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# Physical-chemical properties of low sulphur fuel oils and chemical characteristics and acute toxicity of their WAFs

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# Contents

- Studied oils
- Air measurements during skimmer testing
- Preparation of WAFs (water accommodated fraction)
- Chemical and toxicological characteristics of the WAFs
- Higher PAH contents in low sulphur fuels than conventional fuels?
- Summary and conclusions

# Studied oils and their physical properties

| IM no. | Oil description | Viscosity at 10 °C (cP) | | Density | Pour point |
|---|---|---|---|---|---|
| | | $10\ s^{-1}$ | $100\ s^{-1}$ | 15 °C (calculated) | (°C) |
| **IM-5** | VLSFO, Wakashio | 1199 | 582 | 0.908 | 9 |
| **IM-14** | VLSFO | 13256 | 5183 | 0.929 | 27 (±3) |
| **IM-15** | VLSFO | 9195 | 6729 | 0.946 | 0 (±3) |
| **IM-16*** | ULSFO | 44211 | 9463 | 0.909 | 33 (±3) |

** IM-16: Only oil analyses, not WAF and toxicity*

# Air measurements during skimmer testing

- Objectives
  - Measure the air concentration of VOC after oil release and make an estimate of a "worst-case" situation
  - Measure personal exposure to VOC among persons operating the oil spill tests and compare these levels with the Norwegian Occupational Exposure Limits (OELs)
  - Evaluate the toxic potential of the oils based upon their chemical composition

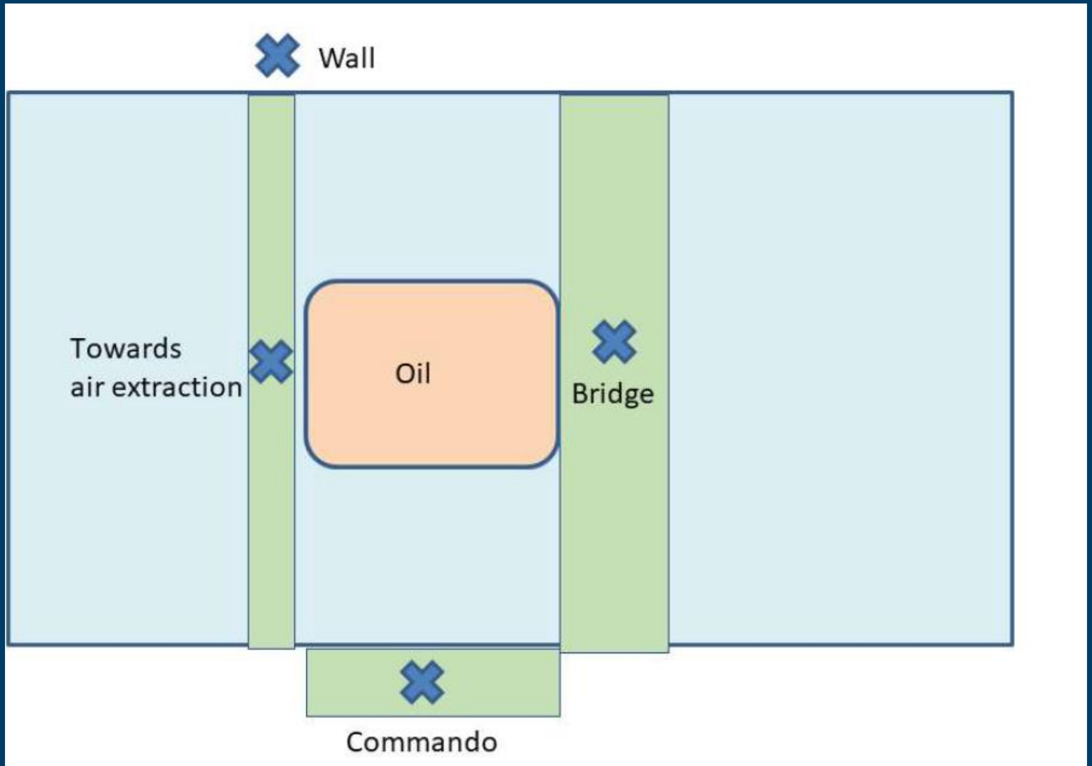
*Measurement performed by the Research Group for Occupational Medicine at the University in Bergen, Norway:*

*Reported in Bråtveit et al. (2022): Air measurements of hydrocarbons emitted from oils during testing of skimmers at National Centre for Testing of oil spill response equipment*

# Air measurements during skimmer testing

- Methods
  - Concentration of VOCs in air
    - PID (photo ionization detector)
      - Personal samples on 2-4 operator
    - TD-tubes (thermal desorption tubes)
      - Four positions in the hall

- Conclusions
  - The measured air concentrations of VOCs and PAHs were low compared to the Norwegian Occupational Exposure Limits




