

# DRAFT 5/8/09

# Exxon Valdez Oil Spill Trustee Council

441 W. 5th Ave., Suite 500 • Anchorage, AK 99501-2340 • 907 278 8012 • fax 907 276 7178

AGENDA EXXON VALDEZ OIL SPILL TRUSTEE COUNCIL May 13, 2009, 10:00 a.m. to 12:00 p.m. Anchorage, Alaska

Trustee Council Members:

RICHARD SVOBODNY Acting Attorney General Alaska Department of Law

LARRY HARTIG Commissioner Alaska Department of Environmental Conservation

DENBY S. LLOYD Commissioner Alaska Department of Fish and Game CRAIG O'CONNOR Special Counsel National Oceanic & Atmospheric Administration U.S. Department of Commerce

KIM ELTON Senior Advisor to the Secretary for Alaska Affairs Office of the Secretary U.S. Department of the Interior

JOE MEADE Forest Supervisor Forest Service U.S. Department of Agriculture

Meeting in Anchorage, Trustee Council Office 441 West 5<sup>th</sup> Avenue, Suite 500 Teleconference number: 800.315.6338. Code: 8205

State Chair:

1. Call to Order – 10:00 a.m.



11.20.04

- 2. Consent Agenda
  - Approval of Agenda\*
  - Approval of Meeting Notes\* March 9, 2009
- 3. Public comment 10:10 a.m. (3 minutes per person)
- Amendment to Boufadel Project 070836A Factors Responsible for Limiting the Degradation Rate of *Exxon Valdez* Oil in Prince William Sound Beaches\*

Elise Hsieh Interim Executive Director Online: Al Venosa, Michel Boufadel, Jacqueline Michel

5. Tentative Executive Session

Adjourn – 12:00 p.m.

\* Indicates action items

Motions

## Motions - May 13, 2009 Trustee Council Teleconference

## Item 2: Agenda and March 9, 2009 Meeting Notes

Motion to approve the May 13, 2009 agenda as presented.

Motion to approve the March 9, 2009 Trustee Council Meeting Notes as presented.

Item 4: Amendment to Project 070836-A, Boufadel

Motion to approve the Boufadel Project 070836-A, Factors Responsible for Limiting the Degradation Rate of Exxon Valdez Oil in Prince William Sound Beaches in the amount of \$437,497; this amount includes G&A (\$36,124).

March 9 Meeting Notes

. 1 .

# DRAFT 4/10/09

# Exxon Valdez Oil Spill Trustee Council

441 W. 5th Ave., Suite 500 • Anchorage, AK 99501-2340 • 907 278 8012 • fax 907 276 7178



## TRUSTEE COUNCIL MEETING NOTES Anchorage, Alaska

March 9, 2009

Chaired by: Craig O'Connor Trustee Council Member

Trustee Council Members Present:

Steve Zemke, USFS \* Rowan Gould, USFWS •Craig O'Connor, NOAA \*\* Craig Tillery, ADOL \*\*\* Denby S. Lloyd, ADF&G Larry Hartig, ADEC

- Chair
- \* Steve Zemke alternate for Joe Meade
- \*\* Craig O'Connor alternate for James Balsiger
- \*\*\* Craig Tillery alternate for Richard Svobodny

The teleconference convened at 9:30 a.m., March 9, 2009 in Anchorage at the EVOS Conference Room.

1. Approval of the Agenda

APPROVED MOTION: Motion to approve the March 9, 2009 draft agenda

Motion by Hartig, second by Lloyd

## 2. Approval of January 16, 2009 meeting notes

APPROVED MOTION: Motion to approve the January 16, 2009 meeting notes

Motion by Hartig, second by Tillery

Public Advisory Committee (PAC) comments: Stacy Studebaker, PAC Chair reported on the February 4, 2009 PAC meeting held during the Alaska Forum on the Environment.

Public comment opened at 9:40 a.m.

## No public comments were offered.

3. Darken Waters Display Resolution 09-03

APPROVED MOTION:	Motion to approve redirecting \$11,254 to apply to the Trustee Council's efforts to create a display for
	use by the 20 <sup>th</sup> Anniversary and for use in venues around Alaska

Motion by Zemke, second by Tillery

## 4. <u>Executive Session</u>

APPROVED MOTION: Motion to go into executive session to discuss personnel and litigation strategies

Motion by Tillery, second by Hartig

Off the record 10:12 a.m.

Teleconference adjourned following Executive Session without any action.

Adjourned at 10:45 a.m.

ļ

r

### Proposal for an Extension to the Project:

## Factors Responsible for Limiting the Degradation Rate of Exxon Valdez Oil in Prince William Sound Beaches

#### Background

The EVOS Trustee Council funded the project Factors Responsible for Limiting the Degradation Rate of Exxon Valdez Oil in Prince William Sound Beaches (the "Limiting Factors" study) in 2007 to understand the physical processes that affect the lingering oil in the subsurface intertidal sediments on some beaches in Prince William Sound. This study is a component of the 2006 Comprehensive Plan for Habitat Restoration Projects Pursuant to Reopener for Unknown Injury that outlined a multi-phase plan to restore shorelines in Prince William Sound and the Gulf of Alaska affected by the Exxon Valdez oil spill. This plan included the following recommended actions to accelerate removal of lingering subsurface oil from those shorelines: (1) locate the remaining lingering oil, using modeling and field sampling; (2) identify the factors that have slowed natural removal of the oil; (3) identify and evaluate candidate bioremediation technologies and, as appropriate, alternative technologies such as tilling and physical removal; (4) pilot test candidate bioremediation technologies; (5) evaluate potential remediation alternatives in a draft restoration implementation plan; and (6) implement the chosen remediation option(s).

The Limiting Factors study design was based on the hypotheses that there were either "environmental" limitations (mainly thought to be nutrients) or "bioavailability" limitations. The hydrologic processes were studied at six beaches in Prince William Sound (PWS) in 2007 and 2008 through installation and monitoring of wells used for tracer studies (Figure 1) and development of models of the groundwater flow patterns and rates. However, the results of two years of field investigations have indicated that there are other factors that have contributed to the persistence of the lingering oil. The Limiting Factor study revealed that the beaches of PWS where lingering oil occurs are made up of two layers: An upper layer with a very high permeability underlain by a lower layer with a very low permeability. The contrast in permeability is around a thousand fold, and subsurface oil in the beaches of PWS resides in the lower layer. Our modeling studies suggested that the concentration of oxygen in the lower layer is probably too low to sustain aerobic biodegradation of oil. Thus, we believe it is likely that at least one factor limiting bioremediation is availability or accessibility of the PAHs to oxygen.

