DEVELOPMENT OF A SURFACE WASHING AGENT EFFECTIVENESS PROTOCOL

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) is developing a protocol for testing the effectiveness of surface washing agents (SWAs) in a laboratory setting. The criteria for evaluating SWA effectiveness is based on the amount of crude oil that can be removed from a substrate with a specified amount of test cleaner. For protocol development and testing, acid washed sand was used as the shoreline substrate. Prudhoe Bay Crude, a medium weight EPA/American Petroleum Institute (API) standard reference oil, and three SWAs were tested. Oil was applied to the sand in 2"x2"x2" stainless steel mesh baskets and allowed to weather for a period of time before the SWA was applied. SWA was applied as a neat solution at a product to oil volume ratio of 2:1. The baskets were then submerged in seawater in 1-L beakers and agitated on a rotary shaker table. The effects of testing variables, including substrate hydration, mode of oil application, oil-weathering time, oil-SWA contact time, mixing speed, and mixing time were evaluated. 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.

INTRODUCTION

Chemical surface washing agents (SWAs) can be used following an oil spill event to enhance the removal of stranded oil from shorelines or other solid surfaces. A SWA is defined as any product that removes oil from a solid surface through a detergency mechanism and does not involve dispersing or solubilizing the oil into the water column (EPA, 1994). The use of SWAs as a remediation tool is recommended when conventional methods are considered invasive, impractical, or detrimental to the natural environment. The decision to use a particular SWA should be based on the potential of the agent to (1) effectively remove oil from substrate surfaces and (2) minimize toxicity to affected aquatic and intertidal communities (Clayton, 1995a).

To be considered for use in the United States, SWAs must be listed on the National Contingency Plan (NCP) product schedule. The NCP, which governs the use of SWAs, as well as oil dispersants, biological additives, and other chemical agents, requires submission of toxicity data for all products listed on the product schedule. Effectiveness data is currently required only for dispersants and bioremediation agents. EPA is in need of an objective laboratory protocol for testing the effectiveness of SWAs prior to listing them on the NCP Product Schedule.

Development of a testing protocol to evaluate the effectiveness of SWAs has been undertaken by numerous research laboratories. The goal of these testing procedures is to quantify the physical removal of oil from non-vegetative substrates as a result of SWA action. The fundamental methodologies for these protocols are similar. They involve the application of oil to a solid substrate (or the use of pre-oiled substrate), weathering of the oil on the substrate, application of SWA, observance of a contact period 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 quantified. Oiled controls without SWA application are also tested.

Fingas *et al.* (1990) developed a testing procedure for Environment Canada that used a stainless steel or porcelain trough as the substrate. Oil was applied to one end of a pre-weighed trough, and the trough was suspended vertically for ten minutes and then reweighed to determine the mass of oil applied. SWA was applied evenly along the trough and allowed to contact the oil for ten minutes. The trough was rinsed, blotted dry, and reweighed. Following solvent extraction of the wash water and the substrate, oil removal was quantified. The investigators reported oil removal efficiencies ranging from 1% to 52% for 26 cleaning agents tested. They also tested the toxicity and dispersant effectiveness of each product and found a negative correlation between dispersant effectiveness and cleaning effectiveness. They concluded that the mechanisms of dispersancy and detergency are different, and thus, a good SWA is a poor dispersant, and vice versa.

Clayton *et al.* (1993) developed and tested a modification of the Environment Canada protocol. They used stainless steel and porcelain coupons instead of troughs. Following application of the oil and SWA, the coupons were lowered into separate beakers containing seawater, the beakers were agitated on a shaker table, and the coupons were subsequently removed, dried and extracted, along with the wash water. They compared this procedure with Environment Canada's protocol using two test oils (Prudhoe Bay Crude and Bunker C) and three cleaning agents (COREXIT 9580,

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Citrikleen XPC, and COREXIT 7664). Comparison of results revealed greater variability with oil type and cleaning agent than with the testing method used.

