Oil level and weathering tracking – Carls (NOAA/NMFS Auke Bay Laboratory, 15120114-S)

FY15 PROJECT PROPOSAL SUMMARY PAGE
Continuing, Multi-Year Projects

Project Title: Long-term Oil Monitoring: Lingering Oil - Extending the Tracking of oil levels and weathering (PAH composition) in PWS through time.

Project Period: February 1, 2015 – January 31, 2016

Primary Investigator(s): Mark Carls and Mandy Lindeberg, NOAA/NMSF Auke Bay Laboratories, 907-789-6019, mark.carls@noaa.gov

Study Location: Sites in western Prince William Sound with persistent oil

Project Website (if applicable): n/a

Abstract*: This project is a component of the integrated Long-term Monitoring of Marine Conditions and Injured Resources and Services submitted by McCammon *et al*. The goal is to provide the EVOSTC with an assessment of persistent *Exxon Valdez* oil in Prince William Sound, describe its chemical characteristics, and initiate a routine, long-term monitoring program that will resample the same sites every five years over the next 20 years. Beaches will be sampled similar to surveys conducted by Auke Bay Laboratories during 2001-05 and sediment samples will be collected to estimate amounts of remaining oil. Mussel and passive samplers will provide information about biologically available oil. Objectives are 1) fingerprint oil, 2) determine oil persistence and weathering over decades, 3) determine oil sources, 4) determine biological availability, and 5) archive hydrocarbon data in the Trustee-sponsored hydrocarbon database. These data, together with an ongoing retrospective analysis of biomarkers, the most environmentally persistent components of the oil, will help investigators understand potential exposure levels (past and present) and linkages to species at higher trophic levels.

Estimated Budget:

EVOSTC Funding Requested* (*must include 9% GA)*:

FY12	FY13	FY14	FY15	FY16	TOTAL
$18	$12	$8	$155.2	$6	$199.2

Non-EVOSTC Funds to be used:

FY12	FY13	FY14	FY15	FY16	TOTAL
n/a	n/a	n/a	n/a	n/a	n/a

Date: September 2, 2014

I. EXECUTIVE SUMMARY

The goal of this project is to provide the EVOSTC with an assessment of persistent *Exxon Valdez* oil in Prince William Sound (PWS) and describe its chemical characteristics. The proposed sampling protocol is designed to be simple and relatively inexpensive so that future assessments of persistence are cost-effective. Intertidal areas in western PWS were extensively coated with *Exxon Valdez* oil (EVO) (Neff, 1995). Despite unprecedented clean-up efforts and decades of natural processes, oil persists in some beaches (Short et al., 2006-07). The end point where EVO is no longer detectable is unknown and thus there is a need for long term monitoring of lingering EVO in PWS. Within the umbrella of the Gulf Watch Alaska long term monitoring program we are proposing to develop a lingering EVO monitoring plan for PWS and conduct a monitoring survey. The design and methodology will be consistent with previous lingering oil surveys funded by the EVOS Trustee Council but slightly modified and focused for manageable long term monitoring. In general our strategy is to revisit and survey about 10 to 12 of the worst case sites with lingering oil in 2015. These sites will become the established long term monitoring sites for lingering oil and be re-sampled every 5 years over the next 20 years (Figure 1). Sites with a history of persistent subsurface oil were prioritized for monitoring based on: heavy subsurface oil surveyed in most recent years, a variety of shore types prone to oil retention, and those sites with a high probability of oil persisting (Michel et al. 2010).

This project fills the following basic information needed for monitoring lingering EVO in the future:

(1) *Fingerprinting oil* – Polynuclear aromatic hydrocarbon (PAH), alkane, and biomarker composition will be measured in sediment samples. The biomarkers (triterpanes, hopanes, and steranes) will provide definitive long-term source oil identification
(2) *Persistence and Weathering of oil* - Understanding the quantity and natural degradation of oil over time in PWS beaches. Monitoring oil loss over time is important for determining full recovery of the habitat; in Alaska, this time course is longer than in lower latitude environments and has already exceeded estimates.
(3) *Bioavailability of oil* - Understanding exposure levels (past and present) for key prey species near lingering oil such as mussels will help make linkages to species recovering at higher trophic levels (e.g. cytochrome P4501 levels in sea otters and sea ducks).
(4) *Archiving Hydrocarbon Analyses* – continued management of the Trustee hydrocarbon database for archiving future analyses.