1

Total Request: \$437,497 Total FY9 Amount: \$437,497 Temple Total Costs w/o G&A = \$401,373

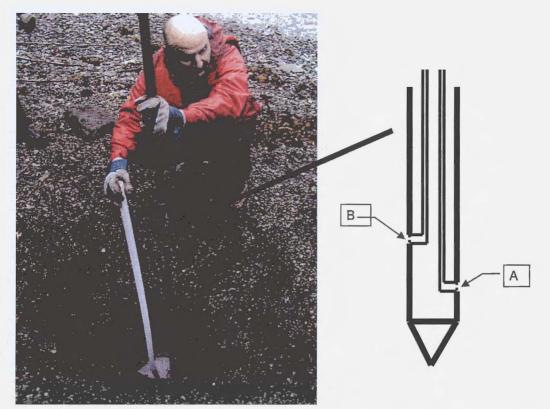


Figure 1: Placement of PVC pipe (white) for measurement of water level and multiport sampling well (stainless steel) in a pit. This approach would be used to monitor the background concentration of oxygen and nutrient in the lower layer of beaches.

Because of these new findings, we request additional funds to conduct additional field work extending the Limiting Factors study to determine if oxygen availability or nutrient availability (or both) in the lower beach layer are below concentrations necessary for the degradation of the lingering oil residues. This information is critical to the third phase of the Comprehensive Plan, that is, identifying and evaluating candidate bioremediation technologies. The proposed research will investigate factors that will inform whether inplace treatment of lingering oil by bioremediation is feasible, and if so, determine how to best stimulate this process through engineered manipulation of the physical or chemical environment of contaminated beaches. Using these results to understand the in-situ biodegradation of oil in the beaches of PWS presents some challenges, as the field conditions are different from those established in the lab. For this reason, we propose to conduct in-situ measurement of background levels of oxygen and nutrients in the summer of 2009.

In addition, we propose to test two alternative approaches to introducing oxygen and nutrients into the lower layer. These approaches will provide data on the hydraulic characteristics of the lower layer at the test beaches. These data will be important in evaluating and deploying pilot testing of candidate bioremediation technologies, should it be determined that the absence of oxygen and/or nutrients in this layer is a key factor in limiting oil biodegradation.

070836-A Proposal

.

#### Proposal for a Modification to the Project:

## Factors Responsible for Limiting the Degradation Rate of Exxon Valdez Oil in Prince William Sound Beaches

## Background

The EVOS Trustee Council funded the project Factors Responsible for Limiting the Degradation Rate of Exxon Valdez Oil in Prince William Sound Beaches (the "Limiting Factors" study) in 2007 to understand the physical processes that affect the lingering oil in the subsurface intertidal sediments on some beaches in Prince William Sound. This study is a component of the 2006 Comprehensive Plan for Habitat Restoration Projects Pursuant to Reopener for Unknown Injury that outlined the multi-phase plan of the United States and the State of Alaska to restore shorelines in Prince William Sound and the Gulf of Alaska affected by the Exxon Valdez oil spill. This plan included the following phases to accelerate removal of lingering subsurface oil from those shorelines by: (1) locating the remaining lingering oil, using modeling and field sampling, the "Lingering Oil" project conducted by Dr. Jacqueline Michel of RPI; (2) identifying the factors that have slowed natural removal of the oil, the "Limiting Factors" project conducted by Michel Boufadel and the "Oil Biodegradability" project conducted by Dr . Albert Venosa of the U.S. Environmental Protection Agency; (3) identifying and evaluating candidate bioremediation technologies and, as appropriate, alternative technologies such as tilling and physical removal; (4) pilot testing of candidate bioremediation technologies; (5) evaluating potential remediation alternatives in a draft restoration implementation plan; and (6) implementing the chosen remediation option(s).

#### SUMMARY OF THE FINDINGS OF THE "LIMITING FACTORS"

We are in the final stages of analyzing and interpreting the data, and we believe that additional field studies are needed to conclusively test the two hypotheses of the project: Environmental Limitations and Oil Bioavailability. A detailed report that would justify our request will be available by July 2009, which would be too late for the "field season" (June through September) on the beaches of Prince William Sound. For this reason, we present herein a summary of the findings, as they addressed testing the two hypotheses.

#### Hypothesis I: Environmental Limitations

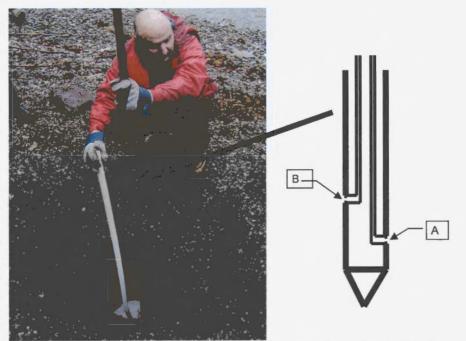
Testing this hypothesis required a better understanding of the hydraulics of the beaches in Prince William Sound and knowledge of the background concentrations of chemicals essential for the biodegradation of oil, such as oxygen and nutrients.

#### Hydraulics

The hydrologic and hydraulics processes were studied at six beaches on Eleanor, Knight, and Smith Islands in Prince William Sound (PWS) in 2007 and 2008 through installation and monitoring of wells used for tracer studies (Figures 1 and 2) and development of models of the groundwater flow patterns and rates.

1

Partial results of the tracer study conducted on EL056C (Eleanor Island) were reported in the Alaska Marine Symposium in January 2008. The presentation is attached herein as Attachment # 1. Attachment # 2 represents a manuscript investigating the hydraulics of EL058B submitted for possible publication in the Journal of Hydrology. It is expected that four additional manuscripts will be available by the end of June.



**Figure 1:** Placement of PVC pipe (white) for measurement of water level and multiport sampling well (stainless steel) in a pit. This approach was used to monitor the water level and concentrations of applied (lithium) and background (nutrients and oxygen) chemicals.

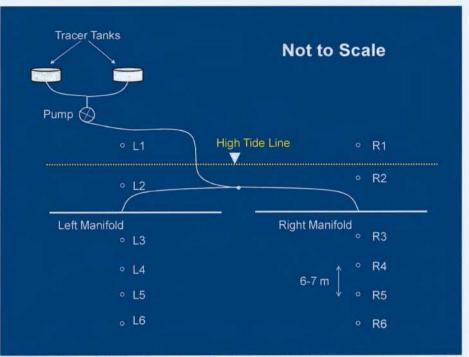


Figure 2: Layout of the field setup showing the manifolds for tracer injection along with the locations of the monitoring wells (Figure 1).

