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Qualification of oil-spill treatment products – Adopting the Baffled Flask Test for testing of dispersant efficacy in the UK

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ABSTRACT

The UK Marine Management Organisation (MMO) tasked the Centre for Environment, Fisheries & Aquaculture Science (Cefas) with reviewing the current UK dispersant efficacy testing procedures. The aim was to identify possibilities to increase standardisation, improve health and safety performance and explore harmonisation possibilities with international dispersant efficacy testing procedures. The US EPA 'Baffled Flask Test' (BFT) was adopted, implemented and validated as a new standard method in the UK. The outputs from this study suggest that dispersant efficacy results from the adopted BFT test and the currently used protocol are in a similar range and results presented by the US EPA.

As a result, the transition to the adopted BFT test will require minimal changes in the assessment of the results or reporting and increase harmonisation between tests used in the UK and North America.

1. Introduction

Oil spills can have disastrous effects on the marine environment (Pezeshki et al., 2000; Helle et al., 2016). Hazardous short-term consequences include toxic effects from the oil itself, reduction of light in the water column and therefore reduction of primary production from algae, as well as choking of local fauna such as marine mammals (Albers, 2003; NRC, 2003; Penela-Arenaz et al., 2009).

The use of dispersants can help in the mitigation of these acute effects by dispersing the oil through the water column, thereby breaking oil layers that have formed on the surface of the water close to the spill site (Brakstad et al., 2015). This effect can potentially increase the biodegradation rate of the spilled oil, reduces the risk of animals choking on the oil or starving due to low primary production (Hazen et al., 2010; Silva et al., 2015).

However, dispersants can be hazardous to the environment if they themselves have harmful ecotoxicological properties (Rahsepar et al., 2016). Furthermore, dispersants do not reduce the amount of oil entering the environment and can add to the toxic effects of the spill underwater since dispersants and dispersed oil under the surface can still be hazardous for marine life (Rahsepar et al., 2016). In consequence, the UK Marine and Coastal Access Act 2009 (Great Britain-Parliament, 2009) requires any substance to be licensed before it can be discharged into UK waters. Therefore, no dispersant can be used in the UK unless it has been approved by the appropriate UK authority, the Secretary of State for the Department for Environment, Food and Rural Affairs (Defra) for the use in English waters, the Scottish Executive for the use in Scottish waters, the Welsh Assembly Government for use in Welsh waters, or the Department of the Environment for Northern Ireland (DoE(NI)) for the use in Northern Irish waters. To be approved, a dispersant has to meet criteria regarding its efficacy (effectiveness) as well as toxicity.

The current UK method for testing the efficacy of oil dispersant products (LR448 Protocol, 1983) has been in use since the 1980s. The advantage of having been used for some time in the UK is that a historical dataset has been built up, meaning that new dispersants can be readily compared to those already tested. However, the use of the established methodology presents both practical and health & safety challenges. The assessment process involves the use of chemicals which are undesirable from a health and safety perspective, such as chloroform and kerosene (LR448 Protocol, 1983), in large, spinning glass apparatus and involves the use of specialist custom-built equipment which reduces the prospect of standardisation and comparability of testing across countries worldwide.

To increase standardisation, improve health & safety performance and explore harmonisation possibilities, the UK Marine Management Organisation (MMO) tasked the Centre for Environment, Fisheries & Aquaculture Science (Cefas) with reviewing the current UK

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dispersant efficacy testing procedures to ensure that, where possible, the methodology is current, in line with best scientific practice and offers better opportunities for global harmonisation of methods.

The resulting method for testing dispersant efficacy presented in this study, was adopted from the 'Baffled Flask Test' (BFT) method used by the United States Environmental Protection Agency (US EPA) for the determination of the efficacy of oil spill dispersants (Venosa et al., 2002; Holder et al., 2015).

1.1. Percentage of oil dispersed

The percentage of oil dispersed (%OD) by an oil spill dispersant is defined as the percentage of the test oil by weight which has been dispersed into the water phase under the conditions of the test.

1.2. Types of dispersant

Type 1: Conventional Hydrocarbon-base - for use primarily undiluted on beaches, but may also be used undiluted at sea from Warren Springs Laboratory (WSL) spray sets using breaker boards or other suitable means of application and agitation.
Type 2: Water-dilutable concentrates - for use at sea after dilution 1:10 with seawater, and sprayed from WSL spray sets using breaker boards or other suitable means of application and agitation.
Type 3: Concentrate - for use undiluted from aircraft, ships or on beaches, using appropriate spray gear.

2. Developing a new dispersant efficacy protocol for the UK

2.1. Objectives

The US EPA BFT method was chosen as a starting point for method development due to its wide application, robustness (Venosa et al., 2002; Holder et al., 2015) and procedural advantages compared to the LR448 protocol, currently used in the UK.

