Chemical and toxicological characterisation of water accommodated fractions relevant for oil spill situations

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Abstract

The laboratory methodology and preliminary findings from an ongoing characterisation study of Water Accommodated Fraction solutions (WAF – water systems with dissolved oil components, which is essentially free of dispersed oil droplets) derived from standardised low energy mixing of oils in seawater is presented.

The study emphasises a tight connection between chemical characterisation and toxicological testing of WAF, and aims at obtaining improved and realistic data on potential environmental effects in the water column after an oil spill situation. Various oil types and the aspect of weathering (evaporative loss and photolysis) of oil is incorporated in the study.

Preliminary results have identified large variation in the composition and toxicity of WAFs depending on the type of crude, oil loading rate (oil:water ratio) and weathering degree of the oils.

Data from the study will be used for improving algorithms in present fate and effect models, which again will be used as quantitative tools in future damage assessment studies and in "Net Environmental Benefit Analysis" of response alternatives in various spill scenarios.

1 Introduction

In connection with assessment of environmental effects from acute oil spills, it is important to identify which chemical components and which concentration levels the marine environment is exposed to in different spill situations. Such knowledge enables toxicological testing under realistic conditions, which is crucial when it comes to using the data as input to models predicting environmental effects.

This study emphasises a tight connection between chemical characterisation and toxicological testing of Water Accommodated Fraction (WAF - water systems consisting of dissolved oil components, which is essentially free of dispersed oil droplets). WAF is of special interest because compounds dissolved from an oil slick or from the dispersed oil droplets beneath the slick have a high bio-availability to marine organisms and the potential for causing acute toxic effects, (e.g. Neff[1] and McAuliffe[2]. WAF is a complex dynamic system of mono-aromatics (Benzene, Toluene, Ethylbenzene, Xylenes and C_3- and C_4-Benzenes), poly-aromatics (2 and 3 ring PAH's) and polar organic compounds (e.g. phenols and acids), and it changes composition over time due to weathering of the oil slick and dilution in the water column.

In the laboratory, the WAF solutions are prepared in closed, low-energy systems consisting of seawater with an oil film on top and a defined headspace. Different oil types, weathering degrees and oil/water ratios are used. Correct design of lab prepared WAF solutions may therefore represent "snapshots" in the dynamic process during a spill situation.

Data from this study will be used for improving algorithms in present fate and effect models, which again will be used as quantitative tools in future damage assessment studies and in "Net Environmental Benefit Analysis" of response alternatives in various spill scenarios.

2 Experimental

2.1 Preparation of Water Accommodated Fraction

Water Accommodated Fractions (WAF) are prepared from both fresh crude oils and weathered oil residues. The weathering of the oils include both evaporation and photolysis. Evaporation of the lighter compounds is obtained by topping the fresh crude according to a modified ASTM-D86/82 distillation (Stiver and Mackay[3]) to a vapour temperature of 150°C, 200°C or 250°C. This gives oil residues with an evaporative loss typically corresponding to respectively a ½ - 1 hour, ½ - 1 day and 2-5 days of weathering of an oil slick at sea (Daling et al.[4]). Photolysis of the oil is achieved by exposing the oil to artificial sunlight. The standardised laboratory weathering methodology is described in e.g. Daling et al.[5].

WAFs are prepared in closed, low energy mixing systems recently internationally adopted through the "CROSERF" forum (Chemical Response to Oil Spills – Ecological Effects Research Forum)[6]. The preparation system is outlined in Figure 1. Bottles of 2 or 5 litres are used.