For all the six beaches, we found that the beach material beneath the armor can be viewed as consisting of two layers: An upper layer with a very high permeability underlain by a lower layer with a very low permeability. We do not treat the armor as a separate layer as done in prior studies, and this is due to two non-exclusive reasons: 1) The coverage of armor was not uniform across the beaches that we studied as indicated in Figure 3, which shows that the armoring disappeared going landward; and 2) as the sediments of the armor were coarse (pebbles and cobbles) with no fine material between them, water flow within the armor occurred freely, and one could view the hydraulics within it to be strongly connected to that of surface flow. Thus, it is unrealistic to treat the armor as a separate layer governed by porous medium hydraulics. Figure 4 provides a schematic of the layers based on our understanding of the geomorphology and hydraulics.

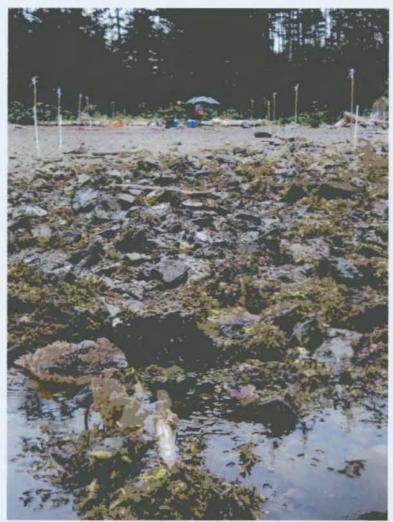


Figure 3: View of EL056C looking landward showing both the right (oiled) and left (clean) transects. Note how the armor disappears going landward.

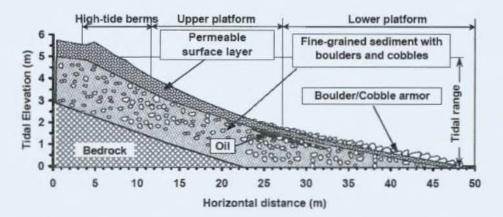
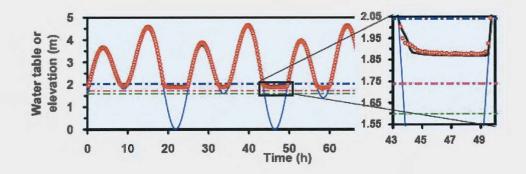


Figure 4: A schematic of the two layers in the beach along with the armor that occupies the seaward portion. The oil typically resides a few centimeters below the interface of the two layers.

The contrast in the permeability of the two beach layers beneath the armor was found to be about a thousand fold based on water level measurements and simulations (see attachment # 2). Figure 5 shows an illustration at a pit (see Figure 2 for explanation). The zero elevation represents the lowest low tide, and coincides with the zero elevation in Figure 4. First note the three horizontal lines: The blue line represents the elevation of the beach surface, the pink line beneath it represents the elevation of the interface of the two layers, and the green line represents the elevation of the pressure sensor. As the tide (blue curve) falls, the observed water level (red dots) follows it closely until the water level approaches the layers' interface where the rate of drop decreases suddenly (becomes mild), suggesting a sudden decrease in the permeability. Modeling results (black line) indicated that the hydraulic conductivity of the upper layer is around a centimeter per second and that of the lower layer around a thousand fold smaller.

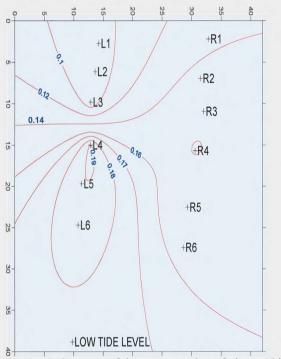


**Figure 5:** Time series of water level at one location. The three horizontal lines are as follows: The blue line represents the elevation of the beach surface, the pink line beneath it represents the elevation of the interface of the two layers, and the green line represents the elevation of the pressure sensor. The blue curve represents the observed tide level. The red dots represent the observed water level and the black curve represents the simulated water levels at the sensors. The maximum difference between simulated and observed results was about 1.0 cm. The zero datum is the same as in Figure 4.

#### **Background Levels**

Prior to conducting tracer studies on a beach, we measured the background concentrations of oxygen and nutrients (nitrate, phosphate, and ammonia) at various locations. Oxygen measurements gave values above 4.0 mg/L suggesting aerobic conditions at the points of measurement. Figure 6 shows the spatial distribution of the average nitrate-N at Beach EL058B (Eleanor). The pattern is being analyzed using the numerical models MARUN (Boufadel et al., 1999a) and SUTRA (USGS, 2003). (The simulations of water flow in Attachment # 2 were obtained using SUTRA). The maximum concentration was around 0.2 mg/L, an order of magnitude lower than the concentration needed for maximum biodegradation of hydrocarbons (2 to 10 mg/L) (Boufadel et al., 1999b, Du et al., 1999).

To conduct the measurements, pits were excavated and wells were placed in them (Figure 1) followed by refilling of the pits. We allowed 24 hours for resettlement of beach materials prior to any measurement of the background concentrations (oxygen and nutrient). However, when the aforementioned approach was conducted, the two-layer configuration was not known, and the "pit effect" disrupted the two-layer configuration and allowed chemical-laden water from the upper layer to enter into the lower zone of the beach near the sensor. Although the "pit effect" was accounted for when modeling and analyzing the movement of chemicals (tracer and nutrients), the field measurements of background concentrations of oxygen and nutrients that we obtained represented unspecified contributions from both layers.



**Figure 6:** Contours of the concentration of nitrate-N in mg/L on EL056B. The distribution was tight varying from a minimum of 0.08 to a maximum of 0.2 with an average of 0.15 mg/L of nitrate-N.

In particular, we conducted various numerical simulations of the movement and consumption of dissolved oxygen, and they all indicated that the lower layer has essentially no oxygen (i.e., an oxygen concentration of 0.0 mg/L), which is in disagreement with the field measurements. In addition, the results of the "Oil Biodegradability" project to date indicate that residual oil from the beaches of PWS biodegrades once exposed to oxygen, even without nutrient amendment, and that the addition of nutrients increases the rate at which biodegradation occurs. Dr.Venosa plans to present the preliminary results of that project on May 5<sup>th</sup> 2009 at Battelle's Bioremediation conference in Baltimore. Based on these results, we hypothesize that oxygen is depleted in the lower layer, and part of the field work described in this proposal will test this hypothesis.

#### Hypothesis II: Bioavailability

This hypothesis states that a "skin" occurred at the oil-water interface resulting in microscopic sheltering of oil from further degradation. In particular, it was thought that either a mineral layer or one made up from asphaltenes might be preventing the biodegradable oil components (alkanes and aromatics) from leaching out from the oil. The proposed testing of this hypothesis was through microscopic measurements in the lab.