The BFT is a procedure used by the US EPA to test the efficacy of dispersants. A pre-mixed solution of crude oil and dispersant shaken for 10 min in a flask containing 100 ml artificial seawater followed by a settling time of 10 min. Subsequently, the dispersed oil mixture is extracted and measured in a spectrophotometer to determine the quantity of dispersed oil present in the water column (Venosa et al., 2002).

The identified main advantages of the BFT compared to the LR448 protocol were that (1) the test equipment is more standardised such that the testing can be readily compared between different laboratories. Using harmonised methods is an important step towards the co-ordination of techniques globally, increasing global expertise and leading to a better understanding of best practice. Furthermore, the use of standard laboratory equipment, apart from some specialist consumables, means that laboratories can run this testing on existing, commercially produced equipment that is easy to replace and update. (2) The BFT method provided the opportunity to eliminate the need to use some of the more hazardous chemicals, such as kerosene and chloroform, mentioned in the LR448 protocol thus improving overall health and safety standards. (3) Product mixing and subsequent chemical analysis could be conducted in a more controlled environment under the BFT procedure. (4) The design of the BFT test could allow for the simultaneous analysis of multiple samples, allowing not only for a potentially improved efficiency, but the capacity to more effectively undertake research into aspects of the test such as effects of mixing ratio, mixing speed, temperature, solvents used, etc.

The objectives for the presented project were to:

- Adopt and validate the US EPA BFT method, including any necessary amendments, to enable it to be considered as a standard method for dispersant efficacy assessment in the UK.
- Establish pass/fail criteria comparable with the standards of the current test procedure.
- Evaluate the comparability of tests results from the adopted and current method and establish "read-across" criteria for test results.

2.2. Method development

Testing was carried out using Kuwait crude oil (batch 04-08-11) as the standard test oil and Corexit EC9500B as a candidate dispersant at a dispersant:oil ratio (DOR) of 1:25 in 125 ml seawater taken from off Lowestoft, UK (settled and filtered at 20 µm prior to use).

The US EPA BFT (Venosa et al., 2002) was used as the basis of an alternative standard method, adapted to meet North Sea specific requirements and to increase the robustness of the method. The primary change compared to the US EPA method was the choice in standard test oil. The US EPA method uses two light and medium crude oils, Prudhoe Bay crude (PBC) and South Louisiana crude (SLC) commonly used in the US (Venosa et al., 2002). However, these oils are not routinely transported or used in the North Sea region.

Kuwait crude oil has been used as the standard oil for UK dispersant toxicity assessments, which made it an ideal candidate as standard test oil for the adopted method. The applicability of Kuwait crude as standardised test oil was assessed by testing (a) the dispersibility of the oil without added dispersant, (b) the % dispersibility of the oil at dispersant oil ratios (DOR) of 1:10, 1:20, 1:32, 1:50 and 1:100, and (c) the % dispersibility for three different dispersants with expected differences in dispersant efficacy based on historical results using the standard UK (LR448) protocol.

The results obtained were that:

a) Without dispersant the Kuwait Crude Oil dispersed < 3% in all 4 tests.
b) The percentage of dispersed oil correlated with the volume of dispersant added (Pearson r = 0.78).
c) The efficacy of different dispersants was discernible at all but the lowest (1:100) DOR; with differences in dispersibility of the tested dispersants between 8% and 25% (with an average of 13% ± 7.1%).

Based on these results it was concluded that Kuwait crude oil is suitable as a standard test oil for the adopted BFT.

Another change from the US EPA method consisted of an increase in the volume of both oil and dispersant to 400 µl oil and 12 µl dispersant, respectively. This increase in pipetting volume significantly increased the robustness of the test method compared to a test set-up with dispersant volumes below 5 µl, because the error in DOR due to pipetting losses is significantly reduced at higher pipetting volumes.

3. Final method

Following the changes and preliminary tests described above, the final method was defined as follows.

3.1. Equipment/apparatus

Modified trypsinizing flask: 150 ml glass trypsinizing flasks with a glass stopcock near the bottom.

Platform shaker: a platform shaker with a variable speed control unit (40–400 rpm) and an orbital diameter of approximately 0.75 in. (2 cm) to create rotational mixing in the test flask liquids.

Micropipettor: an Eppendorf Multipette plus was used, using positive displacement tips capable of dispensing 16 µl of dispersant and 400 µl of oil.

Far UV quartz (170–2700 nm) cuvettes/screw-cap cuvettes with 10 mm path length.

Glassware: glassware consisting of 25 and 100 ml volumetric flasks, 250 ml separating funnels with PTFE stopcocks, disposable glass