Sediment sampling techniques in 2015 will allow extension of time series data (where they exist), detailed examination of hydrocarbons present (including PAHs, alkanes, and biomarkers), verification of hydrocarbon source, weathering state, and estimation of the amount of remaining oil at specific sites. In addition to sediment samples, mussel tissue will also be examined for hydrocarbon loads to determine if PAHs are biologically available without sediment disturbance (such as that created by foraging activities by sea otters and sea ducks). A limited number of passive samplers will also be deployed to detect dissolved oil constituents.

To ensure integration between current projects and with past monitoring, we will also analyze a limited number of sediment samples as needed by other Gulf Watch investigators and maintain the Trustee hydrocarbon database including proper chain of custody and entry of all new sample data.

Ongoing analyses for this project will continue into FY15. Biomarkers in *Exxon Valdez* oil samples collected over time are being analyzed for comparison with contemporary results. Chemical analyses of biomarkers will yield a more complete picture of oil weathering over the last ≥ 25 years and future 20 years because they are more resistant to biodegradation and weathering than alkanes and PAHs. Biomarker data were not originally collected in PWS sediment studies but were incorporated in the bioremediation studies of 2011 - 2012. Thus we are in the process of re-

analyzing past PWS samples to compliment future sampling. Biomarkers are also being measured in several sources (*Exxon Valdez* oil, Constantine Harbor, coal, and Monterey oil) for interpretation. These efforts extend and complement the previous work of EVOS Trustee Council funded remediation studies by Boufadel in 20011-12 as well as the Irvine study outside of PWS in 2011-12. The historical biomarker samples have been processed and most have been run on the GC. Data analysis will commence later this summer.

