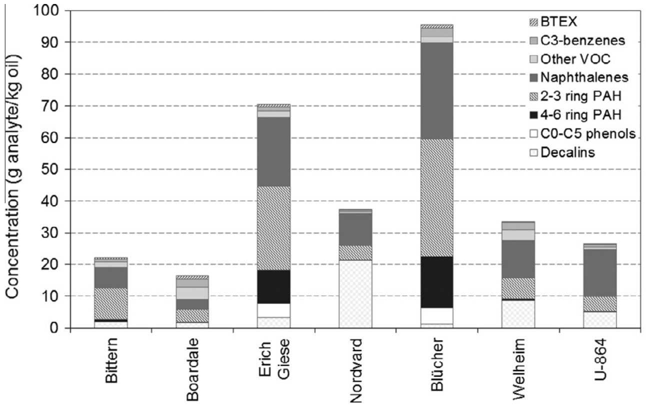

Fig. 3. Chemical compositions of selected components groups from the oils from "Bittern", "Boardale", "Erich Giese", "Nordvard", "Blücher", Welheim", and U-864.

full-boiling-range coal liquids, which is accordance with the results obtained for WAF from "Erich Giese".

The WAFs from the shipwrecks with an oil-to-water loading of 1:40 are compared with WAFs from North Sea crudes in Fig. 4. The total WAF concentration in the lignite oil from "Erich Giese" was in the same range as in the condensates from "Sleipner" and "Snøhvit", but the chemical composition was very different. The volatiles dominate the WAFs from the condensates, while UCM and phenols dominated the WAF with oil from German shipwrecks "Erich Giese" and "Nordvard". The WAFs from the British shipwrecks "Boardale" and "Bittern" have the chemical composition as expected for light bunker oils.

3.2. Acute toxicity of LE-WAFs to marine organisms

There are several ways to present the toxicity results. The toxicity of a chemical is normally quantified as an EC_{50} or LC_{50} value, defined as the concentration causing 50% of the organisms in a test population to die or to show a significant negative effect when they are exposed to a fixed concentration of the chemical for a defined time period (Rand et al., 1995). The EC_{50} and LC_{50} can be given in percentage dilution of the undiluted WAF (relative toxicity, EC or LC_{50} (%)), or as normalized to the total WAF concentration (specific toxicity, EC or LC_{50} (mg/L or ppm)). Low EC_{50} value indicates a high toxicity, while a high EC_{50} corresponds to a lower toxicity.

A summary of the toxicity results are given in Table 1. Specific toxicity is normalized to the total WAF concentration, and has been the traditional approach for expressing toxicity. However, the mass-based analysis neglects the fact that the composition of the WAFs varies both between oil types and with oil-to-water loading. Based on the mass-based approach, "Erich Giese" seems to be the most toxic of the WAFs with an oil-to-water loading of 1:40 to both test organisms. Among the WAFs with oil-to-water loading of 1:10,000, "Erich Giese" was most toxic to the algae, while "Nordvard" was slightly more toxic to copepods.

The relative toxicity (Fig. 5) is presented as EC_{50} and LC_{50} given in percentage of the diluted WAF, and show that no mortality was observed in copepods exposed to the WAFs from the British wrecks with the oil to water loading of 1:10,000. However, WAFs prepared of oils from the German shipwrecks "Erich Giese" and "Nordvard" were more toxic to the tested organisms than the oils from the British wrecks "Bittern" and "Boardale". Studies on the toxicity of the WSF from potential synthetic coal liquids to aquatic organisms that were performed in the early 1980s indicated that relative to petroleum fuels, coal liquids contained a high percentage of readily water-soluble components, including phenols, and therefore posed a greater risk to aquatic environments than mineral fuel oils (e.g. Wright and Dauble, 1986; Dauble et al., 1983).