Figure 7: Sample of oil deposited on sediment used to test Hypothesis 2.

Various authors used microscopic techniques to observe asphaltenes. However, they did not have the constraint that we have, which is not to disturb the sample. Acevedo and Rodrigues (2004) used freeze fracture-transmission electron microscopy (FFTEM) to study the crude oil, however, they precipitated the asphaltene prior to processing. Trejo (2009) precipitated the asphaltene before observing them through Scanning Electron Microscopy (SEM). The approach that we proposed was based on a paper by Bernabeu et al. (2006) who reported observation of asphaltenes on sediments following the Prestige spill on the Spanish coast in 2002. They showed photographs of a granular area that they claimed to be oil. However, they did not conduct elemental analysis through Energy Dispersive X-ray Spectroscopy (EDS) to confirm their visual observation.

We found it extremely difficult to observe the oil structure due to the liquid nature of the oil. All the techniques available for solidifying the oil in place, such as gold coating or freezing, would affect the oil distribution. For this reason, we conducted SEM on the oil that was in the liquid state (Figure 7), a state that was more or less apparent in Figure 8. Figure 9 shows the surface of clean sediments.

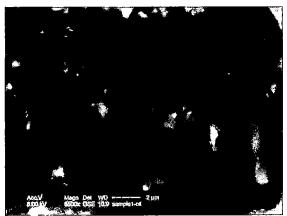
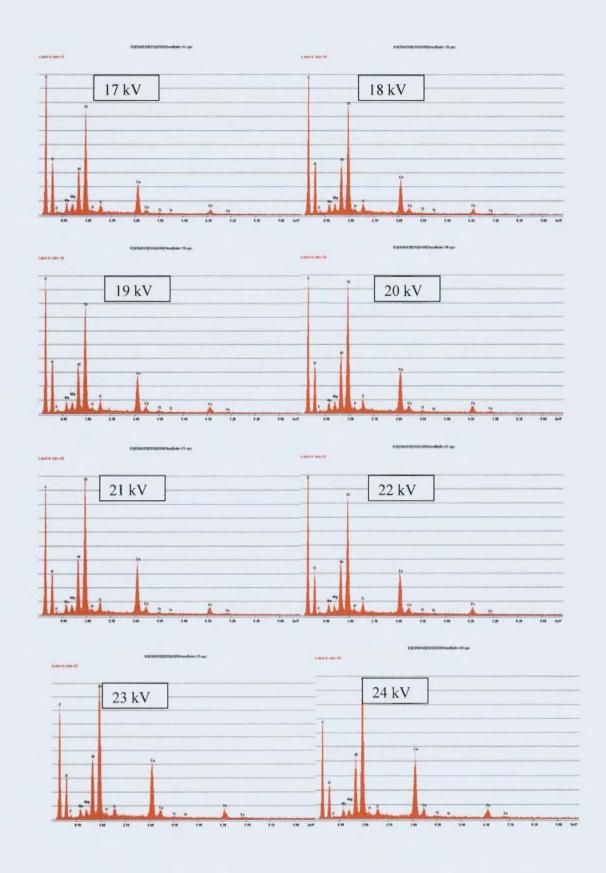


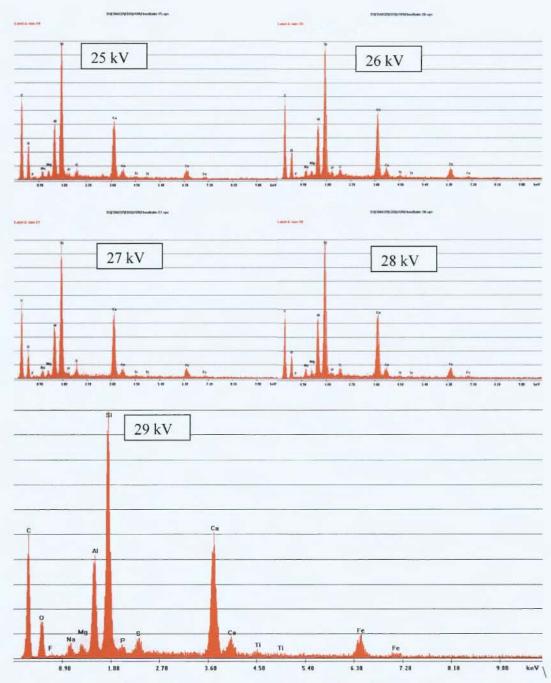
Figure 8: SEM of oil on sediment. The black lakes represent the oil. The "islands" represent sediment crystals.



Figure 9: SEM of the clean sediment surface (control).

We used EDS as a tool for detection of the mineral layer. As the voltage is increased, the depth of penetration of the electrons in the oil layer increases. Thus, if a mineral layer is present at the surface of the oil, the composition of mineral elements (e.g., Si, Al, Ca, O) would be highest at the lowest voltage (i.e., the oil surface) and would decrease as the voltage is increased until the voltage becomes high enough and the depth reaches the sediment. Figure 10, shows that this was not the case, and that the composition of mineral elements increased consistently as the voltage increased. In particular, carbon, C, was highest at the oil surface and decreased with depth until reaching the sediment surface, where Silicon, Si, became the highest. Thus, it is unlikely that a mineral skin existed on the oil.





**Figure 10:** Energy Dispersive X-ray Spectroscopy (EDS) readings of the oil on the sediments. As the voltage increases, the graph incorporates readings at larger depth within the oil layer. At the highest voltage (29kV), the reading reflects mostly the sediment composition.

## **Oil Composition**

We analyzed oil composition in all the oiled pits of the four beaches that we studied in Summer 2008. The beaches were: KN109A, KN114A, SM006B, and SM006C. Figure 11 reports the various fractions of oil normalized by the sum of Chrysenes C2 through

C4, considered relatively recalcitrant compounds. Hopane or stigmastane would have been better compounds for normalization (Atlas and Bragg, 2007), but they were not detected in some of the samples. Figure 11 shows that normalized alkane and aromatic concentrations increased in the seaward direction indicating that oil on seaward locations was less biodegraded. Figure 12 shows that the mass percentage of asphaltene increased as one moves landward, and it was higher than that of the oil present on the Exxon Valdez 11 days after the spill, which was around 4%.

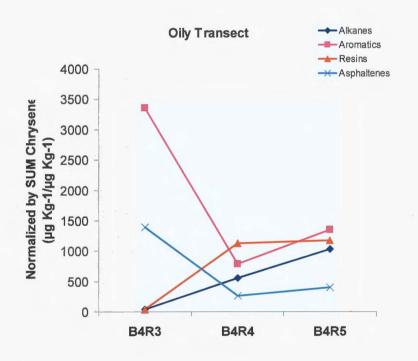


Figure 11: Spatial distribution of hydrocarbon classes on Beach KN114A (labeled Beach 4 in our study).

