

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

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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 trophic 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, 5 α -androstande, 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, C₅-C₉), 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 C₁₀ to C₃₆ 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 C₅ to C₁₀ 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)):

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

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 than 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	C0-C5 phenols	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		Phenol	PH
Naphthalenes	Naphthalene	N	C0-C5 phenols	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	<i>m</i> -xylene	
	C1-fluoranthenes/pyrenes		FL1	<i>p</i> -xylene	
	C2-fluoranthenes/pyrenes	FL2	<i>o</i> -xylene		
	C3-fluoranthenes/pyrenes	FL3	C3-benzenes	Propylbenzene	
	Benzo[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	TPH	C10-C36		
Benzo[k]fluoranthene	BKF		WAF	Sum of VOC and TPH	
Benzo[e]pyrene	BEP			TPH - SVOC	
	Benzo[a]pyrene	BAP	UCM		

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
<i>S. costatum</i> EC50 (%)	45.3	39.1	1.90	8.97	64.6	97.0	7.98	63.3
<i>C. finmarchicus</i> LC50 (%)	54.6	50.7	2.70	14.7	>100*	>100*	29.0	40.9
<i>S. costatum</i> EC50 (ppm)	2.09	2.37	1.61	2.14	0.48	0.90	0.30	1.13
<i>C. finmarchicus</i> 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 calculate 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.

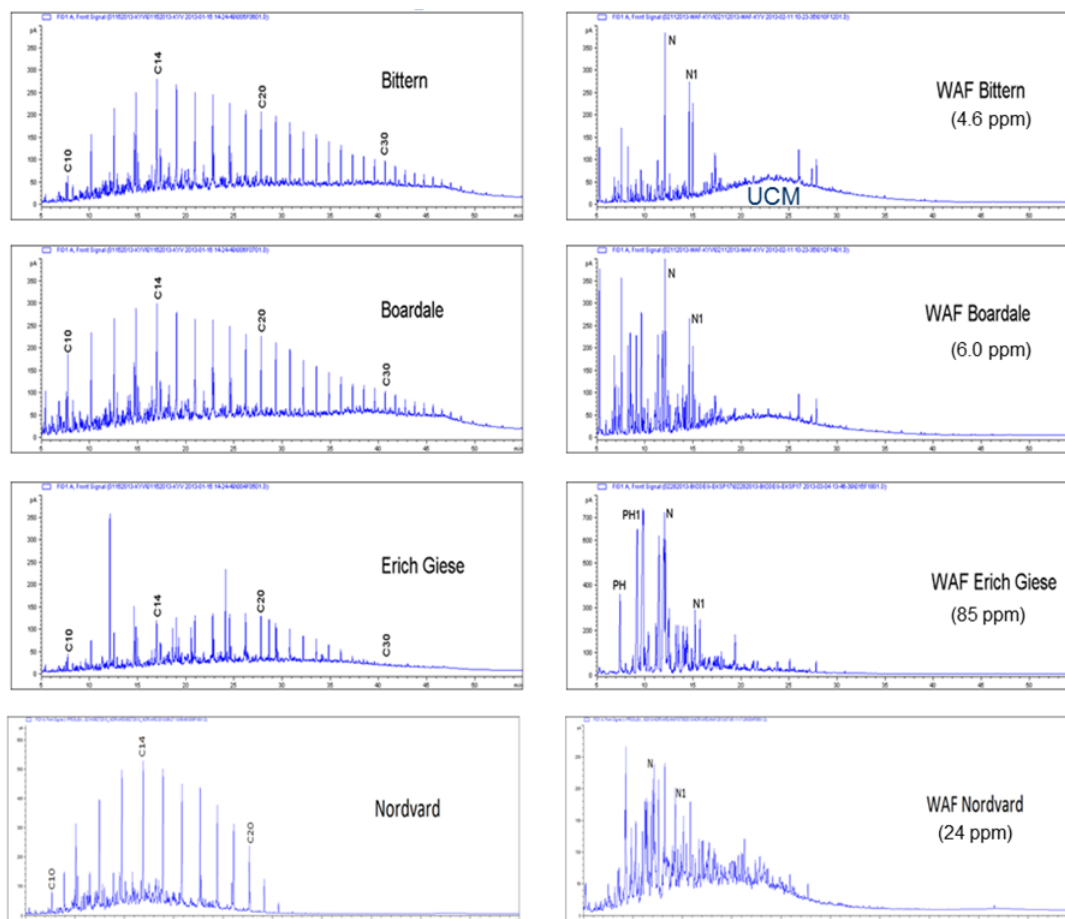


Figure 2. GC chromatograms of the oils and their WAFs (1:40). (N: Naphthalene; N1: C1-naphthalenes; PH: Phenol; PH1: C1-phenols).

