Development of Test Protocols for Effectiveness Testing and Working Mechanisms for Shoreline Cleaning Agents

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Abstract

The use of non-mechanical shoreline cleaning agents (SCAs) is a promising cleanup technique and strategy for oil contaminated shorelines. A large number and wide range of products are marketed worldwide, but the scientific documentation regarding the working mechanisms and effectiveness of these products is limited. No adequate standardized methods for studying SCAs and sorbent effectiveness on oil-contaminated shorelines have until now been available in Norway.

The main objective of this work was to develop test protocols for effectiveness quantification of SCAs (including shoreline washing agents [SWAs], shoreline dispersants [SDs] and biromediation agents) in order to obtain a better understanding of their working mechanisms and effectiveness in treating oil-contaminated shorelines. A suggestion for a stepwise test regime, considering the products ecotoxicology, dispersibility and effectiveness, will be recommended to the Norwegian Climate and Pollution Agency (Klif.no) and presented in this paper. This test regime will contribute to a better background for tactical use of these products in different spill scenarios. Recommended test protocols for ecotoxicity testing of SCAs will be discussed in a separate paper to AMOP (Hansen et al., 2009). Based on data from these studies, guidelines for effective use of these products will be recommended. The present paper includes test protocols and a stepwise test regime.

1 Introduction/Background

The petroleum industry has been in operation for nearly a half century off the Norwegian Coast. During this time period one major spill (Bravo 1977; 21.000 tons) and smaller accidental spills (in the range below thousand tons) have taken place. However, until now no oil from these offshore spills has reached the coastal area and become stranded on the shoreline. On the other hand, freighters have grounded in bad weather with release of several hundred tons of heavy bunker fuel oil (IFO 180/380). Typically the bunker fuel has been emulsified, dispersed and often spread over a relative large area before standing (hours), with relatively low recovery efficacy during the sea operation. The shoreline cleanup operations are in general performed over a very long time period (6 months) with rather low efficacy and generation of large quantities of waste materials. These observations and facts have engendered the need for development and implementation of new and more cost effective shoreline protection, cleanup techniques and strategies.

The need for a more cost-effective shoreline cleanup response contingency is even more important due to the expansion of the petroleum industry on the Norwegian continental shelf. This is directed towards exploration and development

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of oil fields closer to the coast and more vulnerable environmental areas while greater attention is paid to acute releases that can threaten coastal and shoreline areas. Gaining licence to operate, including accessing the new areas, largely depends on the oil companies' ability to meet authority requirements and to win the trust of stakeholders by operating in a responsible manner.

The need for development of oil spill contingency and response in the "new" areas is challenging for several reasons including: the remoteness of some locations, infrastructure and logistics, available personnel and equipment, daylight (polar nights/midnight sun), low temperatures, ice, health, safety and environmental aspects. One of the main strategies to meet the requirements for more cost effective shoreline cleanup and restoration techniques is through taking advantage of self-cleaning processes and stimulating these processes on the shorelines.

Several initiatives have been taken to close the gap in knowledge both from the industry and the authorities. One such initiative is the Coastal Oil Spills - Joint Industry Project (COS-JIP) established by Eni Norge AS, A/S Norske Shell, Det norske oljeselskap ASA and Statoil Petroleum AS, which aims to increase the efficiency of coastal and shoreline oil spill response operations. Emphasis in this program is on developing more efficient alternatives to the present mechanical based cleanup and restoration techniques and strategies. The first phase of this program focused on fate, behaviour and weathering of weathered oil on shoreline during the acute and restoration phase; the present second phase focuses on development of laboratory screening test methods for effectiveness quantification for *in-situ* shoreline treatment agents. The next and third phase will concentrate on algorithm development for weathering and decision support numerical models.

2 Non-mechanical *In-situ* Shoreline Cleanup Techniques

After an accidental release of oil into the marine environment the oil undergoes a number of weathering processes which affect its fate and behaviour. These include evaporation, emulsification, photo-oxidation, dissolution and dispersion. The weathering processes continue after stranding and, in addition, a number of other processes influence the oil properties including: effects of shoreline sediment, flora/fauna and physical exposure. Observations and documentation from numerous spill situations has shown that the nature itself is able to remove the contaminants from the shoreline through the sum of these processes as self-cleaning. This "phenomenon" will be utilized in the development of *in-situ* cleaning techniques or strategies through *e.g.* the supply of chemical agents, or through modification of the properties of the contaminated shoreline, in order to stimulate these processes. Examples of the main processes are agents which modify the properties of the oil (rheological or surface properties), and stimulation of microbiological activities. Also other oil weathering processes (e.g. photo-oxidation, oil fines interaction) can be stimulated, but until now not operationalized in large scale.

A very wide range of products that stimulate various processes are available for the responder, especially during cleanup operations. One of the main challenges for the responder is to compare the different products and their possible potential for contribution to cleanup and restoration of the oil polluted environment. The present Norwegian regulation gives only general criteria for toxicity determined by EC50 testing on the marine algae *Skeletonema costatum,* but nothing on test methods and criteria for effectiveness.

Another important aspect is the working mechanism of any product used for shoreline oil spill cleanup. Often the product is made up of a number of components. Each of the constituent parts could stimulate different processes which could make the effect of treatment unpredictable. It is therefore very important that the combination of toxicity and effectiveness test can be used to document the working mechanism of the product in a spill situation. The most "famous" example of this is the appearance of the so-called "white window" during the Exxon Valdez incident using INIPOL EAP22 (Bragg *et al*., 1992).

In the Coastal Oil Spills – Joint Industry Program (COS-JIP) phase 2 the objective was to develop effectiveness and toxicity testing methods and protocols for chemical shoreline cleaning agents including: shoreline dispersant, shoreline washing agents and bioremediation products. The test methodology and criteria for ecotoxicological assessment were evaluated. In addition, test protocols for sorbent effectiveness on oil shoreline substrates were developed but this is not included in this paper.

The different test protocols do not aim to optimize the effectiveness of the products, but rather select a combination of test parameters that allow the effectiveness of different products to be compared. The tests should also be robust and simple, allowing any laboratory to implement the testing protocol for international use and acceptance.

Different types of chemicals can be used to facilitate cleanup of oil contaminated shorelines. Chemicals used on oil-contaminated shorelines, in combination with washing or natural wave energy, will either be dispersed in the water column (Shoreline dispersants - SD) or washed out at the sea surface for containment and recovery (Shoreline washing agents – SWAs) (Figure 1).

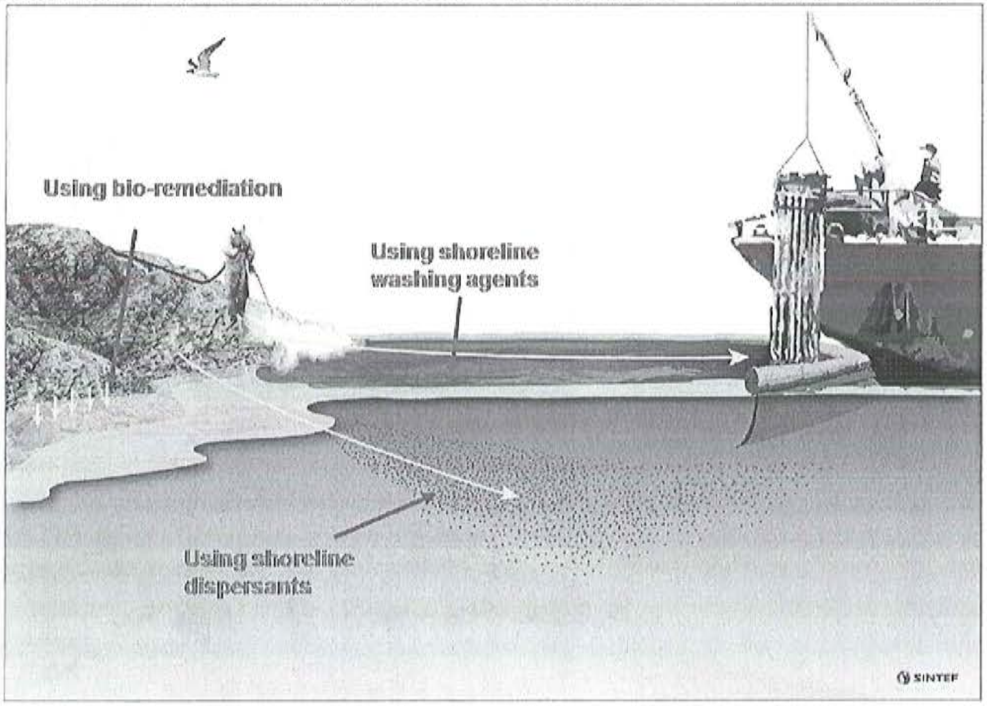

Figure 1 Shoreline Cleaning Agents and Their Working Mechanisms

The SWAs have low dispersible properties compared to the SD, making them a suitable agent group in low energy areas, where the oil properties in combination with the shoreline characteristics makes the shoreline impossible to self clean, and where washing or flooding is required. Experiences from recent oil spills (e.g. Full City, 2009 Norway) (Ramstad *et al.,* 2009) have shown that the effectiveness of the chemicals can be increased by *e.g.* repeated treatments, wetting of shoreline before application and rubbing with e.g. brooms. SD can also be used in combination with washing, but that requires a low sensitive shoreline and/or a minimum water exchange in the area.