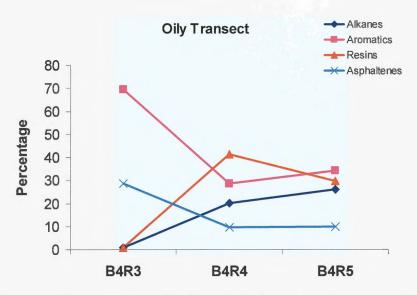


Figure 12: Mass percentage distribution of the hydrocarbon classes on Beach KN114A (Beach 4). A large percentage of asphaltenes indicates a high degree of biodegradation.

The trend of biodegradation was not the same at the beaches that we studied; the extent of biodegradation did not always increase in the landward or seaward direction. However, Figures 11 and 12 are typical in a sense that oil biodegradation was never uniform within a transect, rather it varied greatly, which addresses indirectly the hypothesis of a skin around the oil. If a skin of either minerals or asphaltenes is limiting biodegradation, then it would be unlikely that the extent of biodegradation varies within beaches, as the skin would be the limiting factor and not the distribution of chemicals (nutrient and oxygen). Thus, we are inclined to state there was no "skin" on the oil sheltering it from biodegradation, although data gathered to date do not conclusively disprove the hypothesis. Additionally, the proposed work described below could cast additional light on the viability of this hypothesis by documenting oxygen depletion or nutrient depletion in the lower layer.

#### **PROPOSED WORK**

#### Objective

The proposed work has two objectives: (1) to determine background concentrations of oxygen and nutrients in the lower layer of two beaches in PWS, and (2) to determine the rate of travel of chemicals within the lower layer at the same two beaches.

### Rationale

The proposed work would develop information about the lower layer of PWS beaches that is needed to understand how to best remediate lingering oil in that lower layer. It was initially hoped that lingering oil remediation techniques could be pilot tested in the 2009 field season, based on expected results from both the initial field work of this study and results from the "Oil Biodegradability" study being conducted by Dr. Albert Venosa

of the U.S. Environmental Protection Agency. While both of these studies have developed information that will be useful to designing oil remediation strategies, we believe that the additional information gathered under this proposal will be important, in two respects, for designing pilot studies.

First, by gathering data on background levels of oxygen and nutrients in the lower layer, we will be able to confirm with more precision the extent of oxygen depletion and nutrient depletion in the lower layer. We expect that this will confirm oxygen depletion as the primary factor limiting the biodegradation of oil.

Our field studies indicated that the beaches in Prince William Sound are made up of two layers, and that it is likely that the lower layer is depleted of oxygen. Preliminary results from Dr. Venosa's "Oil Biodegradability" study with funding by the EVOS Trustee Council have revealed that Exxon Valdez oil deposited on sediments biodegrades once placed in microcosms and exposed to oxygen. Even the more weathered oil showed high removal efficiencies for polynuclear aromatic hydrocarbons (PAHs). Thus, it seems likely that the primary factor limiting oil biodegradation is availability or accessibility of the PAHs to oxygen. In addition, as the removal efficiency was higher in microcosms that received nutrients, it is likely the nutrient concentration in the lower layer is not high enough to sustain maximum oil biodegradation.

However, it is at least theoretically possible that both the presence of oxygen and the disruption of the oil-water interface during sample collection and preparation prior to placement into the microcosms caused oil biodegradation. If oxygen concentration measured in the field is found to be high, then it would be likely that the disruption of the oil-water interface caused oil biodegradation in the lab. This would mean that only aggressive mechanical methods could be pursued for remediating the lingering oil. On the other hand, if the oxygen concentration in the lower layer is found to be too low, then remediation of the oil *in situ* could occur by oxygen amendment. In such a case, oxygen measurements are crucial for calculating the amount of oxygen amendment necessary to effect biodegradation of oil. In addition to the measurement of pore water oxygen, it is important to measure the Chemical Oxygen Demand (COD) of the oiled and unoiled sediments, which would provide an upper limit on the amount of oxygen that could be consumed during bioremediation.

The increased biodegradation rate of oil due to the addition of nutrient in the microcosm study suggests that the amount of nutrients in the lower layer also is not sufficiently high. Thus, it would be important to measure in the field the pore water concentration of nutrients to determine the amount that needs to be added. Similar to COD above, measurement of the Total Kjeldahl Nitrogen (TKN) of the sediments would provide essentially an upper limit on the amount of nitrogen that could be utilized during bioremediation.

Given the plausibility of the above competing hypotheses, it seems best to directly determine background oxygen and nutrient levels in the lower layer before designing and

deploying relatively expensive field pilot studies of remediation techniques based on assumptions about the levels of oxygen and/or nutrients in the lower layer.

Second, assuming that oxygen and/or nutrients are depleted in the lower layer, then the effectiveness of remediation methods that add oxygen or nutrients to the lower layer will depend, in part, on the rate at which added oxygen and nutrients travel within the lower layer. The less permeable the lower layer, the slower the rate of travel of added oxygen or nutrients through that layer. That, in turn, will affect the cost, practicality, and effectiveness of methods for adding oxygen or nutrients to the lower layer as a means of remediating lingering oil trapped there.

In sum, the proposed field work would provide important new data on both the likely factors limiting the degradation of lingering oil (oxygen and/or nutrient deficiencies) and characteristics of the lower layer that will strongly influence the kinds of remediation methods that are, and are not, promising candidates for remediating lingering oil.

## Implementation

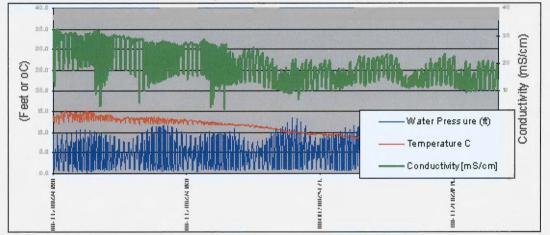
The proposed field work would take place at two beaches in Prince William Sound: EL056C on Eleanor Island and SM006C1 on Smith Island. We propose to monitor these two beaches due to their heavy oiling and difference in geomorphology. The sediments on beach EL056C are dominated by fine gravel, and the beach's bedrock seems to be 10 feet deep. The sediments on beach SM006C1 contain a large percentage of coarse gravel, and the beach's bedrock seems to be 3 to 4 feet deep, especially in the oiled areas. For each beach we propose to place six wells in two transects: three in the oiled transect and three in the clean transect. The time frame for the proposed work is the Summer of 2009, starting in early June.

