

REQUEST FOR AMENDMENT

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ABSTRACT

During the summer of 2011, staff from the Center for Natural Resource Development and Protection at Temple University evaluated the feasibility of enhancing biodegradation (*i.e.*, bioremediation) in order to perform remediation of four Prince William Sound beaches where lingering Exxon Valdez oil persists: EL056C.3 (Eleanor Island), LA015E (Latouche Island), PWS3A44 (Perry Island), and SM006B (Smith Island). Our method relied on injecting beneath the oil layer on each beach a solution of hydrogen peroxide (100 mg/L), lithium nitrate (20 mg N/L), and sodium tripolyphosphate (2 mg P/L). The results from EL056C.3 and SM006B were the only ones available at the time of this request. Those from EL056C.3 showed that the oil in the experimental plots there biodegraded by 30 to 50% within one month. The results from SM006B suggested that no oil biodegradation occurred at that site.

We are proposing to conduct additional feasibility work in Summer 2012 on two beaches: EL056C.3 and SM006B. On EL056C.3 we propose to expand operations in order to determine the maximum extent of biodegradation on the experimental plot used during Summer 2011 and to extend the boundaries of our technique to include the oil-contaminated areas to the right (facing landward) and in the lower intertidal zone. For SM006B, we are proposing to increase the injection pressure, as we believe most of the injected solutions were depleted within a short distance from the well tips. Beach PWS3A44 is similar in morphology to EL056C, while Beach LA015E had little oil. Therefore, pursuing the investigation on these two beaches is not as crucial as on the two beaches for which additional work is proposed.

This request also seeks funding for a two-step process of evaluating, for suitability as candidates for bioremediation, 53 oiled sites identified by Research Planning Incorporated's (RPI's) model for locating lingering oil as having greater than 30% distribution of moderately oiled residue at a 70% predicted probability value. This evaluation will include a desktop exercise as well as field verification.

DISCUSSION

Figure 1 provides a schematic top view of the treatment area for EL056C.3. The injection system was setup in May 2011 during which sediment samples were taken for oil analysis. The injection system started on July 8th and sediment samples from the treatment area were taken on August 10th and September 8th. All oil analyses were conducted at NOAA Auke Bay Laboratory in Alaska. Water samples from the treatment area were also withdrawn on the same dates, and they were analyzed for nutrients and oxygen. The partition of the plot into four zones

(Z1, Z2, Z3, and Z4) was adopted to investigate the effects of increasing transport distance on treatment effectiveness, but there were no geologic differences between these zones.