Bioremediation involves use of products or measures that stimulate biodegradation of oil compounds by the indigenous microorganisms. A very large number of products are available to stimulate the biodegradation of oil and accelerate clean-up activities. In order for bioremediation products to be deemed successful enhanced oil metabolism must be noted over time after the product is applied when compared to non-treated controls. Standardized testing is therefore required to determine the effectiveness and toxicity of such products before they are widely applied in the environment.

3 Test Regime/Protocol

Protocols for toxicity and effectiveness testing from the present project have been used to propose a protocol for testing, documentation and evaluation of any products that aim to stimulate oil removal or restoration of an oil contaminated shoreline. The two main types of shoreline cleaning products are washing/dispersant agents and bioremediation agents, and a flow chart including the relevant tests are presented in Figures 2 and 3, respectively. The suggestions will the basis for updating the present Norwegian regulations by the Climate and Pollution Agency.

3.1 Protocol for Shoreline Washing/dispersing Agent Testing

The stepwise testing and documentation are shown in Figures 2 and 3.

- Toxicity testing: Testing all products as user-concentration by the marine marine algae *Skeletonema costatum* and the sediment reworker *Corophium volutator*. The EC/LC50 should be higher than 100ppm, as an absolute criterion. If LC/EC50 is between 10 and 100ppm the product could be tested as a shoreline dispersant. If EC/LC50 is below 10ppm the product should be diluted or rejected.
- Quantifying the dispersibility properties of products on weathered oil, for evaluation of working mechanism of the product. The standard Warren Spring Laboratory method has been modified to including premixing of agents and oil prior to testing. All products should be tested in two different concentration; AOR (Agent oil ratio) 1/5 and 1/25 representing use as shoreline washing agents and shoreline dispersant respectively. Products with high effectiveness at low dosage should be tested further as a shoreline dispersants (oil droplets into the water column without recovery), and products with low effectiveness at high dosage should be tested as shoreline washing agents (oil recovered at water surface). Products outside these criteria should be rejected as shoreline cleaning agents due to mixed working mechanisms.

- Bioremediation test. Testing the products as bioremediation agents should be considered if used on unconsolidated shoreline substrate. The products could affect the surface properties of the oil, which can increase the oil-water interface in subsurface sediment facilitating microbial oil biodegradation.
- Testing effectiveness as shoreline washing agent using the washing robot, using an AER (agent to oil-emulsion ratio) of 1/5. This represents a washing treatment process and recovery of released oil of the water surface. The effectiveness of products should be ranked according to their effectiveness under standard controlled conditions.
- Testing the effectiveness of dispersing product using the washing robot with an AER of 1/25 using standard test conditions. This represents a washing operation without recovery of mobilized oil. The effectiveness of products should be ranked according to their effectiveness.
- Testing the effectiveness of shoreline dispersants in the "simulated shoreline systems". This represents a scenario where oil is released into the water column due to natural wave action without recovery. The test is performed with an AER of 1/25 under standard test conditions.

The range of tests described above will give important and necessary information to the responder on which products that could be used and tested and documented with a relevant oil in case of an cleanup operation. It is however, important to keep in mind that the oil can behave differently under real treatment, *e.g.* different washing pressure and temperature, different wave exposure and different agent to oil ratios.

3.2 Protocol for Bioremediation Agent

A very large number of bioremediation products are produced and described in the literature. Their composition and working mechanisms varies over a very wide range and can affect a number of natural processes. The need for a thorough documentation on effectiveness and working mechanisms has been demonstrated through previous field studies and response operations (e.g. the "White window" after the Exxon Valdez incident). The protocol for testing bioremediation products in given in Figure 3 and includes the following steps.

- Documentation of composition of the product from the manufacture/distributor. If the product contains microorganisms, necessary documentation should be forwarded to governmental agencies for evaluation of the actual product used in the environment. The present regulation does not allow use of any gene modified organisms.
- Toxicity testing: Testing all products as user-concentration by the marine marine algae *Skeletonema costatum* and the sediment reworker *Corophium volutator*. Approval criteria have to be decided by the pollution authorities, and should reflect loading on the shoreline as with shoreline dispersants and washout agents.
- If the product meets the toxicity requirement, the effectiveness of the bioremediation agent has to be documented using the continuous flow sediment column. This test simulates the main natural processes in oil contaminated shoreline sediment. The effect of the product is quantified by