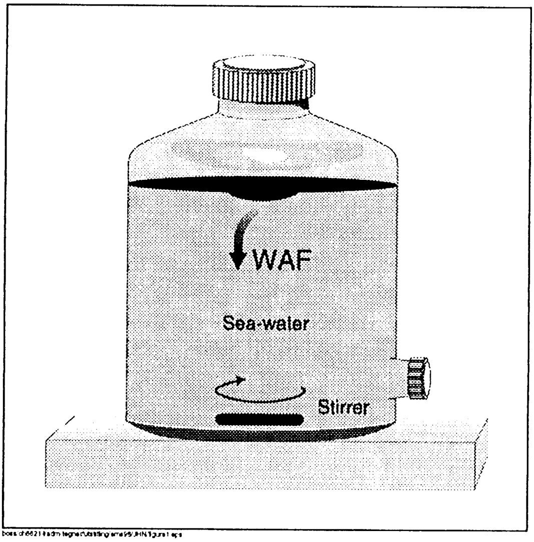

Figure 1: System for preparation of Water Accommodated Fraction (WAF)

A volume of filtered (0.2 μm) seawater giving a water/headspace volume ratio of ~1:4 is added to the bottles. The oil is carefully applied to the water surface. The water is stirred gently with a magnetic stirrer, allowing the oil film to rest on the water surface without creating a vortex and without dispersing any oil droplets into the water. Equilibrium between the oil and water phase is reached within 48 hours. The preparation of WAF is carried out at controlled temperature (climate room). Samples of the WAF are collected through a valve approximately 3 cm above the bottom of the bottle, allowing sampling without disturbing the oil/water interface. Samples for chemical analysis and toxicological testing are collected in glass vials with teflon lined caps, allowing no headspace in the vials. Samples for chemical analysis are acidified (pH<2) to avoid biodegradation.

The oil/water ratio have been varied between 1:40 (25 g /L seawater) and 1:10 000 (100 mg /L seawater). Generally, saturation of WAF is obtained at an oil/water ratio of 1:100 (10 g /L seawater) or higher (Daling and Johnsen[7]).

2.2 Chemical analysis

The oils and the prepared WAFs undergoes a detailed chemical characterisation:

- Quantification of ~40 volatile organic compounds (VOC, C_5-C_9, including benzene, toluene, ethylbenzene and xylenes - BTEX) by Purge and Trap Gas Chromatography – Mass Spectrometry (P&T GC-MS)
- Quantification of ~40 semivolatile compounds (> C_{10}) including polyaromatic hydrocarbons (PAH) and phenols analysed by selected ion monitoring (SIM) GC-MS
- Determination of total extractable organic compounds (TEOC) by Gas Chromatography with Flame Ionisation Detection (GC-FID).
- Relative content of saturates, aromatics, resins and asphaltenes (SARA) by Iatroscan thin layer chromatography (TLC) with FID.

2.3 Assessment of toxicity

Along with the detailed chemical characterisation, the acute toxicity of the WAF solutions is measured by a modified version of the Microtox® Acute Toxicity Test. The acute toxicity is expressed as EC50-values (EC50 is the effective concentration causing 50% effect). The modified method applies closed vials for the test solutions instead of open cuvettes as in the original protocol. This modification implies more controlled conditions for samples with a high content of volatile components. The Microtox testing is performed within the day of sampling of the WAF. The method is described in Johnsen et al.[8].

So far, only Microtox is used in the toxicity characterisation. The Microtox method has been chosen due to its sensitivity for oil WAF fractions, and because it is a rapid and easy test procedure that enables testing of a large number of samples compared to other standard toxicity tests. However, the project intends to use Microtox just as a screening method, forming the basis for selection of samples / WAF systems which should undergo a more thorough toxicological assessment. This will involve other test organisms as well as other test designs (e.g. dynamic systems).

3 Results / Discussion

The preliminary results have identified large variation in the composition and toxicity of WAF depending on the type of crude, oil loading rate and weathering degree (evaporative loss and photolysis) of the oils.

3.1 Effect of oil type

The oil composition of two different North Sea crude oils (Statfjord and Troll) and the composition of WAF generated from the two oils can be seen in Figure 2. The WAF from Statfjord fresh crude has a total concentration (28.1 ppm (mg/L seawater)) more than twice as high as the WAF from Troll fresh crude (12.9 ppm). The BTEX content of the Troll fresh crude WAF is also far lower than it is for the Statfjord WAF.