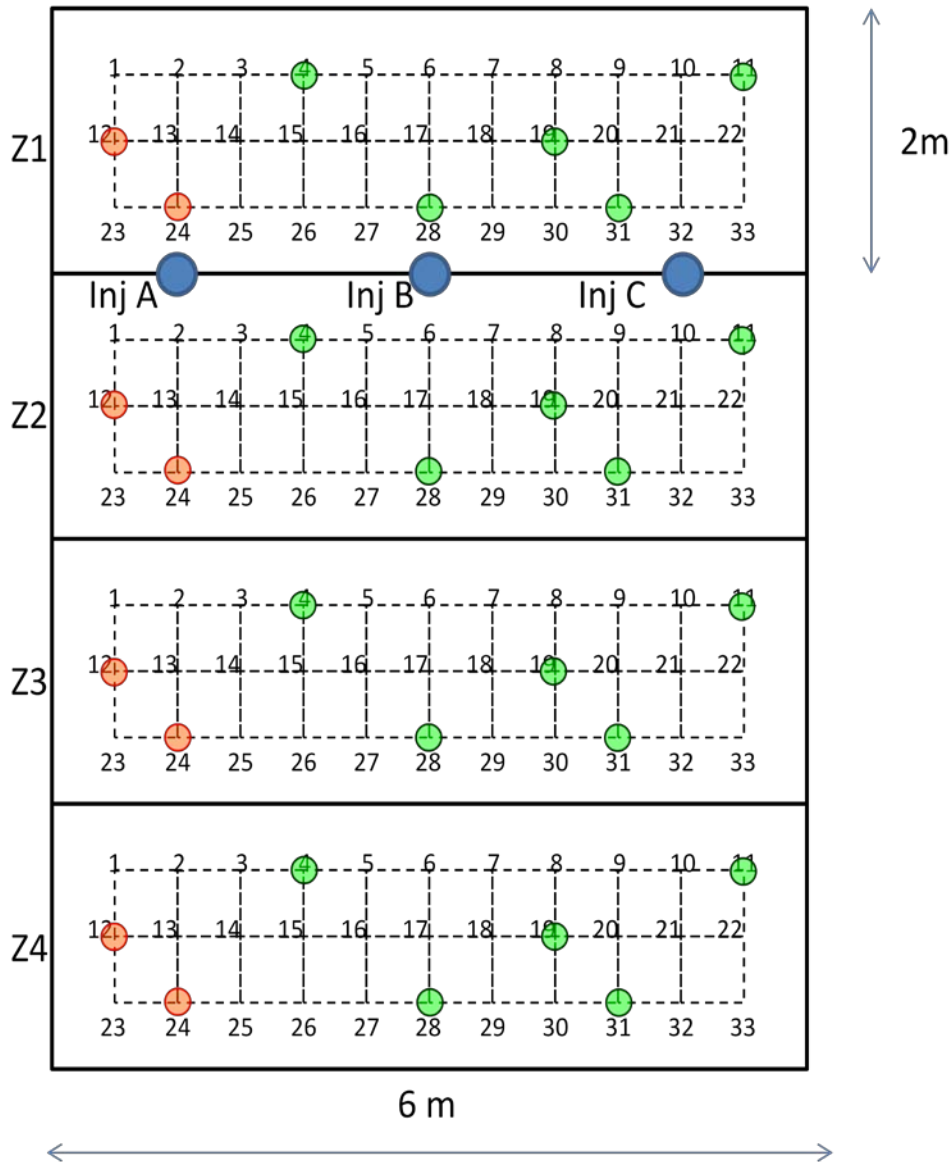


Figure 1: Grid showing the locations of the injection wells (InjA, InjB, and InjC), and four zones (each 2.0 m in the cross shore direction) for sampling for oil biodegradation (the green circles). The orange circles contained oil that was highly degraded prior to the injection (oil was about 63% more degraded in samples from locations indicated by orange circles than locations indicated by green circles). Results from the data points represented by the orange circles and green circles were evaluated separately, as shown in Figures 2 and 3, because the pre-treatment nutrient and TPAH concentrations of the two groups were significantly different.

Figure 2 reports the oil data obtained from each of the four zones in May, August, and September. The top panel of Figure 2 reports the results from each zone. Comparing August to

May, one notes a 90% decrease in the concentration of total polycyclic aromatic hydrocarbons (TPAH) at Z1 (the most landward of the zones), and between 30 to 50% decrease at Z2, Z3, and Z4. The lack of decrease between August and September may have been due to the stoppage of the system due to severe storms that occurred between the August and September sampling trips. Figure 2 clearly demonstrates that bioremediation of the oil in situ is a viable technology, as the biodegraded amount averaged between 30% and 50% within only a month's time. Figure 2 does not include the data from the two leftmost samples on each plot (orange color in Figure 1) because inclusion of the highly weathered oil from those locations would confound the identification of treatment effects. Those results are reported in Figure 3, which shows that extensive biodegradation occurred for both spatial groups, regardless of the initial degree of weathering.