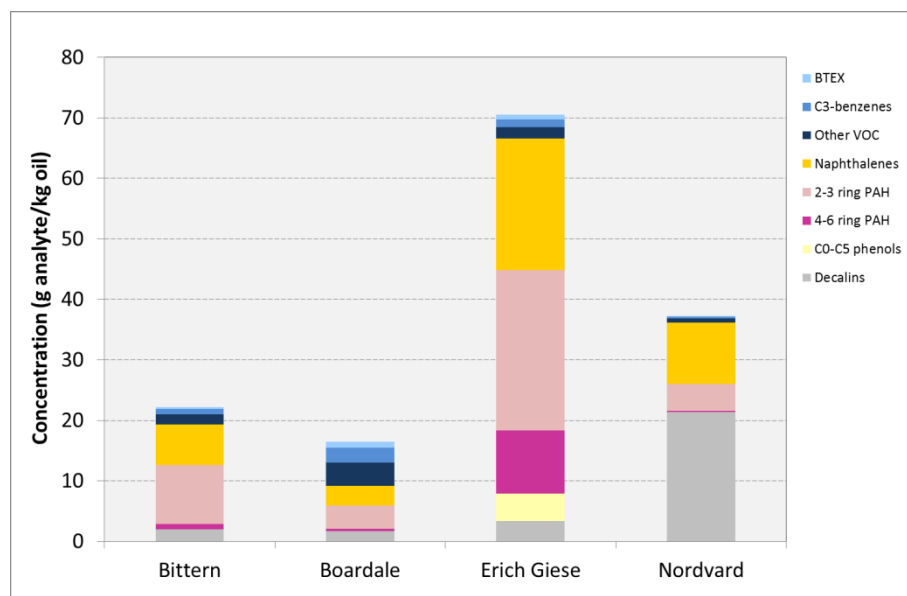


Figure 3. Chemical compositions of selected components groups from the oils from HMS "Bittern", RFA "Boardale", "Erich Giese", and "Nordvard".

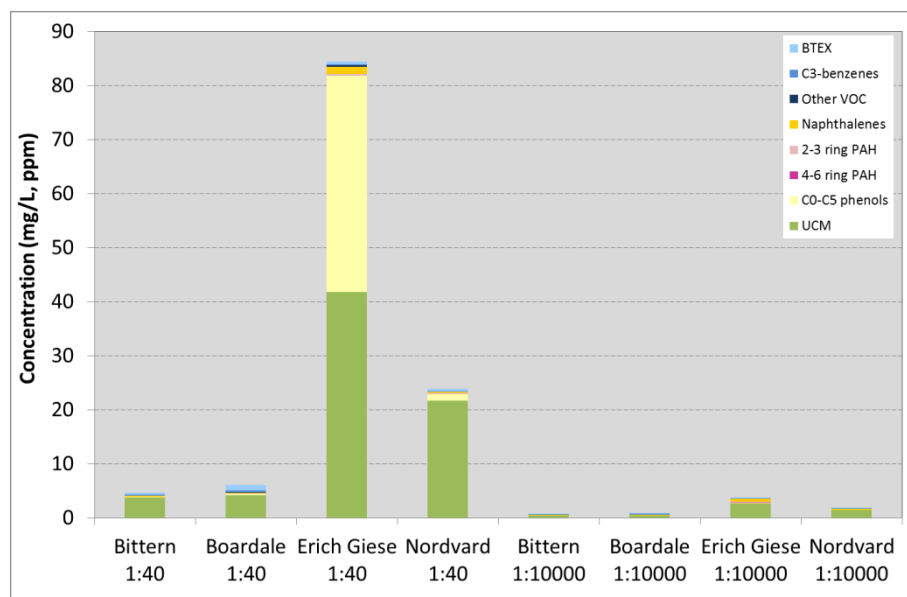


Figure 4. Chemical composition of the WAF systems.

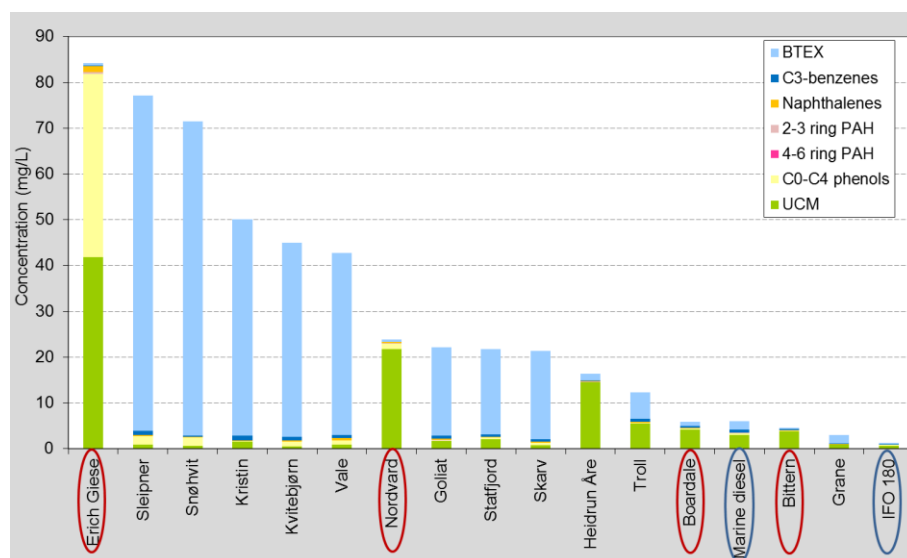


Figure 5. WAF composition of shipwreck oils (red circle), North Sea oils, and the refined products marine diesel and IFO 180 (blue circles). Oil-to-water loading of 1 to 40 in all systems.

