CHEMISTRY AND ENVIRONMENTAL EFFECTS OF THE SHORELINE CLEANER PES-51™

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EXECUTIVE SUMMARY

NOAA evaluated the shoreline cleaner PES-51™ based on chemistry, aquatic toxicity, effectiveness, and personal observations from two recent field tests of the product. This report provides information that may help responders decide whether to use this product for shoreline cleanup of oil spills.

We approach this product as we would any proposed response technique, by determining how its use fits into the overall objectives of an oil spill cleanup. Is the site where the cleaner will be used one that is environmentally sensitive? Is the area heavily used for recreation, making quickly removing oil the primary cleanup objective? What advantages do the responders hope to obtain through using a shoreline cleaner compared with other techniques?

Once these cleanup objectives are clear, the product is evaluated based on two questions: How effective is the product? and What are its likely environmental impacts? Ideally, we would choose a product that is extremely effective and completely non-toxic. However, we know of no such products. Virtually all oil cleaners that can effectively remove oil have some properties that are toxic in the aquatic environment. Therefore, responders must balance the product's effectiveness with its toxicity and environmental fate. If a product is extremely effective and will aid considerably in the response effort, then some degree of toxicity may be acceptable for a resulting overall gain. However, if the site is environmentally sensitive, toxicity will become a more important consideration.

Evaluating a variety of information about PES-51, we conclude that it falls somewhere in a middle ground of the effectiveness/toxicity equation for shoreline cleaners. PES-51 is toxic at certain concentrations in the aquatic environment, though this is based on laboratory analyses only due to a lack of field data on environmental impacts. It is consistently more toxic than another shoreline cleaning product with similar solubility, Corexit 9580, based on toxicity tests using three different species. In terms of effectiveness, NOAA observers at the Prince William Sound, Alaska test were largely positive about
PES-51's apparent ability to liberate submerged weathered oil (visual observations only). In standardized laboratory tests conducted by Environment Canada, however, PES-51 failed to meet the minimum standards for effectiveness as a shoreline cleaner.

A decision will need to be made to consider using this product in the individual context of the situation at hand. The detailed information in this report will assist in this process. Rather than focusing solely on PES-51 or any other individual product, we recommend evaluating a variety of products to obtain the best available balance between maximum effectiveness and minimum environmental impact.

INTRODUCTION

NOAA's Hazardous Materials Response and Assessment Division (HAZMAT) does not endorse or promote specific products for use in oil spill cleanup. We do evaluate effectiveness, toxicity, and conditions or environments where response techniques may be appropriately used to minimize impacts to marine resources from oil spills. In general, we do not evaluate individual spill response products, unless specific requests are made about proposed uses during response events.

We produced this report on PES-51 because, over the summer and fall of 1993, we have observed the use of this product during field tests on two different occasions. This report consolidates the information that we have been able to collect on the chemistry and toxicity of the product, and gives our observations from the field tests where NOAA observers were present.

It continues to be NOAA's position that the appropriate way to choose techniques or products for use during spill response is first to determine the general technique appropriate for the situation at hand (such as beach cleaners or bioremediation,) and then to evaluate objectively the advantages and disadvantages of a number of technical approaches or products. If a commercial product is to be used, then a comparison can be made among the available products that balances effectiveness in performing a specific task, such as shoreline cleaning, with toxicity or other detrimental environmental impacts. Such comprehensive evaluations are, of course, difficult to conduct under the time constraints of a response, and should ideally be performed during the planning process, before an actual spill. The recently completed technical report sponsored by the Marine Spill Response Corporation on Alternative chemical oil spill treating agents (ACOSTA) is an excellent tool for evaluating shoreline cleaners, since it contains information on a number of different products, including toxicity, chemistry, use, and effectiveness evaluations.[1] Our report should be used in conjunction with the ACOSTA manual as well as with other overviews of shoreline cleaners such as EPA's manual on chemical shoreline cleaning agents.[2]

PES-51

The shoreline cleaner PES-51 is marketed by Tesoro Environmental Products Company. PES-51 is one of several currently available shoreline cleaners that consist of wetting agents formulated to effectively remove weathered oil from shoreline surfaces but maintain the oil in a non-dispersed film to be recovered from the water surface. PES-51 is listed on the Environmental Protection Agency National Contingency Plan Product Schedule as a "miscellaneous oil spill response agent."

PES-51 is typically applied by spraying it on a contaminated surface with a hand-held sprayer. Before evaporating, the oil and PES-51 are washed from the surface using water sprayed from a hose with nozzle. The product/oil mixture has a density less than one, allowing it to float until it can be absorbed, skimmed, or vacuumed. According to Tesoro, a temporary protein film remains after treatment on the water surface that prevents the mobilized oil from re-depositing.

