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Report

Chemical characteristics and acute toxicity of field generated in situ burning residues

From Oil-on-water 2018

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ABSTRACT

Water accommodated fraction (WAF) of unburned ULSFO and its ISB residue were characterised with emphasis on chemistry and acute toxicity. Low-energy WAFs were prepared to evaluate the potential impact of ISB residue to the environment.

The total WAF concentrations were low, 1.104 ppm in WAF of unburned (fresh) ULSFO and 0.332 ppm in WAF of ISB residue. *Calanus nauplii* were tested both for WAF of fresh oil and ISB residue, and the results indicate that the nauplii stage is more sensitive than the late copepodite (CV) stage. Specific toxicity is normalized to the total WAF concentration and has been the traditional approach for expressing toxicity. It indicated that WAF of ISB residue was slightly more toxic to nauplii than WAF of fresh oil.

Acute toxicity, expressed as toxic unit (TU), was predicted and TU for both WAFs were below 1, WAF from fresh oil was 0.63 and for WAF from ISB residue was 0.44. The calculations indicate that especially the PAHs are contributing to the toxicity.

It has been assumed the residue after an ISB does not contain water soluble components that can dissolve into the water. However, as seen in the present study, as the residue after an ISB could contain a mixture of burned and unburned/less burned oil. A potential impact on the environment will depend of several factors, e.g. burning effectiveness, residue properties, dilution rate in water.



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Sammendrag

Under "Olje-på-vann" (OPV) i 2018 ble to av 6 planlagte in situ brenneforsøk (ISB) gjennomført. ULSFO (Ultra Low Sulfur Fuel) og Oseberg 200 °C+, begge på ca 6 m³, ble sluppet ut i en Pyro-lense og antent ved hjelp av en Pyro-drone. Etter brenning ble prøver av residuene tatt fra forskjellige posisjoner i lensa. I tillegg mottok SINTEF i ettertid blandingsprøver av ISB-residuene av ULSFO fra Kystverket og av Oseberg 200 °C+ fra NOFO. En karakterisering av de fysikalsk-kjemiske egenskapene til brenne-residuene er rapportert i Faksness og Krause (2018).

Den vannløselige fraksjonen (WAF) av fersk ULSFO og residue etter brenning av ULSFO (fra OPV 2018) ble karakterisert, både mhp kjemisk sammensetning og akutt toksisitetstesting av to stadier av hoppekrepsen *Calanus finmarchicus* (raudåte). Både voksne *Calanus* (CV) og unge nauplii (N3) ble eksponert for WAF fra fersk ULSFO, mens WAF fra ISB residue ble kun testet for nauplii.

Totale WAF konsentrasjoner var lav, 1.104 mg/L i WAF av fersk ULSFO og 0.332 mg/L i WAF av ISB residue. Det viste seg at både olje og WAF fra ISB residue fremdeles inneholdt flyktige komponenter (lavere kokepunkt enn C10), og dette var ikke forventet. Imidlertid kan residuet etter ISB inneholde både brent og ubrent olje, og i dette tilfellet ble residuet varmet opp og homogenisert før tillaging av WAF og innveiling av oljeprøve til kjemisk karakterisering.

Calanus nauplii ble testet både for WAF fra fersk ULSFO og ISB residue. Resultatene viste at nauplii var mer sensitiv til WAF fra fersk olje enn voksne *Calanus* (CV) i dette studiet. Nauplii har langt mindre fett enn de voksne dyrene, slik at de vil ikke oppnå samme beskyttelse ved at tyngre komponenter (PAH) som kommer inn i organismen blir lagret midlertidig i fettreservene og dermed på den måten blir fysiologisk utilgjengelige hos de voksne dyrene. Relativ toksisitet uttrykkes som % fortynnet WAF som kan normaliseres til total WAF konsentrasjon for å få spesifikk toksisitet. Den spesifikke toksisiteten indikerte at WAF fra ISB residue var noe mer toksisk til nauplii enn WAF fra fersk olje. Men, som nevnt over, WAF konsentrasjonen fra ISB-residuet var relativt lav (0.332 mg/L).

Estimert giftighet, uttrykt som "toxic unit" (TU), ble predikert basert på den kjemiske sammensetningen av WAF'en og K_{ow} (oktanol-vann koeffisienten) for de individuelle komponentene. Dersom TU er større enn 1 indikerer dette at WAF-systemet potensielt kan forårsake mer enn 50% dødelighet i testorganismene. Jo høyere TU, desto mer giftig er WAF'en. TU for begge WAF var mindre enn 1, WAF fra fersk ULSFO var 0.63 og WAF fra ISB residue 0.44. Beregningene indikerer at spesielt PAH'ene bidrar til toksisiteten.

Det har tidligere blitt antatt at residuet etter ISB ikke inneholder løselige komponenter som kan lekke ut i vannet. Dette studiet viser at residuet etter ISB allikevel kan bestå av en blanding av brent og ubrent/mindre brent olje. Konsentrasjonen av vannløselige komponenter var 0.332 mg/L, og kan muligens ha en potensiell lokal miljøpåvirkning, men dette vil bl.a. avhenge av brenneeffektivitet, residuets utlekkingspotensiale og fortynningspotensiale i sjøen. I forbindelse med et større feltforsøk hvor Troll råolje (7 m³) ble fulgt i 6 døgn i den marginale issonen i Barentshavet i 2009 (Faksness et al., 2011), ble bl.a. de vannløselige oljekomponenter i vannsøylen målt. De høyeste konsentrasjonene som ble målt i nærheten av oljeflaket på ca 3 meters dyp var 30 ppb, dvs ca 10 ganger lavere enn WAF-konsentrasjonen fra ISB-residuet testet her.

1 Introduction

In situ burning (ISB) of oil has gained large interest both in Norway and Canada as an oil spill response method. In open water, by use of fire-proof booms or herders to contain and thicken the oil and in ice-covered waters even uncontained, provided that the ice contributes to reduce the spreading of the oil. ISB will always leave a burn residue, and the fate, behaviour and effects of the residues are of concern. The characteristics of the burn residue will vary with several factors, such as oil type, weather conditions and burn efficiency.

As a part of the "Oil-on-water" exercise in the North Sea in June 2018, two experimental oil releases (6 m³ each) were performed (ULSFO (Ultra low sulphur fuel oil) and the pre-weathered Norwegian crude, Oseberg Blend). The oils were released and contained into a pyro-boom before ignited by use of a "Pyro-drone". Several samples of burned residues from these two burns were collected at different positions within the boom. A more extensive characterization of the physical-chemical properties of the burned residues is reported in Faksness and Krause (2018).