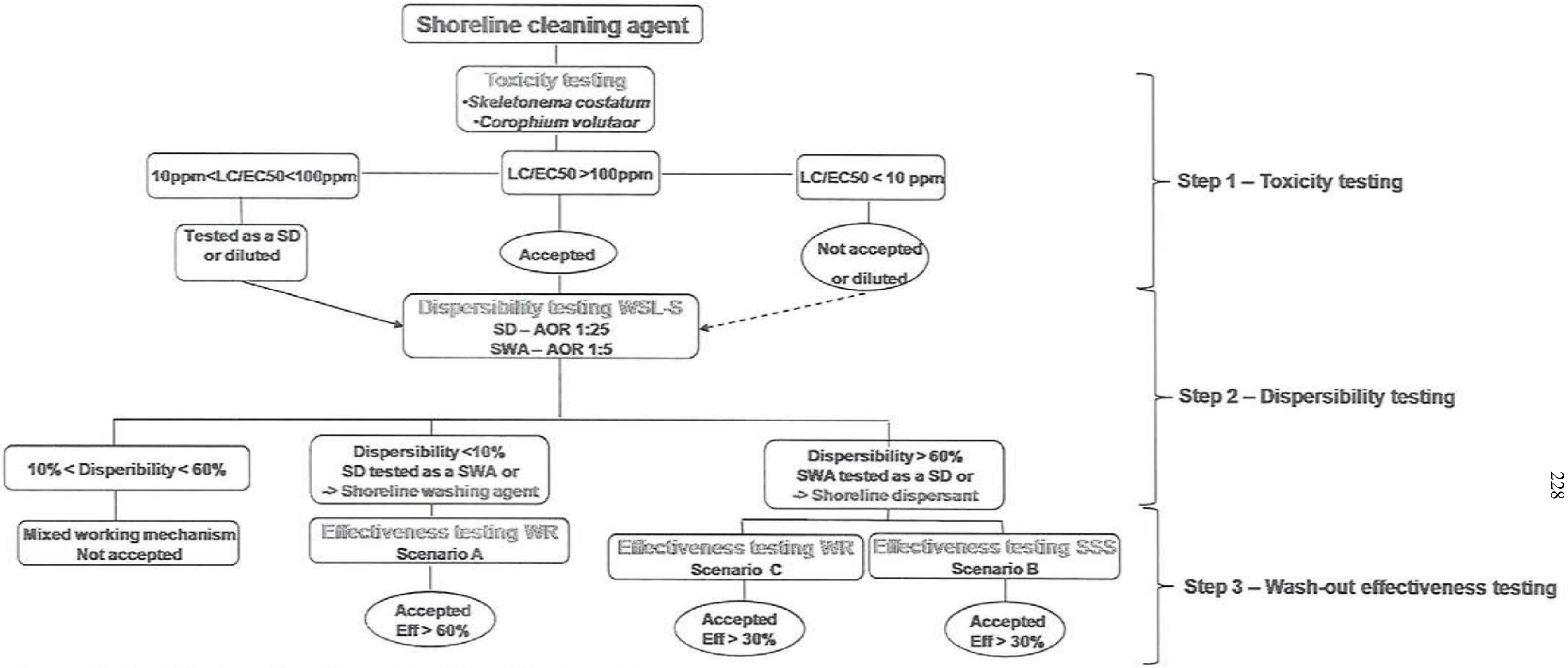

Figure 2 Test Protocol for Shoreline Cleaning Agents

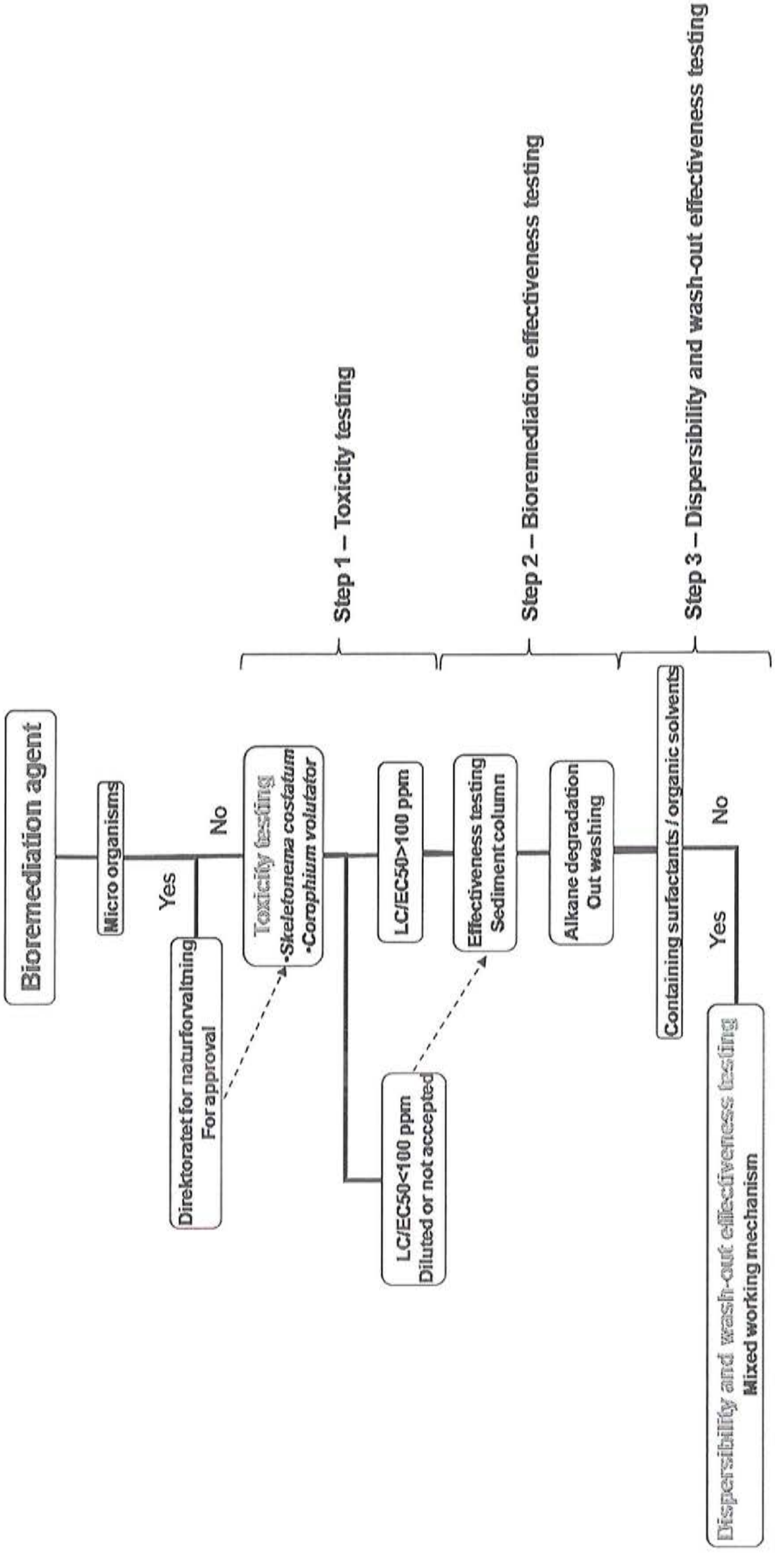

Figure 3 Test Protocol for Bioremediation Agents

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alkane degradation and oil remobilisation and is compared to a non-treatment reference system.

- If the bioremediation product contains surfactants or solvents different from water that can affect the properties of the oil, the product has to undergo the same test protocol as the shoreline dispersants and washout agents as described in Section 3.1.

4 Ecotoxicity Testing

The current regulations for approval of products used for shoreline cleaning in Norway involves ecotoxicity testing of the product using the marine algae test described in the ISO Guideline ISO 10253:2006 "Water quality - Marine algae growth inhibition test with *Skeletonema costatum* and *Phaeodactylum tricornutum*". For offshore use of dispersants the criterion for usage is that the *Skeletonema* test results should have an effect concentration (EC50) above 10 mg/L, whereas the criterion for onshore usage is 100 mg/L.

We have assessed ecotoxicity of nine products (water-based and solvent-based shoreline washing agents and dispersants) using four different species; *Skeletonema costatum* (marine algae), *Acartia tonsa, Calanus finmarchicus* (both pelagic copepods) and the sediment reworker *Corophium volutator* (Hansen *et al.*, 2009). When assessing the ecotoxicity of these nine potential SCA, a high degree of correlation was found in the results obtained through testing of three different pelagic species, including *S. costatum*. Based on that study, it was recommended that the *S. costatum* test should be kept as the standard ecotoxicity test for approval of SCA usage. In addition, because SCA will be used on-shore, and because ecotoxicity levels generated by using the sediment reworker test did not correlated well with the results from the pelagic tests, we recommended also including the *C. volutator* test for approval of SCA usage. The sediment reworker test, described in NS-EN ISO 16712:2005 “Water quality - Determination of acute toxicity of marine or estuarine sediment to amphipods”, is relevant for Norwegian coastal areas since it is a common species in these areas.

5 Dispersibility Testing of Shoreline Cleaning Agents

A test protocol has been elaborated to define the dispersibility and thereby their potential area of use. Dependent on the dispersibility results, the agents will either be defined as a SD or as a SWA. In this work, a test protocol using the Warren Spring Laboratory test – Shorelines (WSL-S), specially developed to study the dispersing properties of shoreline cleaning agents on weathered oil on shore has been elaborated.

5.1 Equipment – Warren Spring Laboratory Test – Shorelines (WSL-S)

The WSL-S test is a modified version of the standardized rotating flask WSL-test (Martinelli, 1984) which is designed to give indications of how well shoreline dispersants contribute to the dispersion of oil at sea. The WSL-S test is specially developed to test the dispersing properties of different shoreline cleaning agents on weathered oil that has been washed out at sea, after being stranded on shore. The experimental setup is shown in Figure 4.

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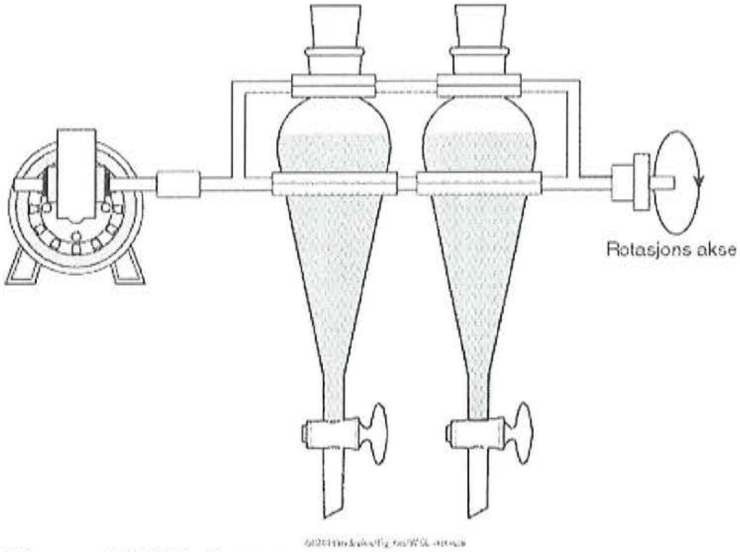

Figure 4 WSL-S Apparatus

The WSL-S test is performed under controlled conditions as e.g. energy and salinity at a test temperature of 10°C. Oil spiked with shoreline cleaning agent is added to the seawater surface in the separating funnels and conditioned for 2 minutes. The system is then rotated around its own axis with a velocity of 33 +/-1 rpm. After the rotation is stopped, a water sample is retrieved from the bottom of the funnel. Dispersed oil is then calculated by extracting the dispersed oil in the water sample with DCM, measuring it on a UV-spectrophotometer at 410 nm wave length, see pictures in Figure 5.