Two field test demonstrations of PES-51 were conducted in 1993 in Prince William Sound, Alaska on oil remaining from the *Exxon Valdez* oil spill and in Tampa Bay, Florida following the *Bouchard 155* oil spill. Field reports from these tests are presented in Appendices A and B.

PRODUCT EVALUATION

Chemistry

As defined by Tesoro, PES-51 is a proprietary biological cleaning agent that removes hydrocarbons from porous and non-porous surfaces. Tesoro's product information indicates that PES-51 is composed of bacterial fermentation by-products that, in combination with the carrier solvent, d-limonene, form a "unique biological mixture" that surrounds hydrocarbon molecules and lifts them from surfaces. The product/oil mixture is stable and water-insoluble. Tesoro claims that water salinity and temperature do not affect product performance (see Table 1 for a summary of physical properties).

The product literature for PES-51 lists four constituents for the material: "biospersans," of microbial origin; "biosurfactant," of microbial origin; d-limonene; and water. This compositional mix is also cited in a field report for the Sleepy Bay PES-51 trial prepared by the Alaska Department of Environmental Conservation.[3] Independent chemical analysis of a PES-51 sample collected at the Sleepy Bay (Prince William Sound) field test in July 1993, performed by Louisiana State University indicated that the major component of the product is limonene, which represents between 90 and 97 percent of PES-51 by weight.[4]

Since limonene is the major component of PES-51, a discussion of known characteristics for limonene follows.

Limonene: General Information

The monoterpene d-limonene is a naturally occurring chemical that is the major component in oil of orange. A number of coniferous tree species also produce limonene, and it is believed that in these, as well as in citrus plants, the compound provides protection against insect pests in concert with other terpenes. Limonene, also known as dipentene, is described in chemical references as a colorless liquid with a lemon-like odor. It is used as a solvent for rosin, waxes, and rubber; as a dispersing agent for oils, resins, paints, lacquers, varnishes, and in floor waxes and furniture polishes.[5] Currently, d-limonene is also widely used as a flavor and fragrance, and is listed as "generally recognized as safe" in food by the U.S. Food and Drug Administration.[6] D-limonene has been shown to cause a male rat-specific kidney toxicity referred to as hyaline droplet nephropathy.[7] However, tests in other mammals have not resulted in a similar pathology, and the validity of extrapolation to other species and to humans has been called into question.[8] Limonene has also been employed as a mosquito larvicide,[9] an aquatic herbicide,[10] and has been found to be effective in killing fleas,[11] but is considered to be of limited utility as a broader-scale insecticide because of the high concentrations necessary to kill or inhibit common pests.[12]

Table 1. Physical properties of limonene, PES-51, and a similar shoreline cleaner, Corexit 9580.

	Flash point (° C)	Solubility (aqueous)	Specific gravity to water
limonene[1]	48	insoluble	0.84 (25°C)
PES-51[2]	51	insoluble	0.84 (25°C)
Corexit 9580[3]	79	insoluble	0.81 (16°C)

1: Material Safety Data Sheet, Aldrich Chemical Co., Inc.
2: Material Safety Data Sheet, Petroleum Environmental Services, Inc.
3: Material Safety Data Sheet, Exxon Chemical

Environmental fate

The PES-51 product literature states that "…the product leaves a 'crude' (impure) protein type film on all treated surfaces. This film does not allow re-deposition of the hydrocarbon to the treated surface which eliminates recontamination during the cleanup process. The film is sensitive to nature and begins to degrade in 96 hr." Laboratory and/or field data were not provided to support the latter claims.

Aquatic degradation products of limonene may closely resemble the pesticide toxaphene and its breakdown products. Researchers[13] studying limonene and related terpenes found that at low pH and when exposed to sunlight, aqueous mixtures produced complex polychlorinated compounds that had “striking similarities” to the organochlorine pesticide toxaphene. Less extensive but still substantial chlorination also took place at higher pH or in the dark. The lower chlorinated compounds could be mistaken for biologically degraded toxaphene in environmental samples, according to the researchers. In these experiments, limonene was the most highly reactive terpene examined, and consistently produced highly chlorinated material. The wider implications of this are not known.

Aquatic toxicity

A substantial body of aquatic toxicity information generated by two facilities under contract to Petroleum Environmental Services and Tesoro is cited in the Alaska Department of Environmental Conservation report on the Alaska test application. These toxicity data for PES-51 are summarized in Tables 2 and 3. Note that, in toxicity tests, a lower LC_{50} value indicates greater toxicity.

Table 2. Toxicity data for PES-51 on test organisms fathead minnow (*Pimephales promelas*), inland silverside (*Menidia beryllina*), and brine shrimp (*Artemia salinas*).