Air measurement positions (blue crosses), approx. 1.5 m above oil level

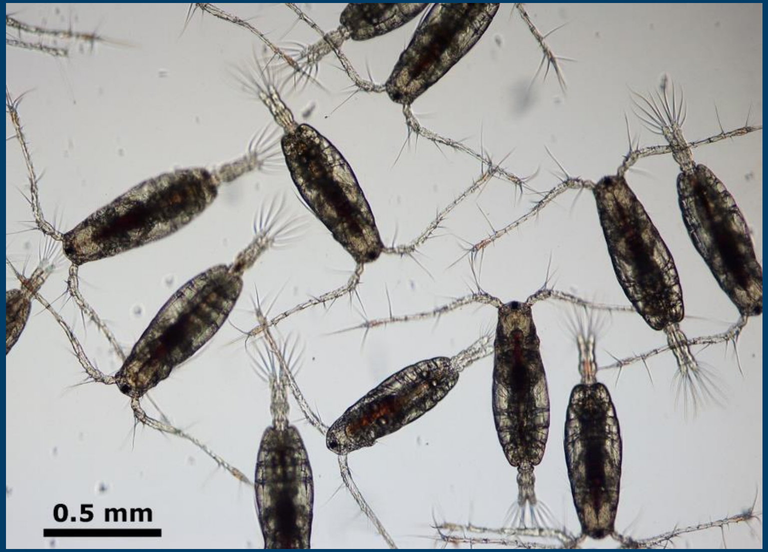
# Preparation of Water Accommodated Fraction (WAF) CROSERF methodology

- A water solution of *dissolved* oil compounds, prepared in lab-system with calm mixing of oil and water
- Headspace: 20-25 %
- Prepared with an oil to water ratio of 1:40 (25 g/L) at 2°C
- Exposure time: 72 hours
- Chemical characterization and toxicity studies

*WAFs of IM-5, IM-14 and IM-15*

# Chemistry and toxicity of the WAFs

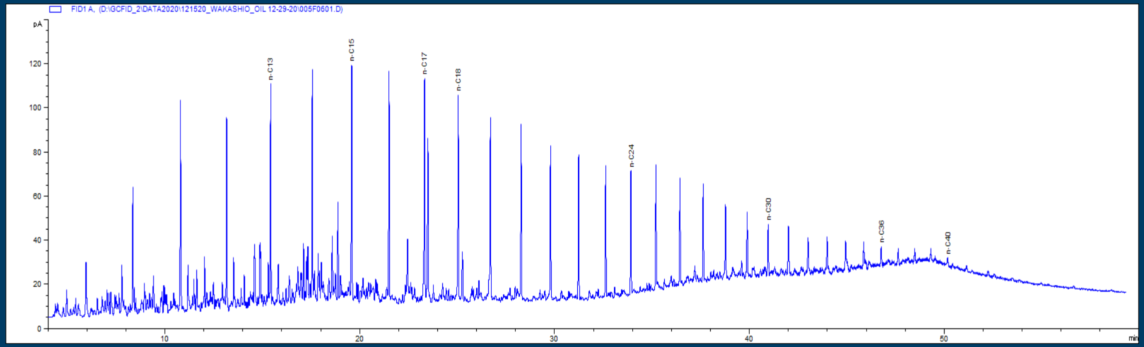
- Detailed chemical characterization of the oils and the WAFs:
  - Volatile components (35 comp, including BTEX)
  - Semi volatile components (55 components, including PAHs and phenols)
  - Total petroleum hydrocarbons ($C_{10}$-$C_{36}$)
- Acute toxicity tests of the WAFs (performed in closed vessels to avoid loss of volatiles):
  - Marine copepod *Acartia tonsa*
    - Mortality monitored after a 48 hours test period at 20 °C
    - Reported as LC-values (Survival of copepods)
  - Marine copepod *Calanus finmarchicus*
    - Mortality monitored after a 96 hours test period at 10 °C
    - Reported as LC-values (Survival of copepods)