Water accommodated fraction (WAF) of unburned ULSFO and its ISB residue were characterised with emphasis on chemistry and acute toxicity. Low-energy WAFs were prepared with an oil-to-water ratio of 1 to 40 to evaluate the potential impact of ISB residue to the environment. A primary consumer, the copepod *Calanus finmarchicus*, were tested, to WAF from unburned oil both CV and nauplii, and to WAF from ISB residue, to only nauplii.

2 Materials and methods

2.1 Oil properties

ULSFO (Ultra Low Sulfur Fuel Oil) was used in this study, both unburned (fresh) and ISB residue. The oils properties are given in Table 2.1.

Table 2.1 Physical properties of the oils used to in-situ burning. Flash point for Grane Blend is given for residue topped to 150 °C+.

SINTEF ID	Oil	Density (15.56 °C)	Viscosity (cP) v/10 °C		Comments
			10 s ⁻¹	100 s ⁻¹	
2018-3881 S1-S2	ULSFO fresh	0,917	62343	10442	Unburned ULSFO (OPV 2018)
2018-3881-S12-S1	ULSFO ISB residue	0,945	131000		Residue collected of OV "Utvær" after ISB of ULSFO

The GC chromatograms of the two oils are shown in Figure 2.1 and Figure 2.2.

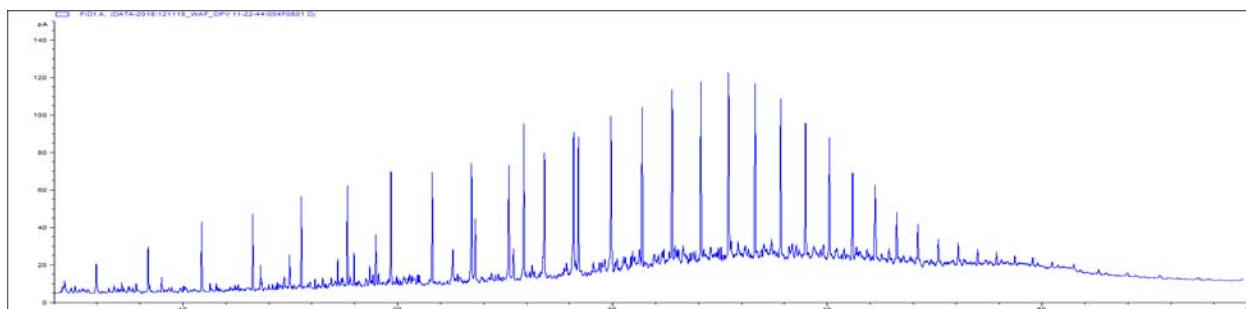


Figure 2.1 GC chromatogram of fresh ULSFO (SINTEF ID 2018-3881-S1-S2)

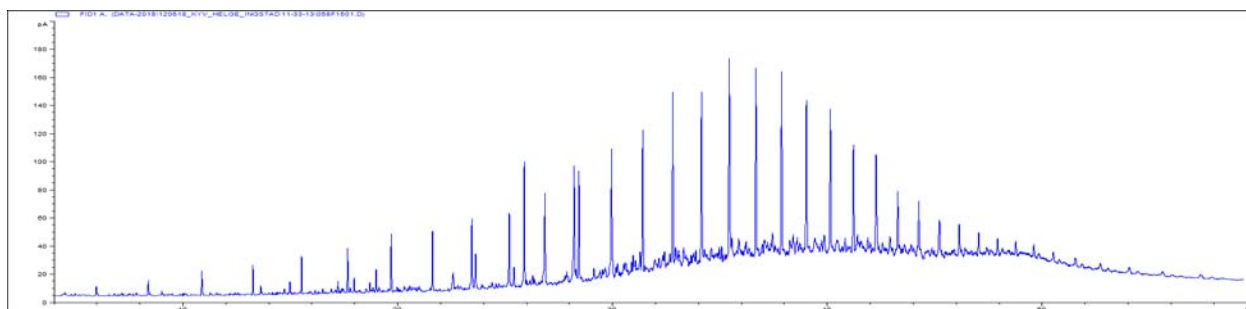


Figure 2.2 GC chromatogram of ISB residue of ULSFO used to WAF (SINTEF ID 2018-3881-S12-S1)

2.2 WAF preparation

Two WAF systems were prepared: ULSFO fresh oil (10 L WAF) and with residue from the offshore burn of ULSFO (2 L WAF). A 2L WAF was prepared of the ISB residue due to that there was a limited amount of ISB residue available. The ISB residue was heated to 50 °C for approximately 2 hours to get them as homogenous as possible prior to weighting and was applied to the water surface while it still was warm to get it as well distributed as possible.

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 to 40 (25 g oil/L water) at room-temperature. 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. The WAFs were generated with a contact time between water and oil for three days before the water was collected for chemical characterization and toxicity tests.

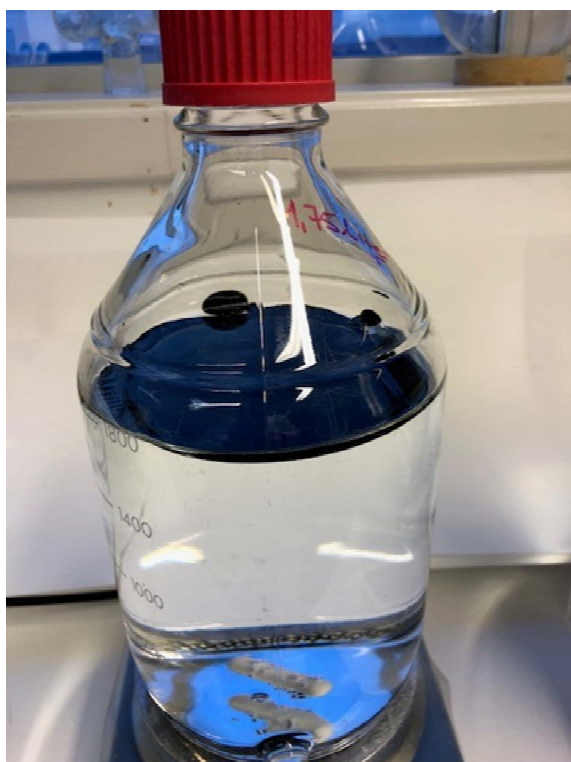


Figure 2.3 WAF of residue from ISB of ULSFO (loading 25 g oil/L water)

2.3 Toxicity of WAF samples

2.3.1 Acute toxicity to *Calanus finmarchicus*

Potential effects on primary consumers were assessed by testing on two life stages, early nauplii (N3) and late copepodites (C5 or CV), of the marine copepod *Calanus finmarchicus*, which is one of the key ecological species in northern boreal to Arctic oceans. The acute toxicity testing was performed as a modification of ISO 14669:1999 (ISO, 1999) with lethal immobilization (LC₅₀) 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 for late stage copepodites or glass vials (5 mL) with screw caps for nauplii to preserve volatiles during exposure. To accommodate for the larger body mass

of *C. finmarchicus* compared to the listed species in the ISO protocol (ISO, 1999), or for testing with nauplii stages, suitable sizes of exposure vessels were accommodated respectively.