	Water	24 hr. LC_{50} (ppm[1])	48 hr. LC_{50} (ppm)	96 hr. LC_{50} (ppm)
PES-51				
P. promelas	Fresh	810	810	810
M. beryllina	Sea	100	100	100
A. salinas	Sea	980	840	N/A
20% PES-51 / 80% #6 Fuel Oil				
P. promelas	Fresh	>1600	>1600	>1600
M. beryllina	Sea	>1600	>1600	>1600
A. salinas	Sea	>1600	>1600	N/A
20% PES-51 / 80% #6 Fuel Oil				
P. promelas	Fresh	>1600	>1600	>1600
M. beryllina	Sea	>1600	>1600	>1600
A. salinas	Sea	>1600	>1600	N/A

[1]parts per million

Table 3. Toxicity data for PES-51 on the test organisms killifish (*Fundulus heteroclitus*), rainbow trout (*Onchorhynchus mykiss*), brine shrimp (*Artemia sp.*), Pacific oyster (*Crassostrea gigas*) and blue mussel (*Mytilus edulis*).

Species	Water	48 hr. LC_{50} (ppm)	96 hr. LC_{50} (ppm)
PES-51			
F. heteroclitus	Sea	1425	1425
O. mykiss	Fresh		98
Artemia sp.	Sea	665	
		48 hr. EC_{50}	NOEC*
M. edulis	Sea	9.6	3.12
C. gigas	Sea	18.7	6.25
O. mykiss	Fresh		62.5
*No observable effects concentration.			

As part of its ongoing evaluations of oil spill remediation products, Environment Canada has independently assessed both the effectiveness and toxicity of PES-51. Results of PES-51 toxicity tests performed by the Atlantic Region Aquatic Toxicology Laboratory for Environment Canada yielded a rainbow trout 96-hour LC_{50} value of 13.6 ppm. This compares with the 98 ppm value obtained by the contracted test facility for Tesoro.

Toxicity Discussion

PES-51 is characterized in both the Material Safety Data Sheet and in product literature as being insoluble in water, which is consistent with the physical characteristics of its major constituent, limonene. This has two implications for assessing aquatic environmental and laboratory toxicity. First, the insolubility of the product suggests that water column exposures would be considerably less than with a water-soluble product. Second, the insolubility of PES-51 makes it difficult to associate results from toxicity tests with a true water-accommodated concentration of the product. None of the aquatic toxicity testing procedures summarized above, including that of Environment Canada, actually measured concentration of the product in test solutions. Because the nominal concentrations were not supplemented with measured values, it is virtually certain that the listed concentrations underestimate the true toxic concentrations for PES-51. By using the volumetric concentrations as the accepted test concentrations, the researchers are assuming that the product is completely soluble—when, in fact, the opposite is true. Any observed toxicity effects may be attributable to a very minute portion of the measured amount of product that either goes into solution, or is in suspension.

This is a significant qualifier that must be considered when nominal concentrations are used for toxicity tests as is confirmed by the comments of aquatic toxicity researchers James Butler and Peter Wells:

> In a test, the insoluble material floats on top of the water and the test organisms are not exposed to it, only to the water-accommodated fraction (including dissolved material, suspended droplets, and material on suspended particulates). If the toxicant is very insoluble, the organisms will be exposed to a much smaller actual concentration than the nominal concentration reported. The result will be to make the toxicant *appear* (authors' emphasis) much less toxic…when in fact the effects observed were…caused by the very much lower water-accommodated fraction…Toxicity threshold based on real concentration is the more appropriate value for determining hazard from real environmental exposure. The use of nominal concentrations makes less-soluble agents appear to be less toxic than they are (or may be), and data from such studies cannot be translated to any situation other than the original experimental apparatus and stirring regime.[14]

These comments by Butler and Wells do not necessarily imply that laboratory toxicity results for PES-51 have no meaning for those tasked with examining potential environmental effects and tradeoffs. PES-51 will remain relatively insoluble in water whether it is a laboratory test solution or whether it is seawater next to a jetty that is being cleaned, and it is still useful to know the unit volume of the product per volume of receiving water that results in a certain level of toxicity. However, it will not be very meaningful to compare toxicity values for PES-51 directly with other compounds, unless these compounds have similar solubility. (See Table 1 for physical properties of PES-51 compared with Corexit 9580).

Because of the way in which PES-51 is used, it could be misleading to rely entirely on extrapolation of lab results to predict field toxicity from operational use. The recommended application technique for the product is to spray it directly onto the oiled substrate, allow it to remain for a few minutes, then rinse it off with ambient temperature seawater. As is noted in product literature, "The only time the product would actually come in contact with the water column of an aquatic ecosystem is when it is rinsed off the rocks." As a consequence, it is difficult to estimate an exposure concentration that nearshore biota might encounter during an application. Available toxicity data are based on volumetric concentrations of the product in water, but during an application it may not be possible to define a meaningful concentration that might occur in nearshore waters. Referring again to the PES-51 product literature, "There is no specific water to PES-51 ratio. Enough water should be used to rinse off the treated rocks thoroughly. One cannot use too much rinse water. Use whatever amount gets the job done." It is reasonable to assume that exposure of water column organisms would be relatively low during this kind of surface-washing operation (assuming that there is good containment and recoverey of oil and product, and that application protocols are adhered to by cleanup crews).