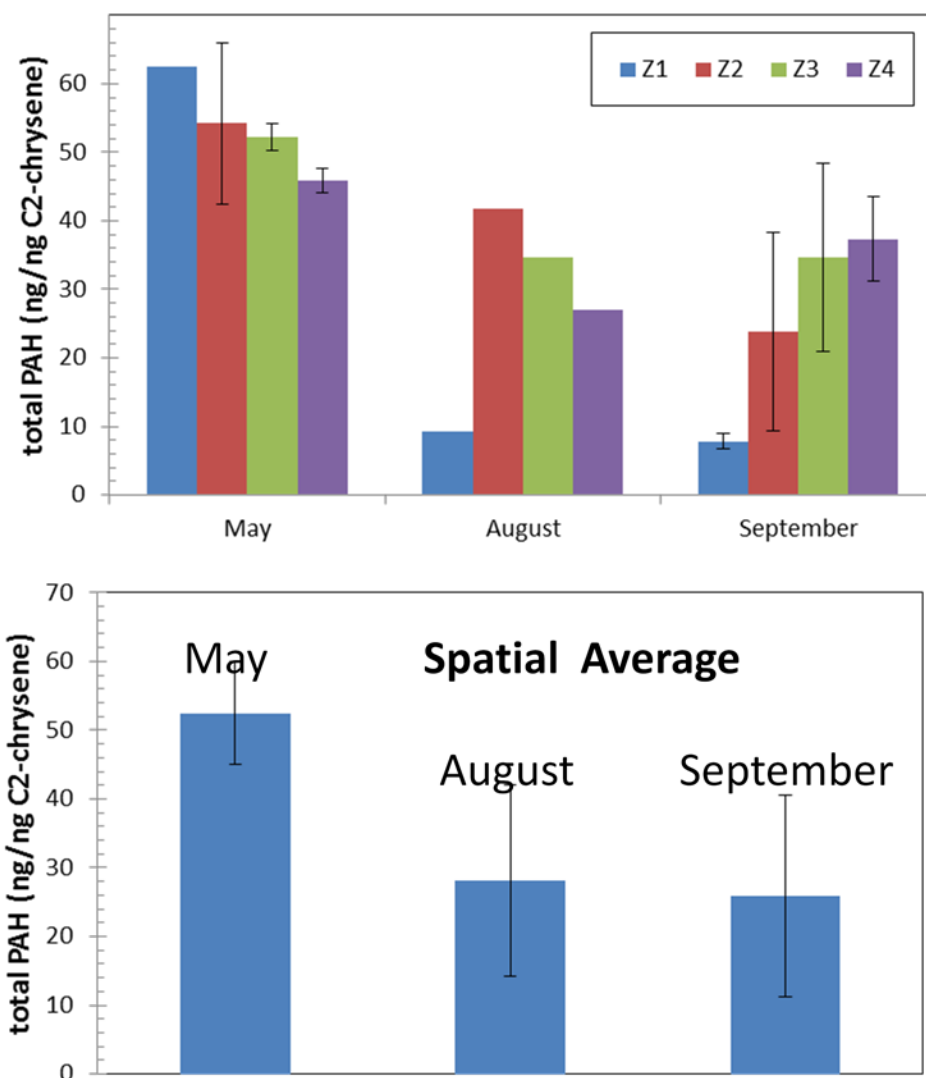


Figure 2: Concentration of total polycyclic aromatic hydrocarbons (TPAHs) as function of space and time. Top panel: Concentration of each zone (Figure 1) at three dates, May (pre injection), and August (10th) and September (8th). Lower panel: Concentration averaged over all zones. Note that injection started on July 8th.

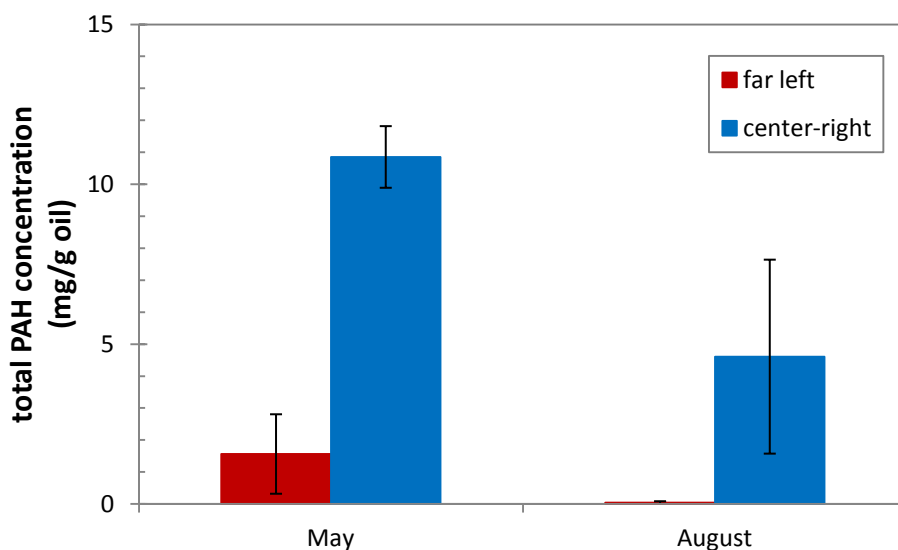


Figure 3: Distribution of oil on EL056C.3 and extent of weathering. Note the high degree of biodegradation of the far left oil.