GC-MS analyses of the semivolatiles (> C_{10} compounds) in WAF from several oils have shown that naphtalenes and phenols are the dominating compounds. Higher PAH-components (3 rings and higher) contribute very little (~0.1% of the total) to the WAF.

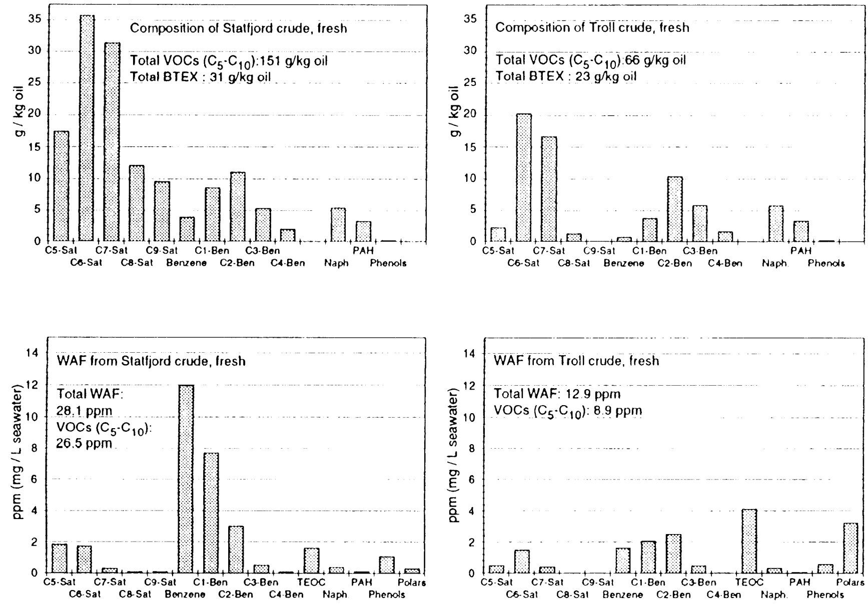

Figure 2: Chemical composition of parent oil and Water Accommodated Fractions (WAF) from two North Sea crudes, Fresh Statfjord crude and fresh Troll crude. Conditions for the WAF preparation: Oil/water ratio 1:40, Temperature: 13°C. The abbreviations used in the figure are listed in Table 1.

3.2 Effect of weathering (evaporative loss and photo-oxidation)

Figure 3 shows the total composition of WAF from different weathered residues of Troll crude. As the weathering degree increases, the most volatile components disappear due to evaporation and the heavier components (>C_{10}) remain. These are mainly polar components. As can be seen, the polar fraction increases significantly if the system is exposed to photolysis (obtained through artificial sunlight).

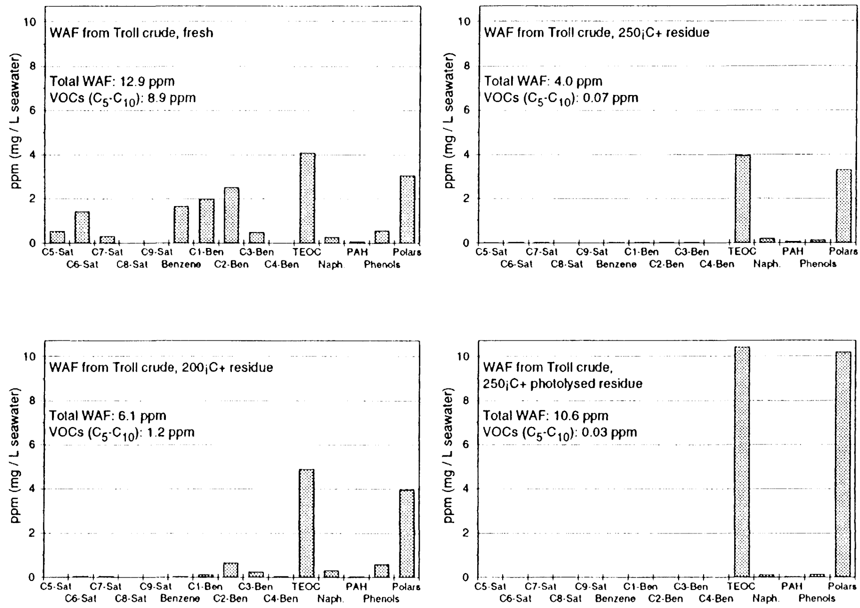

Figure 3: Chemical composition of Water Accommodated Fractions (WAF) from 4 different weathering degrees of Troll crude. Oil/water ratio 1:40. Temperature 13°C.
The abbreviations used in the figure are listed in Table 1.