To measure background concentrations of oxygen and nutrients in the lower layer, we will excavate pits, place wells in them (see Figure 1), and then refill the pits. When this was conducted within the current study, the two-layer configuration (Figure 4) was not evident, and the "pit effect" disrupted the two-layer configuration and allowed water-laden chemicals from the upper layer to enter into the lower zone of the beach near the sensor. Although the "pit effect" was accounted for when analyzing the movement of the applied tracer (Lithium), the measurements of background concentrations of nutrients and oxygen that we obtained represented mostly the upper layer. Therefore, we propose a method that allows us to measure the intrinsic concentration in the lower layer.

The long-term sensors that we placed in two beaches on Eleanor Island (EL056C and EL058B) showed that the temperature and salinity in the groundwater in the beaches fluctuate closely with tide the first month after excavation, and seem to behave independently of it after two months. Figure 13 reports the data of one sensor placed in EL056C. It indicates that the two-layer configuration is reached about two months after excavation, as suggested by the absence of temperature fluctuation. Thus, we propose to start sampling for oxygen and nutrients two months after placement of the sensors into

the beaches, and to conduct the sampling over a duration of six weeks at the frequency of once per week. We will also sample for temperature, salinity, and pH to better understand the geochemical conditions in the lower layer. For example, the pH value determines the state of many compounds (dissolved versus precipitated). As an another example, salinity measurements could used to infer the extent of mixing of saltwater and freshwater.

The measurement of oxygen would be obtained immediately in the field using a flow cell (Troll 9500 Low Flow, In-Situ Inc.), and water and sediment samples will be shipped to Temple University for analysis of nutrient concentration, salinity, and pH. Sediment samples will be taken during excavation and sent to the lab for analysis of TKN (the sediment samples collected for the microcosm contained a high value of 400 mg/kg). These field and laboratory measurements will provide the most accurate depiction of the environmental conditions affecting the oil in the lower layer.



**Figure 13:** Variation of water pressure (blue), temperature (red), and salinity (green) at a sensor placed in Eleanor 056C. Note that temperature fluctuations decrease with time and are absent after 60 days. The large fluctuations of salinity are also absent after 60 days. This indicates that the two-layer configuration is reached within 60 days of refilling the pits (one pit is shown in Figure 1).

To measure the rate of travel through the lower layer at each beach, we propose to introduce a tracer, most likely lithium using methods appropriate to the morphology of each beach. Lithium chemical properties results in its movement through sediments at a rate very similar to those of dissolved oxygen and nutrients. Two means of introducing oxygen and/or nutrients into the lower layer are by fluid injection under pressure and by using a slow release method.

The proposed methods for introducing the tracer at each beach are as follows:

<u>Liquid Injection at EL056C</u>. Injection of water containing oxygen and/or nutrients under pressure at Beach EL056C is considered most promising due to its deep bedrock that allows one to construct wells to depths of five feet or deeper. In practice, liquid injection can be accomplished by either well point injection or injection through buried well screen laterals. The hydraulic parameters used to design horizontal lateral injection laterals are

frequently determined by well point injection testing. Therefore, only well point injection testing will be performed at this time. Two injection wells will be installed in the beach with a screened interval within the lower layer.

The first injection well will be used to test fluid injection rates and pressures to determine the pressure/injection rate at which short circuiting occurs (i.e., water upwelling vertically near the injection pipe). A design injection pressure/flow rate will be selected for tracer injection in the second well that is significantly less than the pressure/injection rate at which short circuiting is determined to occur. The second injection well will be used to introduce an inert tracer (lithium) to evaluate the rates at which introduced solution propagates from the injection point. Monitoring points will be installed down gradient and cross gradient from the injection point. Samples will be collected from the monitoring points over time to determine the rate of tracer propagation within the lower layer.

<u>Slow release method of chemicals at SM006C1</u>. This method is considered most promising for SM006C1 because the beach has a shallow bedrock and injection under pressure would cause shortcircuiting even under low pressure. The slow release will occur either using drip techniques or a membrane that slowly permeates the tracer to the surrounding lower layer. Two transects will be established for this test, one will be in the oiled zone and one in a clean area. Each transect would contain four wells, three of them for monitoring and one for the release of the tracer (lithium). Samples will be collected from the monitoring points over time to determine the rate of tracer propagation within the lower layer.

If this proposal is approved, we would conduct additional detailed design work in May 2009 to specify and acquire the equipment and materials needed to conduct the field work described above. All tests will be conducted in a way that does not interfere with the operation of transects monitoring the background levels.

Finally, it should be noted that the proposed methods for introducing the tracer into the lower layer are also two of the candidate technologies for pilot studies to introduce oxygen and/or nutrients into the lower layer. Thus, the rates of travel data gathered could also confirm the suitability (or unsuitability) of these technologies for later pilot studies. More importantly, these data will be useful in evaluating the suitability of any proposed *in situ* treatment technology for introducing oxygen or nutrients into the lower layer.

#### REFERENCES

- Acevedo, S. and P. Rodriguez (2004). "An electron microscopy study of crude oils and maltenes." <u>Energy & Fuels</u> 18(6): 1757-1763.
- Atlas, R., and Bragg, J. (2007). "Assessing the long-term weathering of petroleum on shorelines: uses of conserved components for calibrating loss and bioremediation potential." Thirtieth Arctic and Marine Oil spill Program (AMOP), 263.

- Bernabeu, A. M., et al. (2006). "Beach morphodynamics forcements in oiled shorelines: Coupled physical and chemical processes during and after fuel burial." <u>Marine</u> <u>Pollution Bulletin</u> 52(10): 1156-1168.
- Boufadel, M.C., M.T. Suidan, and A.D. Venosa. 1999a. A numerical model for densityand-viscosity-dependent flows in two-dimensional variably-saturated porous media. J. Contam. Hydrol. 37: 1-20.
- Boufadel, M.C., Reeser, P., Suidan, M.T., Wrenn, B.A., Cheng, J., Du, X., Huang, T.L., and Venosa, A.D. 1999b. Optimal nitrate concentration for the biodegradation of n-heptadecane in a variably saturated sand column. Environ. Technol. 20: 191-199.
- Du, X., Resser, P., Suidan, M.T., Huang, T., Moteleb, M., Boufadel, M.C., and Venosa, A.D. 1999. Optimum nitrogen concentration supporting maximum crude oil biodegradation in microcosms. In: Proceed., 1999 Int. Oil Spill Conf., pp. 485-488. American Petroleum Institute, Washington, DC.
- Trejo, F., et al. (2009). "Structural Characterization of Asphaltenes Obtained from Hydroprocessed Crude Oils by SEM and TEM." Energy & Fuels 23(1): 429-439

USGS. 2003. http://water.usgs.gov/nrp/gwsoftware/sutra.html

### **Revised Schedule of Measurable Tasks**

#### FY 09, Third Quarter (April 1-June 30, 2009)

- All samples collected in summers 2007 and 2008 are analyzed (nutrients, etc.)
- Modeling of all field studies conducted in summers 2007 and 2008 is completed.
- Designing the pilot study for injection well on EL056C.