However, if the product is injected into the substrate of a beach to remove subsurface oiling (as was done in the Alaska test), organisms may be exposed to higher concentrations for prolonged periods. Intertidal organisms are distributed in a variable manner in and on the substrate, and substrates themselves will be heterogeneous. Moreover, seawater flushing following PES-51 injection is likely to be of variable efficiency. These two facts make it likely that both infaunal organisms (those living in beach sediments) and epibiotic communities (plants and animals attached to substrate surfaces) would be exposed to PES-51 concentrations that approach or exceed toxic levels. Using extended ambient water rinsing through the substrate after PES-51 application would help to mediate such potential exposures.

Toxicity Comparison with Corexit 9580

For the reasons previously described, it is not generally appropriate to compare aquatic toxicity results for those products whose solubilities are very different. For PES-51, a relevant comparison can be made with the shoreline cleaner Corexit 9580. This product is used in a manner similar to PES-51, and is also insoluble in water (see Table 1). Data from toxicity testing using Corexit 9580 are available for several aquatic species[15]. For three of these (killifish, brine shrimp, and oyster), toxicity results are also available for PES-51. In all three cases, Corexit 9580 appears to be less toxic than PES-51 (Table 4). In fact, for the first two species tested, PES-51 toxicity is at least an order of magnitude higher than Corexit 9580.

Table 4. Comparison of toxicity test results of PES-51 and Corexit 9580 M-2.

	PES-51 (ppm)	Corexit 9580 M-2 (ppm)
96 hr. LC_{50} F. heteroclitus	1425	>10000
48 hr. LC_{50} Artemia sp.	665	2800
48 hr. EC_{50} C. gigas	18.7	38

Product effectiveness

Little quantitative information is available on the effectiveness of PES-51 as a shoreline cleaner. Most such information is in the form of promotional videos and observations from two field tests. The only available laboratory measurements on effectiveness are from Environment Canada and were conducted as part of ongoing evaluations of oil spill remediation products. In its test of PES-51 performance as a surface-washing agent, Environment Canada found that the product did not meet their minimum criteria for surface-washing agent performance: measured effectiveness was 22.5 percent in fresh water and 20.6 percent in salt water, while the minimum level of performance established by Environment Canada is 40 percent for surface-washing agents.[16]

Though the Environment Canada tests are the only quantitative data currently available on the product's effectiveness, several field tests have produced qualitative, visual observations on the performance of PES-51. In the Alaska test conducted in Prince William Sound in July 1993, NOAA observers saw "a substantial amount" of oil liberated from the subsurface sediments. At Tampa Bay, test applications of PES-51 were compared with hot-water washing on a concrete walkway and on riprap boulders. Conclusions from this test varied, depending on the observer, from no noticeable difference to less residual stain on PES-51-washed sections of the concrete walkway (Appendices A and B).

FIELD TESTS

NOAA participated in two recent field tests of PES-51. The first test was a pre-planned demonstration applying the product on a cobble/gravel shoreline in Prince William Sound, Alaska containing residual oil from the *Exxon Valdez* spill (four years old at the time of the test in 1993). The second demonstration took place during a spill response in Tampa Bay, Florida and used PES-51 on a cement walkway on top of a riprap bulkhead. Though the Alaska test was much more involved than the test in Tampa Bay, both tests relied on visual observations to determine effectiveness. Each test gathered only anecdotal information about environmental impacts or toxicity to aquatic organisms in the field. Field reports from NOAA observers who were present at each test are presented in Appendices A and B.

NOAA observers at the Alaska test concluded that oil was mobilized from the subsurface following the application of PES-51 and subsequent flushing. Since no true control plot was tested using only cold-water flushing, it could not be definitively concluded that PES-

51 was solely or primarily responsible for the mobilization of the subsurface oil. However, Debbie Payton, one of the NOAA observers, felt that it would be unlikely that four-year old crude oil could have been mobilized by cold-water flushing alone. Sediment and water samples were collected by the University of Alaska before and after the PES-51 application. These samples were scheduled to be analyzed for petroleum hydrocarbons, but results are not yet available. No sampling or analyses designed to address concerns about toxicity or environmental impacts were conducted during this field test.

At the Tampa Bay test, applications of the PES-51 product were compared with hot water washing and with ambient temperature washing on patches of oiled concrete and on boulders on a riprap jetty. Conclusions from visual observations were that hot-water washing and PES-51 both removed the oil coat. On the concrete walkway, more stain remained with the hot-water washing, while the reverse was the case on the boulders. After the test, the responsible party decided to rely on hot-water washing for cleaning these areas, since this technique performed satisfactorily.