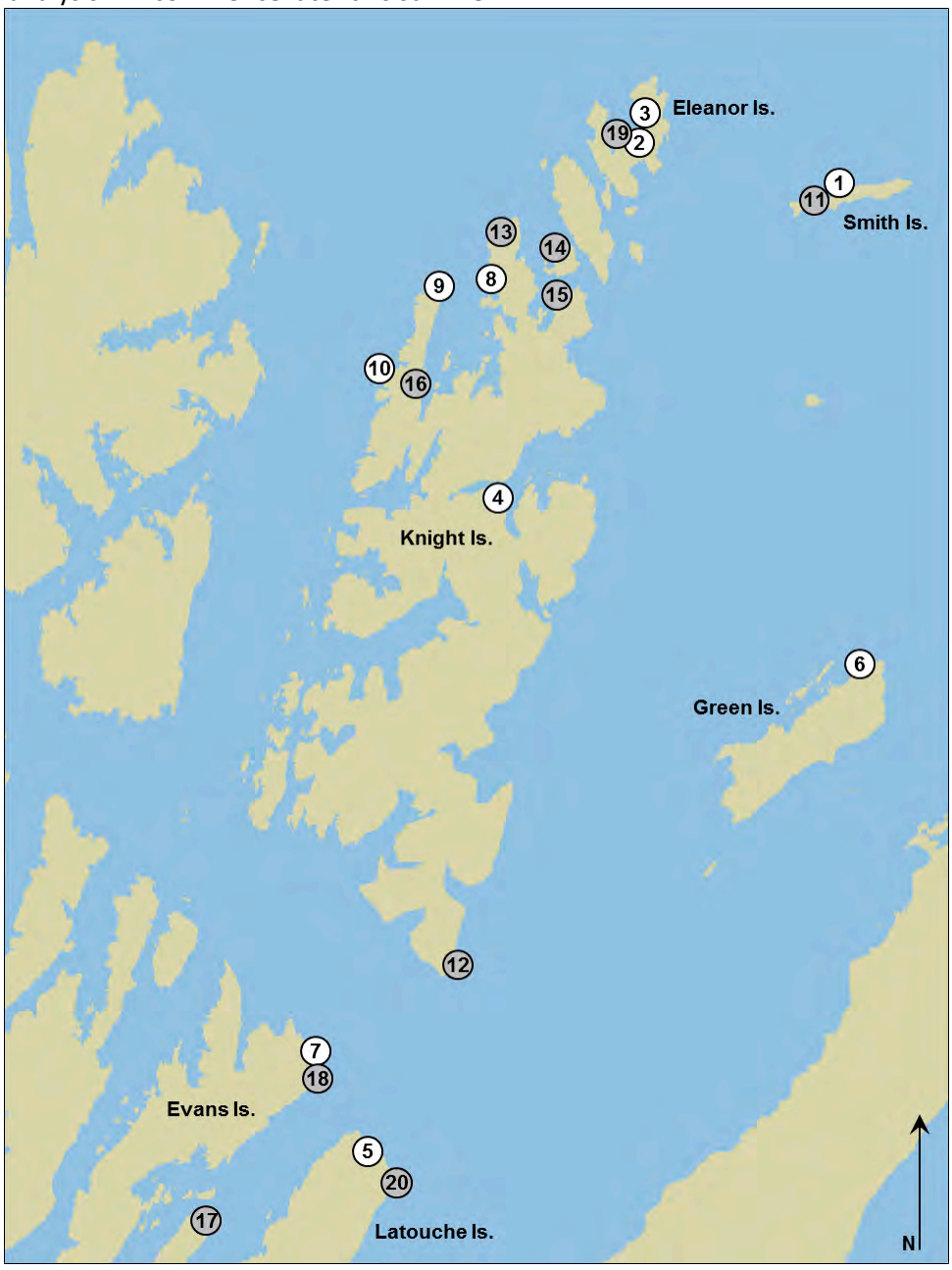

Fig. 1. Map of prioritized sites for monitoring lingering oil in western Prince William Sound. Alternate sites are gray icons, #11-20.

II. COORDINATION AND COLLABORATION

A. Within a EVOTC-Funded Program

This study is closely linked with the benthic component of the Gulf Watch Alaska program and is designed to provide insight into the persistence and nature of EVO in the nearshore ecosystem and a method for long term monitoring. Contaminant samples (mussels and sediments) collected by the benthic component surveys have been sent through Auke Bay Laboratories (ABL) to maintain proper handling and chain of custody. Analyses not provided by ABL were managed by ABL staff to other NOAA contracted labs. ABL staff has also been available for interpretation of these analyses for deliverables and publications.

This project provides a chemical frame of reference for other studies in PWS and the Gulf of Alaska, including 1) definitive long-term source identification of lingering oil, (2) the weathering status of lingering oil, and 3) an understanding of exposure levels (past and present) for key prey species being monitored by the benthic component such as mussels for sea otters and sea ducks. This study complements and extends previous lingering oil work (Short et al., 2004, 06, 07; Michele et al., 2010; Nixon et al., 2013-14), continued management of the Trustee hydrocarbon database, analyses for the remediation studies by Boufadel during 2011-2012, and long term monitoring by Irvine studies outside of PWS (Irvine et al., 1999, 2006).

The field effort in 2015 will require a local charter, a field crew of up to six people. Federal personnel will lead the cruise effort, although contract labor will likely be used for the labor intensive beach surveys. Sample analyses will be completed at the Auke Bay Laboratories in Juneau, Alaska. Senior staff will conduct the instrumental analyses, but sample processing and preparation will be conducted by contractors.

B. With Other EVOSTC-funded Projects

N/A

C. With Trustee or Management Agencies

NOAA has trust responsibilities for oil spill response and restoration. Data collected under this study furthers our understanding of oil persistence in coastal habitats.

III. PROJECT DESIGN – PLAN FOR FY15

A. Objectives for FY15

1. Determine quantity and weathering state on select beaches in PWS, in 2015.
    a. Visit 10-12 beaches known to have lingering EVO, collect sediment samples for PAH concentration and weathering profiles.
    b. Using stratified random sampling (SRS), measure the quantity of oil in samples to estimate the quantity present at each beach.
    c. Collect mussels near oil patches to determine bioavailability in tissues.
    d. Place passive samplers at one beach at the beginning of the cruise and retrieve at the end of the cruise before sampling that beach as an alternative method to sample dissolved PAHs.
    e. Begin chemical analysis of samples using gas chromatography to measure alkane, polynuclear aromatic hydrocarbons, and geochemical biomarker content. Analyses will be completed in study year 5 (FY16).
2. Complete retrospective survey of archived samples to establish biomarker content in historic samples.
3. Supplemental support analyses: support on-going intertidal projects with chemical analyses, such as determining PAH levels in sediments or prey items. This may involve 10-20 samples per year depending on requests from other Gulf Watch investigators.
4. Maintain and expand the Trustee hydrocarbon database and sample collection.

a. Add new information to hydrocarbon database. (This database contains data from all NRDA hydrocarbon samples from 1989 to present, including numerous data sets from investigators outside ABL.)
b. Prepare a complete FOIA (Freedom of Information Act) package. 100% of the chemical analyses have been FOIAed in the past, and these data will likely be FOIAed in the future.

