A New Screening Protocol for Testing the Effectiveness of Surface Washing Agents

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ABSTRACT

The U. S. Environmental Protection Agency (EPA) is conducting research to develop a testing protocol to evaluate the effectiveness of surface washing agents (SWAs) in the laboratory. The purpose of the research is to determine the contribution of several variables on the performance of SWAs to remove crude oil adhered to surfaces such as sand and/or gravel. Variables being considered include substrate type (sand and gravel), SWA concentration, SWA:oil ratio (SOR), contact time between the SWA and the oil, rotational speed of the mixing apparatus, and mixing time. Fixed variables include substrate moisture, drain time, oil volume, oil and SWA application pattern, weathering time, seawater volume, oil type, and temperature. The experiments will be done to test which factors are the most important affecting oil recovery in the presence of surface-washing agents. In preliminary experiments, oil was applied to sand in 125 cm^3 stainless steel mesh baskets and allowed to weather for a period of time before the SWA was applied. The baskets were then submerged in 100 mL artificial seawater in 1-L beakers and agitated on a rotary shaker table. The wash water and sand were extracted separately with DCM and the quantity of oil in the extracts was measured by UV-visible spectrophotometry. The efficiency of the SWA was determined based on the mass of oil released into the wash water relative to the total mass of oil applied. Preliminary results to date indicate that mixing speed, SWA type, SWA concentration, and SOR are the most important factors affecting recovery.

INTRODUCTION

Unintentional releases of oil into coastal waters may result in oil becoming stranded on shorelines. Oil that reaches the shoreline can have a severe effect on the local environment, including toxic exposures and smothering of biota in direct contact with the oil. Surface washing agents (SWAs) are non-dispersing chemical agents intended to enhance the removal of oil from shoreline surfaces, thereby minimizing detrimental effects to impacted biota (EPA, 1994). Before these chemicals are used in the environment, it is necessary to evaluate their potential benefit as a countermeasure treatment for contaminated shorelines.

The U. S. Environmental Protection Agency (EPA) is conducting research to develop a testing protocol to evaluate the effectiveness of SWAs in the laboratory. The testing procedure adopts the same general approach used in previously developed methods (Clayton, et. al., 1995, 1993). The protocol involves applying oil to a substrate, weathering the oil on the substrate, applying SWA, observing of a contact time for SWA penetration, and washing of the substrate with water. The fraction of oil removed in the wash water and the fraction remaining on the substrate

are extracted and quantified. SWA performance is evaluated relative to the washing efficiency of water without SWA.

Preliminary research has been conducted to determine the effect of protocol variables on the effectiveness of surface washing agents (SWA) to remove Prudhoe Bay crude oil from sand. The following variables were tested at multiple levels: substrate hydration (wet/dry sand), substrate drain time (for wet sand applications), mode/pattern of oil application, oil application volume, oil weathering time, SWA application volume, SWA dilution, SWA-to-oil ratio (SOR), oil-SWA contact time, rotational mixing speed, and mixing time. Preliminary testing revealed that some variables did not significantly affect protocol performance; thus these values were fixed at values convenient for testing purposes (Koran, et. al., 2005). The work presented here examines the effects of SWA dilution, SOR and oil volumes on protocol performance.

MATERIALS AND METHODS

Prudhoe Bay Crude (PBC), a medium weight EPA/American Petroleum Institute (API) standard reference oil, was used in this study. One SWA was selected from those listed on the NCP Product Schedule and will be designated "SWA" to maintain manufacturer anonymity. Artificial seawater was prepared at a concentration of 34 parts per thousand (ppt) using the synthetic sea salt "Instant Ocean" (Aquarium Systems, Mentor, OH). Pesticide quality dichloromethane (DCM) was used as the extraction solvent for standards and samples.

Sand was selected as a representative shoreline substrate and was acid washed prior to use. The sand was contained in 125 cm^3 baskets constructed of 30-mesh stainless steel wire cloth and supported by a stainless steel frame (Hillside Wire Cloth Co., Inc., Bloomfield, NJ). A Brinkmann Eppendorf Research Pro Pipette capable of dispensing 5 µL-100 µL was used to dispense the required volumes of oil and SWA. Pyrex 600-mL beakers were used to contain the submerged baskets during seawater washing and DCM extraction. A LabLine 3520 orbital platform shaker was used to provide washing agitation. Aqueous sample and aqueous standard extractions were performed in 250-mL separatory funnels with ground glass stoppers and Teflon stopcocks. An Agilent 8453 UV/visible spectrophotometer with standard silica 10 mm path length rectangular cell was used for quantitation of oil in the sample extracts. This methodology was chosen to create reproducible and repeatable conditions for a valid testing protocol. Acceptance criteria for reproducibility and SWA performance are yet to be determined.