Clayton further modified the testing protocol for on-site field testing of SWAs (Clayton, 1995b). The revised protocol was applied to natural substrates and readily adaptable to field situations. Three natural substrates were used: gravel, fragments of rock riprap, and blades of the eelgrass *Zostera marina*. Two oils (Bunker C and Bonny Light) and two SWAs (PES-51 and COREXIT 9580) were also tested. Substrates were placed in a wire mesh container and submerged in seawater. A known quantity of oil was applied as a slick to the surface of the seawater, and the mesh container was pulled vertically through the slick. The oiled substrate was allowed to weather at ambient temperatures for 18-22 hours, and gravel and rock substrates were weathered in a 60°C drying oven for an additional 1-2 hours. A known quantity of SWA was applied to the substrate using a spray applicator. Following a contact period, the substrate was washed with seawater, and the wash water and substrates were extracted with solvent. Cleaning performance varied with substrate; the greatest efficiency was achieved with gravel while the rip-rap and eelgrass results were comparable. The Corexit product performed better than PES-51 for all 3 substrates, and Bonny Light was less easily from gravel surfaces than Bunker C.

Preliminary research reported in this paper was conducted to develop a standardized and reproducible testing protocol to evaluate the cleaning effectiveness of chemical SWAs for the purpose of listing successful products on the NCP Product Schedule. To accomplish this objective, a testing procedure was proposed that adopts the same general approach used in previously developed methods. The test procedure was performed under various operational conditions to determine which factors had the greatest impact on the method results. Factors such as substrate hydration, mode of oil application, oil weathering time, oil-SWA contact time, rotational mixing speed, and mixing time were evaluated. SWA performance was evaluated relative to the washing efficiency of water without SWA.

MATERIALS AND METHODS

Prudhoe Bay Crude (PBC), a medium weight EPA/American Petroleum Institute (API) standard reference oil, was used in this study. Three SWAs were selected from those listed on the NCP Product Schedule. Two of the agents were water-soluble, the other oil-soluble. The SWAs were randomly assigned the letters A, B, or C to maintain manufacturer anonymity. Artificial seawater was prepared at a concentration of 34 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 2"x2"x2" 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 mL-100 mL 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.

SWA Effectiveness Procedure

The SWA effectiveness tests were conducted at 20 ± 3°C. A 25-mL volume of sand was added to stainless steel baskets using a 25-mL graduated cylinder. For experiments conducted with wet sand, the baskets were submerged in artificial seawater for 5 min to wet the surface of the sand particles and then permitted to drain for 10 min prior to oil application. Using an electronic pipette, 90 mL oil was applied to the level surface of the sand. With the exception of the "oil application experiment" described later, PBC oil was applied as nine 10 mL drops in a 3x3 block pattern. The oil was allowed to weather on the sand for a period of time prior to application of SWA. Weathering times ranging from 5 min to 18 hours were evaluated. Undiluted SWA was applied to the oiled sand in the same 9 drop pattern at a product-to-oil ratio (POR) of 2:1. Following an oil-SWA contact period (evaluated experimentally from 5 min to 6 hr), the baskets were submerged in 100 mL seawater and agitated on an orbital shaker platform for a predetermined period of time (5, 10 or 20 min) at a specific rotational speed (100, 150, or 250 rpm). Baskets were elevated above the water level and allowed to drain for 5 minutes. 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 40-mL aliquots of DCM by shaking at 150 rpm for 10 min on the orbital shaker. A 40-mL volume was sufficient to cover the surface of the sand contained in the basket. The extracts were collected in 150-mL graduated cylinders, brought to a final volume of 150 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 Procedure

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.

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 calibration curve plotted as concentration versus area.

EXPERIMENTAL RESULTS AND DISCUSSION

Substrate Hydration Effects

The effect of substrate hydration on protocol performance was evaluated by conducting experiments on dry and wet sand. The weathering time and oil-SWA contact time for this set of experiments were fixed at 15 min and 5 min, respectively. The rotational mixing speed was 150 rpm, and the mixing time was 5 min. SWA was applied undiluted at an POR of 2:1. Two untreated control replicates and four treatment replicates were included in each experimental run.

The primary difference between dry and wet experiments was evident in the untreated control (Figure 1). When oil was applied directly to dry sand, the oil bonded to the sand particles and was not released by washing with water alone. This gave a clear differentiation between treated and untreated samples, which is an important consideration when evaluating a testing protocol. When oil was applied to wet sand, the oil did not strongly adhere to the sand particles, and significant amounts of oil were released in the untreated controls. This difference was not observed in samples treated with SWA. The mass of oil removed in SWA-treated samples was similar for both dry and wet sand experiments.