To ensure that the observed effects were approaching the incipient toxicity level of LC₅₀ for the species, the exposure time was increased to 96 hours for late copepodite and 72 hours for nauplii 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 for late copepodites and quadruple for nauplii. Seawater only was used as negative control in duplicate of the exposure concentrations; i.e. six bottles for late copepodites and eight vials for the nauplii. For positive control 0.8 mg/L of 3,5-dichlorophenol were used in same replication as for the exposure dilutions. The exposure vessels were filled with minimal headspace to keep potential evaporative loss to a minimum during exposure, and the respective exposure vessel was stocked with seven copepodite V or nominally 20-25 nauplii of *C. finmarchicus* at onset exposure. Mortality was monitored at 24, 48, 72 and 96 hours for late copepodites and at end of exposure after 72 hours for the nauplii. 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.

Both life stages of *Calanus* (early nauplii (N3) and late copepodites (C5)) were exposed to WAF from fresh ULSFO, while only nauplii (N3) was exposed to WAF from the ISB residue.

2.3.2 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. (1992; 1993) and Di Toro et al. (2007)):

$$\log LC_{50} = m \log (K_{ow}) + b \quad (1)$$

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. (2002). The LC₅₀ (mg/L) is calculated for each component by use of equation (1). Different regression coefficients can be used to calculate TU relative to different species (McGrath and DiToro, 2009), resulting in other values of the TU than these calculated here. However, all oils used for comparison in this report are calculated using the same equation.

In the WAFs, the TUs of the individual components are summed up 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.

2.4 Sample preparation and chemical analysis

An aliquot of the unburned oil and the ISB residue were weighted directly into a graduated flask (10 mL). Dichloro methane (DCM) was used as a solvent. The residues were heated at 50 °C for approximately 2 hours to get them as homogenous as possible prior to weighting. Water samples from the WAF were processed using liquid-liquid extraction with DCM.

All samples were added internal standards for quantitative analysis on gas chromatograph with flame ionisation detector (GC/FID) and gas chromatograph with mass spectrometer (GC/MS). For GC/FID *o*-terphenyl and 5 α -androstane were added, and for the GC/MS analysis naphthalene-*d*₈, phenanthrene-*d*₁₀, chrysene-*d*₁₂, fluorene-*d*₁₀, and acenaphthene-*d*₁₀ were added.

All samples were analyzed for SVOC (decalins, PAHs and hopane) using GC/MS and for TPH using GC/FID. In addition, the water samples were analyzed 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 Appendix B (Table B 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 analysed in a full scan mode.

3 Results and discussion

ULSFO (Ultra Low Sulfur Fuel Oil) was used in this study, both unburned (fresh) and ISB residue from large scale offshore burn during the "Oil on water" exercise in 2018. More detailed results are provided in Appendix A.

3.1 Chemical composition of the oils and the WAFs

GC chromatograms of the oils are shown in Figure 2.1 Figure 2.2 and of the WAFs in Figure 3.1 and Figure 3.2. The GC chromatograms illustrate that there were still lighter components present after ISB, but that there were less of them. The concentrations of TPH were 705 µg/L for WAF of fresh oil and 268 µg/L for WAF of ISB residue. Total WAF concentrations (including VOC) were 1104 µg/L and 332 µg/L, respective.

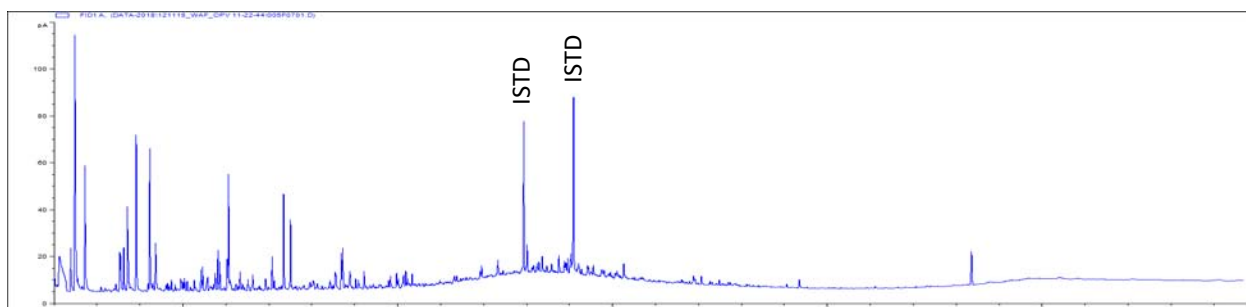


Figure 3.1 GC chromatogram of WAF of unburned ULSFO (peaks at approx. 26 and 28 min are added internal standards (ISTD)).

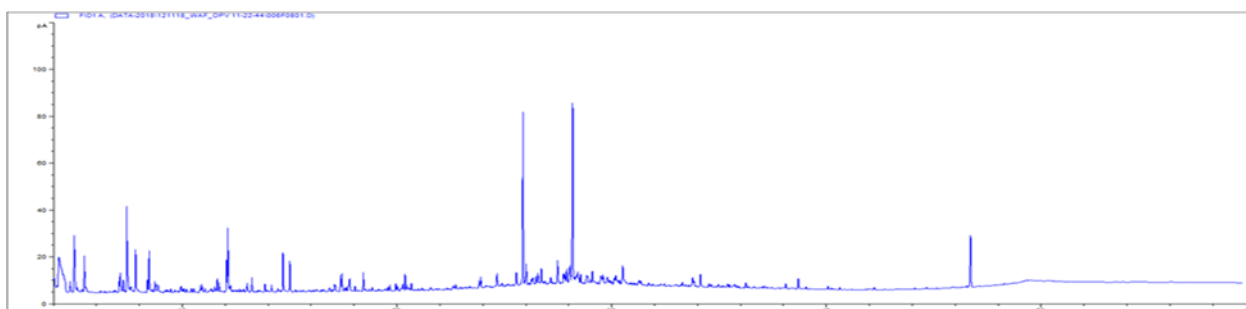


Figure 3.2 GC chromatogram of WAF of ISB-residue (peaks at approx. 26 and 28 min are added internal standards).