FY 09, Fourth Quarter (July 1-September 30, 2009)

- June 2009, Placement of long term wells along with pilot injection system.
- August 2009. Testing of pilot injection system.
- August 2009. Sampling for oxygen and nutrients from both layers of beaches.

## FY 10, First Quarter (October 1-December 31, 2009)

- Analyses of half of the samples for all nutrients.
- Numerical evaluation of pilot tests.

## FY 10, Second Quarter (January 1-March 30, 2010)

- All samples are analyzed.
- Numerical evaluation of pilot tests.
- Circulation of draft final report.
- FY 10, Third Quarter (April 1-June 30, 2010)
- Final report is submitted.

## BUDGET

## Total Request: \$437,497 Total FY9 Amount: \$437,497 Temple Total Costs w/o G&A = \$401,373

<u>Item</u>	<u>Cost \$</u>			
Travel first trip (five people from philadelphia)	7500			
Boat Aucklet- ten days	16750			
Boat Alexandra- ten days	14750			
6 diggers	15000			
Shipping	15000			
Travel second trip	5500			
Lodging and perdiem for 1.5 months	15300			
Boat, 2nd part trip	20800			
Oxygen cell	10,000			
Nutrient analysis	45,000			
Sediment analysis for COD and TKN	16,000			
Salary four graduate students (3 months)	24,000			
Beach Injection (2 wells)	15,000			
Postdoc/engineer	65,000			
Summer Salary	18,000			
Direct Temple	303600			
Direct RPI	7150			
Direct Farallon	7800			
Total Direct	318550			
Overhead at 26%	82823			
Total cost	401373			
Total cost with G&A at 9%	437497			

## **BUDGET JUSTIFICATION**

Five people will travel from Philadelphia to Whittier to take the boat. The airline ticket per person is estimated at \$1,000. In each direction, a one night stay in an Anchorage hotel at \$200. Per diem for two days is \$100. Thus, for five people 5X\$1500=\$7,500.

The boat Auklet will be rented to house six people during 10 days to conduct the installation. Costs are 1,675/day for 10 days = 16,750.

Another boat will be rented for 10 days to house the remaining people, expected to be six diggers Costs are 1,475/day for 10 days = 14,750.

Six local diggers will be contracted for 10 days at 250/day = 15,000.

Shipping of equipment through carrier (e.g., ABF) to Anchorage and transport via rented trucks to Whittier for loading on the boats. Returning the equipment to Philadelphia. Shipping nutrient and sediment samples to Philadelphia. Total costs estimated at \$15,000.

Four students will travel in early August to conduct the sampling. 4X\$1,000/per ticket=\$4,000. One senior personnel will travel and spend a week in the beginning of the monitoring and injection testing.

Four students stationed in a hostel in Anchorage for 45 days (August through September). Housing and per diem costs for the students are  $85 \text{ day } \times 4 \text{ persons } \times 45 \text{ days} = 15,300$ .

The four students will travel to the field once a week to collect samples and return them to Anchorage. Six trips are planned at the approximate rate of two days for the boat. To account for inclement weather days, eight trips will be budgeted. 8 trips at 2 days/trip @\$1300/day = \$20,800.

An Oxygen Cell (Troll 9500, Low Flow, In Situ Inc) to be used in the field to measure oxygen in situ would be purchased at \$10,000.

Nutrient analysis will be conducted. The budget includes 600 samples at the cost of \$75 per sample = \$45,000.

The budget requires chemical analysis of 50 sediment samples: 25 for total Kjehldahl nitrogen (TKN) and 25 for Chemical Oxygen Demand (COD). Cost is estimated at \$16,000.

Four graduate students will be paid for three months (the summer semester) to work on this project. 4 X \$2000/monthX 3 months=\$24,000.

Beach injection setup for two wells along with the slow release test. Estimated at \$15,000.

Postdoc/engineer to design the pilot study and to conduct analysis of measurements for optimizing the system, and for conducting simulations of possible chemical consumptions. The estimated base salary is \$53,000. With a fringe benefit percentage of 25%, this would result in approximately \$65,000.

Salary for Boufadel to be in the field for 15 days and support for additional three weeks to supervise the installation and the testing.

### **RPI Contractual Support**

The budget includes a subcontract to RPI to provide logistical support during the planning and implementation of the field studies, and technical support for data interpretation. The costs are based on the following level of effort:

Dr. Jacqueline Michel: 30 hours @\$195/hour = \$5,850 David Betenbaugh: 20 hours @\$65/hour = \$1,300 Total RPI costs = \$7,150

### **Farallon Engineering Contractual Support.**

The budget includes a subcontract to Farallon Engineering for Rich McManus to assist in the design of the injection system.

Rich McManus: 40 hours @195/hour=\$7,800

070836-A Justification

<u>.</u> . .

.

-

-

.

## Justification for the 2009 Limiting Factors Field Study Modification

This document briefly describes the rationale for a proposed modification to the study titled "*Factors Responsible for Limiting the Degradation Rate of Exxon Valdez Oil in Prince William Sound Beaches.*" The activities outlined in the proposed modification would be conducted during the 2009 field season. An important assumption behind the field work proposed for 2009 is that the Trustee Council will seek to fund pilot studies in 2010 of promising methods for remediating lingering oil. We believe that the activities proposed for 2009 will improve both the likelihood of success and the cost-effectiveness of pilot studies conducted in 2010, for the reasons that follow.