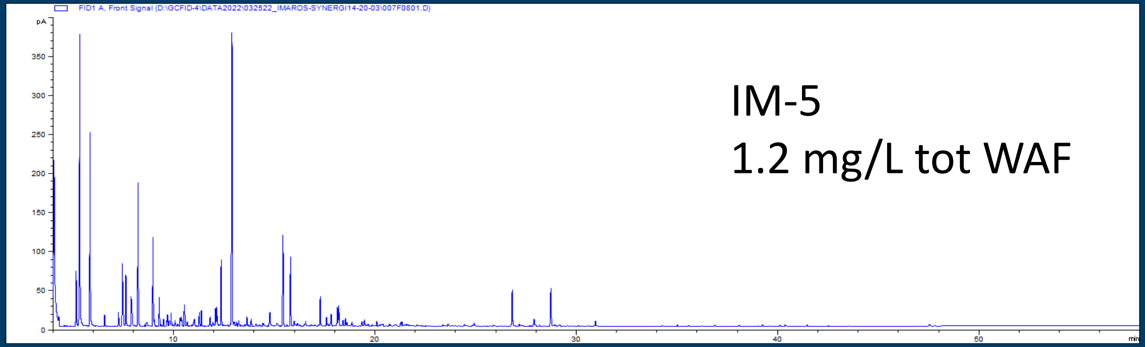


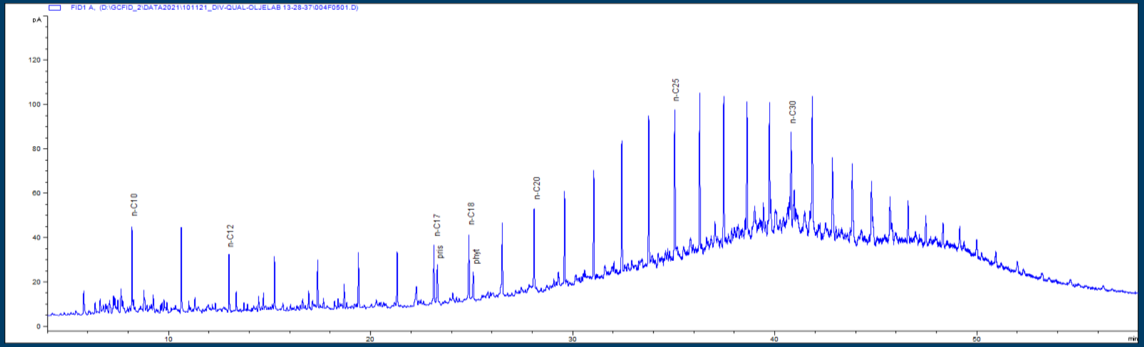

*Acartia tonsa* (Photo: D. Altin)

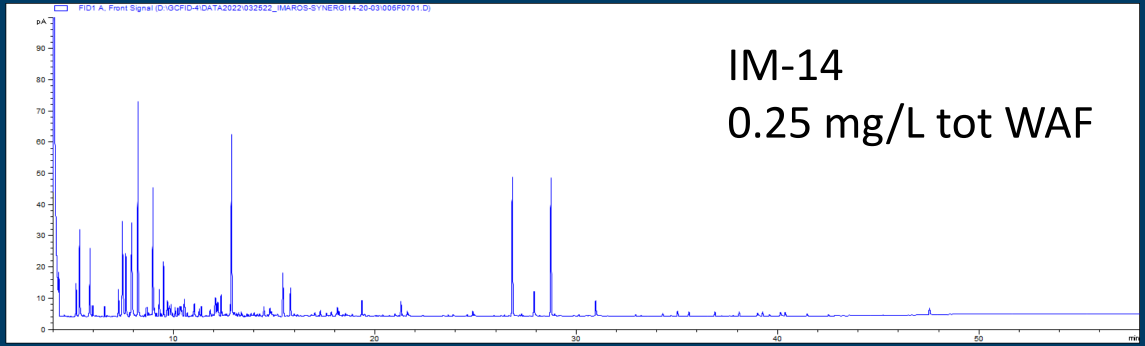

*Calanus finmarchicus*, Copepodite V (CV)

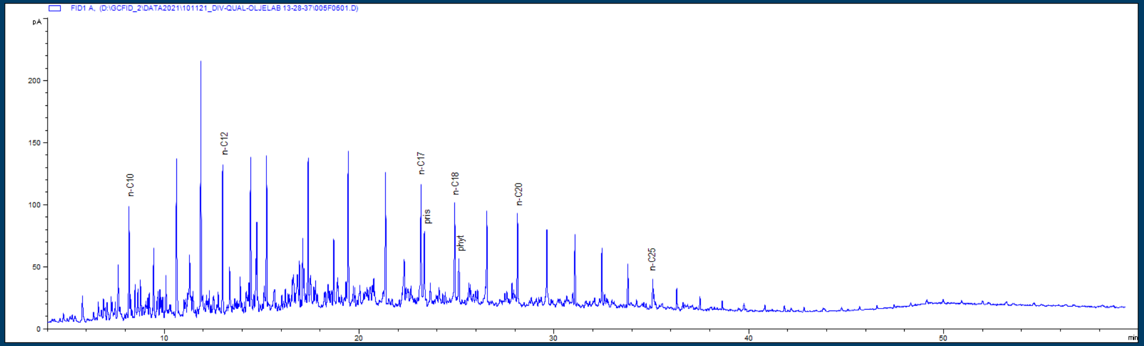
# GC chromatograms of the oils and their WAFs