Figure 3.3 summarizes the composition of the main groups of aromatics in the oils (left) and their WAFs (right). The data are also provided in Table A 1. The contribution of the different component groups reflects the effect ISB has on the chemical composition of the oil. It was somewhat surprising that the oil and WAF of ISB residue still contained volatiles (Table A 3). However, the residue after a burn could contain both burned and unburned oil, and here the residue was heated and homogenized before the WAF was prepared. The "chemical profile" of a WAF is unlike that of its parent oil. Decalins, 4-6 ring PAH and some of the 2-3 ring PAH have low solubility in water, and this is also reflected in the chemical composition of the WAFs. More detailed SVOC results are provided in Table A 2. UCM (unresolved complex materials) contributed to approximately 55% of the concentration of WAF from fresh oil and 70% of WAF from ISB residue.

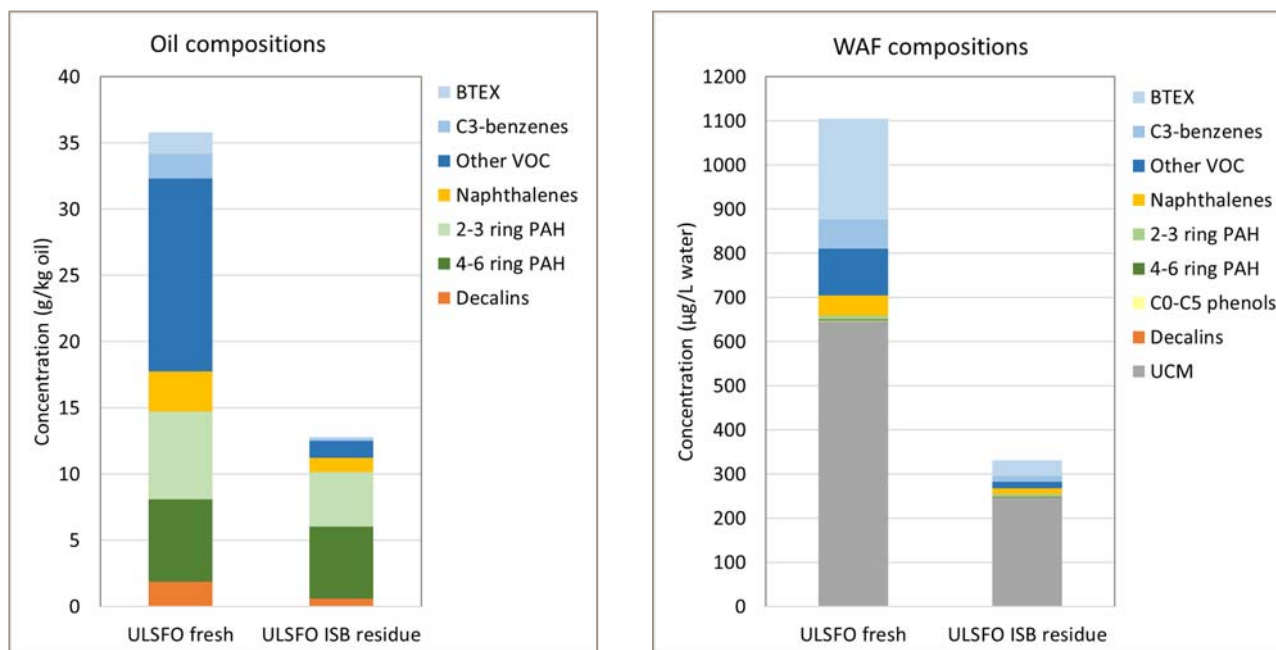


Figure 3.4 Chemical composition of selected component groups (aromatics) in ULSFO oils in left figure, and in WAFs of ULSFO in right figure (ULSFO fresh, unburned oil, and ISB residue).

3.2 Acute toxicity of WAFs to *Calanus finmarchicus*

The acute toxicity, expressed as LC_{50} , can be given in percent dilution of the undiluted (or 100%) WAF (relative toxicity, LC_{50} in percent (%)) or as normalized to the total WAF concentration (specific toxicity, LC_{50} in mg/L or ppm). Low values of LC_{50} indicate a high toxicity, while a high value of LC_{50} corresponds to lower toxicity. The two approaches to express toxicity have different applications: Specific toxicity expresses the toxicity of the WAF of a selected oil and test condition and is associated with the chemical composition of the WAF. Relative toxicity expresses a given dilution to obtain a predefined effect (e.g. LC_{50}) and can e.g. be used to compare WAFs from different oil with different WAF compositions.

In Figure 3.5, the relative toxicity (left graph) and the specific toxicity (right graph) to the two WAFs are shown. *Calanus nauplii* were tested both for fresh oil and ISB residue to have a common point for comparing the effects of the two WAF systems. The toxicity results are also provided in Table A 4.

Relative toxicity is expressed as percent WAF diluted in seawater to obtain a predefined effect concentration, typically LC_{50} . This gives a measure of the toxic potential of the WAF; i.e. a WAF with a LC_{50} -value of 50% will not produce a LC_{50} -value if diluted in the same volume, whereas a WAF with a LC_{50} -value of 10% need to be diluted 10 times its own volume to reach the same level of toxicity. The results from this study indicates that the naupliar stage tested is more sensitive to WAF of fresh oil than the late copepodite (CV) stage when expressed as relative toxicity, and the WAF of ISB residue is less toxic to nauplii than WAF of fresh oils. The nauplii have limited fat reserves and are therefore less protected than the grown organisms where heavier components (PAHs) will be stored temporary in the fat reserves and in that way be physiological unavailable.

Specific toxicity is normalized to the total WAF concentration (1.104 mg/L in fresh WAF and 0.332 mg/L in WAF of ISB residue) and has been the traditional approach for expressing toxicity. However, the concept of comparing toxicity based on analytical mass ignores the fact that the composition of the WAFs varies between oils, and that WAFs from different oils with the same concentration can have different toxicity. The specific toxicity indicates that WAF of ISB residue is more toxic to nauplii than WAF of fresh oil. However, as

mentioned above, the WAF concentration of ISB residue is relatively low (0.332 mg/L). Faksness et al. (2011) measured the water-soluble oil components in the water during a 6-day experimental release of Troll crude oil (7 m³) in the marginal ice zone in the Barents Sea in 2009. The highest concentrations measured close to the oil slick (3 m depth) was 30 ppb, which is 10 times lower than the WAF concentrations of the ISB-residue tested here.