Preliminary data from SM006B indicate that oil there did not biodegrade, and we believe it is due to a combination of biochemical and hydraulic factors. Specifically, Venosa et al. (2010) conducted microcosm biodegradation studies on oiled sediments from three beaches: EL107, KN114A, and SM006B. They found that, when the microcosms were amended with nutrient, the oil biodegraded to 7%, 1% and 20% of the initial concentrations within 160 days at EL107, KN114A, and SM006B, respectively. Venosa et al. (2010) fitted a first-order decay expression to the data and estimated the decay constants for each beach. We used their estimated values to plot the variation of TPAH concentration as function of time in Figure 4. The figure clearly shows that the oil biodegradation at SM006B is slower than at the other beaches. Therefore, it is possible that there was not sufficient time in the project as undertaken to observe measurable biodegradation of the SM006B oil. The lack of observed biodegradation at SM006B may have been caused by unnecessarily low injection rates, in addition to insufficient injection time. To avoid blowout conditions at SM006B, we used injection flows that are relatively small -- 0.2 liter/minute per well in comparison with 1.0 liter/minute per well at EL056C.3. Our data revealed that the injected oxygen was consumed within a short distance of the injection wells. As the gauge pressure reading within the wells was essentially equal to zero psi (pound per square inch), we believe that we could increase the pressure by at least one psi, which would increase the flow rate by five- to ten-fold to 1.0 liter/minute.

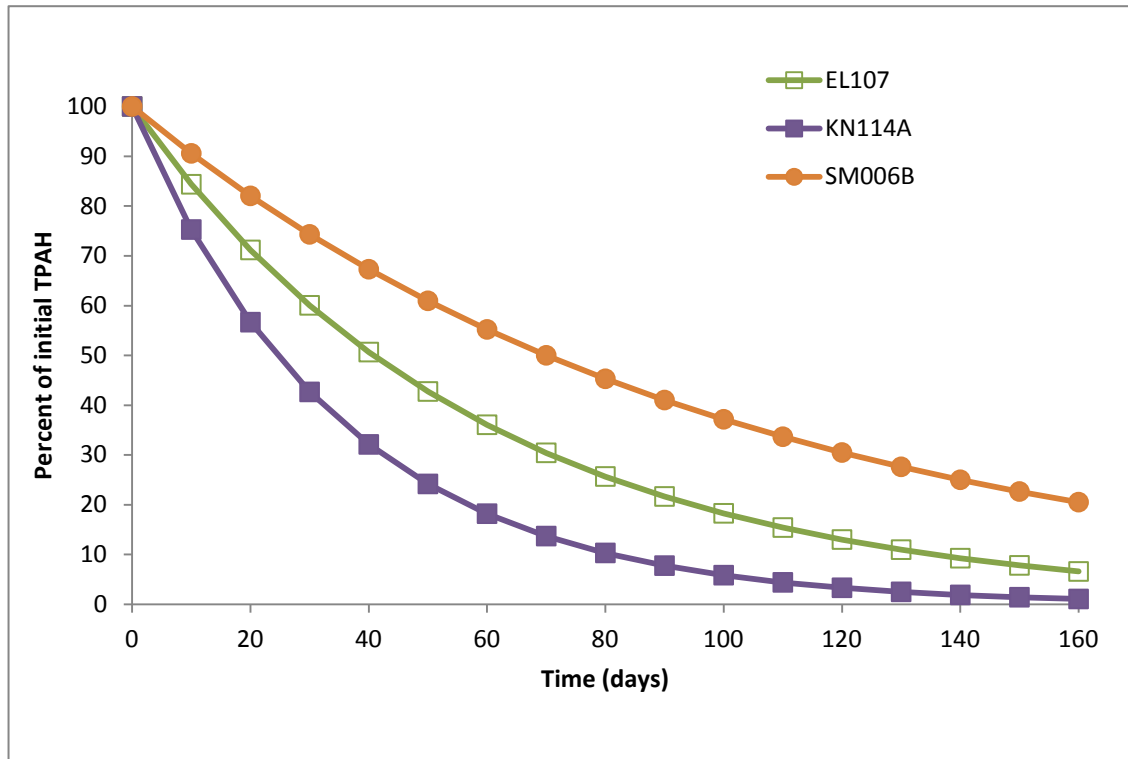


Figure 4: Concentration of TPAH as function of time in the microcosms amended by nutrients in Venosa et al. (2010). The parameters of the curves were obtained by Venosa et al. (2010) by fitting to observed data.

