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25 June 1991

To: John Strand
Restoration Manager

From: John F. Karinen and Malin M. Babcock
Principal Investigators
Recovery Monitoring Study: Pre-spill and Post- spill Concentrations of Hydrocarbons in Sediments and Mussels at Intertidal Sites in Prince William Sound

Thru: Stanley D. Rice, Program Manager
Habitat Investigations

Subject: Justification for August, 1991 Sampling Trip.

We present data and graphs of petroleum hydrocarbon levels in sediments taken at the study sites in 1989 and 1990. The data presented indicate good justification for funding a second field trip (August) in 1991.

The historical data (1977-80) showed seasonal trends in aromatic and alkane levels in sediments, and alkanes in mussels. Total aromatics and alkanes were usually lower in fall than in spring or summer; ranging from 10 to 25% of spring levels.

Sediment data from 1989 and 1990 are more complicated than the historical data of the 1970's. Oil levels in 1989 did change with time because of active oiling, intense beach cleaning and natural processes, masking usual seasonal trends. Environmental physical processes prevailed in the winter - leading to increased contamination (>2.5x) at some sites (Elrington and Bay of Isles), and decreased levels at Sleepy Bay in April, 1990. Oiling and cleaning were such dominant processes in 1989 that we have only one year, 1990, to evaluate seasonal trends.

Total mean aromatic hydrocarbons in sediments at Elrington Island and Bay of Isles declined from April to August 1990, but essentially remained the same at Sleepy Bay. Mean concentrations decreased to 7% (Elrington) and 33% (Bay of Isles) of spring values by August (Table 1). This decline at Elrington Island approached the level of the reference sites, Bligh Island and Olsen Bay (Figure 1). Grouped aromatics in sediments (phenanthrenes, dibenzothiophenes, fluorenes, and chrysenes) followed this seasonal change, in 1989, at the reference sites, Bligh Island and Olsen Bay (Figure 2); and at Elrington Island and Bay of Isles in 1990.

Just one season (1990) to evaluate seasonal trends in hydrocarbon contamination is not adequate. At least a second year (1991) of 2 sampling trips are needed to gain an understanding of the dynamics of physical and biological processes from hydrocarbon contamination in sediments and mussels. We strongly recommend that samples be taken in August 1991 to document these changes.

Figure 1. Mean total aromatic hydrocarbons in sediments from selected sites in Prince William Sound after the EXXON VALDEZ oil oil spill. Refer to Table 1 for sample size and standard error values.