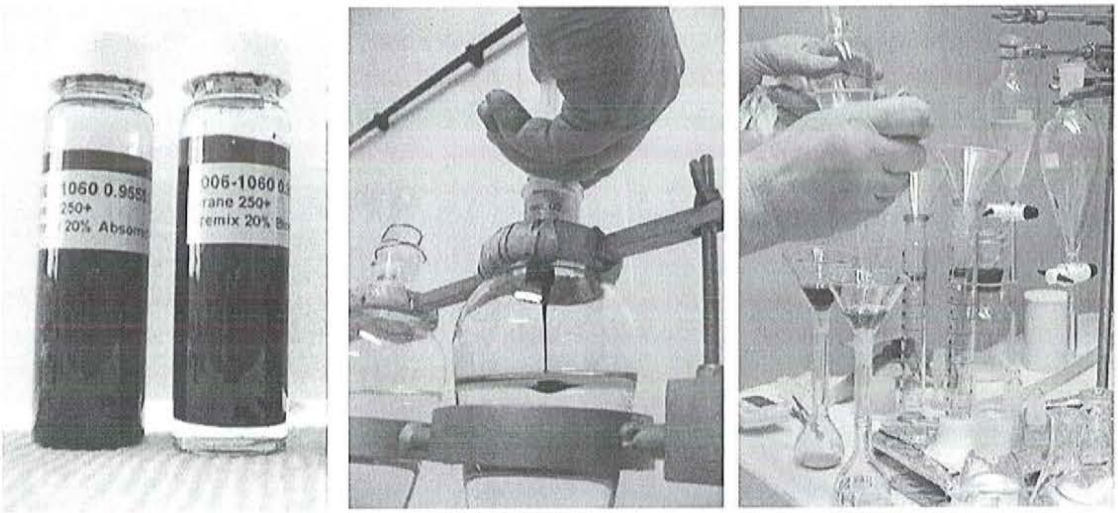

Figure 5 Dispersibility Testing of Oil Spiked with SCA using the WSL-S Test

5.2 Development of Test Parameters for the WSL-S Dispersibilty Test

To elaborate the test protocol for the dispersibility testing, several test parameters were tested; oil type, agent to oil ratio (AOR), rotating time and settling time. The main objective was to find a standard test oil, showing the width in the data set when testing different shoreline cleaning agents.

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Settling time

To find the optimal settling time, an asphaltenic crude oil, using one of the most promising shoreline dispersant at an AOR at 1:50, were tested at a settling time of 1 and 5 min. The results showed quite low dispersibility (<10%) for both settling times and was predicted to be even lower for bunker fuel oils. It was therefore decided to use a settling time of 1 min, which also is used as a standard in WSL procedures (Martinelli, 1984). In addition, it was decided to increase the AOR to 1:25 to obtain a greater dispersibility.

Rotating time

Using an AOR of 1:25 instead of 1:50 increased the dispersibility considerably (from <10% to about 80%), for both 2 and 5 min rotation time for the same asphaltenic crude oil. In contrast, tests performed using an IFO 180 bunker fuel oil showed a dispersibility of only 17-23%. Based on these results a rotating time of 2 min was decided to be used.

Agent testing and modifications of test parameters

One SD, one SB-SWA and one WB-SWA was used to study the potential range of the dataset for different agents, using. The results showed a low dispersibility, <3%, for both SWA on both test oils. Based on these results, it was decided to increase the AOR from 1:25 to 1:5 for the SWAs, resulting in a minor increase of dispersibility for the asphaltenic crude oil. Based on these results it was decided to use the asphaltenic crude as test oil for the dispersibility testing with an AOR of 1:5 for the SWAs and an AOR of 1:25 for the SDs. Dispersibility results for 3 selected WB-SWAs, 3 WB-SWAS and 3 SDs, using the standard test parameters elaborated, is given in Figure 6.

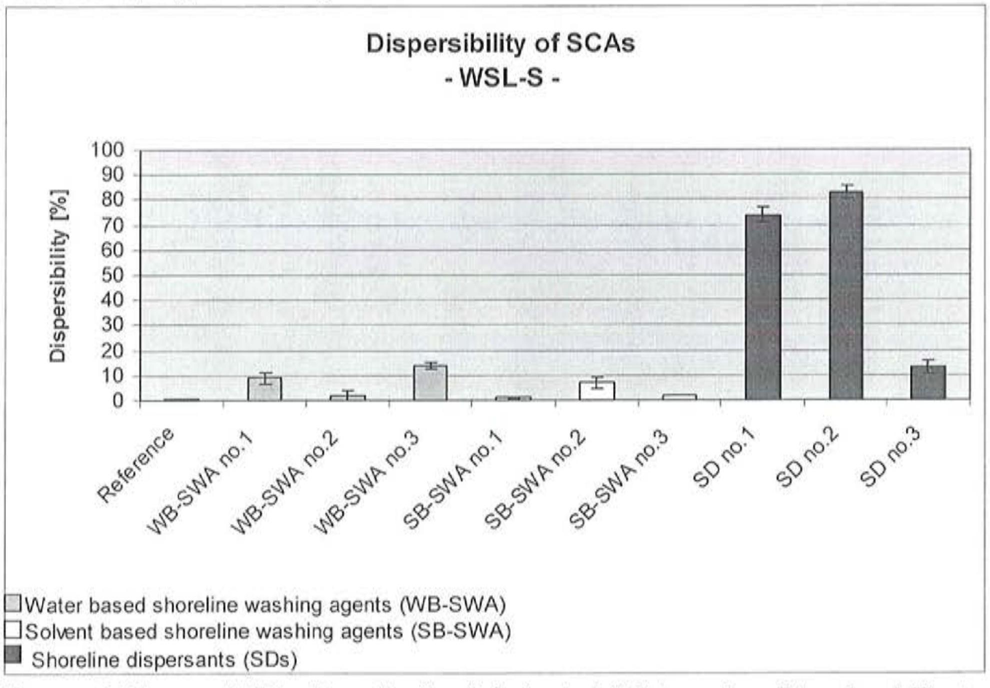

Figure 6 Dispersibility Results for 9 Selected SCAs using Standard Test Parameters; Asphalthenic crude 250°C+, AOR of 1:25 for SD and an AOR of 1:5 for SWA, 2 min rotation time and 1 min settling time at a test temperature at 10°C.

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The test protocol for disperibility testing of SCAs elaborated in this work were found to be both simple and efficient. The protocol showed a good range in data and repeatebility results, resulting in a good st.dev (<±4%). For the agents tested several times over a period of time, the test method also showed reproducibility. The test protocol was therefore found to be well suited for determing the working mechanisms for different SCAs.

5.3 Test Protocol for Dispersibility Testing of SCAs

Depending on the results from the toxicity testing, the water based SWA have to be diluted to match the criteria's set by the government. In Norway the criteria's for use of SWA are set to be $EC_{50} > 100$ mg/L.

Depending on the specifications from the fabricant, an agent to oil ratio (AOR) of 1:25 is recommended to be used for SD and an AOR of 1:5 for the SWA.

Test temperature: 10°C
Oil type: Asphalthic crude oil 250°C+ fraction
Equipment: Temperature controlled room, separating funnel, rotating device

Procedure - Performing the WSL-S test

1. Add 30 ml of heated oil (50°C) to 1:25 AOR (4% agent) or 1:5 AOR (20% agent) in a glass container for mixing. Shake the spiked oil for 2 min in room temperature. Let the mixture rest in room temperature until its acclimated (about 4 hours).
2. Add 250 ml acclimated sea water (10°C) to a 250 ml separating funnel placed in a temperature controlled room at test temperature.
3. Shake the mixture again for 2 min, before applying 5 ml to the water surface.
4. Let the mixture acclimate on the water surface for 2 min before starting the rotation. Let the apparatus rotate around its own axis with a velocity of 33 +/-1 rpm for 2 min, then let it settle for 1 min.
5. Retrieve a 50 ml sample for the funnel using a graded cylinder.