To leverage resources while we are in PWS, we propose to select the additional sites that, from an engineering standpoint, would be most suitable for bioremediation. This will be done through a two step process: 1) We will start from the results of RPI (Michel et al., 2010), where the modeling identified 53 sites with >30% distribution of moderately oiled residue (MOR) at a 70% predicted probability value. We will review the most recent ShoreZone videography associated with each of these sites, and sort them based on features that favor the presence of oil.

According to Michel et al. (2010), these features are:

- 1) Armored, low-angle beaches
- 2) Tombolos (gravel bars connecting the shoreline to an island)
- 3) Natural breakwaters formed by large boulders or bedrock outcrops
- 4) Large rubble accumulations
- 5) Edge effects of adjacent bedrock outcrops

We will also consider the presence of fine-scale sediments that are either in beaches with low wave energy or sheltered from waves due to armoring. These sediments should possess sufficient permeability and thickness to retain lingering subsurface oil and to allow transport of injected solutions. We will develop additional criteria in early 2012 (*i.e.*, prior to field work). The 53 sites will then be ranked from highest to lowest in terms of their potential for effective treatment using in-situ bioremediation, and sites with the highest priority will be selected for field validation of the RPI model and evaluation of potential for bioremediation.

We will visit up to twenty of the sites generated by the desktop review over the course of a one-month period to evaluate the feasibility of bioremediation on these beaches and further validate the model at these additional sites. To validate the model, we will excavate pits at select

locations in the beach (based on a grid determined beforehand) as was done during the model refinement process in 2007. Comparison of the amount of oiling to model prediction will provide a direct validation of the model. To evaluate the suitability of an individual beach for bioremediation, we will use criteria that include: actual presence of oil and patch size, depth to bedrock, and logistical factors. The results of the field work would be used to generate a list of sites that are candidates for bioremediation.

PROPOSED ADDITIONAL WORK

In summary, we propose to conduct another season of work in PWS in Summer 2012 to achieve the following tasks:

- 1) Continue our work at EL056C.3 to determine the maximum amount of enhanced biodegradation achievable and extend our bioremediation technique into the lower intertidal zone. This will entail the addition of approximately 20 injection wells to the beach, six of them in the lower intertidal zone, as well as rebuilding of a structure to house the pumps, the control equipment and the power system; reconnecting the pumps to the wells; reinstalling monitoring wells; and replacing the equipment used to fill the seawater storage tank.
- 2) Revise the bioremediation technique at SM006B by increasing the injection flow rate to 1.0 liter/minute. We will try to establish monitoring zones as far seaward from the injection well sites as possible. However, the lower intertidal zone of this beach is completely covered with boulders, and is therefore not suitable for bioremediation. Restarting the bioremediation system will require the rebuilding of a structure to house the pumps, the control equipment and the power system; reconnecting the pumps to the wells; reinstalling monitoring wells; and replacing equipment used to fill the seawater storage tank.
- 3) Conduct field visits to those oiled beaches within Prince William Sound that have the highest potential (based on modeling results and criteria generated by the pilot study) for treatment using in-situ bioremediation. These visits would be conducted by a survey team for a one-month period at up to twenty sites.

BUDGET

Item	Cost
Mobilization of equipment from Anchorage and Valdez	20,000
Installation at Eleanor and Smith	120,000
ship time (50 days @ \$2K/day)	100,000
Operation for three months	125,000
Oil and nutrient analysis	100,000
Site inspections	95,000
Temple Personnel (design + field personnel)	60,000
Travel	30,000
Total direct	650,000
Temple overhead (26%)	169,000
Total	819,000
G&A 9% of the cost (for NOAA to manage the grant)	73,710
Total cost to EVOSTC	892,710