3.3 Effect of oil loading rate

As shown in Figure 4, the WAF composition is influenced by oil loading rate. This is in accordance with observations done by e.g. Blenkinsopp[9].

WAF from systems with oil/water ratios from 25 g oil/ L sea water down to 10 mg oil/ L sea water have been analysed. The highest loading rates imply oil/water systems with excess of oil (i.e. saturated oil-water systems), while the lowest loading rates implies equilibrium between the oil and water phase. In the equilibrium systems a depletion of the most water soluble components will occur from the oil phase. The differences in relative chemical composition influence the toxicity of the WAF from systems with different oil loading. Therefore, in connection with toxicity testing it is essential that individual loading rates are prepared for each concentration of interest.

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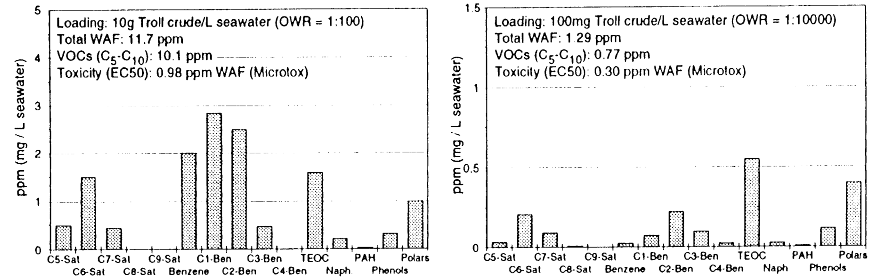

Figure 4: Chemical composition of Water Accommodated Fraction (WAF) from fresh Troll crude. – Effect of oil loading rate. The abbreviations used in the figure are listed in Table 1.

Table 1: Abbreviations used for groups / analytes in the diagrams in Figures 2-4.

Abbreviations	Group composition/ Analytes
C5-Sat	C5-Saturates: n-Pentane, Isopentane, Cyclopentane
C6-Sat	C6-Saturates: n-Hexane, 2-Methylpentane, 3-Methylpentane, Methylcyclopentane, Cyclohexane
C7-Sat	C7-Saturates: n-Heptane, 2-Methylhexane, 3-Methylhexane, 2,3-Dimethylpentane, Methylcyclohexane
C8-Sat	C8-Saturates: n-Octane
C9-Sat	C9-Saturates: n-Nonane
Benzene	Benzene
C1-Ben	C1-Benzene: Toluene
C2-Ben	C2-Benzenes: Ethylbenzene, *o,m,p*-Xylenes
C3-Ben	C3-Benzenes
C4-Ben	C4-Benzenes
TEOC	Total extractable organic compounds (C_{10} –C_{40})
Naph.	Naphtalenes; C_0-C_4 alkylated
PAH	Polyaromatic Hydrocarbons (2 rings or more)
Phenols	Phenols; C_0-C_4 alkylated
Polars	Polar components (C_{10} –C_{40})

3.4 Results from Microtox-assay

EC50 values obtained from Microtox testing of WAF from different weathering degrees of two different North Sea crudes are given in Table 2. The EC50 values are calculated from testing of a dilution series of 8 dilutions of the original WAF. The EC50 values are given both in % of the original WAF (original WAF = 100%), and in calculated absolute effect concentration – EC_{50} (ppm). A low EC50 implies high toxicity.