The decision to apply the oil to wet sand is reasonable since interstitial water will be a factor in real world applications. However, in order to be useful, the testing protocol must be able to distinguish between good and bad performance relative to controls that receive no treatment. The amount of oil released from untreated controls should be minimized experimentally so that a distinction in performance can be readily observed. Two operational variables that can influence the release of oil from sand are the water content of the sand at the oiled surface and the amount of time the oil has to adhere to the sand prior to SWA treatment.

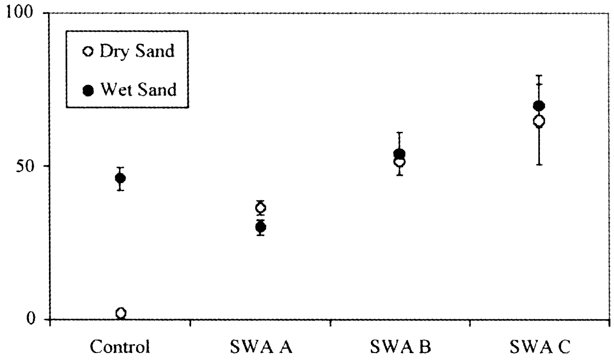

FIGURE 1. REMOVAL OF PBC OIL FROM DRY AND WET SAND AFTER 15 MIN WEATHERING

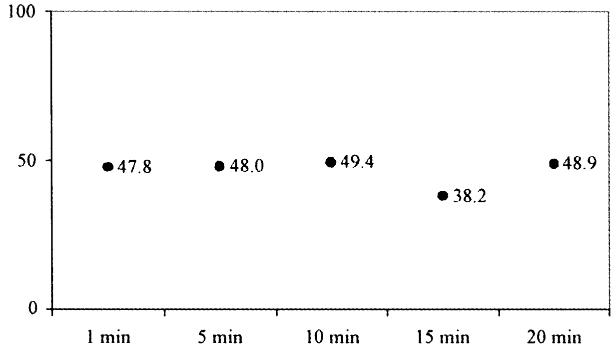

FIGURE 2. EFFECT OF SUBSTRATE DRAINAGE TIME ON PBC REMOVAL FROM WET SAND AFTER 15 MIN WEATHERING

Substrate hydration will 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. To evaluate this effect, experiments were conducted in which the substrate drainage time prior to oil application was varied. Baskets were submerged in seawater for 5 min and allowed to drain by gravity for 1, 5, 10, 15 or 20 min. The protocol was then performed under the following conditions: 15 min weathering time, 150 rpm mixing speed, and 5 min mixing time. SWA was not applied. The various drainage times from 1 to 20 min did not have a significant effect on oil release (Figure 2). The relative standard deviation (RSD) for samples across all treatments was 8.9% with no apparent trend. Therefore, a 5 min drainage time was chosen for the protocol.

Another factor that can influence the mass of oil released is the amount of time the oil is in contact with the sand prior to SWA treatment. In this protocol, increasing the time between oil application and SWA application allows for (1) evaporation and drainage of some interstitial water, (2) spreading of oil on the substrate surface, (3) evaporative loss of volatile fractions from the oil, and (4) formation of adhesive bonds between the oil and substrate. Weathering of the oil on wet sand for different lengths of time was evaluated in the second phase of testing.

Oil Application and Weathering Effects

There are numerous possible methods for applying oil to the substrate, including pulling the basket of sand through a slick on the surface of the water, using a specific weight or volume of preoiled substrate, and dispensing a specific volume using a positive displacement pipetter. For a standardized protocol, it is important to know the total mass of oil applied so that a mass balance can be performed. Therefore, the pipetter approach is preferred. However, due to the viscosity of oil, pipette dispensing can be a source of error. It is recommended that an electronic pipetter be used for increased accuracy.

The mode of oil application was tested using a total applied volume of 100 mL PBC dispensed as 1, 2, 5, or 10 drops. The protocol was conducted on wet sand under the operating conditions described above. The removal of PBC from sand by washing without SWA treatment was 57.7%, 59.5%, 56.3% and 54.1% for the 1, 2, 5 and 10 drop application methods, respectively. No significant difference 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.