CONCLUSIONS

Ideally, toxicity results for this or any other chemical agent that may be considered for use in cleaning up an oil spill will be factored into a much broader evaluation of environmental tradeoffs. Consideration of how well the product performs, in terms of operational efficiency, certainly is an important aspect. If an agent under consideration does not significantly improve the removal of oil from the environment and is also toxic to organisms exposed to it, there would seem to be little reason for considering its use any further. On the other hand, if a product is highly effective in speeding the removal of oil but is also toxic, the Federal On-Scene Coordinator may be willing to consider the tradeoff to provide a longer-term benefit to the environment.

PES-51 is toxic in aquatic environments at certain concentrations. It contains a very high percentage of limonene, which has demonstrated toxicity. In fact, limonene has even been used as a standalone herbicide and pesticide. However, it is not possible to compare the toxicity of PES-51 to other reference toxicants, or even many other oil spill chemical agents, for reasons previously discussed and summarized below. Although an implicit assumption is made that the bacterial fermentation products in PES-51 are less toxic than the limonene carrier, this has not been confirmed and should not necessarily be accepted as a given.

While the other listed PES-51 components (i.e., "biospersans" and "biosurfactant") may contribute to the advertised functional characteristics of the product, the proportional distribution of the constituents suggests that this is less a bacterial fermentation by-product supplemented with limonene, than it is limonene with a relatively small component of a biological additive.

Whether PES-51 (or, for that matter, any other chemical shoreline agent) is effective at removing oil is independent from other considerations and should be evaluated at face value. Environment Canada attempts to do so in an objective way. However, the need or desire for a "natural" product is another factor that should be addressed explicitly; if this is judged to be an important criterion in making a selection, then the claim by PES-51 vendors that their product is indeed a "unique biological mixture" should be examined critically.

Similarly, the role of the biological component in enhancing the performance of the product would be interesting to ascertain and document. That is, how do the shoreline cleanup capabilities of PES-51 compare to pure limonene? Is it the microbial by-product component that gives PES-51 its cleanup potential, or is it the limonene carrier?
Toxicity results generated thus far for PES-51 must be interpreted with due caution, because concentrations for test solutions are nominal (i.e., based only on mixed amounts) and not actually measured in the test solutions. Since PES-51 is apparently virtually insoluble in water, toxicity results based on nominal concentrations would represent a significant underestimate of true aquatic toxicity. Currently available toxicity results for PES-51 are not comparable to those for other compounds, with the possible exception of products with similar solubility characteristics. PES-51 does resemble another shoreline cleaner, Corexit 9580 M-2, in its insolubility and its mode of application. In the three toxicity tests in which the same organisms were used, PES-51 was more toxic than Corexit 9580 M-2.

In tests cited in the PES-51 product literature, the product was found to have a relatively brief environmental half-life. However, there is some evidence that aquatic degradation products of limonene may closely resemble the pesticide toxaphene and its breakdown products. The wider implications of this are not known.

Though observers show PES-51 liberating residual subsurface oil in Prince William Sound, laboratory tests conducted by Environment Canada show that it does not meet minimum qualifications for effectiveness as a surface-washing agent. The Tampa Bay demonstration shows that PES-51 does work to wash oil off concrete and boulders, but not significantly more so than using hot-water washing. Based on this limited information, it would seem that PES-51 has some potential as a surface-washing agent, but that its effectiveness needs to be further evaluated in the field.

PES-51 does appear to hold some promise as a shoreline cleaner, as demonstrated primarily in the test application in Prince William Sound and in tank demonstrations by Tesoro. However, that promise is not completely without consequence, as use of the product also results in a certain level of environmental toxicity, and may also result in introducing stable chlorinated organic compounds into the environment, whose consequence is not entirely understood. In an ideal world, all of the product applied would be recovered—the reality, however, does not approach this level of efficiency. The need to remove oil from the environment may outweigh the potential effects from use of PES-51, but it is important that those charged with making the choices are aware of the known implications.

APPENDIX A: OBSERVATIONS OF PES-51 APPLICATION IN PRINCE WILLIAM SOUND

July 1-4, 1993

NOAA Observers: Debbie Payton, Seattle, Washington
John Whitney, Anchorage, Alaska

Background

Tesoro Oil Company is marketing a product, PES-51, for removing hydrocarbons from beaches. They proposed to the State of Alaska's Hazardous Substance Spill Technology Review Council to apply PES-51 to a portion of beach in Prince William Sound (Sleepy Bay, La Touche Island, segment LA-19A) that had subsurface oil bound to the sediments. Tesoro received funding from the Council for a test application and pre- and post-monitoring of the area. They requested approval from the Alaska Regional Response Team (ARRT), although it is not clear that there is any requirement for such approval. The ARRT, through Mark Miller, requested that NOAA review and comment on the test plan. Tesoro invited NOAA and other agencies to observe the test.