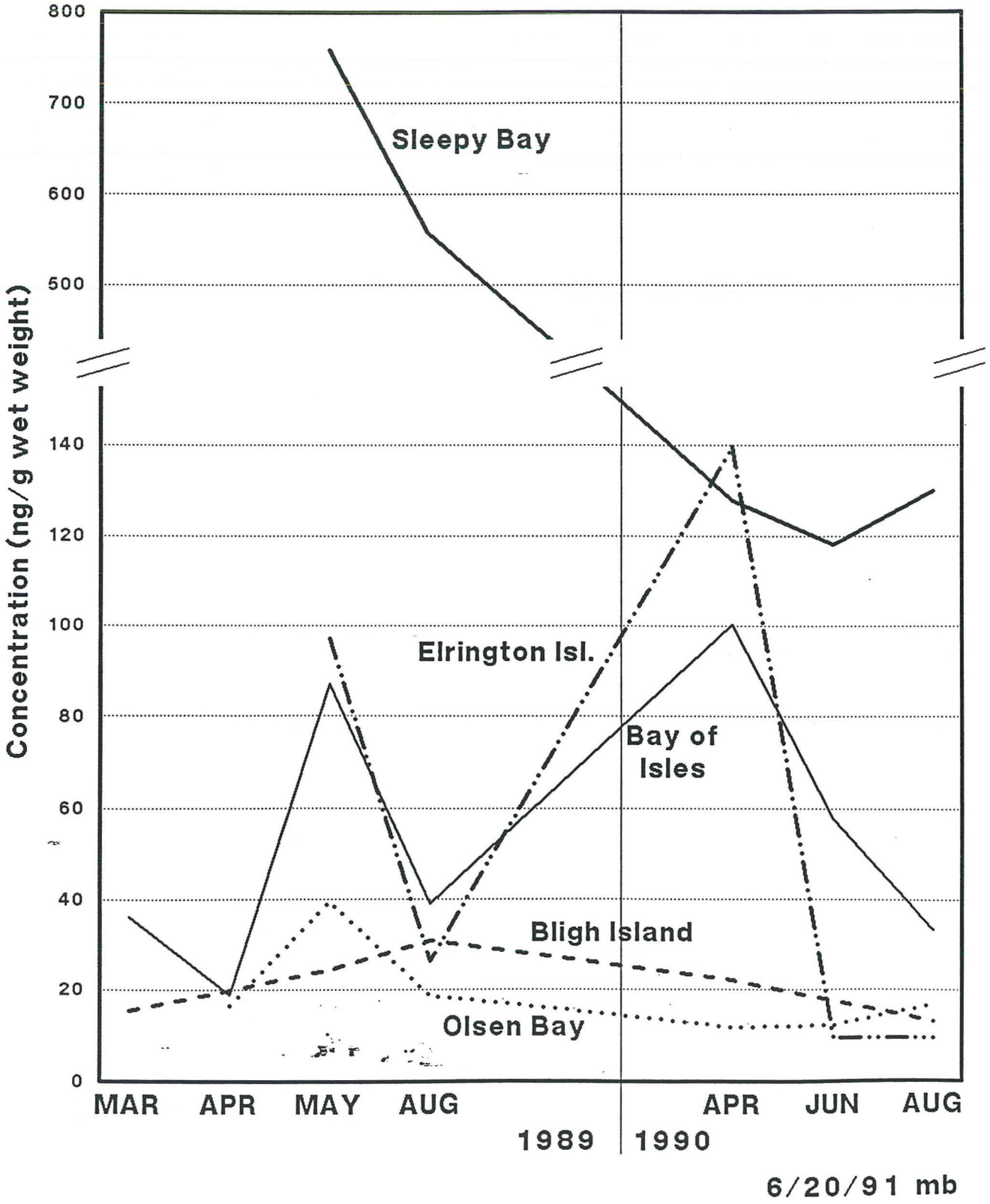
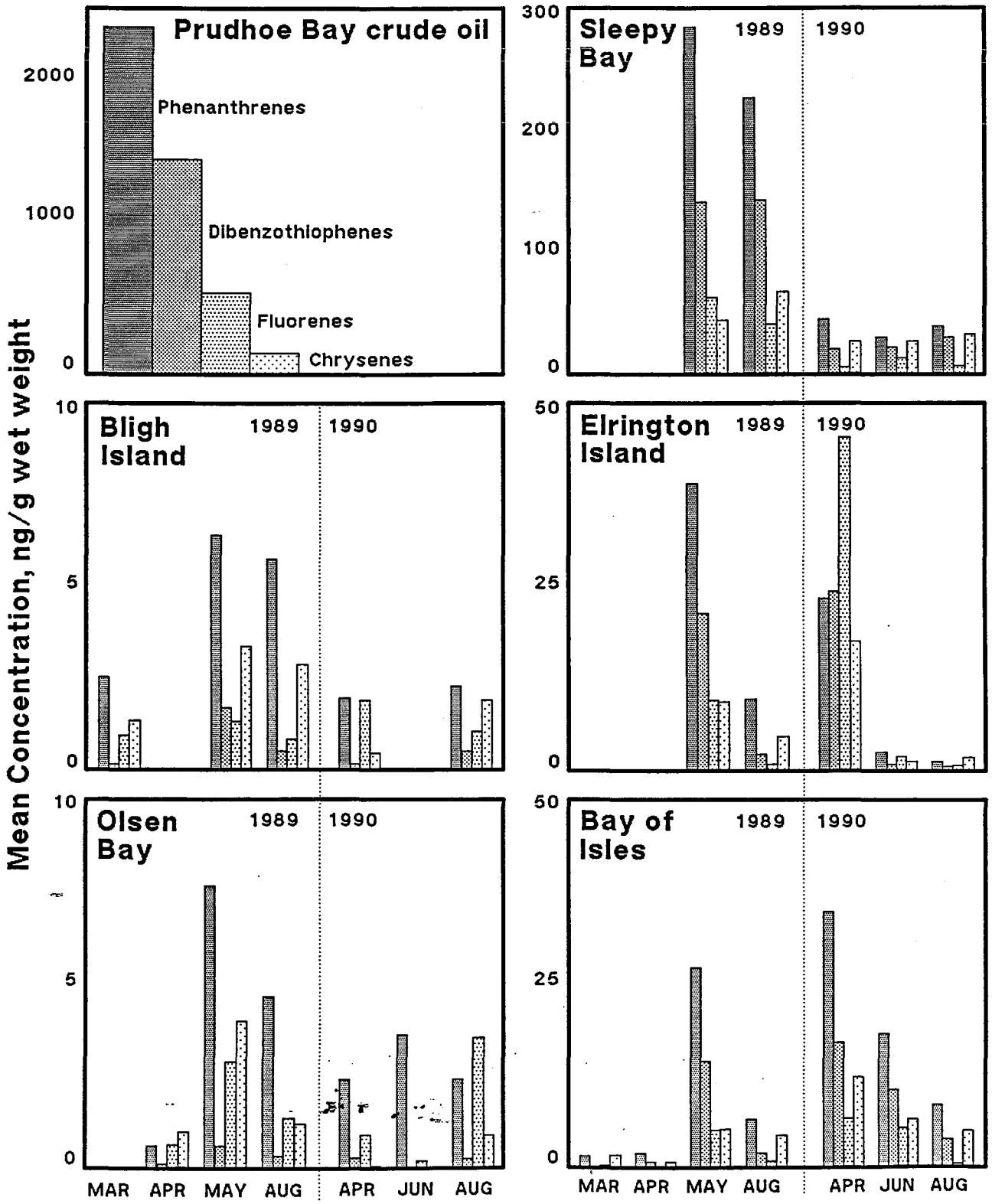