BUDGET JUSTIFICATION

Installation at Eleanor and Smith Islands

The installation costs include all expenses to restart the bioremediation systems on Eleanor Island (EL056C.3) and Smith Island (SM006B). At Smith Island, the costs will include rebuilding the structure housing the pumps, control equipment and power system, reconnecting the wells to the pump, and reinstalling monitoring wells. Bioremediation of the entire oil-contaminated zone on EL056C.3 (about 200 m²) will require installation of about 20 additional injection wells (in two transects: one in the upper intertidal zone and one in the lower intertidal zone) in addition to the same types of activities that will be conducted to restart the bioremediation system at Smith Island. At both beaches, all of the equipment used to fill the seawater storage tank, which is used to feed nutrient-amended seawater to the injection wells (e.g., submersible pumps, protective canisters, piping, gabions) must be replaced. Labor, supplies for the setup at both beaches, along with demobilization is expected to be about \$120K.

Ship time

Approximately 50 days of boat charter will be required to support this study (\$100K). This time will be divided among five charters: 20 days to set up and restart the bioremediation systems, and 7 days for each of four sample-collection trips. The boat charter estimates include time lost due to weather.

Operation for three months

Maintenance of the bioremediation systems at EL056C.3 and SM006B will require weekly maintenance visits throughout the period of operation (18 to 20 weeks) to replace propane tanks and to inspect the equipment (\$100K). Based on experience from 2011, some equipment repair and/or replacement will be needed, and in some cases, the repairs will require additional site visits. Therefore, the maintenance budget was increased by 25% over the base cost to accommodate the expected additional effort. Hence, the \$125K.

Oil and Nutrient Analysis

Samples will be collected using a similar approach as last year, except that only a portion of the EL056C.3 site will be designated for detailed monitoring. The 25-m wide oil-contaminated area will be divided into three approximately 8-m wide sections, and each section will be divided into five treatment zones at different horizontal distances from the most landward transect of injection wells. Sediment samples will be collected for analysis of oil concentration and composition monthly from each of the five treatment zones in one of the three sections, but they will only be collected at the beginning and end of the study in the other two sections (total of 90 samples for oil analysis). The oil concentration in the four treatment zones at Smith Island will be monitored monthly throughout the summer (total of 40 samples for oil analysis). Water samples will be collected from all possible sample locations on a monthly basis at both sites (about 250 samples), and the concentrations of dissolved oxygen, nutrients (nitrite, nitrate, ammonia, phosphate), lithium, salinity, and sulfate will be measured. One full-time analyst will be required for six months to support this level of analysis of water samples. This would total into \$100K.

Site Inspection

Travel by boat to 20 locations to evaluate the predictive model of Michel et al. (2010) through establishment of detailed beach surveys. The cost, \$95K, is mainly for boat rental for 30 days.

Personnel

At least \$10K will be for RPI for providing a mid-level staff to assist in calibrating the model of Michel et al. (2010). For Temple, one senior personnel and two junior staff will dedicate (each) 5 months to this project. They will develop drawings for the installation, work with the technicians during installation, and interpret the results. A group of them will also inspect the 20 beaches for calibrating the model of Michel et al. (2010) and will review recent ShoreZone videography to evaluate each of these sites and grade them according to the site criteria that would be developed from the results of the pilot study. Their contribution is expected to be \$50K. Thus, the total for personnel is \$60K.

Travel

Travel to sites from Anchorage and Philadelphia through Whittier. For one person travelling from Philadelphia, it would be \$700 for airline, \$500 for lodging in Anchorage for two nights, and \$200 for per diem and transportation. Thus, \$1500 per person. As it is required to have four people travelling three times to Alaska, this would total in \$18K. Shipment of samples to Auke Bay Lab and to Temple University is estimated at \$8K. Travel to conferences to present the results \$4K. The total is thus \$30K.

REFERENCES

- Venosa, A. D., P. Campo, M. T. Suidan, Biodegradability of lingering crude oil 19 years after the Exxon Valdez oil spill. *Environmental Science and Technology*, 44(19):7613-21, 2010.
- Michel, J., Zachary Nixon, Miles O. Hayes, Jeffrey Short, Gail Irvine, David Betenbaugh, Christine Boring, and Daniel Mann, Final Report, Distribution of Subsurface Oil from the *Exxon Valdez* Oil Spill Restoration Project 070801. Exxon Valdez Trustee Council web site <http://www.evostc.state.ak.us/>