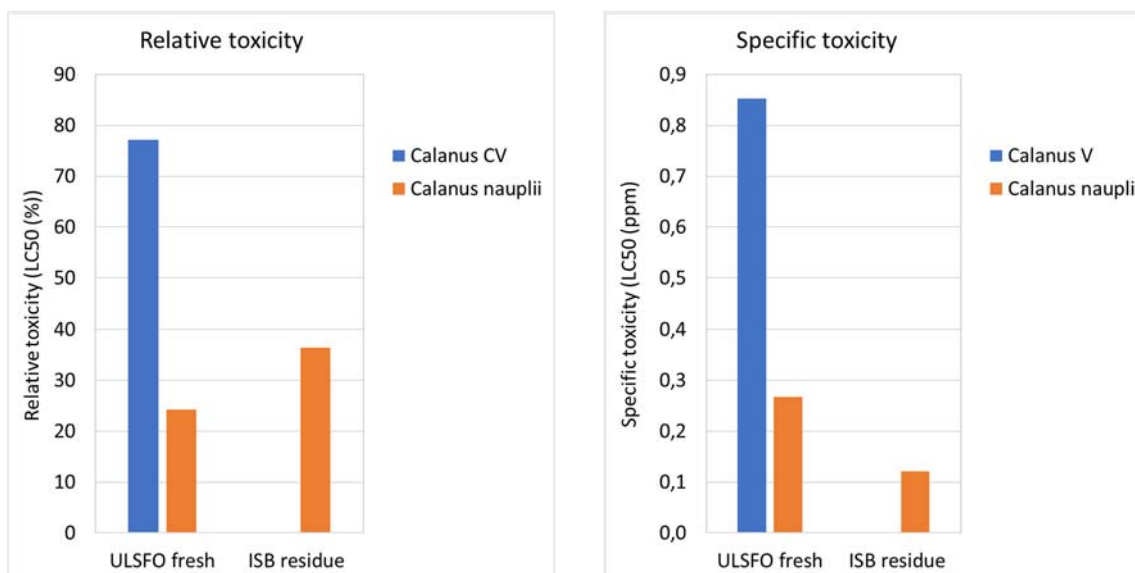


Figure 3.5 Acute toxicity expressed as relative toxicity (left figure) and specific toxicity (right figure) for WAF of fresh, unburned ULSFO and ISB residue of ULSFO. Fresh ULSFO was tested both for *Calanus CV* (blue) and *nauplii* (orange), WAF of ISB residue only for *nauplii*. Lower bars indicate higher toxicity.

In Figure 3.6, copepod survival is plotted as a function of the total WAF concentration. The left graph, illustrating *Calanus CV* exposed to WAF of fresh ULSFO, shows that the percent dead copepods increase with time, and a mortality of approximately 70% was observed at test endpoint in undiluted WAF. The right graph compares the survival for *Calanus nauplii* exposed to WAF of fresh ULSFO (blue line) and ISB residue (black line). At test endpoint (72 hours), the observed mortality was approximately 100% in both WAFs. As mentioned above, the specific toxicity indicates that WAF of ISB residue was more toxic to *nauplii* than WAF of fresh oil.

Acute toxicity, expressed as toxic unit (TU), was predicted based on the chemical composition of the WAFs and the K_{ow} for the individual components. A $TU > 1$ for the total WAF implies that it is expected to cause more than 50% mortality in the test organisms. TU for the WAFs are computed and provided in Table A 5. TU for both WAFs were below 1, WAF from fresh oil was 0.63 and for WAF from ISB residue was 0.44.

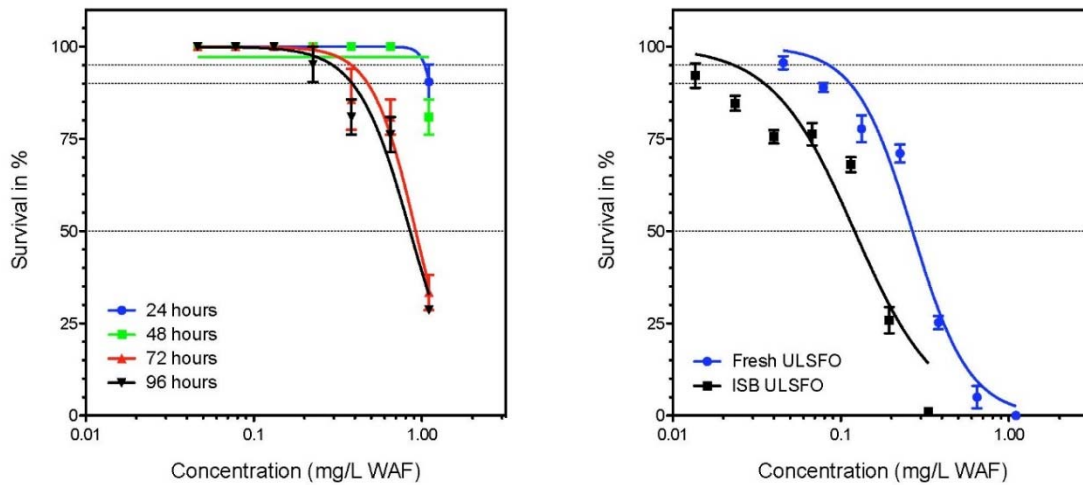


Figure 3.6 Survival of *Calanus finmarchicus* (y-axis) as a function of WAF concentration. Left graph: *Calanus* (CV) exposed to WAF of fresh ULSFO, survival after 24, 48, 72, and 96 hours. Right graph: *Calanus nauplii* exposed to WAF of fresh ULSFO (blue line) and ISB residue (black line), survival after 72 hours.

3.3 Comparison with WAFs from other oil products

WAF concentrations and TU for the WAFs were compared with other oil products in Figure 3.7 and Figure 3.8. Although the concentrations in WAFs of unburned and burned ULSFO are lower than the other WAFs in Figure 3.7, the computed TU are higher than some of the other oils (Figure 3.8). The calculations indicate that especially the PAHs are contributing to the toxicity. WAF of "ULSFO 2016" is another batch of ULSFO, which contained more volatile components than the ULSFO burned during "Oil-on-water" in 2018, had a TU lower than the WAFs of unburned and burned ULSFO studied here. Of the oils presented in Figure 3.8, only a marine gas oil has a TU>1, all other WAFs were below 1.