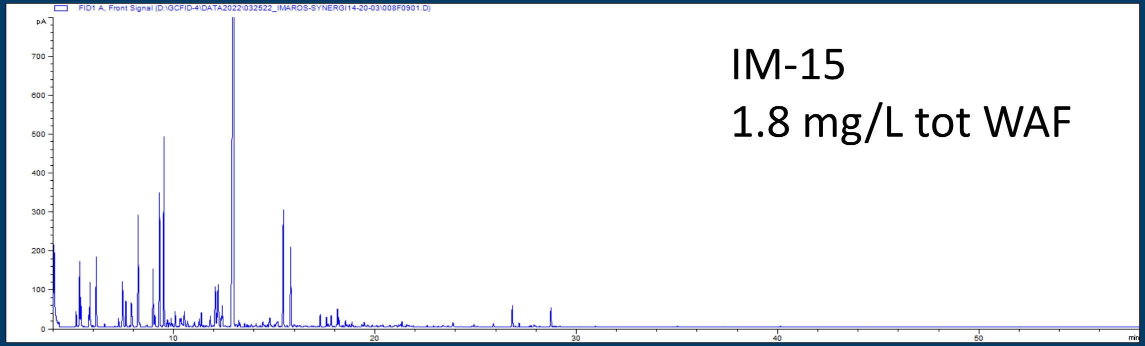


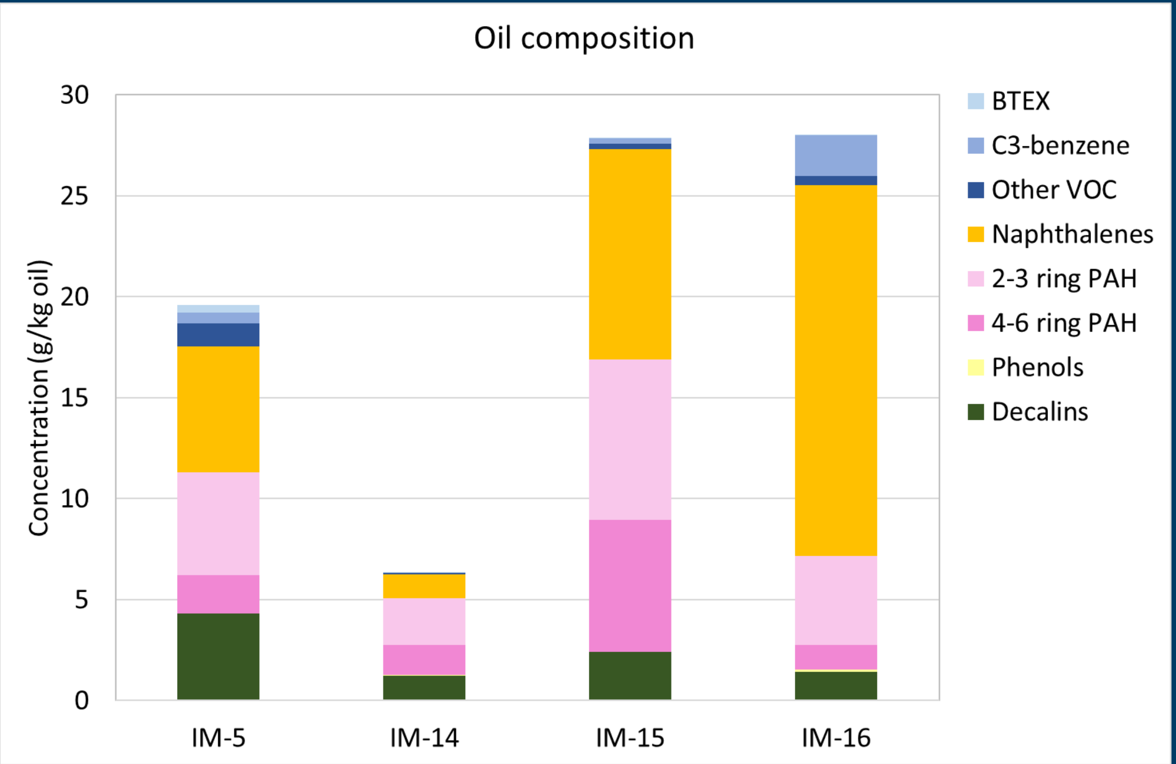



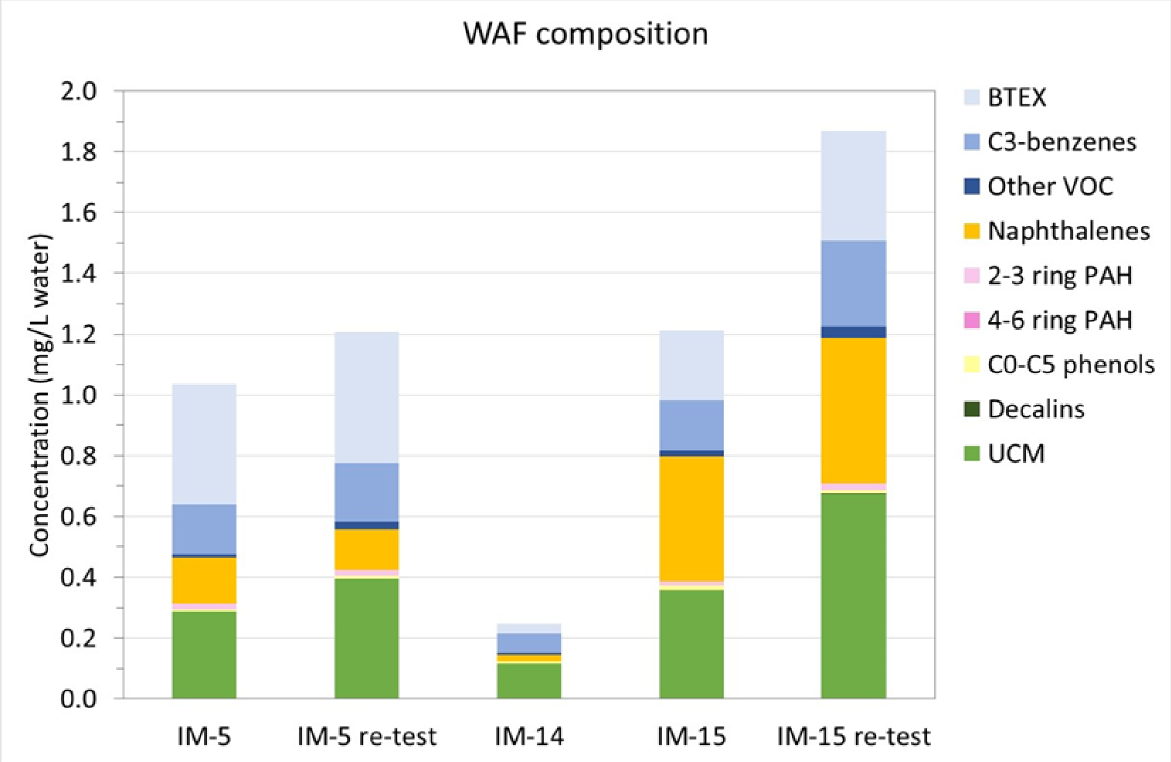



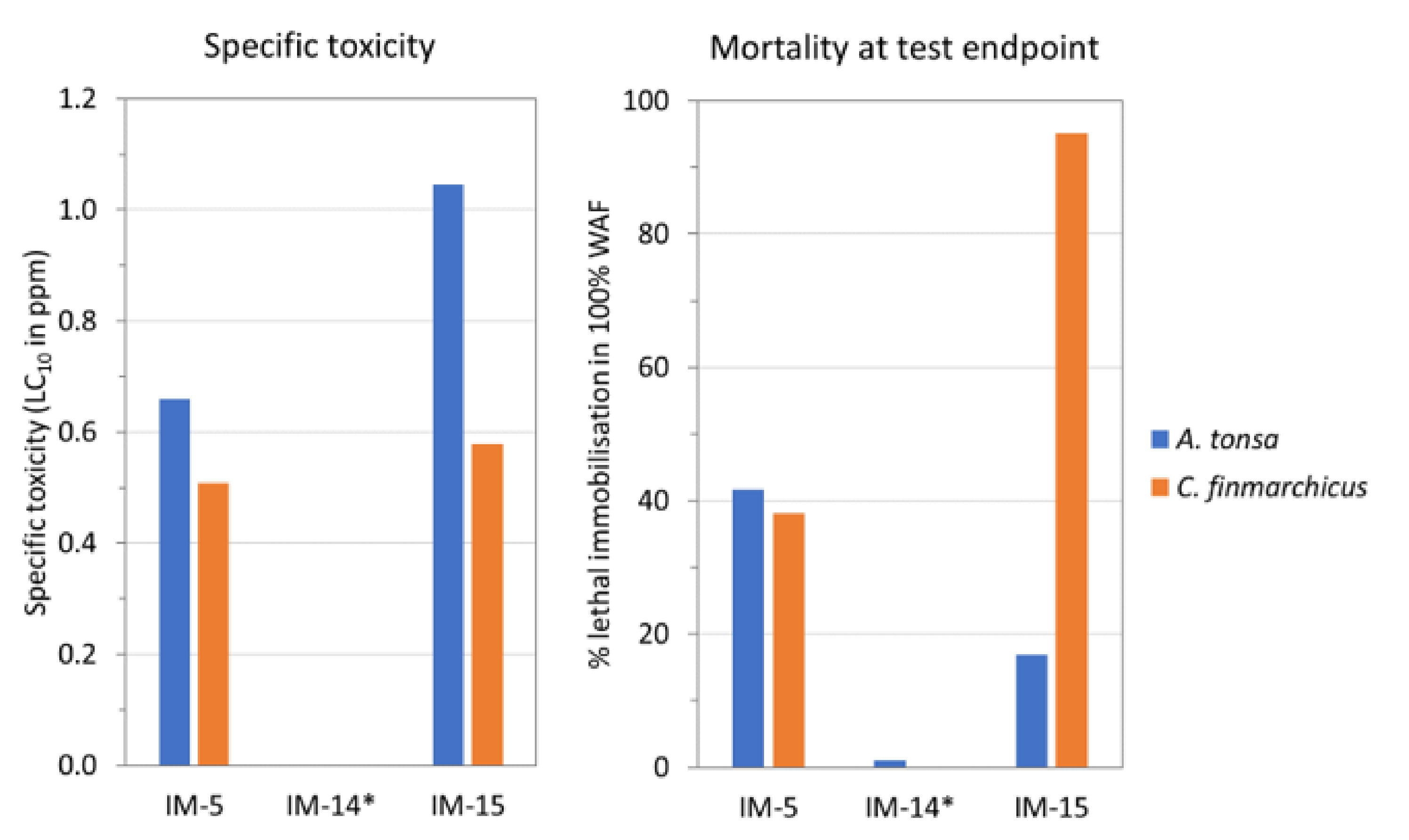



# Chemical composition of the oils and the WAFs



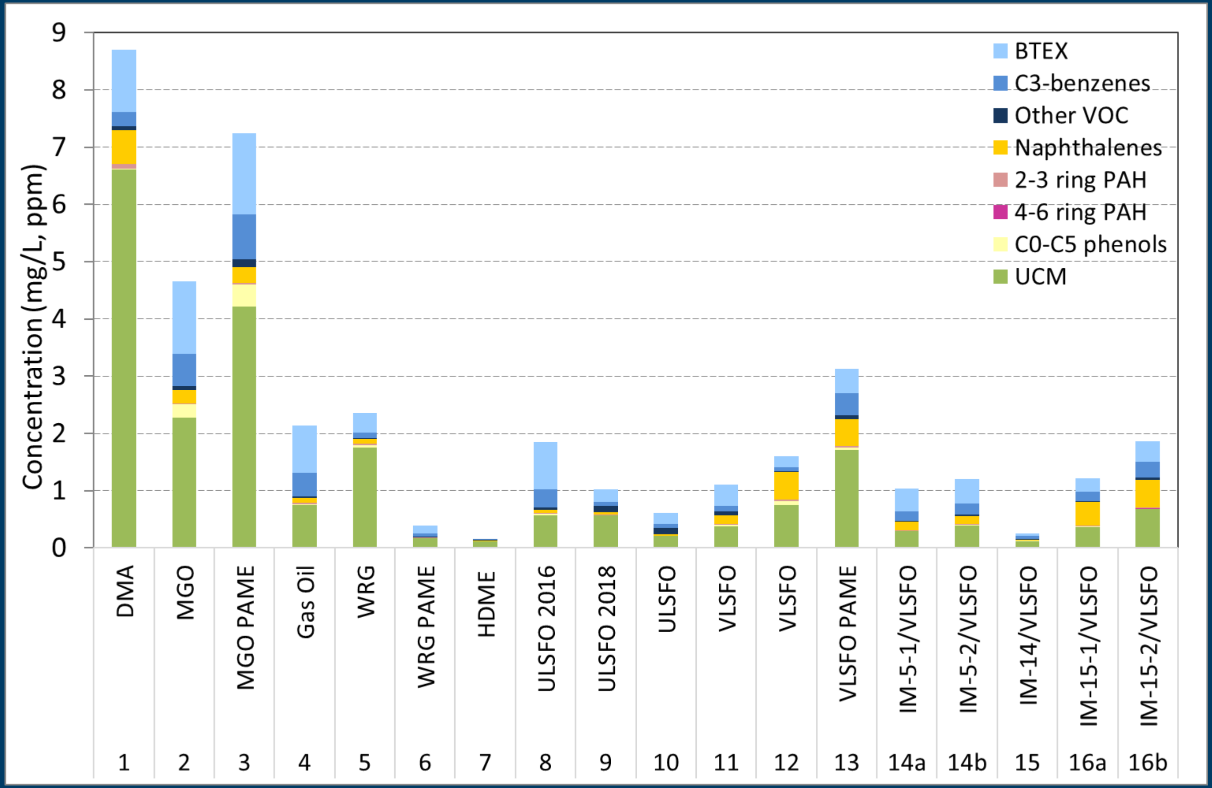
# Toxicity in the WAFs

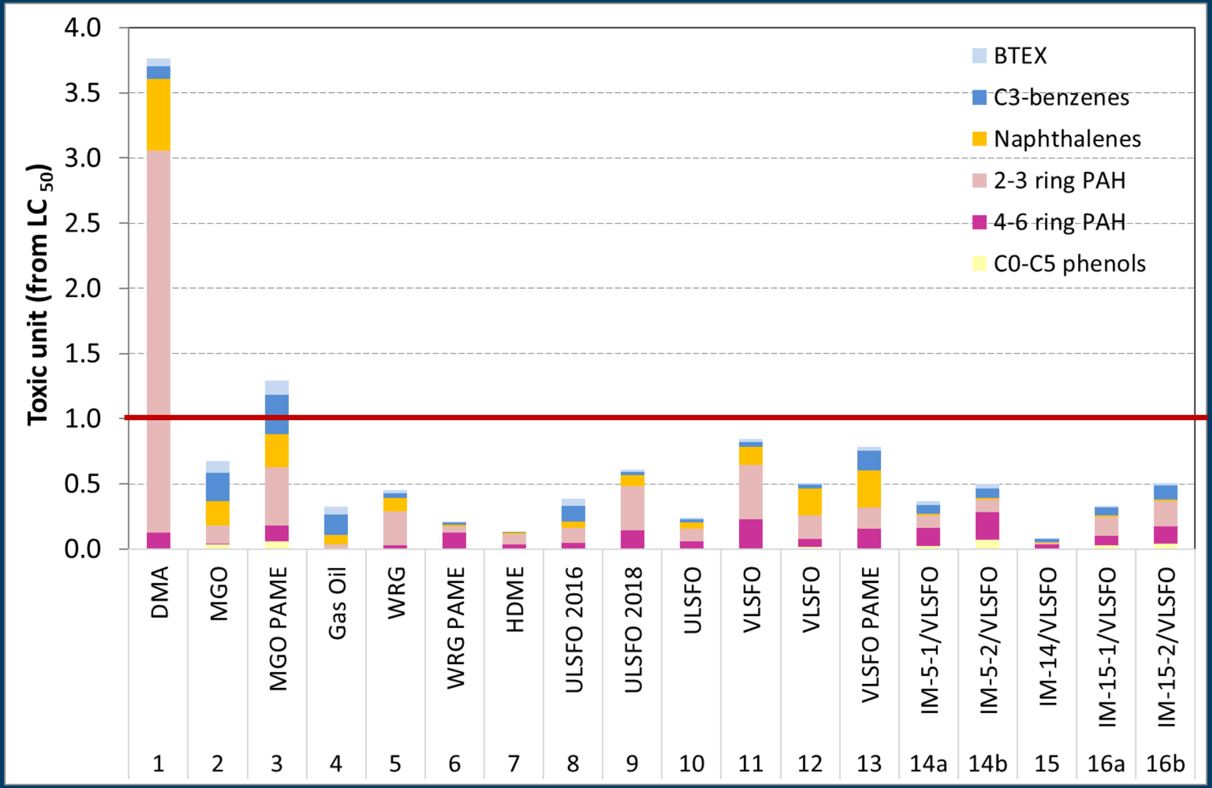