- 1. The proposed 2009 field program will gather important data that are presently lacking about groundwater flow in the lower layer of the beaches. In designing effective *in-situ* remedial techniques, it is critical to know the flow rates in the lower layer, the "area of influence" of an injection well under different injection pressures, and the maximum injection pressure that can be reliably applied while maintaining well integrity. Similarly, where slow-release application at beaches with a shallow oil layer is proposed, information on the rate of flow within the oil layer and the area of influence from the point of application of slow release material is critical. The proposed 2009 field program will gather this information using a tracer (probably a lithium-based compound) with flow rate characteristics similar to oxygen and nutrient compounds that would be used in remediation pilot studies.
- 2. At the same time that data on groundwater flow in the lower layer is gathered, it is both costefficient and prudent to take measurements of oxygen and nutrient levels in the lower layer. Based on studies conducted to date, particularly by Dr. Venosa, it is quite likely that lack of oxygen in the lower layer is the key factor limiting decomposition of lingering oil, with nutrient availability in the lower layer as a lesser but measurable factor. However, oxygen and nutrient levels in the oiled layers of the beaches have not yet been directly measured in the field, and before conducting expensive field studies of proposed remedial techniques, it would be prudent to confirm this hypothesis at a relatively low cost. This will also allow remediation field studies to determine with more precision the quantities of oxygen and nutrients to introduce to the oiled layer.
- 3. The two-layer characteristic of the beaches also limits the time and methods used for gathering the data described above. In order to measure the above parameters in the field, we want to wait for at least 2 months after well installation for the sediments to return to their natural condition. Therefore, with well installation in June, field measurements can only start in August and must terminate by mid-September because of weather conditions (maybe even earlier on Smith Island). This limited time period is workable for measurements of lithium tracer and direct sampling of oxygen and nutrients in the lower layer. However, if we were going to directly test injection of oxygen and nutrients, there would not be enough time to measure any actual changes in oil composition after just 30 days of treatment. Many of the wells installed in 2009 can be used in 2010 remediation trials, so there should be less delay in starting actual pilot tests of different remediation strategies. Data collected in 2009 will also confirm the actual wait period between well installation and return to natural condition.

- 4. The two proposed sites for continued work in 2009 represent two different types of beaches that contain significant amounts of lingering subsurface oil. The site on Eleanor Island has a thicker accumulation of finer gravel and is representative of potential treatment sites located at, for example, Sleepy Bay, Herring Bay, Perry Island, Evans Island, and parts of Knight Island. The site on Smith Island has a thinner sediment accumulation that is armored; it is representative of potential treatment sites located, for example, on other parts of Smith Island, Green Island, Latouche Island, Herring Bay, and Bay of Isles. We cannot say what percent of the potential treatment sites is represented by these two study sites, but they should be similar to many of the sites with the greatest amount of lingering subsurface oil and thus would be priority areas for remediation.
- 5. The results of the proposed 2009 field work will be available in early fall and can be used as part of a RFP to solicit from the public the best approaches for *in-situ* remediation. With these additional feasibility studies already conducted, all new proposals will be better designed and likely to be more effective and cost-efficient. For example, the data on flow rates and area of influence in the lower layer will inform important design decisions such as the distance between surface injection points or wells, the injection pressure for wells, and the amounts of oxygen and nutrients to be injected, whether by well or surface injection. It will also help design the distance between wells or injection points and monitoring locations. Conversely, another outcome of the proposed 2009 work could be a determination that some or all technologies cannot effectively inject oxidants at PWS beaches. This result, while disappointing, would also be very important to the Trustee Council and the public in deciding whether to fund field tests of particular remedial technologies.
- 6. Further to the issue of providing data to improve new proposals for pilot testing of remedial strategies, the results of the 2009 studies will provide the basis for evaluating the design of different methods such as: use of wells versus lateral trenches for injection of oxidants and nutrients; application rates of oxidants and nutrients (there are currently insufficient data from which to estimate the oxygen demand of the oiled sediments which includes biogenic hydrocarbons); whether injection of slow-release compounds will be effective at reaching the oiled layer; formulations of oxidants (slow release versus dissolved formulations); and the potential formulation of new products that will be most effective under the hydrological conditions on beaches in PWS. It is important to note that most oxidant formulations have been developed for use in terrestrial applications. Manufacturers may have to modify their formulations to meet the application conditions in the intertidal zone of PWS.

Resolution 09-04

.

# DRAFT 5/12/09

## RESOLUTION 09-04 OF THE EXXON VALDEZ OIL SPILL TRUSTEE COUNCIL REGARDING AUTHORIZATION FOR ADDITIONAL FUNDS FOR PROJECT 070836-A

We, the undersigned, duly authorized members of the *Exxon Valdez* Oil Spill Trustee Council do hereby certify that, in accordance with the Memorandum of Agreement and Consent Decree entered as settlement of <u>United States of America v.</u> <u>State of Alaska</u>, No. A91-081 Civil, U.S. District Court for the District of Alaska, and after public meetings, unanimous agreement has been reached to expend funds received in settlement of <u>State of Alaska v. Exxon Corporation, et al.</u>, No. A91-083 CIV, and <u>United States of America v. Exxon Corporation, et al.</u>, No. A91-082 CIV, U.S. District Court for the District of Alaska, for necessary natural resource damage assessment and restoration activities in the amount of \$437,497 for fiscal year 2009 as described in Attachment A. The monies are to be distributed according to the following schedule:

TOTAL APPROVED	\$437,497
TOTAL TO UNITED STATES OF AMERICA	\$437,497
National Oceanic & Atmospheric Administration	\$437,497

Funds shall be spent in accordance with Attachment A.

By unanimous consent, we hereby request the Alaska Department of Law and the Assistant Attorney General of the Environmental and Natural Resources Division of the United States Department of Justice to take such steps as may be necessary to make available additional funds for Boufadel Project/070836-A, Factors Limiting the

1

# DRAFT 5/12/09

Degradation Rate of Exxon Valdez Oil on Prince William Sound Beaches from the

appropriate account designated by the Executive Director.

Approved by the Council at its meeting of May 13, 2009 held in Anchorage, Alaska as affirmed by our signatures affixed below.

JOE L. MEADE Forest Supervisor Forest Service Alaska Region U.S. Department of Agriculture RICHARD SVOBODNY Acting Attorney General Alaska Department of Law

KIM ELTON Senior Advisor to the Secretary for Alaska Affairs U.S. Department of the Interior CRAIG R. O'CONNOR Special Counsel National Oceanic & Atmospheric Administration U.S. Department of Commerce

DENBY S. LLOYD Commissioner Alaska Department of Fish and Game LARRY HARTIG Commissioner Alaska Department of Environmental Conservation

Attachment A: Funding Distribution



Project # PI	Project Title	-	FY09 Direct cost approved	FY 09 PJ Mgmt Approved	FY09 G&A Approved	Total Resolution 09-04
					F	FY09 approved
070836-A Boufadel	Factors Responsible for Limiting the Degradation Rate of Exxon Valdez Oil in Prince William Sound Beaches		\$401,373	\$0		\$437,497
		NOAA	\$401,373	\$0	\$36,124	\$437,497
	Total to the United States o	f America		*		\$437,497
	Total Approved Resolut	tion 09-04				\$437,497

,

-

\$

\*NOAA has declined project management funds for this project