5. Products: prepare annual and final reports as needed; supply collaborators with appropriate data (e.g. Gulf Watch benthic monitoring). Prepare synthesis manuscript summarizing environmental progress after 25 years in study year 5.

Methods.

1. *Chemical analyses*: Standard operating procedures developed at the Auke Bay Laboratories for hydrocarbon analysis will be used for all sample analyses (Short, 1996; Carls, 2004). These have resulted in numerous peer-reviewed publications. Senior staff will conduct the instrumental analyses, but the processing effort will be by contractors.
    a. Analytes: alkanes, PAHs, biomarkers

2. *Site Selection*:
   Prioritization of beaches selected for monitoring lingering subsurface oil (SSO) is summarized in Table 1. Factors considered for prioritization were based on: initial oiling, shore types prone to oil retention (Michel and Hayes, 1993; Hayes and Michel, 1998-99; Michel et al., 2010), past oil surveys to aid our understanding of loss rates (NOAA ORR 1989-1992; Gibeaut and Piper, 1993; NOAA ABL 2001-05; Research Planning, Inc. 2007-08), most recently observed oil in heaviest categories (HOR and MOR), and a high probability of oil persistence (Michel model).

   We acknowledge sites selected for long term monitoring have a history of man-made disturbance and loss of SSO could be variable among these sites over time. Since the onset of the spill, oiled beaches have been surveyed and treated using a gamut of techniques: mechanical removal (high pressure water flushing, berm relocation), and remediation (Inipol EAP22, Customblen, Corexit, PES-51®). Certain sites were identified with persistent SSO and repeatedly excavated in the 2000s by EVOSTC and Exxon Corporation surveys. Additional experimental remediation techniques by Boufadel were applied to a suite of sites in recent years. Due to these factors we will estimate loss of SSO at each site individually, not stratified by initial oiling or treatment history. We have selected alternate sites in case additional survey time is available or weather becomes an issue on more exposed sites. Further review and consideration of the prioritized sites will be conducted prior to the summer 2015 surveys and Table 1 will be finalized.

Table 1. This is a list of prioritized sites for monitoring lingering oil on beaches in Prince William Sound. Summarized here are the various treatments and surveys these sites had in the past. Priority has been given to sites with heavy subsurface oil (SSO) surveyed in most recent years, a variety of shore types prone to oil retention, and a high probability of oil persisting. Prioritization of alternative sites have been included (shaded in gray) if needed.

	Location Name	Shore Segment	Initial oiling/cleanup	Remediation	Oil Survey Excavation History	Shore type prone to persistent oil	Michel Model Heavy SSO
1	Smith Is.	SM006B	Heavy oil 1990-1993	Boufadel 2005-12	1989-92[1], 2001[3], 2008[4]	armored	>30%
2	Northwest Bay, Eleanor Is.	EL056C	Medium oil 1990-1993	Boufadel 2005-12	2001[3], 2007[4]	rubble accumulations	>30%
3	Northwest Bay, Eleanor Is.	EL058B	Heavy oil1989 only	Boufadel 2005-12	2001[3], 2005[3]	breakwater	>30%
4	Bay of Isles, Knight Is.	KN0136A	Heavy oil 1989 only		1993[2], 2003[3], 2008[3]	lagoon, peat	5-15%
5	Sleepy Bay, Latouche Is.	LA018A-1	Heavy oil1990-1993		1989-92[1], 2001[3], 2005[3]	rubble, slope	5-15%
6	Green Is.	GR103B	Heavy oil 1990-1993		2001[3], 2005[3], 2007[4]	armored, slope	1-5%
7	N. Evans Is.	EV039A	Heavy oil 1990-1993	PES-51® 1997	1993[2], 2005[3]	edge effect	1-5%
8	Herring Bay, Knight Is.	KN0114A	Heavy oil1990-1993		2003[3]	breakwater	>30%
9	Herring Pt., Knight Is.	KN0300A-2	Medium oil 1990-1993		1993[2], 2005[3]	breakwater	1-5%
10	Herring Pt., Knight Is.	KN0506A	Heavy oil 1990-1993		2001[3], 2005[3]	edge effect	0-1%
11	Smith Is.	SM006C-1	Heavy oil 1990-1993	Boufadel 2005-12	2001[3]	armored	>30%
12	Pt Helen, Knight Island	KN0405A-1	Heavy oil1990-1993		2001[3], 2008[4]	armored	5-15%
13	NW Pt. of Knight Island	KN0109A	Medium oil1990-1993	Boufadel 2005-12	2003[3], 2007[4]	breakwater	5-15%
14	Disk Is.	DI067A	Medium oil 1990-1993		1993[2], 2003[3]	rubble accumulations	5-15%
15	Louis Bay, Knight Island	KN0107	Heavy oil1990-1993		2003[3], 2008[4]	rubble accumulations	1-5%
16	Herring Bay, Knight Is.	KN0132D	Medium oil 1990-1993		2001[3], 2005[3]	rubble accumulations	1-5%
17	Elrington Is.	ER020B	Heavy oil 1990-1993		1993[2], 2001[3], 2005[3]	edge effect	1-5%
18	Northwest Bay, Eleanor Is.	EL056A	Heavy oil 1990-1993		2001[3], 2005[3]	rubble accumulations	1-5%
19	N. Evans Is.	EV037A	Medium oil 1990-1993	PES-51® 1997	2001[3]	edge effect	1-5%
20	N. Latouche Is.	LA015E	Heavy oil 1990-1993	Boufadel 2011	1989-92[1], 2001[3]	armored	1-5%

