Environmental Technology

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Chemical and toxicological characterization of water accommodated fraction (WAF) of crude oils

SINTEF has established a laboratory methodology for preparation and chemical and toxicological characterization of water accommodated fraction (WAF) of crude oils and refined products. The study aims at obtaining improved and realistic data on potential environmental effects to the water column of various oils released and weathered at sea. Such data will be used for improving algorithms in present fate and effect models for damage assessment studies and "Net Environmental Benefit Analysis" (NEBA) of response alternatives in various spill scenarios.

What is WAF?

The WAF is representing the water soluble oil compounds (e.g. BTEX, naphthalenes, PAHs, phenols and polar components) with high bioavailability towards marine organisms and is relevant for both acute oil spills and regular discharges for studying toxicity effects.



Figure 1. System for preparation of WAF

The test systems

WAF solutions from different oils at different weathering degrees and with variable oil-loading rates are prepared in a closed, low energy mixing system following the guidelines established by the CROSERF (Chemical Response to Oil Spills – Ecological effects Research Forum), see Figure 1.

WAFs are prepared from different weathering degrees, and usually with two oil-to-water ratios (1 to 40 and 1 to 10 000). These different WAFs illustrate "snapshots" in the dynamic process of weathering and dissolution occurring during a spill situation. The oil-to-water ratio of 1 to 40 (40 g oil/L seawater) is considered to be unrealistic high, and the data generated gives a kind of "worst case scenario" conditions representing a conservative estimate of concentrations foreseeable in the field. An oil-to-water ratio of 1 to 10 000 (100 mg oil/L water) is often considered to be a more realistic approach in an oil spill release (e.g. after use of chemical dispersants).

The chemical characterization of WAFs and oils includes quantification of

- Approximately 35 target volatile analytes (VOC) in the C5 to C10 range by use of Purge and Trap Gas Chromatography/Mass Spectrometry (P&T GC/MS).
- Approximately 60 semi-volatile organic compounds (SVOC) in the C10 – C22 range included aromatic hydrocarbons (PAH/NPD), decalines, and phenols by use of Gas Chromatography/Mass Spectrometry (GC/MS)
- Total Petroleum Hydrocarbons (TPH) in the C10

 C40 range by use of Gas Chromatograph with a Flame Ionization Detector (GC/FID).





Figure 2 illustrates the large variation in chemical

Figure 2. Chemical composition of WAFs from Norwegian crudes, oils from World War II shipwrecks (red circles), and refined products (oil-to-water ratio of 1 to 40 in all systems).

Toxicity

Microtox[®] bioassay and acute toxicity tests are performed to establish the EC or LC50 values for organisms of two trophic levels: The unicellular marine algae *Skeletonema costatum* and the marine pelagic copepods *Calanus finmarchicus* or *Acartia tonsa*. The results can be compared to results from other bioassays of WAFs from different oils performed under similar conditions. In addition, the toxicity, expressed as toxic unit (TU) of the WAFs can be predicted by estimating LC50 values based on octanol-water partitioning coefficient (K_{ow}) of the individual components in the WAFs (see Figure 3).



Use of data

Data from such studies can be used for improving present fate and effect models, which again can be used in damage assessment studies and in NEBA of spill scenarios. The characterization of the water-soluble oil fraction is considered important in relation to oil spill response and aftermath monitoring, e.g. if dispersants is a part of the oil spill response plan.

The study is relevant as a part of the documentation to an operational oil spill contingency plan for new and existing oil fields. The specific composition of the oil and the water soluble fraction of the oil are used as input to the OSCAR model (Oil Spill Contingency and Response model). The OSCAR model system has been developed to supply a tool for objective analysis of alternative spill response strategies. OSCAR is intended to help achieve a balance between the costs of preparedness in the form of available, maintained spill response capability on the one hand, and potential environmental impacts on the other.

Recently, the methodology has been used for assessment of the potential environmental risk of oil leakage from shipwrecks in Norway by giving valuable input to the decision maker's recommendations of how to deal with old shipwrecks containing oil.

Figure 3. Predicted acute toxicity expressed as toxic unit of WAFs from Norwegian crudes, oils from World War II shipwrecks (red circles), and refined products (oil-towater ratio of 1 to 40 in all systems). A TU>1 indicates mortality for more than 50% of the tested organisms.



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