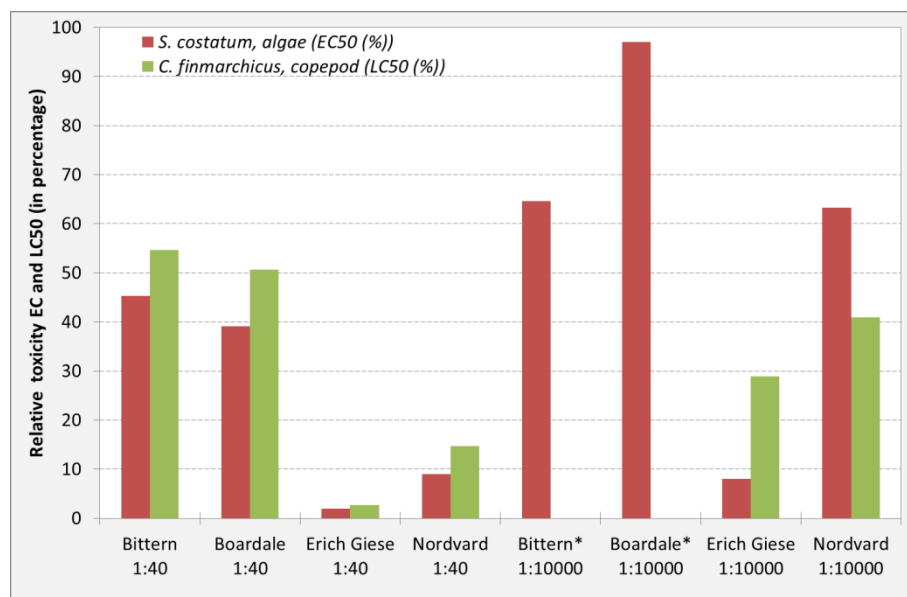


Figure 6. Relative toxicity of the WAFs given as EC50 and LC50 (in % of the WAF dilution). Lower bars indicate higher toxicity. No bars indicate absence of an observed effect on the test organisms (*). See Table 2.

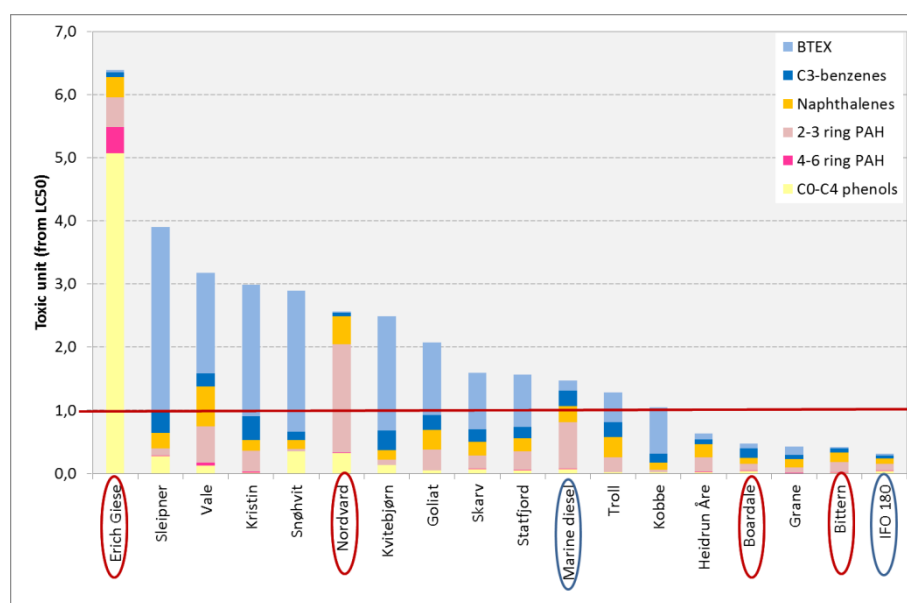


Figure 7. Predicted acute toxicity expressed as toxic unit (TU) for WAFs with an oil-to-water loading of 1 to 40. WAFs from the shipwrecks are marked with red circles, and the refined products marine diesel and IFO 180 with blue circles. A $TU > 1$ indicates mortality for more than 50% of the tested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