Note for oil survey excavation history: 1. NOAA ORR surveys; 2. Gibeaut surveys; 3. NOAA ABL surveys; 4. Michel surveys.

3. *Field logistics*: Beaches will be accessed by charter boat during spring or summer months during one cruise. Federal personnel will lead the cruise effort, although some contract labor will likely be used for the labor intensive beach surveys. The crew size will be ≤ 6.

4. *Site Surveys*: Our methods will follow those established by ABL in 2001 and then modified in 2003 (Short et al., 2004, 2006).
    a. Survey Grid – using surveying equipment, a typical 100 m length of shoreline will be divided into 5 contiguous columns of 20 m width, each of which is partitioned into 5 rectangular blocks by 1-m vertical tidal elevation intervals, beginning at – 0.2 m and extending to + 4.8 m tide height. Shorter shoreline segments are divided into correspondingly fewer ~ 20 m sampling columns. We will randomly locate two sampling quadrats (each 0.25 m^2) within each block, resulting in a maximum of 50 quadrats per 100 m of shoreline distributed throughout nearly the full range of the tidal excursion (MHHW to zero tide).
    b. Quadrat Sampling - Each quadrat will be examined visually for the presence of surface oil and subsurface oil, using the oil classification scheme given by (Gibeaut and Piper, 1998). After examining the uppermost 5 cm of sediments for surface oil, quadrats will be excavated to a depth of 0.5 m, or until boulders or bedrock are encountered, and examined for oil by sight and smell. Surface oil classifications include asphalt pavement (AP), surface oil residue (SOR), oil coat or oil cover (CT/CV), tar balls (TB) and oil film (OF). Subsurface oil classifications include light, medium and heavy oil residue (LOR, MOR, HOR). Additional methods may be field tested to classify oil in a more rigorous scheme. All oiled quadrats will be photo documented.

5. *Hydrocarbon Sampling Effort and Analysis*: standard hydrocarbon sampling protocols established at ABL will be followed to maintain Chain of Custody and quality assurance requirements.
    a. Sediment. Oiled sediment samples will be collected and archived from all oiled quadrats. If no visible oil is found, sediment will be collected at 2 random quadrats from each meter vertical drop block (upper, middle, and lower; n= 6). We have budgeted for 100 gravimetric samples and 50 GC analyses (PAH, alkanes, and biomarkers). If more samples are collected in the field, then an analysis subset will be chosen at random within beach, column, and zone.
    b. Mussels. Two composite mussel samples will be collected from each beach. One of these will be collected as close as possible to the most oiled quadrat on that beach (~25 individuals). The other will be collected randomly within the mussel zone across the entire beach to represent general conditions. If no oil is discovered, both samples will be collected across the entire beach. We have budgeted for 30 tissue samples.
    c. Passive samplers will be placed on one beach at the beginning of the cruise and picked up at the end before any digging on that beach. Paired samplers will be placed in each of the vertical zones for a total of six. They will be anchored in the intertidal using bolts or duck bill anchors depending on the substrate. All passive samplers will be analyzed.