SWA Effectiveness Testing Protocol

The SWA effectiveness tests were conducted at 20 ± 3ºC. Four replicate treatments and 2 replicate controls were included in every experiment. A 25-mL volume of sand was added to each stainless steel basket using a 25-mL graduated cylinder. The baskets were submerged in artificial seawater for 30 sec to wet the surface of the sand particles and then permitted to drain for 10 min prior to oil application. Using an electronic pipette, PBC oil was applied to the level surface of the sand as nine 10 µL drops in a 3x3 block pattern for a total application volume of 90 uL. The oil was weathered on the sand for 18 hr at room temperature in a well

ventilated hood prior to application of SWA. SWA was applied to the oiled sand in the same 9 drop pattern. Following a 15 min oil-SWA contact period, the baskets were submerged in 100 mL seawater and agitated on an orbital shaker platform for 5 min at 150 rpm. Baskets were elevated above the water level and allowed to drain for 5 minutes. Figure 1 shows oiled sand before and after washing. The wash water was transferred to 250-mL separatory funnels and extracted with three 15-mL aliquots of DCM. The extracts were adjusted to a final volume of 50 mL and stored at 5°C in 50-mL glass vials with air-tight caps and Teflon-lined septa. Baskets were placed in clean 600-mL beakers and extracted with three 50-mL aliquots of DCM by shaking at 150 rpm for 5 min on the orbital shaker. A 50-mL volume was sufficient to cover the surface of the sand contained in the basket. The extracts were collected in 250-mL graduated cylinders, brought to a final volume of 180 mL, and stored at 5°C in glass vials with air-tight caps and Teflon-lined septa. All extracts were analyzed by UV/visible spectrophotometry within 48 hours of collection.

Oil Standards Preparation

A stock solution of oil in DCM was prepared at a concentration of 10% oil by volume. Six calibration standards were then prepared by adding a specific volume of stock solution to 100 mL synthetic seawater in each of six 250-mL separatory funnels. The standards were extracted with three 15-mL aliquots of DCM and the final extract volume was adjusted to 40 mL. The final extracts were stored at 5°C in 50-mL crimp style glass vials with aluminum/Teflon seals.

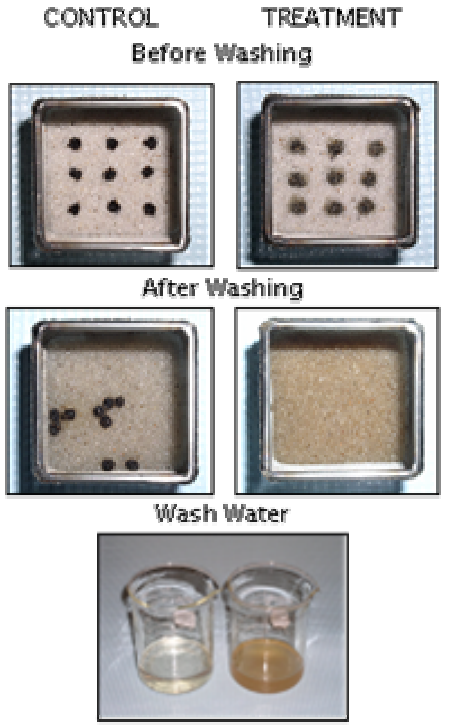


Figure 1. Oiled sand before and after washing for control and SWA treatment

Analytical Methods

The Agilent 8453 UV/Visible Spectrophotometer is a diode array and gave complete sample scans over the range of wavelengths. Absorbance measurements at 340, 370, and 400 nm were used to calculate the area under the absorbance curve for standards and samples. Sample concentrations were calculated from the six-point standard calibration curve plotted as concentration versus area under the absorbance curve.