The acute toxicity, expressed as TU, can be predicted based on the chemical composition of the WAFs and the K_{ow} for the individual components. TU for the WAFs are computed and are compared with other oils in Fig. 6. A TU > 1 for the total WAF implies that it is expected to cause more than 50% mortality in the test organisms. Although the UCM is not included in the calculated TU, the results indicate that the German oils studied are more toxic than the British oils, and especially "Erich Giese", where the phenols seem to contribute to nearly 80% of the TU. This is in accordance with the results presented in Table 1 and Fig. 6, and reflects that the chemical composition of a WAF is an important factor when observed toxicity should be evaluated.

Based on the chemical composition of the oils that have not been tested for toxicity, one can assume that the oil from "Blücher" most likely is at least as toxic as the oil from "Erich Giese", as both are lignite oils. The oils from "Welheim" and "U-864" are probably a blend of synthetic and mineral diesel, as "Nordvard". Their chemical composition, and that both are from German wrecks, could indicate that they possibly are as toxic as "Bittern" and "Boardale".

Table 1

Summary of toxicity and chemistry results of the WAFs. Toxicity is expressed as reduction in growth rate for *S. costatum* and mortality for *C. finmarchicus*. The acute toxicity is given both as relative toxicity (LC_{50} (%)) and as specific toxicity (LC_{50} (ppm)). The chemical composition given in ppm (mg/L), and the component groups are described in Table 2.

Oil	Bittern	Boardale	Erich Giese	Nordvard	Bittern	Boardale	Erich Giese	Nordvard
Oil to water loading	1:40	1:40	1:40	1:40	1:10,000	1:10,000	1:10,000	1:10,000
S. costatum EC_{50} (%)	45.3	39.1	1.90	8.97	64.6	97.0	7.98	63.3
C. finmarchicus LC_{50} (%)	54.6	50.7	2.70	14.7	>100[a]	>100[a]	29.0	40.9
S. costatum EC_{50} (ppm)	2.09	2.37	1.61	2.14	0.48	0.90	0.30	1.13
C. finmarchicus LC_{50} (ppm)	2.51	3.07	2.28	3.51	>0.750[a]	>0.928[a]	1.07	0.73
Total WAF (ppm)	4.60	6.05	84.5	23.9	0.750	0.928	3.70	1.79
BTEX (ppm)	0.35	0.93	0.53	0.43	0.063	0.146	0.08	0.06
C_3-benzenes (ppm)	0.18	0.39	0.15	0.10	0.110	0.187	0.09	0.06
Other VOCs (ppm)	0.02	0.14	0.29	0.08	0.014	0.020	0.03	0.04
Naphthalenes (ppm)	0.19	0.12	1.31	0.20	0.112	0.086	0.52	0.13
2–3 ring PAH (ppm)	0.03	0.03	0.41	0.19	0.022	0.017	0.16	0.05
4–6 ring PAH (ppm)	ND	ND	ND	ND	ND	ND	ND	ND
C_0–C_5 phenols (ppm)	0.08	0.30	39.9	1.17	0.002	0.003	0.14	0.03
UCM (ppm)	3.76	4.14	41.8	21.7	0.428	0.467	2.67	1.41

ND: not detected.

[a] No mortality observed in the non-diluted WAFs, not possible to calculated LC_{50}.

Table 2
Overview of the component groups and abbreviations (abb).