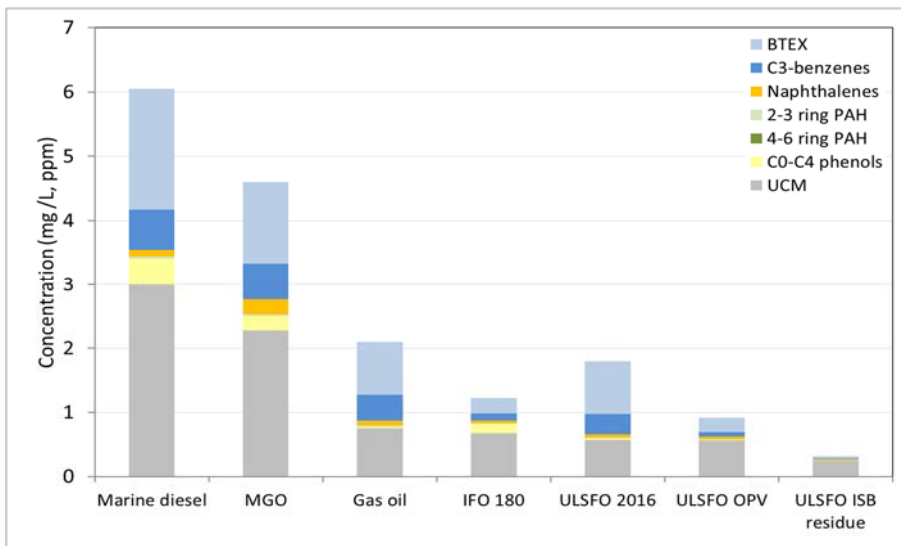


Figure 3.7 WAF concentrations of oil products tested in previous studies at SINTEF, compared with the WAF studied here: Unburned ULSFO (ULSFO OPV) and ISB residue (ULSFO ISB residues)

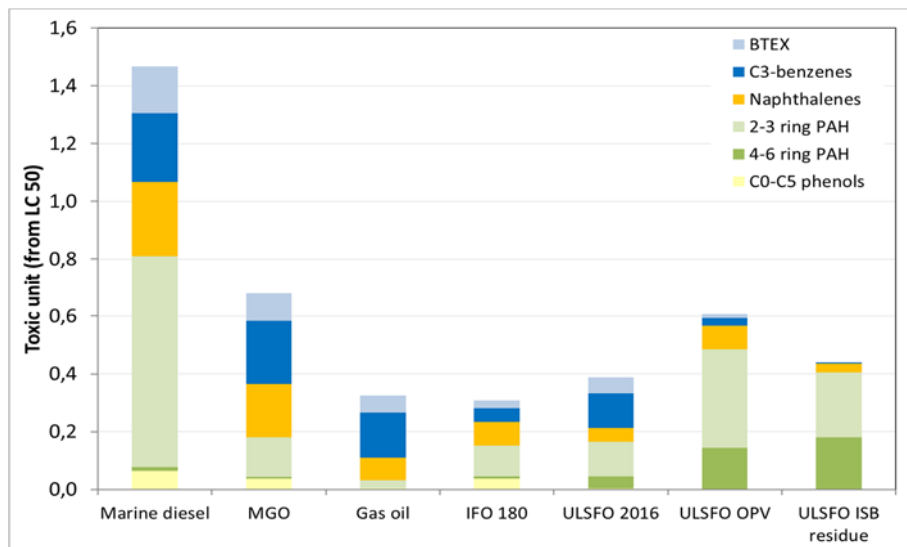


Figure 3.8 Predicted acute toxicity expressed as TU for WAFs of oil products tested in previous studies at SINTEF, compared with the WAF studied here: Unburned ULSFO (ULSFO OPV) and ISB residue (ULSFO ISB residues). A TU > 1 indicated a mortality of 50% for the tested organisms.

4 Summary and conclusions

Water accommodated fraction (WAF) of unburned ULSFO and its ISB residue were studied with emphasis on chemistry and acute toxicity. Low-energy WAFs were prepared with an oil-to-water ratio of 1 to 40 to evaluate the potential impact of ISB residue to the environment. The primary consumer, the copepod *Calanus finmarchicus*, were tested, to WAF from unburned oil both CV and nauplii, and to WAF from ISB residue, only by nauplii.

The total WAF concentrations were low, 1.104 ppm in WAF of unburned (fresh) ULSFO and 0.332 ppm in WAF of ISB residue. The oil and WAF of ISB residue still contained volatiles, and this was unexpected. However, the residue after a burn could contain both burned and unburned oil, and here the residue was heated and homogenized before the WAF was prepared.

Calanus nauplii were tested both for WAF of fresh oil and ISB residue, and the results indicate that the nauplii stage is more sensitive to WAF of fresh oil than the late copepodite (CV) stage. The nauplii have limited fat reserves and are therefore less protected than the grown organisms where heavier components (PAHs) will be stored temporary in the fat reserves and in that way be physiological unavailable.

Specific toxicity is normalized to the total WAF concentration and has been the traditional approach for expressing toxicity and indicated that WAF of ISB residue was more toxic to nauplii than WAF of fresh oil. However, as mentioned above, the WAF concentration is relatively low (0.332 ppm).

Acute toxicity, expressed as toxic unit (TU), was predicted based on the chemical composition of the WAFs and the K_{ow} for the individual components. A $TU > 1$ for the total WAF implies that it is expected to cause more than 50% mortality in the test organisms. TU for both WAFs were below 1, WAF from fresh oil was 0.63 and for WAF from ISB residue was 0.44. The calculations indicate that especially the PAHs are contributing to the toxicity.

It has been assumed the residue after an ISB does not contain water soluble components that can dissolve into the water. However, as seen in the present study, as the residue after an ISB could contain a mixture of burned and unburned/less burned oil, the concentration and composition of water-soluble components from the residue could reach a level that may have an impact on marine organisms. A potential impact on the environment will depend of several factors, e.g. burning effectiveness, residue properties, dilution rate in water. Faksness et al. (2011) measured the water-soluble oil components in the water during a 6-day experimental release of Troll crude oil (7 m³) in the marginal ice zone in the Barents Sea in 2009. The highest concentrations measured close to the oil slick (3 m depth) was 30 ppb, which is 10 times lower than the WAF concentrations of the ISB-residue tested here.

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A Appendix A Additional results of chemical analysis and toxicity

Table A 1 Summary of the chemical composition of the oils (in g analyte/kg oil) and their WAFs (in µg analyte/L water). Total WAF concentration, TPH and UCM are not quantified in the oils (ND: Not detected).