<u>Extraction of dispersed oil in water</u>

6. Add the sample to a 100 ml separating funnel.
7. Clean the graded cylinder with 10-20 mL DCM. Add the oil containing DCM to the separating funnel.
8. Shake the separating funnel for 2 min, let it then settle to separate the two phases (water and DCM) (minimum 5 min.) before retrieving the DCM phase.
9. Extract the DCM-phase through a funnel containing a dehydrating agent (Na2SO4) to remove water from the sample. Repeat the extracting procedure two times, but then only by using 10 ml DCM.
10. Shake the sample from side to side ten times to get it homogenized.
11. Find the oil concentration by using a UV spectrophotometer at a wave length of 410 nm.

If the dispersibility of the SWA is >60%, the SWA should be tested as a shoreline dispersant at an AOR of 1:25.

6 Wash-out Effectiveness Testing of Shoreline Dispersant (SD) on Oil-contaminated Bedrock using the Simulated Shoreline System

It is suggested that wash-out effectiveness (removal of oil by simulated wave action) testing of SD on oil contaminated bedrock in combination natural wave exposure is performed using a simulated shoreline system (SSS). In this work, test protocols for effectiveness testing of SD, has been elaborated.

6.1 Equipment – The Simulated Shoreline System (SSS)

The "Shoreline Simlulation System" was designed to simulate the natural environment wave exposure, representing a low to moderate wave energy level. The Shoreline Simulation System was constructed based on a similar system developed at Cedre in Brest (Jezequel *et al.*, 1999) and is in this work used to study the natural wash-out effectiveness of different shoreline cleaning agents on weathered oil.

The system contains 24 reservoirs, distributed over 2 identical experimental systems. Seawater is added to each of the reservoirs for water exposure, covering the tile totally at the incoming wave, leaving the tile free of water at the maximum outgoing wave. The water is temperated before exposure to the shale tiles. The construction of the Shoreline Simulation System is shown in Figure 7.

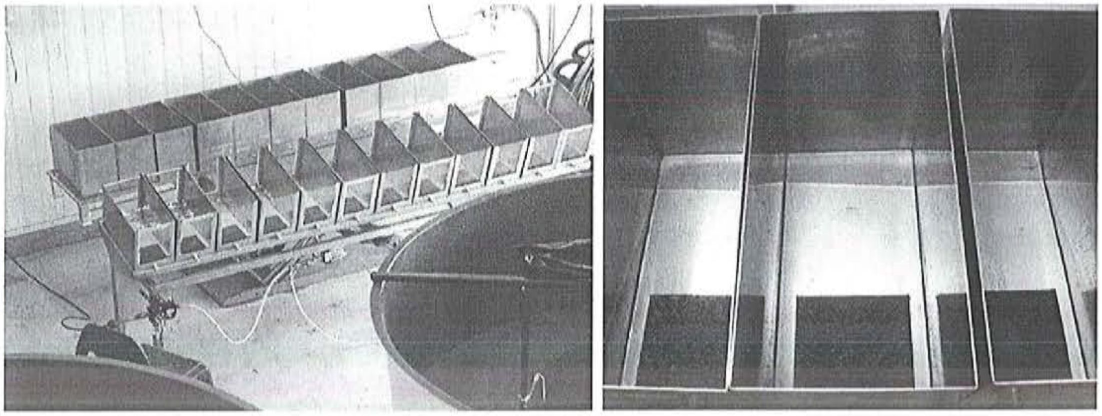

Figure 7 Simulated Shoreline Systems (SSS)

The SSS test is performed at a test temperature of 10°C. Weathered oil (evaporated and emulsified crude oil 22.50g +/-0.25g) is applied to shale tiles (15x15 cm) and stored horizontally in a temperature controlled room at test temperature for 24 hours. Agent is added using a vaporizer or a pipette depending on the viscosity. The agent is allowed to soak before the tiles are transfered to the shoreline simulation system. The shale tiles are exposed for wave energy using a standard oscillating interval program. After the treatment, the remained oil is quantified gravimetrically and/or analysed spectrophotometeric (410 nm) after extracting the sample in dichloromethane (DCM).

6.2 Test Parameters for the Dispersion Effectiveness Test

To elaborate the test protocol for the wash-out effectiveness test using the simulated shoreline system, several parameters was tested; oil type, exposure conditions and soak time. The main objective was to find a standard test oil showing the width in the data set when testing different shoreline cleaning agents. Based on the knowledge that dispersants at sea usually are applied with an AER of 1:25 to 1:50, an AER of 1:25 was used.

Wave energy – water load

An IFO 380 bunker fuel oil was tested at 3 different exposure conditions in the SSS system; 1, 2 and 4 litres, using a SB-SWA. The results showed little effect using this agent at different water loads, only 2-4 % effectiveness. Based on this knowledge, it was decided to use a water load of 2 litres, providing the greatest exposure conditions. It was also decided to study a bunker fuel oil having a lower pour point (15°C versus 3°C), probably showing higher washout effectiveness.

Oil type and soak time

The bunker fuel having the lower pour point showed very limited washout of oil in the SSS system. Due to the small change in washout effectiveness, a soak time of 20 min was decided used. The limited washout effectiveness observed was considered to be due to the high viscosity of the oil. Bunker fuel oil was considered unsuitable as test oil.

Weathered emulsion of one paraffinic, one napthenic, one waxy and one asphaltenic crude oil were evaluated as possible standard test oils in the SSS. The asphaltenic crude oil was more resistant to washout. The asphaltenic crude oil showed both a good range in data (reference vs. use of agent) and sufficient effectiveness level and thereby best suited as a standard test oil.

Exposure period

Exposure period in the range of 15-120 minutes was tested in the SSS system to find the optimal exposure period for the asphaltenic crude oil. The optimal exposure period were found to be 30 min, which was in accordance with the Server oil study (Carlsen and Ramstad, 2007), showing a good range in data.

Effectiveness results for 3 selected WB-SWAs, 3 WB-SWAS and 3 SDs, using the standard test parameters elaborated for the simulated shoreline system is given Figure 8.

Considering the SWAs low effectiveness, only SDs is recommended to be used in combination with natural wash-out energy. The test protocol for natural wash-out effectiveness testing using the SSS in combination with SDs elaborated in this work, were found to be both simple and efficient. Based on the results, the protocol showed a good reroducibility, resulting in an acceptable standard deviation (<5%) and a moderate range in data between different agents. The test protocol is well suited for determing effectiveness for different agents in combination with washout due to natural wave energy.

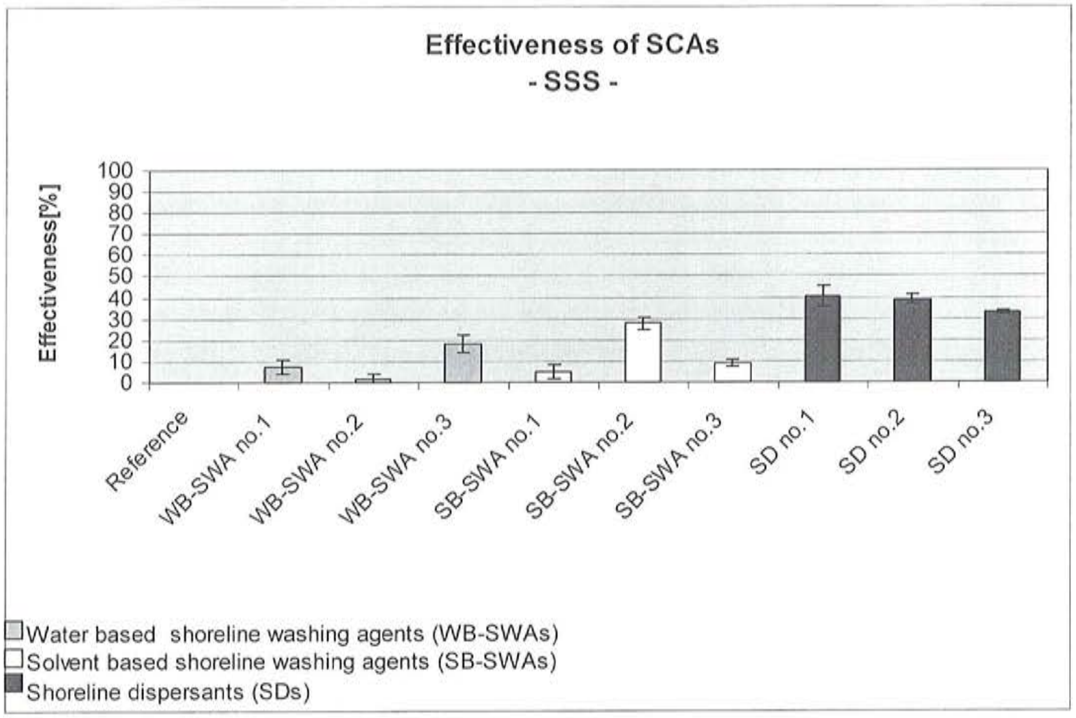

Figure 8 Effectiveness Results for 9 Selected SCAs using Standard Test Parameters for the Simulated Shoreline System (SSS); Asphaltheinic crude 250°C+, 40% emulsion, AER of 1:25 for SD and an AER of 1:5 for SWA, 2 liters water load, 20 min agent soak time and an exposure period of 30 min at a test temperature at 10°C.