Figure 2. Means of aromatic hydrocarbon groups in sediments from sites in Prince William Sound. See Table 1 for additional data.



NOTE: Y-axis scale differs!

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Table 1. Means, sample numbers ("N"), and standard errors ("se") of total aromatic hydrocarbons and selected aromatic hydrocarbon groups (phenanthrenes, dibenzothiophenes, fluorenes, and chrysenes) from sediments taken at selected Coastal Habitat 1b sites in Prince William Sound, 1989 and 1990.

			AROMATICS		PHENANTHRENE		DIBENZOTH.		FLUORENES		CHRYSENES	
SITE	DATECOL	N	Mean	se	Mean	se	Mean	se	Mean	se	Mean	se
BLIGH ISLAND	28-Mar-89	1	15.5		2.4		0.1		0.9		1.2	
BLIGH ISLAND	02-May-89	3	24.5	10.8	6.0	2.6	1.6	1.2	1.2	0.3	3.1	1.7
BLIGH ISLAND	15-Aug-89	3	31.0	9.8	5.4	3.2	0.5	0.1	0.8	0.4	2.7	1.0
BLIGH ISLAND	28-Apr-90	2	22.1	8.6	1.8	0.7	0.1	0.1	1.8	1.1	0.4	0.4
BLIGH ISLAND	Aug 1990	2	13.2	0.5	2.1	0.1	0.5	0.1	1.0	0.3	1.8	0.5
BAY OF ISLES	30-Mar-89	3	36.2	6.0	1.4	0.4	0.1	0.1	0.2	0.1	1.6	0.8
BAY OF ISLES	08-Apr-89	2	19.0	8.2	1.8	1.8	0.6	0.5	0.0	0.0	0.7	0.5
BAY OF ISLES	06-May-89	3	87.1	32.7	27.1	13.4	14.4	5.4	5.0	2.6	5.1	2.0
BAY OF ISLES	16-Aug-89	3	39.1	5.3	6.4	3.0	1.8	1.2	0.7	0.1	4.3	1.2
BAY OF ISLES	25-Apr-90	2	100.5	0.7	34.5	2.0	16.9	1.0	6.5	0.1	12.1	3.3
BAY OF ISLES	22-Jun-90	2	57.7	0.5	18.1	1.2	10.4	2.4	5.2	1.9	6.4	0.2
BAY OF ISLES	Aug 1990	1	33.5		8.5		3.7		0.4		5.0	
ELRINGTON ISL.	10-May-89	3	97.1	27.1	39.0	10.5	21.4	7.4	9.5	3.6	9.3	1.6
ELRINGTON ISL.	17-Aug-89	3	26.5	14.1	9.7	5.6	2.1	0.6	0.7	0.4	4.5	2.5
ELRINGTON ISL.	26-Apr-90	2	139.7	72.0	23.4	8.0	24.3	9.6	45.5	28.2	17.6	17.2
ELRINGTON ISL.	23-Jun-90	2	9.6	8.7	2.4	2.4	0.8	0.7	1.8	1.8	1.1	1.1
ELRINGTON ISL.	Aug 1990	3	9.4	2.0	1.1	0.4	0.5	0.2	0.6	0.1	1.6	0.1
OLSEN BAY	06-Apr-89	3	16.5	1.7	0.6	0.2	0.1	0.1	0.6	0.1	1.0	0.1
OLSEN BAY	01-May-89	3	39.5	11.6	7.9	3.5	0.6	0.3	3.0	1.3	4.1	1.9
OLSEN BAY	16-Aug-89	3	18.7	3.1	4.8	1.4	0.3	0.0	1.4	0.3	1.2	0.6
OLSEN BAY	28-Apr-90	2	11.9	1.5	2.5	0.5	0.3	0.0	0.9	0.3	0.0	0.0
OLSEN BAY	26-Jun-90	1	12.3		3.7		0.0		0.2		0.0	
OLSEN BAY	09-Aug-90	3	16.8	5.3	2.5	0.6	0.2	0.2	3.6	3.0	0.9	0.2
SLEEPY BAY	07-May-89	3	756.2	327.2	289.5	112.8	142.8	53.8	64.0	32.4	44.6	13.8
SLEEPY BAY	17-Aug-89	2	536.0	44.0	229.9	29.1	144.9	11.6	41.6	13.9	68.8	8.2
SLEEPY BAY	26-Apr-90	2	127.9	20.2	44.2	8.9	20.2	7.1	5.8	2.2	26.2	0.5
SLEEPY BAY	23-Jun-90	2	118.3	9.4	29.2	0.5	21.2	2.9	12.7	7.9	25.9	3.1
SLEEPY BAY	Aug 1990	3	130.0	32.4	38.4	12.7	29.3	8.8	6.7	2.4	32.3	6.7