EXPERIMENTAL RESULTS AND DISCUSSION

Fixed Variables

Protocol variables were tested at multiple levels to determine their effect on protocol performance. Variables that did not significantly affect protocol performance were fixed at values convenient for testing purposes (Koran, et. al., 2005). These include substrate hydration, substrate drain time, oil and SWA application patterns,

oil-SWA contact time, mixing time, and seawater volume. Organic carbon (OC) content of the substrate was not a variable chosen for study since it would be difficult to acquire a shoreline substrate with consistent and reproducible OC content. Weathering time and mixing speed were also fixed based on results from preliminary testing (Koran, et. al., 2005). Only one oil type and temperature were considered for this study. A heavy refined oil and additional temperatures will be tested in future experiments.

The decision was made to apply oil to wet sand rather than dry sand because this is a closer reflection of real world applications. Previous data reveal SWA performance for dry and wet sand applications did not differ significantly. However, the mass of oil released from controls due to washing with water alone (without SWA) was significantly higher for wet sand. In order to be useful, the protocol must differentiate between good and bad performance relative to controls that receive only water as the treatment. Therefore the amount of oil released from water-treated controls that have not had sufficient time for oil to adhere should be minimized experimentally so that a distinction in performance can be readily observed. To allow sufficient time for oil to adhere and bond to the sand, a weathering time of 18 hours was selected as described below.

Substrate moisture can affect the spreading of oil on the sand as well as the bonding of the oil to the sand. Standing water in pore spaces near the substrate surface may result in high release of oil from the untreated controls. Substrate drainage times from 1 to 20 min were previously tested, and no effect was observed on oil release from controls (RSD 8.9%). Therefore, a 10 min drainage time was chosen for the protocol.

The mode of oil application had been tested using a total applied volume of 100 µL PBC dispensed as 1, 2, 5, or 10 drops. No significant difference in percent oil release was observed among the application methods (RSD 3.5%). However, applying the oil as multiple drops across the surface of the sand serves the primary purpose of ensuring increased contact surface area between the sand and the oil. For the protocol, a 9-drop pattern in a 3x3 block design was chosen. The application of SWA to the oiled surface follows the same 9-drop pattern.

The effect of oil weathering time was tested by varying the amount of time the oil remained on the sand prior to SWA application. Oil weathering times of 5 min, 15 min, 1 hr, 6 hr, and 18 hr were examined. Only control samples with no SWA application were included in this experiment since the primary interest was to reduce the oil removed in the controls. Weathering times less than 60 min did not appear to alter oil release from the controls. After 6 hours, a small decrease was noticed, but 43% of the applied oil was still released. At 18 hr, the oil released was reduced to 22%, and the mass of oil remaining on the sand was significantly greater than the mass released into the wash water. Because applying oil to wet sand is a closer approximation of real world applications and minimizing oil release from controls is an important factor in the protocol, a weathering time of 18 hr was fixed for this protocol.

The effect of oil-SWA contact time was examined on wet sand using undiluted SWA at an SOR of 2:1. Samples were washed at 5 min, 15 min, 30 min, 1 hr, 3 hr,

and 6 hr after SWA application. For both a water-soluble and oil-soluble SWA, the length of time the SWA contacted the oil prior to washing did not have a statistically significant effect on SWA effectiveness. Based on these findings, an oil-SWA contact time of 15 min was chosen for subsequent experiments.

The effects of rotational mixing speed and length of mixing were evaluated at 3 levels in a factorial experimental design. Mixing speed was tested at 100, 150, and 200 rpm and oil removal from treatments and controls was shown to increase significantly with rpm. The maximum difference between treatments and controls occurred at 150 rpm, while 200 rpm was determined to be excessively rigorous and 100 rpm yielded low release from treatments and controls. Differences in protocol performance for the treatment and control were not strongly linked to the length of mixing time. The relative standard deviation (RSD) for SWA efficiency at 5, 10, and 20 min mixing was less than 2% for 150 and 200 rpm conditions. For the control under the same conditions, the RSD was less than 6%. Based on these preliminary data, a rotational mixing speed of 150 rpm and mixing time of 10 minutes was selected.

SWA Dilution Effects

Each SWA listed on the NCP Product Schedule has a manufacturer-recommended application rate and procedure. Some vendors recommend neat application, while others recommend dilution (solution concentrations ranging from 0.6% to 50%). In order for the testing protocol to be standardized, a decision must be made regarding how the SWA will be applied during testing. One option is to use the manufacturers' recommended application procedures, which would result in each SWA being tested under different application conditions. Alternately, the protocol could specify that each product be tested at full-strength and at one or two specified dilutions. For water-insoluble SWAs, only undiluted application would apply.