6. *Statistical methods*:
Oil area at each beach segment and tidal zone (5 zones) will be calculated based on the proportion of oiled quadrats to total quadrats sampled and expanded to total area in the given tidal zone. The total oiled area for a given beach segment will then be calculated by summing the oiled areas at each tidal zone.

$$\hat{A}_i = \sum_{j=1}^{5} \sum_{k=1}^{C} N_{ijk} \frac{o_{ijk}}{n_{ijk}},$$

Where: $\hat{A}_i$ is the total oiled area in ith beach segment, N_{ijk} is the total number of 0.25 m^2 quadrats at ith beach, jth tidal zone (j=1,2,3,4,5) and kth column, .o_{ijk} is the number of oiled quadrats found (0,1,2) at ith beach, jth tidal zone and kth column. n_{ijk} is the number of quadrats sampled (2 in this case) at ith

beach, jth tidal zone and kth column. $\frac{o_{ijk}}{n_{ijk}}$ can also be written as p_{ijk}, or the proportion of oiled quadrats at ith beach, jth tidal zone and kth column. Additionally, each quadrat where oil is detected will be sampled for oil volume and weight. First, all oiled substrate within the 0.25 m^2 by 0.5 meter deep quadrat will be collected. Subsequently gravimetric analysis on the substrate will be done in the field or the laboratory in order to obtain total oil volume and weight contained within each of the oiled quadrats. Oil volume and weight calculations for each beach segment will be done in the same fashion as oil area except the amount of oil in each quadrat will be used for the computation:

$$\widehat{W}_i = \sum_{j=1}^{5} \sum_{k=1}^{C} N_{ijk} \widehat{\omega}_{ijk} p_{ijk},$$

Where W_i is the total weight of oil at ith beach, $\widehat{\omega}_{ijk}$ is the estimated weight of oil found from gravimetric analysis in the jth tidal zone, and kth column of ith beach segment. p_{ijk} is the proportion of oiled quadrats in the jth tidal zone, and kth column of ith beach segment. Variance calculations will be done using standard stratified (blocked) design methods.

$$\widehat{var}(A_i) = \sum_{j=1}^{5} \sum_{k=1}^{C} N_{ijk}^2 \frac{s_{ijk}^2}{n_{ijk}} \frac{N_{ijk} - n_{ijk}}{N_{ijk}}$$

B. Changes to Project Design

The project design remains as proposed and implemented in FY14, which delayed the field effort by one year.

IV. SCHEDULE

A. Project Milestones for FY 15

Objective 1. Determine oil quantity and weathering in 12 PWS beaches 25 years post spill.
To be met by September 2016. (Field work will be completed in 2015; measurements and analysis will be completed in 2016)

Objective 2. Supplemental analyses as needed.
To be met yearly as information is requested by other long-term monitoring collaborators

Objective 3. Maintain and add new data to the hydrocarbon database
Additions to the data base to be met yearly.

Objective 3. Prepare annual and final reports
To be met annually. A synthesis manuscript is expected in 2016.

B. Measurable Project Tasks for FY 15

FFY 15, 1st quarter (Feb 1, 2015-Apr 30, 2015)
February — *Prepare for field sampling*
FFY 15, 2nd quarter (May 1, 2015-Jul 31, 2015)
May — *Field sampling this quarter*
FFY 15, 3rd quarter (Aug 1, 2015-Oct 31, 2015)
September 30 — *Begin analysis of new samples*
FFY 16, 1st quarter (Feb 1, 2015-April 30, 2016)
December — *Summarize available data*
January — *Annual Marine Science Symposium, meetings*

V. PROJECT PERSONNEL – CHANGES AND UPDATES

NA

VI. BUDGET

A. Budget Forms

Please see program workbook for completed budget forms.

B. Changes from Original Proposal

The project design remains as proposed and implemented in FY14, which delayed the field effort by one year.

C. Sources of Additional Funding

N/A

VII. Highlights of Work to Date

1. An expanded, revised hydrocarbon database was released to the Trustees.

2. A retrospective analysis of geochemical biomarkers in PWS sediment is underway; this effort has been delayed by litigation-driven demands involving another major PWS study (bioremediation).

3. New analytical tools developed for other ongoing projects are in place and will aid interpretation of the historical biomarker analyses.

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