Objectives

Tesoro's stated objectives were to
1) test the effectiveness of PES-51;
2) measure the levels of hydrocarbons in the water resulting from the application; and
3) measure the microbial response to PES-51 treatment.

NOAA's objectives for observing the test were to
1) make qualitative observations of effectiveness;
2) note the application procedure and logistics requirements;
3) observe beach type of both test and control areas; and
4) note any obvious acute effects to organisms.

Both John Whitney and Debbie Payton made qualitative observations. In addition, the Coast Guard sent an observer from Marine Safety Office Valdez, MST1 Mike Rudolph, and the Alaska Department of Environmental Conservation sent Leslie Pearson to observe. On one of the days a representative from the Regional Citizens' Advisory Council, John Hayes, also observed the application.

Pre-Application Observations

Test beach

Biota

The lower-mid intertidal area had good coverage of yellow-brown algae (*Fucus sp*.) attached to the rocks, numerous seastars, mussels, limpets, and periwinkles (*Nucella sp.*), anemones, isopods, and small minnow-like fish were occasionally observed in the water. In the mid-intertidal area mussels, barnacles, limpets, and littorine snails were present., with barnacles and littorine snails in the upper intertidal.

Beach type

The test area was bordered to the west by a large bedrock outcropping and on the east by a number of large boulders. The area between the large boulders and bedrock outcropping was mostly small boulder to large cobble overlaying bedrock or gravel, with large, angular boulders scattered throughout the area.

Oiling

Very little surface oil was seen in the area. On the extreme east and west sides of the test area, heavy oiling was seen behind and between some of the large boulders. A sheen was observed on the standing water in some of these boulder areas. Subsurface oil was seen in an approximately 3-meter wide swath in the upper intertidal area across the whole test area. Some of the boulders and cobbles had oil staining in the form of non-flaky black spots. Oil also stained the cobble and pebble in the upper storm berm.

Control Beach

Biota

The lower-mid intertidal area and the mid intertidal area were similar to the test beach but had fewer barnacles and littorine snails in the upper intertidal area.

Beach Type

The western portion of the control beach consisted of large boulders, fading to smaller boulders and cobble to the east. Boulder and cobble size decreased eastward across the control beach to medium-sized cobble over pebble.

Oiling

Very little surface oil was seen. The surface oil that was found was on the extreme western portion of the beach (the eastern side of the test beach), behind large, angular boulders. There did not appear to be a swath of subsurface oiling in this area, although some patches were found at approximately the same level of the beach.

Application Method

An area of the beach measuring 135 feet by 120 feet was selected for the test site. The area was surrounded by two parallel hard booms. Absorbent boom was placed abutting sections of the hard boom. NOAA observed three applications: the first had no absorbent boom, the second had absorbent boom placed behind portions of the first hard boom, and the third had absorbent boom placed half in front, half behind portions of the first boom. A clamshell-shaped skimmer (Man-O-Ray) was placed in the eastern portion of the inner boom, and oil and water were skimmed into a storage tank onboard the landing craft. After gravity separation, the water was pumped back into the Sound. Air knives were attached to a two-gallon can of PES-51 and to compressed air. The knives used compressed air at about 150 pounds per square inch (psi). The proposed cold water deluge system did not work, so cold-water, low-pressure flushing from two fire hoses (2-3 inch diameter) was used. The PES-51 was injected, via the knives, into the sediment at depths that looked to range from a few inches to almost a foot (this does not include how far down the air may have penetrated). The first applications were done in the upper tidal area on the eastern 50 feet of beach, where there was no sampling either before or after the application). The following applications were done in a pattern that went from the lower beach area (zone 2), parallel to the water and then up the beach to the next zone. Most of zones 5 and 6 were untreated when the NOAA observers departed.

The area to be treated by PES-51 was sometimes wetted first, the PES-51 injected, then the area flooded. At other times, the PES-51 crew was ahead of the water and the injection was done, followed anywhere from a few seconds to minutes later by the fire hose flushing. Injection sites were randomly selected (mostly dictated by where injection could be done due to the large boulders); flow rate of product was not controlled. The average application rate (over three applications) was one gallon per 170 square feet. The first application observed was done on a falling tide; subsequent applications were on a rising tide. Before observations, approximately three to four gallons of PES-51 were applied during an equipment shakedown, which was mostly concentrated on the upper eastern quarter of the test area.

Sampling

The University of Alaska at Fairbanks was contracted to sample the sediment, water column, and microbiota before, during, and after the testing. They had conducted sampling at the test and control beaches in June. During the first part of the test in July, they had two persons on-scene to conduct the sampling, Mark Tumeo and Tamara Venerator. Tamara planned to stay through the entire testing period.