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1991 RESTORATION SCIENCE PROGRAM

RECOVERY MONITORING STUDY:

PRE-SPILL AND POST-SPILL CONCENTRATIONS OF HYDROCARBONS IN SEDIMENTS AND MUSSELS AT INTERTIDAL SITES IN PRINCE WILLIAM SOUND

PRINCIPAL INVESTIGATORS

John F. Karinen and Malin M. Babcock

Auke Bay Laboratory
Alaska Fisheries Science Center
National Marine Fisheries Service, NOAA
11305 Glacier Highway, Juneau, Alaska 99801

Study No. 11

Lead Agency: National Marine Fisheries Service,
National Oceanic and Atmospheric Administration

Cost: $83.9K

Effective Dates: 1 March 1991 to 29 February 1992

AUTHORIZATION:

	Signature	Date
Restoration Manager: John Strand (907) 789-6605	John Strand	3/28/91
Chief, Office of Oil Spill Damage Assessment and Restoration: Byron Morris (907) 789-6000	Byron Morris	5/28/91

PRE-SPILL AND POST-SPILL CONCENTRATIONS OF HYDROCARBONS IN SEDIMENTS AND MUSSELS AT INTERTIDAL SITES IN PRINCE WILLIAM SOUND

Recovery Monitoring Study Number 11

John F. Karinen and Malin M. Babcock
Principal Investigators

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Alaska Fisheries Science Center
National Marine Fisheries Service, NOAA
P.O. Box 210155, Auke Bay, Alaska 99821

Lead Agency - NOAA, NMFS

Cost - $83.9 K

Dates of Study Plan - 1 March 1991 to 29 February 1992

	Signature	Date
Project Leader: John Karinen (907) 789-6054	John F. Karinen	21 Feb. 91
Oil Spill Damage Assessment Coordinator: Stanley Rice (907) 789-6020	Stan Rice	21 feb 91
Organizational Leader: George Snyder (907) 789-6000	George Snyder	2/21/91
Financial Officer: Deborah Rathbone (907) 789-6006	Debi Rathbone	2-22-91

INTRODUCTION

The extent of weathering and release of persistent hydrocarbons (HC) to the environment from oil buried both intertidally and subtidally in the oil spill area is largely unknown. Oily sheens from buried oil are still evident two years after the *EXXON VALDEZ* oil spill. The potential for long-term effects on marine life suggests that a monitoring program be initiated to follow the fate of unrecovered oil on beaches of Prince William Sound and adjacent waters.