6.3 Test Protocol for Wash-out Effectiveness Testing of SDs using the SSS

The agents showing a dispersibility > 60%, hence the SDs are recommended to be tested in the simulated shoreline system and should be tested at an agent to emulsion ratio (AER) of 1:25.

Test temperature: 10°C
Oil type: Asphalthenic crude 250°C+, 50% w/o- emulsion
Equipment: Temperature controlled room, simulated shoreline basin; tilting angle; 8 and 16° at a 4.70 sec. and 0.75 sec. interval, shale tiles (15x15 cm).

Procedure - Performing the SSS effectiveness test

1. Number, weigh and acclimate the shale tiles to test temperature
2. Add 22.50 +- 0.5 g weathered oil to the shale tiles.
3. Set the shale tiles applied the weathered oil for conditioning for 24 h at test temperature.
4. Weigh the shale tiles covered with weathered oil again to find the emulsion loss during the conditioning.
5. Add acclimated SDs (10°C) at a 1:25 AER and let it soak for 20 min.
6. Expose the polluted shale tiles to wave exposure at the given test settings.
7. Weigh the shale tiles containing the left over emulsions to calculate the effectiveness of the exposure process.

8. The effectiveness is calculated either by quantifying the shale tiles containing the left over emulsions gravimetrically and/or by analyses in a UV-spectrophotometer at a wave length of 410 nm extracting the sample in dichloromethane (DCM).

7 Washing Effectiveness Testing of Shoreline Cleaning Agents

It is suggested that washing effectiveness quantification of SCAs on oil contaminated bedrock, is performed using a washing robot (WR). Test protocols, using the WR for effectiveness testing of SCAs, have been elaborated. Experiences gained from the Previous laboratory testing (Carlsen and Ramstad, 2007) project were used as a basis for the WR method.

7.1 Equipment – The Washing Robot

The "Washing robot" was developed in close cooperation between Cedre in France and SINTEF, and was designed for simulating washing as a countermeasure for the removal of oil from bedrock (Jezequel, 2009). SINTEF and Cedre have over the last years used the washing robot to study the effectiveness of different shoreline cleaning agents. The construction of the washing robot is shown in Figure 9.

Figure 9 Washing Robot (WR)

The effectiveness test, using the WR, is performed at a test temperature of 10°C. Weathered oil (10.00g +/-0.25g) is applied to shale tiles measuring 10x10 cm and stored horizontally in a temperature controlled room at test temperature for 24 hours. Shoreline cleaning agent is then added using a vaporizer or a pipette depending on the viscosity. The agent is then allowed to soak for some time before the tiles are mounted on a test rack and placed in the robot. The shale tiles are exposed for washing only for a few seconds, following a standard movement already set in the robot program. After the treatment, the remained oil are quantified gravimetrically and/or analysed in a UV-spectrophotometer at a wave length of 410 nm extracting the sample in dichloromethane (DCM).

7.2 Development of Test Parameters for the WR Effectiveness Test

To elaborate the test protocol for the effectiveness testing using the washing robot, two test parameters was tested; oil type, and washing pressure. The main objective was to find an oil to be used as standard test oil. It was important that the oils chosen could show the span in the data set when testing different shoreline cleaning agents. Based on the knowledge that dispersants at sea usually are applied with an AER of 1:25 to 1:50, an AER of 1:25 was first used.

Oil type and washing pressure

Two different IFO 380 bunker fuel oil was tested in combination with a SB-SWA, representing oils having both high and low pour points (15°C and 3°C). The bunker fuel having the lower pour point showed greatest potential and was tested at a range of washing pressures, 14, 30 and 60 bar. The results showed quite low washout effectiveness, from approx. 0-40% effectiveness, and were not being able to show the potential of the SCA tested. The IFO 380 bunker fuel oils were therefore considered unsuitable due to the low washout effectiveness.

Considering results from similar tests elaborated for Server IFO 180 (Carlsen and Ramstad, 2007), it was decided to test an oil having a lower viscosity, an IFO 180 bunker fuel oil. The results showed a good range between the reference and the treated tiles and sufficient washout effectiveness (60%), using a water pressure of 14 bar. The IFO 180 was therefore considered suitable as a standard oil for effectiveness testing of shoreline cleaning agents in the WR system.

Effectiveness results for 3 selected WB-SWA, 3 WB-SWA and 3 SD, using the standard test parameters elaborated for the washing robot is given Figure 10.

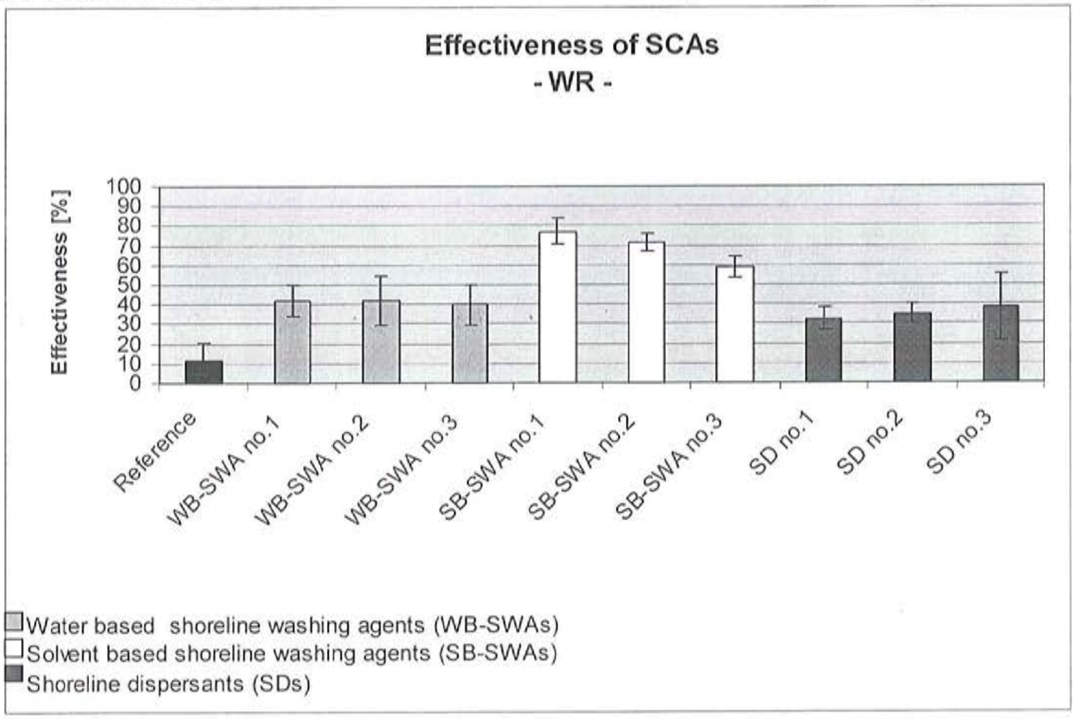

Figure 10 Effectiveness results for 9 selected SCAs using standard test parameters for the simulated shoreline system (SSS); Vysotsk IFO 180, 40% emulsion, AER of 1:25 for SDs and an AER of 1:5 for SWAs, 20 min agent soak time and a washing pressure of 14 bar at a test temperature at 10°C.

Ramstad, S., B.H. Hansen, P.S. Daling, M. Frenzel, J.H.C. Øksenvåg, and F.-X. Merlin, Development of Test Protocols for Effectiveness Testing and Working Mechanisms for Shoreline Cleaning Agents, Proceedings of the Thirty-third AMOP Technical Seminar on Environmental Contamination and Response, Environment Canada, Ottawa, ON, pp. 223-244, 2010.

The test protocol for effectiveness testing using the WR in combination with SCAs elaborated in this work, were found to be both simple and efficient. Based on the results in this work, the protocol showed a moderate repeatebility, giving a standard deviation of <(8 % (average for the agents tested using 3 parallells) and a good range in data between different SCA. For the agents tested several times over a period of time, the test method also showed good reproducibility. The test protocol is therefore found to be well suited for determing effectiveness for different SCAs in combination with washing as a countermeasure.