Group	Compound	Abb	Group	Compound	Abb
SVOC	Decalin	DE	C_0–C_5 phenols	Phenol	PH
	C1-decalins	DE1		C1-phenols	PH1
	C2-decalins	DE2		C2-phenols	PH2
	C3-decalins	DE3		C3-phenols	PH3
	C4-decalins	DE4		C4-phenols	PH4
	Benzo(b)thiophene	BT		C5-phenols	PH5
Naphthalenes	Naphthalene	N			
	C1-naphthalenes	N1	Other VOC	Isopentane	
	C2-naphthalenes	N2		Pentane	
	C3-naphthalenes	N3		Cyclopentane	
	C4-naphthalenes	N4		2-Methylpentane	
2–3 ring PAHs	Biphenyl	B		3-Methylpentane	
	Acenaphthylene	ANY		Hexane	
	Acenaphthene	ANA		Methylcyclopentane	
	Dibenzofuran	DBF		Cyclohexane	
	Fluorene	F		2,3-dimethylpentane	
	C1-fluorenes	F1		3-Methylhexane	
	C2-fluorenes	F2		Heptane	
	C3-fluorenes	F3		Methylcyclohexane	
	Phenanthrene	P		2,4-Dimethylhexane	
	Anthracene	A		2-Methylheptane	
	C1-phenanthrenes/anthracenes	P1		Octane	
	C2-phenanthrenes/anthracenes	P2		Nonane	
	C3-phenanthrenes/anthracenes	P3		Decane	
	C4-phenanthrenes/anthracenes	P4		n-Butylbenzene	
	Dibenzothiophene	D		1,2,4,5-Tetramethylbenzene	
	C1-dibenzothiophenes	D1		n-Pentylbenzene	
	C2-dibenzothiophenes	D2		C4-benzenes	
	C3-dibenzothiophenes	D3		C5-benzenes	
	C4-dibenzothiophenes	D4	BTEX	Benzene	
4–6 ring PAHs	Fluoranthene	FL		Toluene	
	Pyrene	PY		Ethylbenzene	
	C1-fluoranthrenes/pyrenes	FL1		*m*-Xylene	
	C2-fluoranthenes/pyrenes	FL2		*p*-Xylene	
	C3-fluoranthenes/pyrenes	FL3		*o*-Xylene	
	Benz[*a*]anthracene	BA	C3-benzenes	Propylbenzene	
	Chrysene	C		1-Methyl-3-ethylbenzene	
	C1-chrysenes	C1		1-Methyl-4-ethylbenzene	
	C2-chrysenes	C2		1,3,5-Trimethylbenzene	
	C3-chrysenes	C3		1-Methyl-2-ethylbenzene	
	C4-chrysenes	C4		1,2,4-Trimethylbenzene	
	Benzo[*b*]fluoranthene	BBF		1,2,3-Trimethylbenzene	
	Benzo[*k*]fluoranthene	BKF			
	Benzo[*e*]pyrene	BEP	TPH	C_{10}–C_{36}	
	Benzo[*a*]pyrene	BAP	WAF	Sum of VOC and TPH	
	Perylene	PE	UCM	TPH–SVOC	
	Indeno[1,2,3-*c*,*d*]pyrene	IN			
	Dibenz[*a*,*h*]anthracene	DBA			
	Benzo(g,h,i)perylene	BPE			

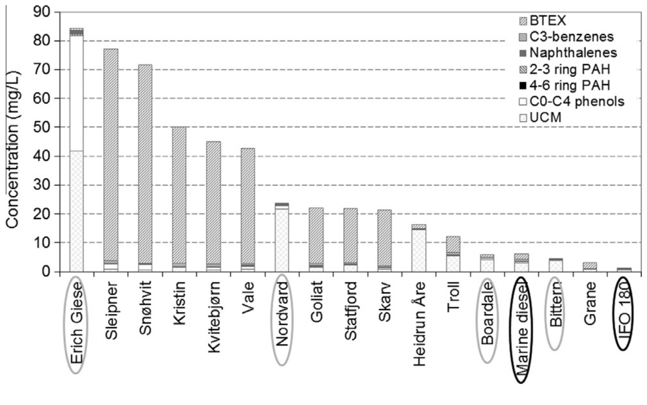

Fig. 4. WAF composition of shipwreck oils (grey circles), North Sea oils, and the refined products marine diesel and IFO 180 (black circles). Oil-to-water loading of 1:40 in all systems.