- Toxic level too low to calculate $LC_{50}$s: Less than 50% mortality in all system exept one
- No toxic effect observed in tests on IM-14

$LC_{10}$ is defined as the concentration causing a negative effect on 10% of the test organisms

# Chemical composition and Toxic Unit of WAFs of low sulphur oils




Use log $K_{OW}$ to estimate the LC50 for each component using the linear regression model

log LC50 = *m* log $K_{OW}$ + *b (McCarty et al, 1992 and 1993)*

TU > 1 implies that the WAF is expected to cause 50% mortality in the test organisms

# Higher PAH contents in low sulphur fuels than conventional fuels?

- Have been reported that some of the "new" LSFOs contain more than 90% PAHs (IMO (2020); Behrends (2021)
- Not described how these values were calculated, but reported as > 90% PAHs in LSFO:
  - 90% of the analysed components?
  - 90% of the total oil content (0.9 kg PAH in 1 kg oil)?
- We have evaluated and compared the chemical composition of 53 fuels oils, including 13 IM-oils from Cedre

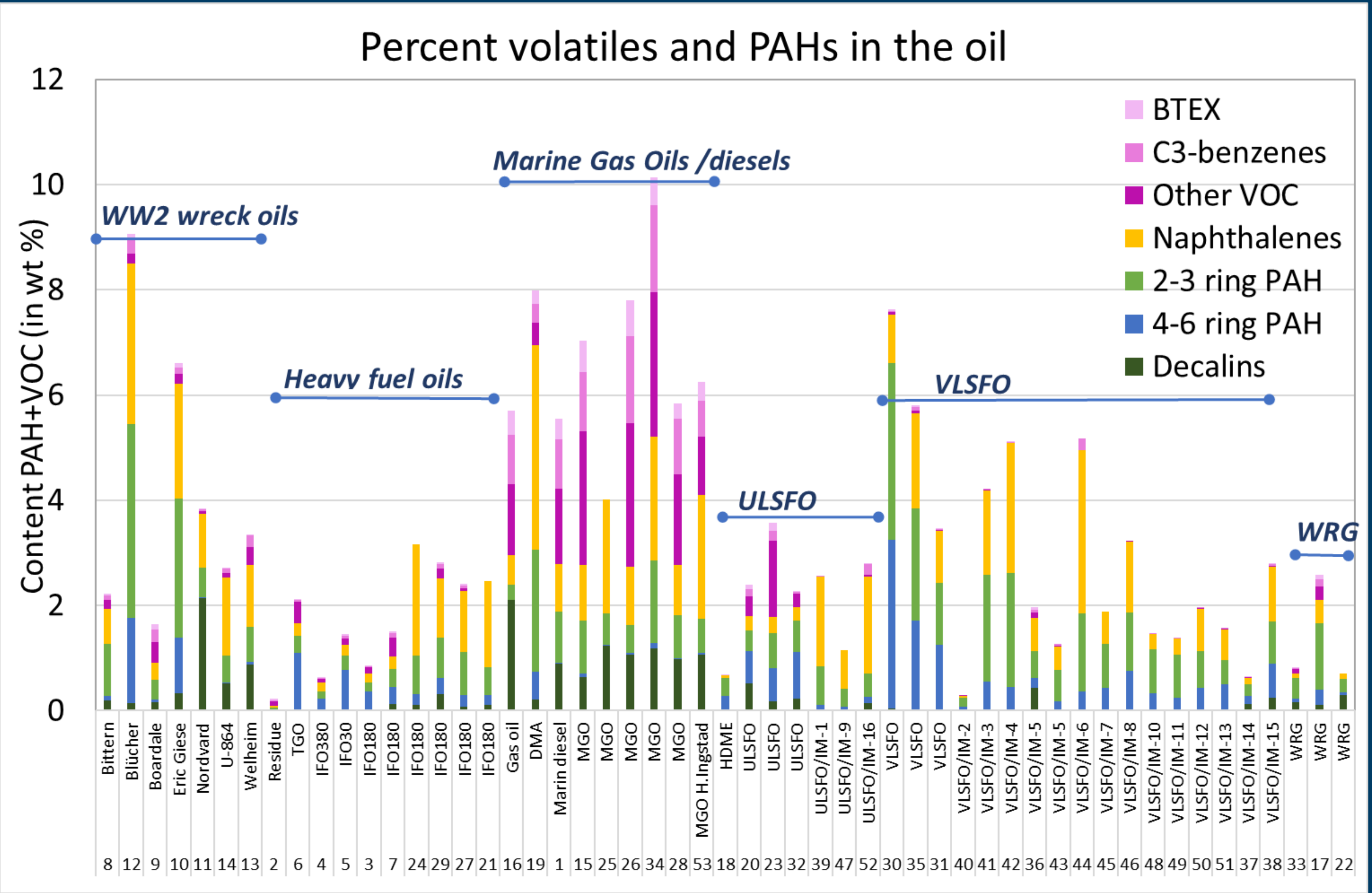
Table from IMO and Behrends:

**Table 4: Chemical groups of the major compounds of the VLSFOs after GC x GC-HRTOFMS analysis. Grey shaded lines represent the aromatic compounds**

| Type of hydrocarbon | Chemical groups including the alkylated compounds | Unit | VLSFO (73.7%) | VLSFO (83.1%) | VLSFO (97.3%) |
|---|---|---|---|---|---|
| paraffinic | n-Alkanes | % | 4.37 | 6.70 | 1.67 |
| | iso-Alkanes | % | 9.45 | 5.69 | 0.59 |
| | Naphthenes/Olefines | % | 3.41 | 2.91 | 0.00 |
| | Dinaphthenes/Olefines | % | 4.91 | 0.75 | 0.00 |
| aromatic | Alkylbenzenes | % | 6.64 | 6.25 | 3.83 |
| | Naphthobenzenes | % | 8.30 | 7.94 | 6.71 |
| | Indenes | % | 7.34 | 9.05 | 10.47 |
| polycyclic aromatic | Naphthalenes | % | 25.51 | 40.81 | 54.64 |
| | Biph./Diph.meth./Acenaphthenes | % | 10.82 | 8.67 | 9.62 |
| | Fluorenes | % | 6.14 | 4.71 | 5.11 |
| | Phenanthrenes | % | 6.85 | 5.08 | 6.18 |
| | Pyrenes/Fluoranthenes | % | 0.91 | 0.31 | 0.47 |

*IMO PPR 8/5/1: Reduction of the impact on the Arctic of emission of Black Carbon from international shipping*

# Comparison of 53 fuel oils (approx 90 comp)




- 7 of 53 oils > 5% SVOC
  - 7.5% in VLSFO (Multipartner)
  - 6.7% in DMA (Rotterdam)
  - 6.3% in MGO (H.Ingstad)
  - 5.6% in VLSFO PAME
  - 5.1% in VLSFO (IM-4)
- MGO PAME has highest content of total VOC+SVOC (10%)
- 11 fuels < 1% SVOC
- Content of SVOC varies:
  - From 0.5 to 7.5% for VLSFO
  - From 1.2 to 2.8% for ULSFO
  - From 0.7 to 3% in traditional heavy bunker oils

# Summary and conclusions

- The measured exposure of VOCs and PAHs to operating personnel during skimmer testing were low compared with the Norwegian Occupational Exposure Limits
- The WAFs were dominated of volatiles and naphthalenes, which are the most water soluble component and the total WAF concentrations were low in IM -14 (0.25 mg/L), and in the same range as other LSFOs in IM-5 and IM-15 (between 1 and 1.9 mg).
- In general, the toxicity in the WAF systems were low, as the observed lethal immobilisation was less than 50% in 5 of 6 tests, and calculated TUs were less than 1 in all systems.
- There are no significant differences in relative content of the component groups between the new LSFOs compared to the more traditional heavy fuel oils.
  - There was a span in PAH content from 0.5% to 7.5% in the VLSFOs and from 1.2% to 2.8% in the ULSFOs. In the traditional IFO180s, the PAH content varied from 0.7 to 3%.

- There are no indications that these tested LSFOs contain non-analysed components that would enhance the toxic potential to the marine environment

# Acknowledgements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- Dag Altin (Biotrix)