The University of Alaska team divided the beach into six zones, each 20 feet deep. Zone 1 started at the lower intertidal; zone 6 ended approximately 20-25 feet seaward of the upper storm berm. In each zone they collected a composite sediment sample from five places randomly spaced along the zone. The microbiology sample was a composite from all 30 holes. In addition, there were some “hot spots” from which sediment samples were taken. Water samples were collected as a composite from three places just offshore of the middle third of the zone, six inches below the surface. On the control beach, UAF collected composite sediment samples from five places along zones 2, 4, and 6; the microbiology sample was a composite from all 15 holes, and water samples were again collected offshore.

During this testing period, the first samples were to be collected immediately before application, with another suite of samples taken just after the test was completed. Water samples were to be taken after each application. Due to communication problems, samples were not taken for the “shakedown” and the eastern upper beach application (19-20 gallons), but were taken after the subsequent zonal applications.

Observations

Weather

It rained intermittently during the testing period, winds were mostly out of the north to northeast at 5-10 knots when PES-51 was being applied. A storm on the night of July 2 broke off and stranded *Fucus sp.* in the upper tidal area. No applications were conducted during stormy weather.

Application

In general, the product application was quite effective at liberating oil from sediments. As long as water remained on the application area, surface sheens and free-floating brown/black oil could be seen.

During and immediately after application, strong citrus smells were observed in the area. By the following day, there was no smell of citrus except in the few “hot spot” areas. In these areas, a limonene scent was noticeable by turning over rocks.

During the application, the oily/water/PES-51 mixture adhered to a hand, although oil did not stick. The sticky mixture was easily wiped off. Similarly, the mixture did not stick or adsorb onto the rocks (attributed to a biologically derived lipid/saccharine protein put into PES-51 specifically to prevent sticking). By the next day, the oil did stick, as normal oils do.

The amount of surface oiling significantly increased after the first application (and all subsequent ones that NOAA observed). This was probably due to the fact that the product application was working well, but there were insufficient quantities of water to get the oil off the beach and into the water where it could be collected in the boom.

NOAA documented a patch of mussels in the lower intertidal and observed no obvious changes. The only obvious biological impact was the displacement of littorine snails, probably from the water pressure.

Light sheens filled the inner boom area within approximately one hour of the application (July 4). Some of the sheen entrained and moved to the east during all applications. Very little brown/black oily product was in the boom area (it was spread too thin by then).

Absorbent pads worked very well in absorbing the oily mixture.

For up to at least two hours after the application of PES-51, re-introduction of water liberated more oils/sheens. Since surface oiling was increased because of the previous application, it was hard to tell whether the PES-51 was still having any cleaning effect the next morning when plain water was introduced.

There seemed to be a general consensus that, with more water, significantly less PES-51 would be needed.

Much of the floating product acted like it had a lot of surfactant; it didn’t stick and made discrete small droplets.

Some of the personnel applying PES-51 (from the Chenega Corporation) complained of headaches after the first application and requested organic vapor canisters respirators that they used for the remainder of the test.   Debbie Payton, who is very sensitive to smells, did not observe anything other than dry hands and a slight headache from the smell, which was not offensive.

Conclusions

This application of PES-51 appeared to work very well at cleaning oil off rocky areas and out of the substrate.   This test addressed only effectiveness and was not designed so that any conclusions could be reached on environmental effects.   (Toxicity tests of PES-51 are being independently conducted by Tesoro. Note: these tests were evaluated in the toxicity section of this report). PES-51 may be a valuable response tool if it proves to be relatively non-toxic, short-lived, and not downwardly mobile. However, significantly greater quantities of water would be needed and careful attention must be paid to collection in the offshore area.

APPENDIX B: PES-51 TEST DEMONSTRATION AT THE *BOUCHARD 155* OIL SPILL

John's Pass, Florida
August 31, 1993

NOAA Observers: Ruth Yender (Biological Assessment Team)
Brad Benggio (Scientific Support Coordinator)

Background

On August 10, 1993, three vessels collided at the entrance to the channel leading to Tampa Bay, Florida, one mile south of Mullet Key. An estimated 325,000 gallons of No. 6 fuel oil were released and by August 15 had oiled the Florida beaches of Pass-A-Grille, St. Petersburg, Treasure Island, Madeira, and Redington. Oil also moved into Boca Ciega Bay through John's Pass, oiling mangroves, seagrass beds, marshes, beaches, sea walls, and boats. Cleanup efforts began immediately, employing a variety of techniques and equipment.

Request to Use PES-51

A proposal for use of the chemical product PES-51 to assist in the spill cleanup was submitted to the On-Scene Coordinator on August 26 by Martech, a cleanup contractor employed by the responsible party, Bouchard. The proposal suggested using PES-51 on jetties, sea walls, and oiled boats. Oiled sea walls and boats were already being cleaned using methods recommended by the Shoreline Cleanup Technical Committee, which was composed of representatives from NOAA, the State of Florida, and the responsible party.