Baseline (pre-spill) hydrocarbon data (water, sediments, mussels, fish) are available for 10 sites in Prince William Sound (PWS) sampled over a four year period from 1977 to 1981. This period represents the first four years of oil transport from Port Valdez. All sampling sites were located on low-energy, low-gradient beaches, often associated with eel grass. All sites had adjacent bands of mussels (*Mytilus trossulus*).

In 1989, the 10 historically (1977-1981) established intertidal baseline sites in PWS were resampled in response to the *EXXON VALDEZ* oil spill. Additionally, 10 sites (6 in PWS and 4 on the Kenai Peninsula) were established along the spill trajectory before oiling, and sampled both before and after oiling to measure the increase of hydrocarbon levels in sediments and mussels (Figure 1). Sampling was continued in 1990. Analyses of sediments for HC are currently being conducted; preliminary results indicate that the March/April, 1989, sampling was successful in establishing pre-impact HC levels at the historically established and some newly established sites. Results also indicate a seasonal effect on HC concentrations in the intertidal environment, i.e., HC concentrations tend to increase over the winter storm period (August to April) and tend to decrease over the more biologically-active summer period (April to August).

Most of the new sites are also located on low-energy, fine-grained beaches at the head of embayments. Some of these show significantly elevated levels of HC and can be expected to retain their HC burdens over longer periods of time when compared to higher energy beaches or beaches that have been cleaned.

Previously, this study was supported by the Natural Resource Damage Assessment (NRDA) Program (Coastal Habitat Intertidal Study 1B). Sampling was conducted five times in 1989 and three times in 1990 (Table 1). In 1991, the NRDA will only support a spring sampling effort. This proposal addresses the need to conduct, at minimum, a second sampling in the summer of 1991 of sites in PWS. This proposal also establishes the vehicle for potential sampling in 1992 and beyond, as part of the long-term ecological monitoring of natural recovery within the spill area. Sites on the Kenai Peninsula are not scheduled for continued monitoring under this proposal.

Figure 1. Intertidal baseline sampling sites.
▲ = historical sites ■ = established in 1989.