To resolve this issue, the effect of diluting an SWA during the application process was tested 1) by applying 100%, 50%, and 10% solutions of SWA using a fixed solution volume, and 2) by applying the same mass of SWA using multiple concentration-volume combinations. In the first set of experiments, 90 µL PBC was applied to wet sand in a 9-drop pattern according to the protocol. Following the 18-hr weathering period, 180 µL of SWA solution was applied using 100%, 50%, and 10% solutions. These correspond to SORs of 2:1, 1:1, and 1:5, respectively. Controls with no SWA treatment were also evaluated. In general, SWA efficiency increased with solution concentration and SOR, ranging from 22.2% oil removal in untreated controls to 69.0% removal with a neat solution at 2:1 SOR (Figure 2). For this particular SWA, which had a recommended dilution of 50%, there was no significant difference between applying the undiluted solution at 2:1 SOR (69.0% removal, 7.6% stdev), and the 50% solution at 1:1 SOR (66.6% removal, 3.1% stdev). Applying a 10% solution (1:5 SOR) yielded an intermediate efficiency of 40.1%. The conclusion for this SWA is that the manufacturer-recommended dilution is optimal under these testing conditions.

In the second set of experiments, an SOR of 2:1 was maintained while varying SWA concentrations and volumes. As in the first experiments, 90 µL PBC was applied to wet sand in a 9-drop pattern and an 18-hr weathering period was

observed. SWA was then applied according to the following conditions: 180 µL undiluted SWA; 600 µL 30% solution; 1800 µL 10% solution; 6000 µL 3% solution. Untreated controls were also tested during each experimental run, with average release of oil ranging from 14.9% to 24.6%. Data indicate that diluting the SWA did not impair efficiency as long as the total mass of SWA applied was constant (Figure 3). Average efficiencies of 69.0%, 66.9%, 64.7% and 66.8% were obtained for the undiluted, 30%, 10%, and 3% solution concentrations, respectively. Thus, it appears that SWA solution concentration is less critical than the overall mass of SWA applied to treat a given amount of oil.

SWA-to-Oil Ratio and Oil Volume Effects

One objective of developing a testing protocol is to provide data that will be predictive of SWA performance in the field. Since real world applications will involve treating large volumes of oil, it is important to demonstrate that oil volume does not