As stated previously, the length of time the oil contacts the sand prior to treatment may affect the release of oil from the sand. It is desirable to minimize this release in untreated controls in order to maximize the differences between control and treated samples. The effect of oil weathering time on the protocol was tested by varying the amount of time the oil remained on the sand prior to SWA application. Oil weathering times of 5, 15, 60, 360 and 1080 min were examined. Experiments were conducted on wet sand with 5 min contact time, 150 rpm mixing speed, and 5 min mixing time. 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.

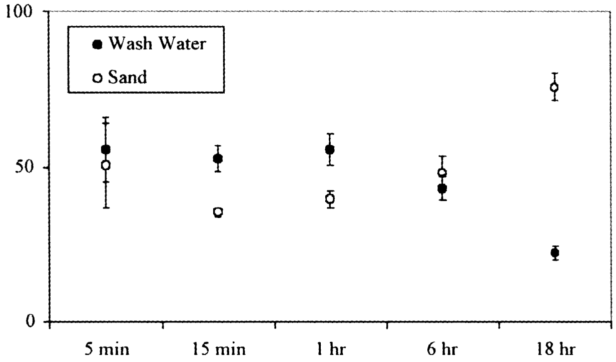

FIGURE 3. EFFECT OF OIL WEATHERING TIME ON PBC RELEASE FROM WET SAND

Weathering times less than 60 min did not appear to alter oil release from the controls (Figure 3). At 5, 15 and 60 min, the oil recovered from the wash water was 52% to 56% of the total oil applied. After 6 hours, a small decrease was noticed, but 43% of the applied oil was still released. At 18 hrs, 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. Since 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, all subsequent experiments were conducted on wet sand with a weathering time of 18 hr.

Oil-SWA Contact Time Effects

The effect of oil-SWA contact time was examined on wet sand under the following operating conditions: 18 hr weathering time, 150 rpm mixing speed, and 5 min mixing time. After the oil had weathered, undiluted SWA was applied at a POR of 2:1. Samples were then washed at 5, 15, 30, 60, 180 and 360 min after SWA application.

For both the water-soluble and oil-soluble SWAs, the length of time the SWA contacted the oil prior to washing did not have an effect on SWA effectiveness (Figure 4). Based on analysis of variance (ANOVA) statistics, the differences in mean values among the groups are not great enough to exclude the possibility that the difference is due to random sampling variability. Therefore, we can conclude that there is no significant difference in SWA performance as a result of contact time for SWAs A or B ($P = 0.849$ for SWA B). Based on these findings, an oil-SWA contact time of 15 min was chosen for subsequent experiments.

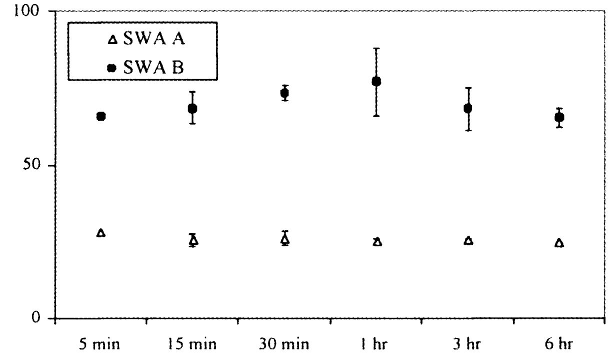

FIGURE 4. EFFECT OF CONTACT TIME ON REMOVAL OF PBC BY SWAS A AND B

Mixing Effects

Experiments were conducted to test operational variables associated with washing of the substrate following SWA treatment. The effects of rotational mixing speed and length of mixing were evaluated at 3 levels in a factorial experimental design. The levels tested were 100, 150 and 200 rpm and 5, 10 and 20 min washing. Other operational variables were held constant as follows: 18 hr weathering time and 5 min oil-SWA contact time. SWA B was tested along with untreated controls.

Mixing speed had the greatest effect on oil removal (Figures 5a and 5b). The release of oil in the control averaged 4.6 ± 2.9% at 100 rpm and 71.0 ± 1.2% at 200 rpm across the three mixing times. For SWA treatments, the release ranged from 20.9 ± 4.4% at 100 rpm and 89.4±1.1% at 200 rpm. Differentiation in performance between the treatment and control was evident at each level, with 15% to 28% more oil released by SWA B. From an observational standpoint, 200 rpm was an excessively rigorous mixing speed and resulted in the breakage of some beakers. Thus, it would be an impractical operating speed for the protocol. A mixing speed of 100 rpm yielded low release of oil from the controls, but also lower efficiencies for SWA B. The maximum difference between SWA B and the control occurred at 150 rpm at each of the three mixing times.