The Regional Response Team (RRT) met by conference call on August 30, 1993 to consider approving use of PES-51 on oiled jetties and a concrete walkway at John's Pass. The RRT requested a test demonstration of PES-51 before making a decision. They also requested a demonstration of high-pressure, hot-water washing, which was being used successfully on the sea walls but had not been attempted on the jetty. Tesoro Environmental Products Company, marketer of PES-51, conducted two test demonstrations on August 31, 1993. (Due to malfunctioning hot-water equipment and other preparation problems at the morning demonstration, a second demonstration was conducted in the afternoon.)

Demonstration

The PES-51 demonstrations were conducted on the north jetty at John's Pass, where riprap boulders and a concrete walkway had been oiled. Though Bouchard had conducted some manual cleanup with sorbent materials at this location, a coat of oil remained. Invertebrates and other organisms were not abundant on the riprap or the underlying sandy substrate in the immediate area of the demonstration.

At both demonstrations, each cleaning method was tested on a small section of cement walkway (approximately 50 square feet) and on the tops of two to three boulders at the upper part of the riprap pile, just below the walkway. A sheet of sorbent material had been stretched along the edge of the walkway on top of the riprap. An arc of snare, sorbent, and containment boom had been deployed in the water at the base of the riprap.

The morning demonstration was conducted at 0800 on a rising tide (about + 1.3 feet). A small section of concrete walkway was sprayed with PES-51 using a hand-held sprayer, scrubbed with a bristle broom, and flushed with low-pressure, ambient-temperature seawater. Boulders at the edge of the sidewalk were then sprayed with PES-51 and flushed with low-pressure, ambient-temperature seawater. An nearby section of sidewalk and boulders were cleaned with high-pressure, ambient seawater. The hot-water unit was not functioning at that time.

The afternoon demonstration was conducted at 1600 on a falling tide (about + 1.4). PES-51 was applied to a small section of concrete walkway and flushed with low-pressure, ambient temperature seawater. Two or three boulders next to the walkway were treated in the same manner. A nearby section of sidewalk and boulders was cleaned using high-pressure, hot-water washing, then flushed with ambient-temperature, low-pressure seawater.

Visual Observations

Concrete Walkway

Both PES-51 and high-pressure, hot water effectively removed the oil coat from the walkway, although slightly less stain remained on the PES-51 treated section. Brushing during the morning demonstration did not appear to significantly enhance PES-51 effectiveness. High-pressure, ambient-temperature seawater was least effective of the three methods, leaving substantially heavier oil coat and stain.

The water flushed after PES-51 applications to the walkway clearly contained mobilized oil. It should be noted that, for both demonstrations, insufficient sorbent material had been deployed on the riprap to recover all of the oil flushed over the edge of the walkway. In contrast to the chemdical action of PES-51, high-pressure, hot-water washing appeared to remove the oil physically, blasting the weathered oil coat from the concrete surface and scattering oil particles along with the reflected water spray. Cleaning was accomplished more quickly with PES-51 than with high-pressure, hot-water washing.

Riprap Boulders

Both PES-51 and high-pressure, hot water effectively removed the oil coat from the riprap boulders, though high-pressure hot water appeared to leave less stain. High-pressure ambient seawater was much less effective than the other two methods. Variability in the composition of the boulders made these results more difficult to compare than the treated concrete walkway patches.

PES-51 is applied undiluted, with a recommended application ratio of approximately one gallon per 100-150 square feet. At the morning demonstration, it appeared that about three gallons were applied to about 50 square feet of walkway and about three riprap boulders, which would indicate a much higher application rate than recommended. After the demonstration, Tesoro representatives did indicate that there had been an “overuse” of product on the riprap.

No toxicity or other biological testing was conducted.

RRT Approval

On September 1, 1993, the RRT approved using PES-51 “to assist in cleaning rock jetties, concrete walkways, metal railings, and wooden walkways in the vicinity of John’s Pass and Blind Pass that were affected by the spill.”

Actual Jetty Cleanup

The actual method used by Bouchard to clean the John’s Pass jetties and walkway was high-pressure, hot water, as had been used on oiled sea walls. PES-51 was not used. According to Robert Stoll, Response Manager for Bouchard, the walkway was cleaned on September 2 and 3, and the riprap boulders were cleaned several days later, after the Labor Day weekend. The walkway, which had been re-oiled by tourists who had climbed around on the oiled riprap, was re-cleaned at that time. Based on NOAA observations made on

September 3, this method was successful at removing the oil coat from the walkway, though some light stain remained after cleaning. Stoll indicated that Bouchard selected high-pressure, hot water as a sufficiently effective cleaning technique for this location and was satisfied with the results it achieved. They viewed the PES-51 test as simply a Tesoro demonstration.

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