Figure 2. Dilution Effects with Same SWA Volume

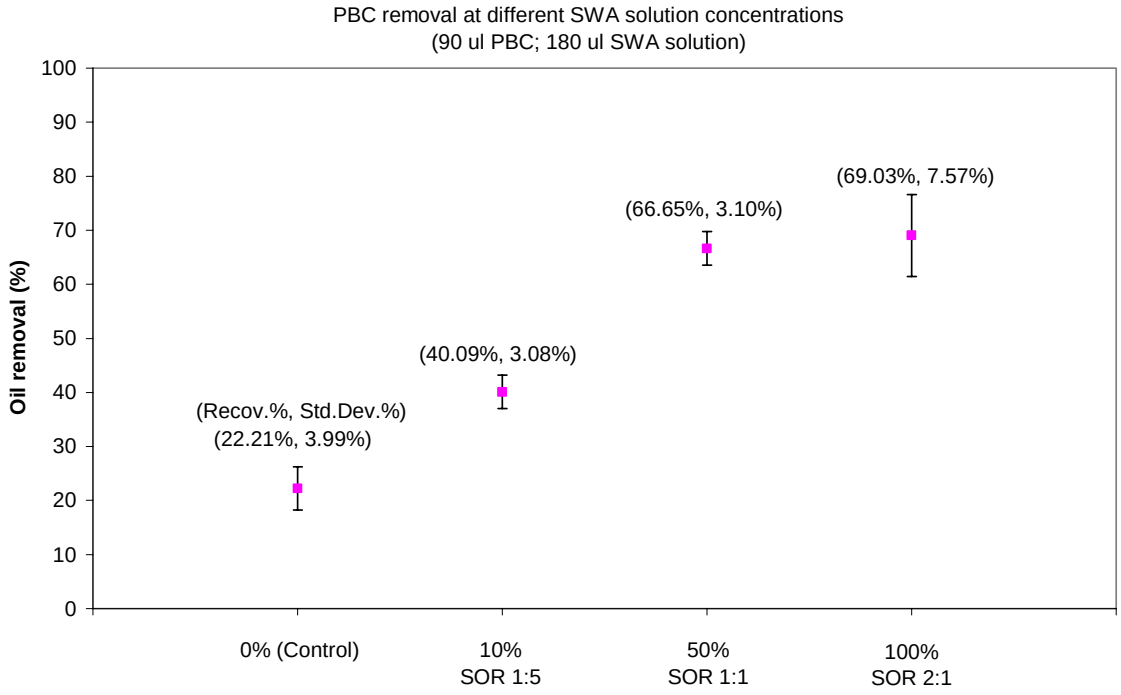
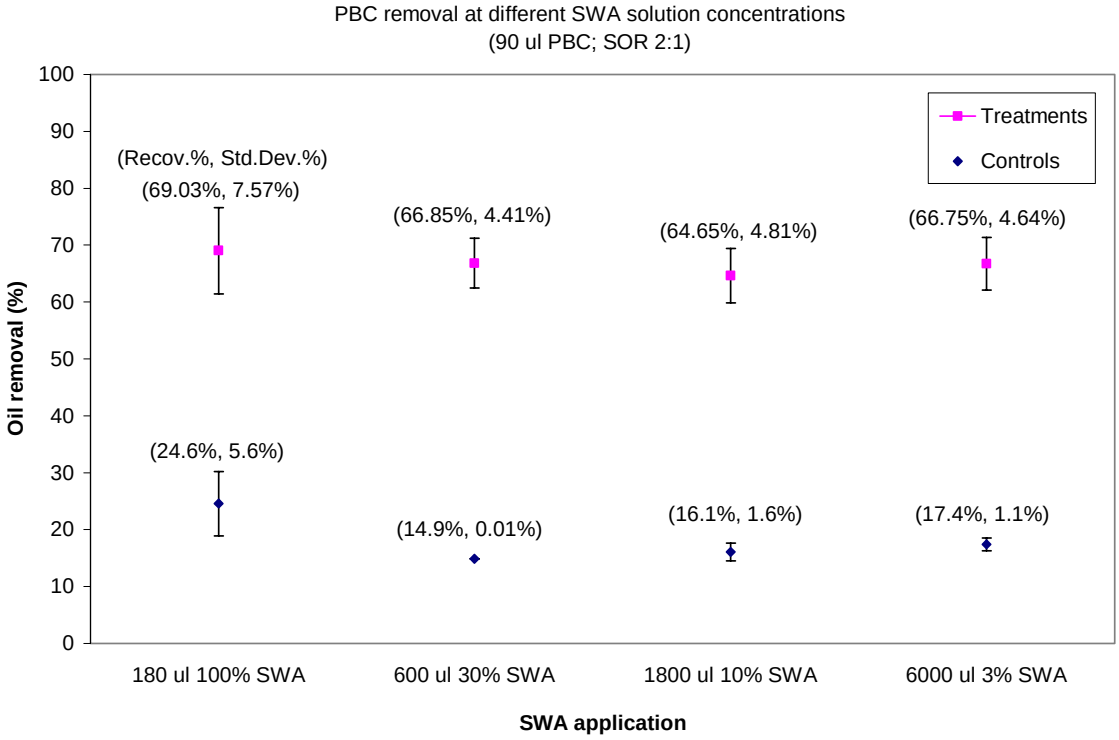