Microtox testing of WAF have so far indicated that – as expected – toxicity of the original (non-diluted) WAF is reduced with increased weathering degree of the oil. This is because of loss of volatile components (mainly BTEX) during weathering. However, what is more remarkable, is that for some oils (e.g. Statfjord), the EC50 with respect to total WAF concentration, EC50 (ppm), indicates that the WAF from the weathered oil is relatively more toxic than the WAF from the fresh oil. For example, even though the total concentration of the WAF from Statfjord 200°C+ residue is far lower (~3 ppm) than that from fresh Statfjord crude (~28 ppm), the EC50 (ppm) of the "200°C + WAF" is lower (EC50 ≈ 0.3 ppm), i.e. more toxic, than that of the "fresh WAF" (EC50 ≈ 2 ppm). This indicates that some of the heavier components that remain after weathering (e.g. polars) are rather potent toxicants.

Table 2: Results from Microtox testing of saturated WAF solutions. Oil/water ratio = 1:40 (25 g oil/L seawater).

WAF (oil type)	**Total VOC (C5-C10) (ppm)**	**Total WAF (ppm)**	**EC50 (% dilution)***	**EC50 (ppm)**
Statfjord crude, fresh	26.55	28.08	7.4	2.08
Statfjord, 200°C+ topped	1.61	3.07	9.2	0.28
Statfjord, 250°C+ topped	0.14	1.45	47	0.68
Statfjord 260°C+Photo (on water)	0.06	3.76	34	1.28
Troll crude (1994), fresh	8.86	12.95	8.3	1.08
Troll (1994), 200°C+ topped	1.18	6.06	32	1.94
Troll (1994), 250°C +topped	0.07	3.98	46	1.83
Troll (1994), 250°C +Photo (water)	0.03	10.61	47	4.99

*) Non-diluted WAF = 100%

Microtox testing of WAF solutions prepared in systems with different oil/water ratio (Table 3) indicate that toxicity decrease (EC 50 (%dilution) increase) as the oil/water ratio is lowered (due to lower total WAF-concentration). However, the relative toxicity with regard to concentration (EC50 (ppm)) increases at lower oil/water ratio. This is because of a change in the relative composition of WAF since relatively more of the larger and more toxic compounds go into solution at lower oil/water ratio.

Table 3: Results from Microtox testing of WAF solutions from fresh Troll crude.Different oil/water ratios

Oil / water ratio	Total VOC (C5-C10) (ppm)	Total WAF (ppm)	EC50 (% dilution)*	EC50 (ppm)
1 : 100 (10 g oil / L seawater)	10.08	11.71	8.4	0.98
1 : 1000 (1 g oil / L seawater)	5.87	6.73	12.9	0.87
1 : 10 000 (100 mg oil / L seawater)	0.77	1.29	23.2	0.30
1 : 100 000 (10mg oil / L seawater)	0.07	0.17	79.0	0.13

.*) Non-diluted WAF = 100%

4 Summary and further work

The preliminary results have identified large variation in the composition and toxicity of WAF depending on the type of crude, oil loading rate and weathering degree (evaporative loss and photolysis) of the oils.

Other oil types, for instance Mediterranean and Arctic crudes as well as condensates and refined products, will be taken in the next phase of this research program.

More effort will be put into the chemical characterisation of WAF from weathered oils, aiming at identification of those components causing the WAF from some weathered oils to be relatively (with respect to concentration) more toxic than the WAF from the fresh oil. Here the focus will be on the polar components (phenols and organic acids) in the area C_{10}- C_{20}.

Other approaches to toxicity testing will be included in order to evaluate whether the trends observed with Microtox are general and also observed with other test organisms (i.e. correlation studies between Microtox and other standard toxicity tests. Toxicological studies of selected WAFs in a flow-through system with relevant organisms in realistic, spiked exposure regimes will also be performed.

Data obtained from testing at realistic and controlled conditions are fundamental for reliable modelling of environmental effects, which again is necessary for good Net Environmental Benefit Analysis (NEBA) of spill scenarios and contingency planning around e.g. refineries, oil terminals and offshore installations.

5 Acknowledgements

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