7.3 Protocol for Effectiveness Testing of SCA using the Washing Robot

Dependent on the results from the dispersability test, the effectiveness test using the washing robot will be used applying an:

- AER of 1:5 for the agents showing a potential as a shoreline washing agent - dispersibility < 10%
- AER of 1:25 for the agents showing a potential as a shoreline dispersant - dispersibility > 60%

Test temperature: 10°C
Oil type: IFO 180, 40% w/o- emulsion
Equipment: Temperature controlled room, washing robot (1.5mm opening, 25^o angle and 33 cm distance at 14 bar pressure), shale tiles (10*10 cm)

Procedure - Performing the WR effectiveness test:

1. Number, weigh and acclimate the shale tiles to test temperature
2. Add 10.00 +- 0.50 g weathered oil to the shale tiles.
3. Set the shale tiles added the weathered oil for conditioning for 24 h at test temperature.
4. Weigh the shale tiles covered with weathered oil again to find the emulsion loss.
5. Add acclimated (10°C) SCA and let it soak for 20 min.
6. Expose the polluted shale tiles to washout at the given test settings.
9. The effectiveness is calculated either by quantifying the shale tiles containing the left over emulsions gravimetrically and/or by analyses in a UV-spectrophotometer at a wave length of 410 nm extracting the sample in dichloromethane (DCM).

8 Bioremediation Agent Effectiveness

Both the U.K. and U.S. regulation includes standard bioremediation product test procedures that incorporate a shake flask system. The U.K. system, as described by Swannell *et al.*, (1997), is based on determining the extent of oil biodegradation in Erlenmeyer flasks treated with the product, compared to untreated controls. Products are tested on a standard inoculum of oil-degrading bacteria; *Micrococcus luteus* NCIMB 13267, *Pseudomonas fluorescens* NCIMB 9046, *Pseudomonas putida* NCIMB 9571, *Pseudomonas nautical*, and *Alteromonas* sp.; a standard amount of 250°C+ Forties crude oil; and a standard amount of nutrient. A positive control is included to ensure that the system is operating. If evidence of enhanced metabolism is observed in the flask experiments then the product is tested further in microcosm tests. A products is deemed to pass if it significantly enhances oil biodegradation above that of untreated controls ($p<0.05$).

In contrast, the U.S. test system is based on the premise that oil degrading microorganisms naturally present in seawater can biodegrade a large portion of crude oil within 28 days when supplemented with simple nutrients (National Environmental Technology Applications Corporation, 1993). In order for a bioremediation product to be considered effective it must demonstrate statistically greater biodegradation of the oil compared to a control of natural seawater supplemented with simple mineral nutrients. The difference must be statistically significant for both alkanes and aromatics as measured by GC-MS. The U.S. test system does not include microcosm and field monitoring studies, due to the costs involved in running such tests.

Herein a sediment column system has been recommended for testing the efficacy of bioremediation agents. The test includes plexiglas columns filled with sediment, the upper 10 cm of which is mixed with oil to simulate an oiled shoreline. Seawater is pumped into and out of the columns from the bottom, simulating tidal variation. Bioremediation products may be mixed with the oiled sediment for applied to the surface, mimicking real-world application. No bacterial inoculum is added to the system, the naturally-occurring bacteria within the seawater are used to biodegrade the oil. The extent of oil biodegradation can be ascertained at time points of interest by sampling the sediment from the column and extracting the oil using a standard solvent extraction. It is also possible to study effects at different depths using such a system.

In comparison with an alternative flask system it was found that the column system gave consistently reproducible results between experiments. This was not observed in the flask system, where the efficacy of products was not consistent between tests.

The column system requires a longer period of testing and incurs a greater cost than a flask system; however, due to the constant influx and efflux of seawater in the columns this system is more realistic. This constant mixing also overcomes any problems that may result from heterogeneous bacterial populations within a flask system. We therefore recommend the use of the column system in investigating the effectiveness of bioremediation agents.

8.1 Equipment

8.1.1 Column Design

The columns have a length of 70 cm and an inner diameter of 10 cm; they are made of plexiglas for observation of oil behaviour. To prevent sediment infiltrating into the pipes, two filters with different mesh size are placed in the bottom of each column. The system consists of 16 columns, where a series of 4 columns are operated individually. A reservoir with temperate seawater is connected to the column system and the in- and output of seawater is placed at the bottom of the columns for tidal simulation (Figure 11). A computer program is used to simulate the tidal variation by controlling the number of tidal period and cycles. The water fluctuation takes the form of a sine curve, which is similar to natural tidal cycles.

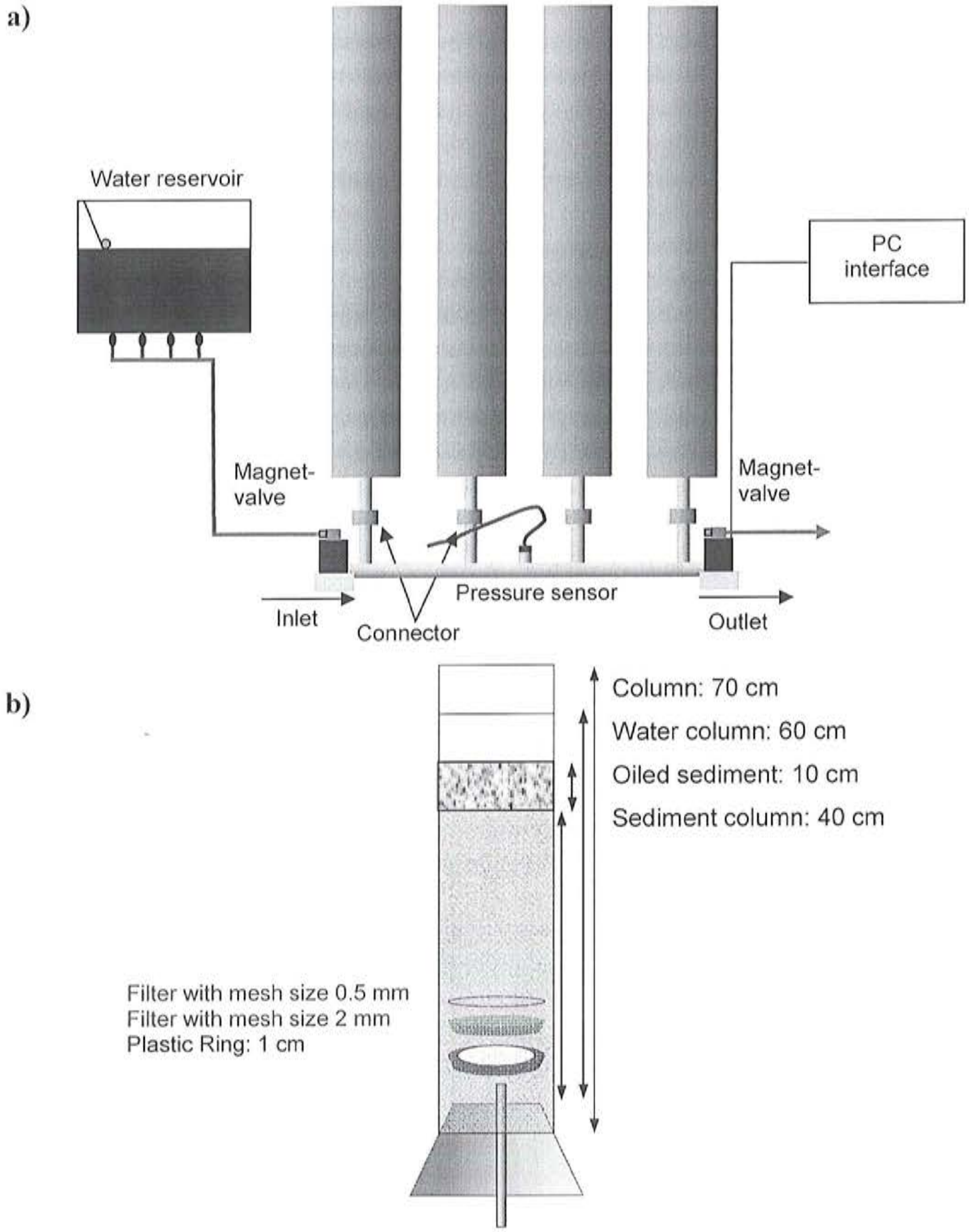

Figure 11 a) The column system setup used. b) Overview of a single sediment column indicating the size of the column itself, enclosed sediment column and water column. Filter sizes are also shown.