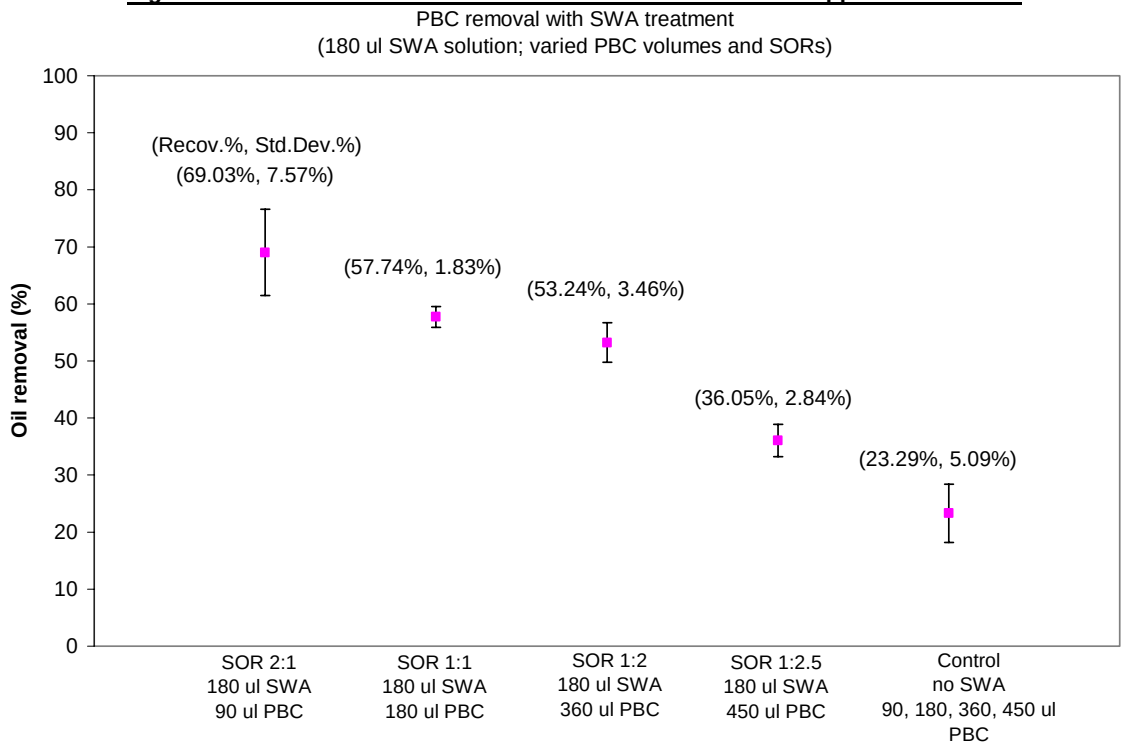
Figure 3. Dilution Effects with Same SWA Application Mass



significantly affect protocol performance for a given SOR condition. The relative ratio of SWA:oil had been determined to be significant. However, since preliminary testing had been primarily conducted using an oil volume of 90 uL, this had only been tested on a small volume scale. Additional testing determined the applicability of the protocol to larger oil volumes.

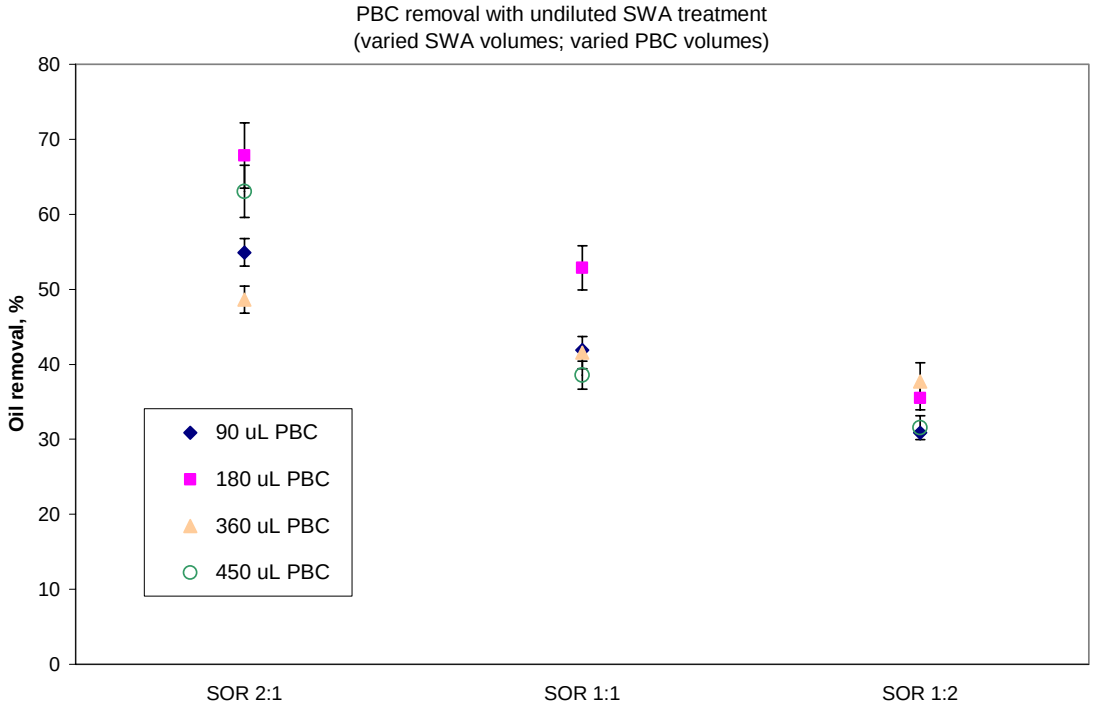
Two sets of experiments were conducted to determine the importance of SOR and oil volume on protocol performance. In the first set of experiments, a fixed volume of undiluted SWA (180 uL) was applied to a range of PBC volumes (90, 180, 360, and 450 uL), resulting in SORs of 2:1, 1:1, 1:2, and 1:2.5. Larger volumes of oil were attempted, but the oil penetrated the sand matrix and spilled out of the basket during application. Untreated controls were run for each PBC volume, with oil releases ranging from 16.9% to 30.7%. As expected, SWA efficiency increased with SOR (Figure 4). The 2:1 SOR yielded a SWA efficiency of 69.0%, while the 1:2.5 SOR yielded 36.0% efficiency. These data confirm that the relative ratio of SWA:oil is important and that the release of oil from untreated controls is independent of oil volume for the volumes tested.