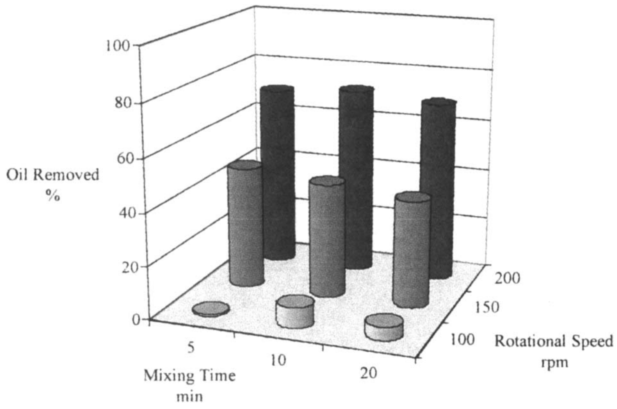

FIGURE 5A. EFFECTS OF MIXING ON PBC REMOVAL IN CONTROLS

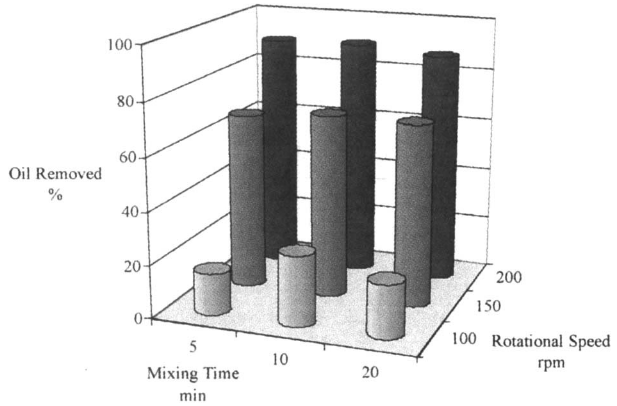

FIGURE 5B. EFFECTS OF MIXING ON PBC REMOVAL BY SWA B

Differences in protocol performance for the control and SWA B were not strongly linked to the length of mixing time. The relative standard deviation (RSD) for SWA B performance across the three mixing times was less than 2% for 150 and 200 rpm conditions. For the control under the same conditions, the RSD was less than 6 %. The greatest variability across mixing times was observed at 100 rpm where high RSD values were a result of lower oil removals on average and a 10 min mixing time yielded the highest removal. Based on these preliminary data, a rotational mixing speed of 150 rpm and mixing time of 10 minutes will be proposed.

SUMMARY AND CONCLUSIONS

The goal of this work was to develop a standardized laboratory protocol for evaluating SWA effectiveness. A series of experiments were designed to determine the effects of substrate hydration, oil weathering time, oil-SWA contact time, rotational mixing speed, and mixing time on protocol performance. The protocol was most sensitive to rotational mixing speed and oil weathering and was not greatly affected by contact time or mixing time. Based on preliminary testing results, the following operational conditions are recommended: 10 min drainage time, 9 drop oil pattern on wet sand, 18 hr weathering time, 15 min contact time, 150 rpm mixing speed, and 10 min mixing time.

There are many other factors to be tested before a final protocol is proposed. In this study, only one oil and three SWAs were considered. Future experiments will be conducted using South

Louisiana crude oil and additional SWAs. Questions of how to apply the SWA and at what concentration still need to be addressed. SWAs in the current study were applied as neat solutions in order to have a uniform guideline for handling all SWAs. However, most water-soluble SWAs are intended to be applied in diluted form, according to the manufacturers. Appropriate dilutions will be considered in future testing. In addition, other substrates such as gravel can be tested to evaluate the impact of substrate on SWA performance. All protocol proposals will be published in the Federal Register and will be open for public comment.

BIOGRAPHY

Karen Koran is a Research Associate and Ph.D. Candidate in the Department of Civil and Environmental Engineering at the University of Cincinnati. She serves as the On-Site Manager for the University of Cincinnati Contract Staff working at the U.S. EPA in Cincinnati, OH.

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