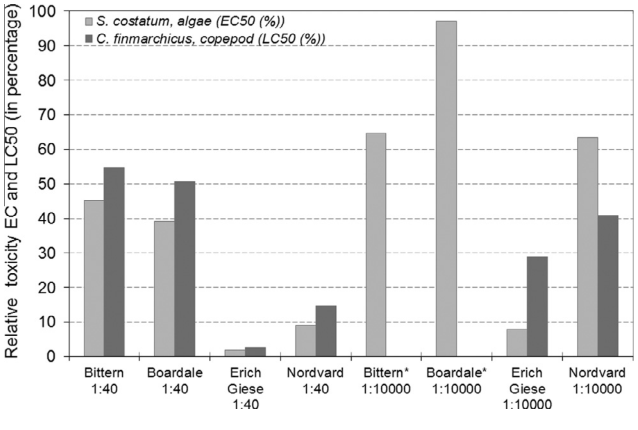

Fig. 5. Relative toxicity of the WAFs given as EC_{50} and LC_{50} (in% of the WAF dilution). Lower bars indicate higher toxicity. No bars indicate absence of an observed effect on the test organisms (*). See Table 1.

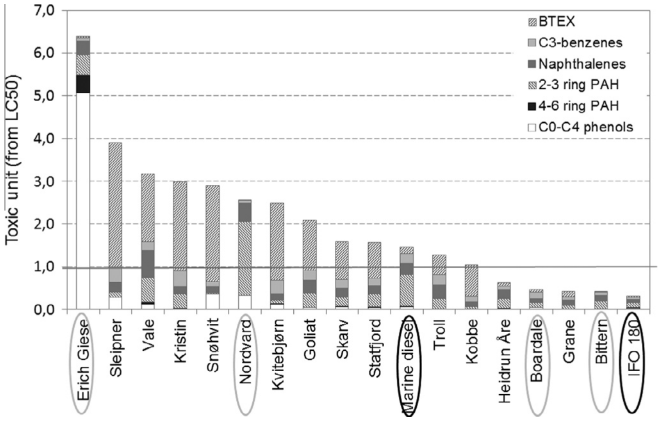

Fig. 6. Predicted acute toxicity expressed as toxic unit (TU) for WAFs with an oil-to-water loading of 1:40. WAFs from the shipwrecks are marked with grey circles, and the refined products marine diesel and IFO 180 with black circles. A TU > 1 indicates mortality for more than 50% of the tested organisms.

4. Conclusions

The water accommodated fractions (WAFs) of oils from four WWII shipwrecks have been studied with special emphasis on chemistry and biological effects (algae growth of *S. costatum*) and copepod mortality (*C. finmarchicus*)). The oils were from the British sloop HMS "Bittern", the British carrier tanker RFA "Boardale", the German destroyer "Erich Giese", and the German cargo ship MS "Nordvard". The oils from the British shipwrecks seem to be bunker oils (IFO 20–30), the oil from "Nordvard" was probably a blend of synthetic and mineral diesel, while "Erich Giese" carried lignite oil (produced through coal hydrogenation).

The total WAF concentration in the oils from the shipwrecks varied, and the highest concentrations are quantified in the WAFs from "Erich Giese". These WAFs were also the most toxic for both algae and copepods, and it is suggested that the high content of phenols and other polar compounds (in the UCM) have impact on the toxicity. WAFs from "Nordvard" were also more toxic than the WAFs from "Bittern" and "Boardale". The results from these studies indicate that the more "synthetic produced" oils from German WWII shipwrecks seem to have higher toxicity to marine organisms than the "mineral" oils from the British shipwrecks studied. Based on the chemical composition of the oils that have not been tested for toxicity, one can assume that the oil from "Blücher" most likely is at least as toxic as the oil from "Erich Giese", as both probably are lignite oils.

Worldwide there are nearly 8000 wrecks from WWII that have now been underwater for approximately 70 years. The risk of pollution from these WWII shipwrecks will not simply disappear with time, but rather continue and increase as corrosion will lead to that these wrecks will eventually disintegrate and release their oil, resulting in potential adverse impacts to the environment. The methodology used here has become the basic standard methodology for assessment on of the potential environmental risk of oil leakage from shipwrecks in Norway. The project has given valuable input to the decision maker's recommendations of how to deal with old shipwrecks containing oil, and have also resulted in an altering of the priority list for future oil recovery from WWII wrecks due to the potential for higher impact on the marine environment of coal based oils.

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