	2018-3881 ULSFO fresh g/kg	2018-5304 ULSFO ISB residue g/kg	2018-3881 WAF ULSFO fersk µg/L	2018-5304 WAF ULSFO ISB residue µg/L
Tot WAF			1104	332
TPH			705	268
UCM			566	247
Sum SVOC	17,8	11,3	58,8	20,8
Sum VOC	18,0	1,53	399	64,1
Decalins	1,85	0,59	0,18	0,03
Naphthalenes	3,04	1,10	45,7	12,4
2-3 ring PAH	6,63	4,10	9,44	6,27
4-6 ring PAH	6,24	5,46	1,75	1,81
C0-C5 phenols	ND	ND	1,70	0,20
BTEX	1,63	0,16	227	36,7
C3-benzenes	1,84	0,14	67,0	12,0
Other VOC	14,6	1,23	105	15,4

Table A 2 Semi-volatiles in oils and WAFs of unburned ULSFO and ISB residues (ND: Not detected).

SINTEF ID	2018-3881-S1	2018-5304-S12	2018-3881-S1-S1	2018-5304-S12-S2
Sample ID	ULSFO fresh oil g/kg	ULSFO ISB-residue g/kg	WAF ULSFO µg/L	WAF ISB residue µg/L
Decalin	0,11	0,03	0,08	0,01
C1-decalins	0,26	0,07	0,05	0,01
C2-decalins	0,33	0,10	0,05	0,01
C3-decalins	0,63	0,21	ND	ND
C4-decalins	0,52	0,19	ND	ND
Benzo(b)thiophene	ND	ND	ND	ND
Naphthalene	0,06	0,02	11,6	3,16
C1-naphthalenes	0,29	0,09	18,4	3,61
C2-naphthalenes	0,80	0,26	9,74	3,23
C3-naphthalenes	1,16	0,42	4,80	1,89
C4-naphthalenes	0,73	0,30	1,24	0,56
Biphenyl	0,01	0,01	0,26	0,12
Acenaphthylene	ND	ND	0,07	0,45
Acenaphthene	0,01	ND	0,22	0,11
Dibenzofuran	0,01	ND	0,10	0,05
Fluorene	0,03	0,01	0,62	0,31
C1-fluorenes	0,10	0,05	0,63	0,33
C2-fluorenes	0,31	0,16	0,63	0,40
C3-fluorenes	0,34	0,19	0,26	0,16

SINTEF ID	2018-3881-S1	2018-5304-S12	2018-3881-S1-S1	2018-5304-S12-S2
Sample ID	ULSFO fresh oil	ULSFO ISB-residue	WAF ULSFO	WAF ISB residue
	g/kg	g/kg	µg/L	µg/L
Phenanthrene	0,12	0,07	1,08	0,75
Anthracene	0,01	0,01	0,19	0,13
C1-phenanthrenes/anthracenes	0,55	0,32	1,59	1,00
C2-phenanthrenes/anthracenes	1,56	0,94	1,60	1,08
C3-phenanthrenes/anthracenes	1,97	1,26	0,67	0,51
C4-phenanthrenes/anthracenes	1,27	0,87	0,15	0,13
Dibenzothiophene	ND	ND	0,06	0,04
C1-dibenzothiophenes	0,04	0,02	0,16	0,09
C2-dibenzothiophenes	0,09	0,05	0,26	0,14
C3-dibenzothiophenes	0,12	0,08	0,73	0,39
C4-dibenzothiophenes	0,08	0,06	0,16	0,08
Fluoranthene	0,03	0,03	0,09	0,10
Pyrene	0,25	0,18	0,46	0,45
C1-fluoranthenes/pyrenes	0,99	0,73	0,65	0,55
C2-fluoranthenes/pyrenes	0,20	0,20	0,08	0,09
C3-fluoranthenes/pyrenes	1,06	0,87	0,10	0,20
Benz(a)anthracene	0,15	0,13	0,07	0,09
Chrysene	0,20	0,16	0,08	0,09
C1-chrysenes	0,89	0,82	0,12	0,14
C2-chrysenes	1,09	1,07	0,07	0,07
C3-chrysenes	0,76	0,65	0,02	0,02
C4-chrysenes	0,37	0,27	ND	ND
Benzo(b)fluoranthene	0,04	0,04	ND	0,01
Benzo(k)fluoranthene	0,01	0,01	ND	ND
Benzo(e)pyrene	0,09	0,11	0,01	0,01
Benzo(a)pyrene	0,06	0,06	ND	0,01
Perylene	0,02	0,03	ND	ND
Indeno(1,2,3-c,d)pyrene	0,01	0,02	ND	ND
Dibenz(a,h)anthracene	0,02	0,02	ND	ND
Benzo(g,h,i)perylene	ND	0,06	ND	ND
Phenol	ND	ND	0,95	0,13
C1-Phenols (o- og p-cresol)	ND	ND	0,75	0,07
C2-Phenols	ND	ND	ND	ND
C3-Phenols	ND	ND	ND	ND
C4-Phenols	ND	ND	ND	ND
C5-Phenols	ND	ND	ND	ND
30 ab hopane	0,50	0,49	ND	ND
Sum all compounds	17,8	11,3	58,8	20,8
Sum decalins	1,85	0,59	0,18	0,03
Naphthalenes	3,04	1,10	45,7	12,4
2-3 ring PAHs	6,63	4,10	9,44	6,27
4-6 ring PAHs	6,24	5,46	1,75	1,81
C0-C5 Phenols	ND	ND	1,70	0,20

Table A 3 Composition of volatiles in oils and WAFs of unburned ULSFO and ISB residues (ND: Not detected).