Figure 4. SOR Effects at Different Oil Volumes with Same SWA Application Volume



The next set of experiments tested four oil volumes (90, 180, 360, 450 uL) at three SORs (2:1, 1:1, 1:2). Thus, the effect of oil volume was evaluated at each SOR. As before, efficiency increased with SOR for each level of oil volume tested (Figure 5). However, for a given SOR, there was no trend with oil volume. Volumes that produced the highest removal efficiencies at one SOR had lower efficiencies at other SORs. The greatest spread in data occurred for the 2:1 SOR, but the overall variability was not unreasonable. RSDs for average efficiencies across all oil volumes were as follows: 14.6% at 2:1; 14.4% for 1:1, and 9.6% for 1:2. The variability was far greater across SORs, with RSDs of 28.2% for 90 µL oil, 31.1% for 180 uL, 13.0% for 360, and 37.3% for 450 uL. These data suggest that SOR is a more significant variable than oil volume in determining SWA performance.

Figure 5. SOR Effects at Different Oil Volumes with Same SWA Application Mass



SUMMARY AND CONCLUSIONS

The goal of this work is to develop a standardized laboratory protocol for evaluating SWA effectiveness. Protocol variables were tested at multiple levels to determine their effect on protocol performance. Previous research had determined that certain variables did not significantly affect protocol performance, including substrate hydration, substrate drain time, oil and SWA application patterns, oil-SWA contact time, mixing time, and seawater volume. These variables were fixed at values convenient for testing purposes. Weathering time and mixing speed were also fixed based on results from preliminary testing.

In this study, the effects of SWA dilution, SOR, and oil volume were evaluated for one SWA and PBC oil. The SWA was water soluble and had a manufacturer recommended dilution factor of 2 (50% solution). Testing at 2:1 SOR revealed that the 50% solution was as effective as the undiluted SWA at removing PBC. However, when the same mass of SWA was applied, similar efficiencies were achieved regardless of dilution. This suggests that total applied mass is more important than dilution for this SWA.

SOR was found to be a critical variable affecting SWA performance. Efficiency increased with SOR for ratios ranging from 1:2.5 to 2:1 and oil volumes ranging from 90 µL to 450 uL. No trend was observed with oil volume at a given SOR, and the RSD for average efficiencies across oil volumes was significantly less than the RSDs across SORs. This indicates that SOR is a more significant variable than oil volume in determining SWA performance.

Future experiments will be conducted using additional SWAs, a heavier weight refined oil, and gravel as an alternate substrate. All protocol proposals will be published in the Federal Register and will be open for public comment.

DISCLAIMER

The material in this document has been subjected to Agency technical and policy review, and approved for publication as an EPA report. The views expressed by individual authors, however, are their own, and do not necessarily reflect those of the U.S. Environmental Protection Agency.

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