8.2 Test Parameters

In order to examine the performance of the column system under different conditions several test parameters were examined: product dose, repeat applications of product and duration of test.

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Product dose

Product doses of 10-, 20- and 40 g were mixed with the oiled surface layer of sediment. Application of increased amounts of product did appear to be more effective than lower doses; however, doubling the amount of product added did not double the amount of oil biodegraded. The system was able to provide data for different product dose regimes, covering the application guidelines of each product.

Repeat applications of product

Repeated applications of product were also examined using the column system; it was found the re-application of the product did result in greater biodegradation of the oil, and that product re-application did not interfere with the test. The ability to re-apply product in the test system is required when testing products that require repeated use to be effective.

Duration of test

Test durations of one, two and three weeks were tested. Differences in the amount of oil biodegraded could be observed after one week's incubation, though best results were obtained after two weeks. Bioremediation is a long-term strategy is it informative to be able to run the column system for longer periods.

Biodegradation results for products after, one-, two-, and three weeks, at different doses and after re-application are shown in Figure 13.

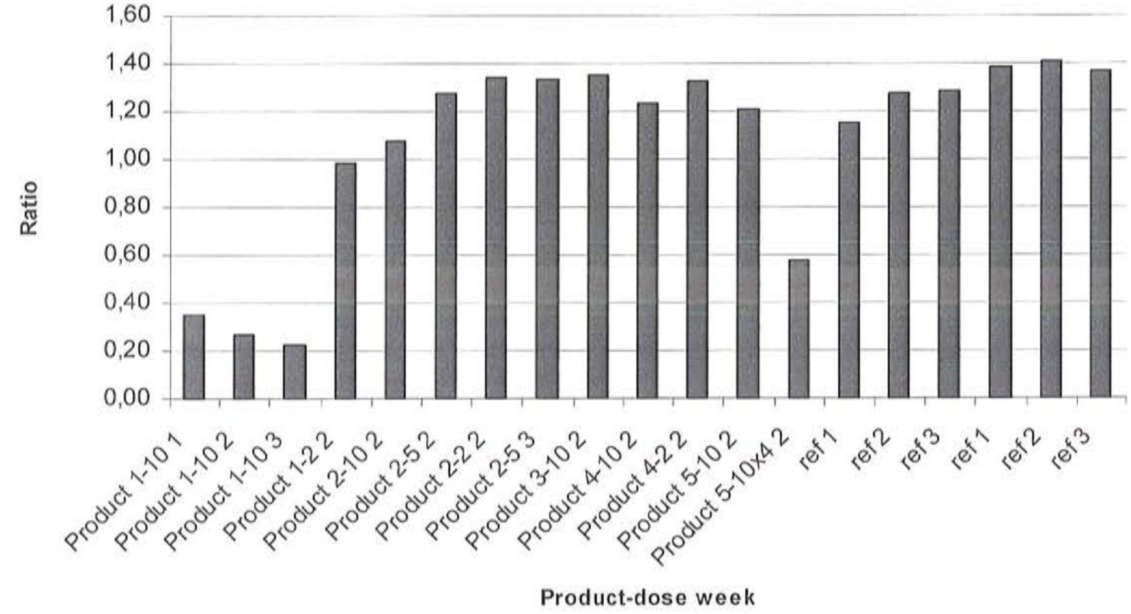

Figure 13 Ratios of n-C_{18}/phytane in the remaining oil extracted from the column system after different treatment regimes. The treatments are labelled in the format product-dose week: Product 1-10 1 therefore refers to incubation with 10 g of Product 1 sampled after one week's incubation; ref = reference column (no treatment).

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The column system requires a longer period of testing and incurs a greater cost than a flask system; however, due to the constant influx and efflux of seawater in the columns this system is more realistic. This constant mixing also overcomes any problems that may result from a heterogeneous bacterial population within a flask system. If required this system also allows sampling at different depths within the sediment column to investigate the biodegradation and loss of stranded oil below the sediment surface.

8.3 Protocol for Effectiveness Testing of Bioremediation Products

Test temperature: 13°C
Oil type: Paraffinic oil evaporated 250°C+ fraction
Equipment: Temperature controlled room, pre-washed sediment (2–6 mm), Plexiglas columns and rig.

1. The sediment columns are established in a temperature-controlled room at 13 °C.
2. Each column is packed with clean, pre-washed sediment (2–6 mm) to a height of 40 cm.
3. A further 20 L of sediment (2–6 mm, washed) is mixed with 200 mL of the test oil in a cement mixer (1 minute, 20°C). This may be stored at the test temperature until required.
4. 750 mL of the oil-contaminated sediment is mixed with the bioremediation agent under investigation (10 g) for one minute.
5. The sediment/oil/agent mixture is then transferred to the top of the clean sediment in the column to give a layer approximately 10 cm thick.
6. The seawater supply is started and exchanged 3 hours after mixing, with a tidal period of 3 hours.
7. The test is run for a period of 14 days, with daily inspection and observation of the columns.
8. At sampling times the sediment is removed from the column using a hydraulic jack to push the sediment from the bottom of the column. Samples are taken as 2 cm sections using a solvent-washed spatula.
9. Extraction of oil fraction is by standard methods, and composition determined by GC-FID analysis. Oil quantification; Spectroscopic 410 nm
10. Biodegradation is evaluated by comparison of *n*-C17/pristine and *n*-C18/phytane ratios and TOC with unfertilized columns operated under identical conditions.

GC-FID Analysis

The GC-FID analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph fitted with a flame ionization detector. The column was a HP-5 fused silica capillary column (30 m x 0.25 mm internal diameter [i.d.] x 0.25 mm film thickness). The carrier gas was hydrogen at a constant flow of 2.0 ml/min and the make-up gas was helium at a constant flow of 30 ml/min. A 1.0-ml sample was injected into a 275°C splitless injector. The oven temperature was programmed from 40°C (held 5 min) to 310°C at 6°C/min and held for 10 min. The flame ionization detector was operated at a temperature of 325°C and supplied with air (360 ml/min) and hydrogen (30 ml/min). Data and chromatograms were monitored and recorded by ChemStation software (Agilent Technologies).

9 Acknowledgements

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10 References

Bragg, J.R, R.C. Prince, J.B. Wilkinson and R.M. Atlas, "Bioremediation for Shoreline Cleanup Following the 1989 Alaska Oil Spill", Exxon Company, USA, Houston TX, 1992.

Carlsen, J.H. and S. Ramstad, *Screening Laboratory Testing of Shorline Cleaning Agents,* Coastal Oil Spill JIP, 2007.

Hansen, B.H., D. Altin, K. Bonaunet, and O.G. Brakstad, *C13 – Ecotoxicity Testing of Shoreline Cleaning Agents (SCA) used for Treatment of Oil Spills on Shore,* Coastal Oil Spills JIP, 2009.

Jezequel, R., F.X. Merlin and K. Lee, *The Influence of Microorganisms on Oil-Mineral Fine Interactions in Low Energy Coastal Environment*, 1999.

Jezequel, R., J. Lebastard and F.X. Merlin, *Influence of Weathering of Heavy Fuel Oil on High Pressure Washing Efficiency With and Without Cleaning Agent,* 2009.

Martinelli, F.N., *The Status of the Warren Spring Laboratory`s Rolling Flask Test*, Allen, T.E., Oil Spill Chemical Dispersants - Research, Experience, and Recommendations, pp. 55-68, 1984.

National Environmental Technology Applications Corporation, *Oil Spill Bioremediation Products Testing Protocol Methods Manual*, Pittsburgh, Pennsylvania, University of Pittsburgh Applied Research Center, 1993.

Ramstad, S., P.S. Daling and J.H.C. Øksenvåg, *Testing og dokumentasjon av strandvaskemiddel ved Full City aksjonen*, SINTEF Report A13099, 2009.

Swannell, R. P., D. J. Mitchell and A. J. Flemming, *Protocol for the Testing of Bioremediation Products*, 1997.

Ramstad, S., B.H. Hansen, P.S. Daling, M. Frenzel, J.H.C. Øksenvåg, and F.-X. Merlin, Development of Test Protocols for Effectiveness Testing and Working Mechanisms for Shoreline Cleaning Agents, Proceedings of the Thirty-third AMOP Technical Seminar on Environmental Contamination and Response, Environment Canada, Ottawa, ON, pp. 223-244, 2010.