SINTEF ID	2018-3881-S1	2018-5304-S12	2018-3881-S1-S1	2018-5304-S12-S2
Sample ID	ULSFO fresh oil	ULSFO ISB-residue	WAF ULSFO	WAF ISB residue
	g/kg	g/kg	µg/L	µg/L
Isopentane	0,52	ND	16,0	3,01
n-C5 (Pentane)	0,82	ND	16,3	2,01
Cyclopentane	0,30	ND	14,2	1,38
2-methylpentane	0,49	0,01	4,25	0,58
3-Methylpentane	0,26	0,01	2,38	0,33
n-C6 (Hexane)	0,82	0,09	3,90	0,44
Methylcyclopentane	0,55	0,04	14,1	2,10
Benzene	0,07	0,01	41,7	9,39
Cyclohexane	0,49	0,03	15,4	2,47
2,3-Dimethylpentane	0,11	ND	0,36	0,05
3-methylhexane	0,37	0,01	0,70	0,13
n-C7 (Heptane)	1,16	0,12	0,97	ND
Methylcyclohexane	1,51	0,09	12,2	1,89
Toluene	0,39	0,04	82,0	11,2
2,4 diethylhexane	ND	ND	ND	ND
2-Methylheptane	0,58	0,02	ND	ND
n-C8 (Octane)	1,58	0,19	ND	ND
Ethylbenzene	0,12	0,01	10,5	1,69
m-Xylene	0,64	0,06	55,8	8,79
p-Xylene	0,21	0,02	13,9	1,81
o-Xylene	0,21	0,02	23,5	3,84
n-C9 (Nonane)	1,99	0,24	0,08	ND
Propylbenzene	0,05	0,01	1,20	0,21
1-Methyl-3-ethylbenzene	0,20	0,02	6,55	1,13
1-Methyl-4-ethylbenzene	0,14	0,01	3,82	0,63
1,3,5-trimethylbenzene	0,23	0,02	6,94	1,22
1-Methyl-2-ethylbenzene	0,08	0,01	3,27	0,61
1,2,4-Trimethylbenzene	0,66	0,05	22,6	4,01
n-C10 (Decane)	2,85	0,36	0,18	0,11
1,2,3-Trimethylbenzene	0,47	0,03	22,6	4,18
n-Butylbenzene	ND	ND	0,16	0,03
1,2,4,5-Tetramethylbenzene	0,19	0,01	2,72	0,52
n-Pentylbenzene	ND	ND	1,32	0,31
C4-Benzenes	1,41	0,10	19,1	3,72
C5-Benzenes	1,53	0,08	6,70	1,56
Sum all VOC	18,0	1,53	399	64,1
Sum BTEX	1,63	0,16	227	36,7
Sum C3-benzenes	1,84	0,14	67,0	12,0
Sum other VOC	14,6	1,23	105	15,4

Table A 4 Acute toxicity for *Calanus finmarchicus* after 96 hours to WAFs of unburned ULSFO (adult/CV) and after 72 hours for WAFs of ISB-residue (nauplii). Acute specific toxicities are normalized to total WAF concentration and are given as LC50. In addition, percent mortality in 100% WAF at test endpoint are shown.

WAF-system:	LC ₅₀ (% WAF)	95%CI	LC ₅₀ (mg/L WAF)	% mortality in 100% WAF at test endpoint
2018-3881:				
Unburned 1:40				
Cons.: 1 104 µg/L				
Adult/CV (96 hours)	77.2	70.1 - 85.1	0.952	71.4
Nauplii (72 hours)	24.2	22.2 - 26.4	0.267	100
2018-5304:				
ISB residue 1:40				
Cons.: 332 µg/L				
Nauplii (72 hours)	36.4	31.0 - 42.8	0.121	99.0

Table A 5 Predicted acute toxicity expressed as toxic unit (TU) for WAFs of fresh ULSFO and ISB residue.

	BTEX	C3-benzenes	Decalins	Naphthalenes	2-3 ring PAH	4-6 ring PAH	C0-C5 phenols	Total TU
ULSFO OPV	0,014	0,026	0,021	0,0825	0,3410	0,14376	0,0001	0,63
ISB residue	0,002	0,005	0,004	0,0305	0,2243	0,17957	ND	0,45

B Appendix B Overview of target analytes and component groups

Table B 1 Overview target analytes with abbreviation (SVOC: Semi volatile organic compounds, VOC: Volatile organic compounds, TPH: Total petroleum hydrocarbons, UCM: Unresolved organic materials).

Gruppe	Compound	Abb	Gruppe	Compound	Abb
SVOC	Decalin	DE	C0-C5 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
Naphthalenes	Naphthalene	N	C5-phenols	PH5	
	C1-naphthalenes	N1	Hopane	17 α (H),21 β (H)-hopane (C30)	HOP
	C2-naphthalenes	N2	Other VOC	Isopentane	
	C3-naphthalenes	N3		n-C5 (Pentane)	
C4-naphthalenes	N4	Cyclopentane			
2-3 ring PAHs	Benzo(b)thiophene	BT		2-methylpentane	
	Biphenyl	B		3-methylpentane	
	Acenaphthylene	ANY		n-C6 (Hexane)	
	Acenaphthene	ANA		Methylcyclopentane	
	Dibenzofuran	DBF		Cyclohexane	
	Fluorene	F		2,3-dimethylpentane	
	C1-fluorenes	F1		3-methylhexane	
	C2-fluorenes	F2		n-C7 (Heptane)	
	C3-fluorenes	F3		Methylcyclohexane	
	Phenanthrene	P		2,4-dimethylhexane	
4-6 ring PAHs	Anthracene	A		2-methylheptane	
	C1-phenanthrenes/anthracenes	P1		n-C8 (Octane)	
	C2-phenanthrenes/anthracenes	P2	n-C9 (Nonane)		
	C3-phenanthrenes/anthracenes	P3	n-C10 (Decane)		
	C4-phenanthrenes/anthracenes	P4	n-Butylbenzene		
	Dibenzothiophene	D	1,2,4,5-tetramethylbenzene		
	C1-dibenzothiophenes	D1	n-pentylbenzene		
	C2-dibenzothiophenes	D2	BTEX	Benzene	
	C3-dibenzothiophenes	D3		Toluene	
	C4-dibenzothiophenes	D4		Ethylbenzene	
	Fluoranthene	FL		<i>m</i> -xylene	
	Pyrene	PY		<i>p</i> -xylene	
	C1-fluoranthrenes/pyrenes	FL1	<i>o</i> -xylene		
	C2-fluoranthrenes/pyrenes	FL2	C3-benzenes	Propylbenzene	
	C3-fluoranthrenes/pyrenes	FL3		1-methyl-3-ethylbenzene	
	Benz[<i>a</i>]anthracene	BA		1-methyl-4-ethylbenzene	
	Chrysene	C		1,3,5-Trimethylbenzene	
	C1-chrysenes	C1		1-methyl-2-ethylbenzene	
	C2-chrysenes	C2		1,2,4-trimethylbenzene	
	C3-chrysenes	C3		1,2,3-trimethylbenzene	
C4-chrysenes	C4				
Benzo[<i>b</i>]fluoranthene	BBF				
Benzo[<i>k</i>]fluoranthene	BKF				
Benzo[<i>e</i>]pyrene	BEP	TPH	C10-C40		
Benzo[<i>a</i>]pyrene	BAP	WAF	Sum of VOC and TPH		
Perylene	PE	UCM	TPH - SVOC		
Indeno[1,2,3- <i>c,d</i>]pyrene	IN				
Dibenz[<i>a,h</i>]anthracene	DBA				
Benzo[<i>g,h,i</i>]perylene	BPE				