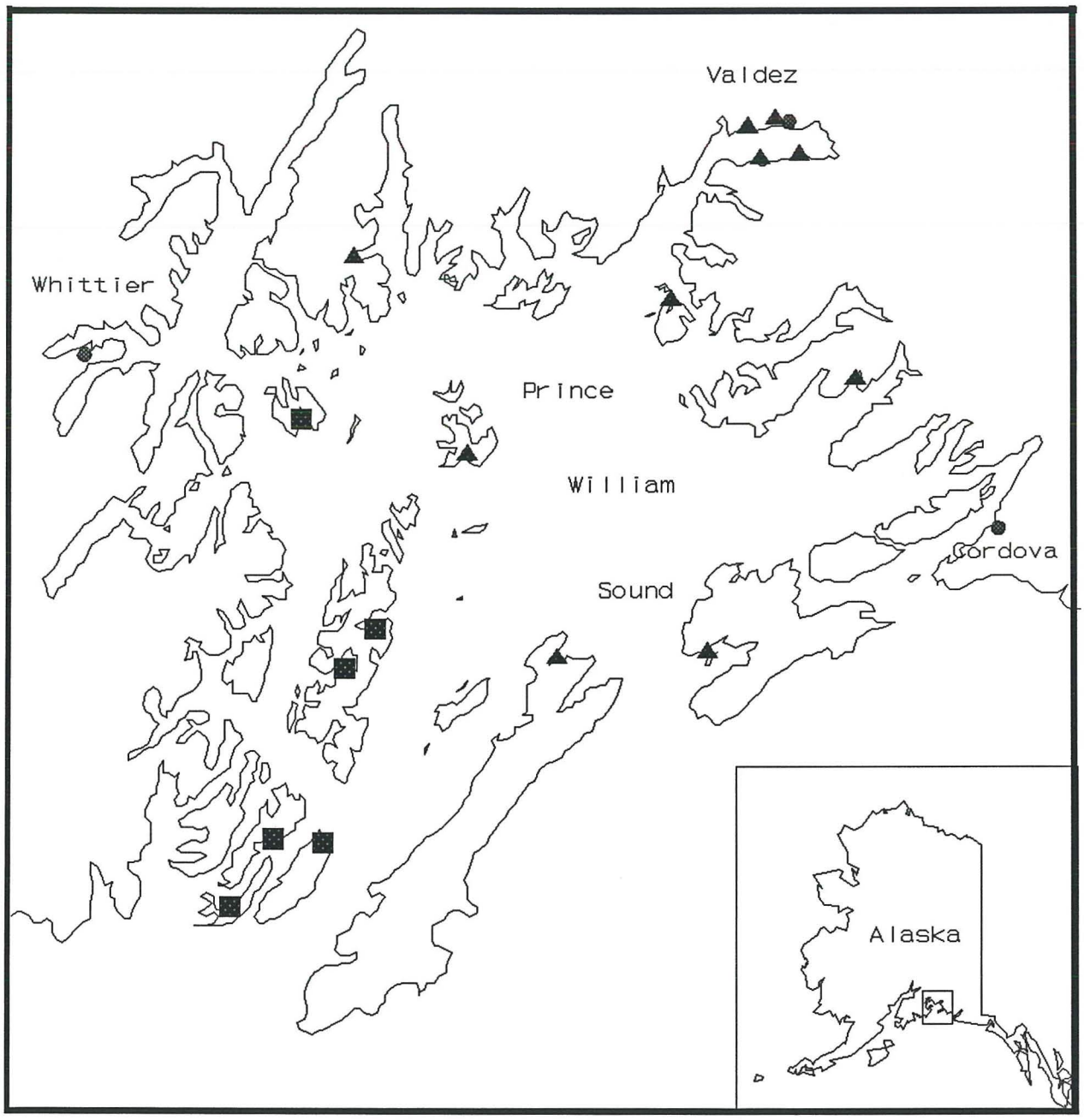

Table 1. Field Sampling Frequency for NRDA Coastal Habitat Study Sites in Prince William Sound

YEAR/MONTH	MARCH	APRIL	MAY	JUNE	JULY	AUGUST
1989	X	X	X	X		X
1990		X		X		X
1991		X				X
(FUTURE) 1992-95		?		?		?

Depuration and recovery (return to background levels) of sediments and mussels is undoubtedly seasonally mediated. Redistribution of hydrocarbons from abiotic to biotic sinks is perhaps greatest during severe storms as experienced during the late fall, winter and early spring. The time from April to early September is characterized by relatively mild weather conditions and higher temperatures that serve to enhance microbial degradation and other physiological processes. Sediment and mussel samples collected in August, 1991, will measure depuration rate over this more biologically-active time period, whereas the spring samples measure redistribution.

This study will provide linkage to studies of higher trophic level organisms; i.e., hydrocarbons in mussels accumulate in fish, birds, mammals and other shellfish (crabs) that feed on mussels and can affect their survival, physiology and reproduction. Some HC concentrations found in mussels following the spill are equivalent to levels known to affect survival, reproduction, or behavior in molluscs in general; and/or exposed mussels do not retain their forage value for other organisms in the food web as a result of oil contamination.

Recovery of intertidal sediments to pre-spill levels of petroleum hydrocarbons is expected to take several years but could take longer where oil is buried. Bioavailability of HC to flora and fauna is expected to decline rapidly, and recovery of some biota to pre-spill numbers may occur in three to five years. Results of this study will increase our understanding of the potential effects of seasonal factors on recovery of oiled sediments. Results of this study also will provide estimates of recovery rates for oiled sites; and when compared with the levels of petroleum hydrocarbons at reference sites, will allow prediction of the times to recovery.

OBJECTIVES

1. For all sites sampled during the NRDA process - to estimate the hydrocarbon concentrations in mussels and sediments such that the estimate is within 15% of the actual concentration 95% of the time when total aromatic concentrations are greater than 200 ng/g dry wt.

2. To compare petroleum hydrocarbon levels at all sites over all sampling periods. This second sampling trip will provide information on recovery of HC levels over a biologically active period (April - August) 2+ years after the accident.

METHODS

Sampling. Transect lines for sediment samples are thirty meters (m) in length and located parallel to the water line at -0.75 m to +0.75 m (depending on specific site). Sediment samples will be collected in triplicate at each site by compositing 10 cores (dia 3.2 cm x depth 1.25 cm) taken at random along the transect for each sample. Composite sediments will be placed in chemically clean jars, placed in an ice chest with artificial ice and transported. These will be frozen within 2-3 hours of collection. One blank sample will be taken at each site.

Mussel transects are located in mussel bands, parallel to the water line, usually just up (+1 m tide level) from the sediment transects. Triplicate mussel samples will be collected by taking approximately 30 2-5 cm. mussels (enough to produce $\geq$10 gm tissue) at random along the 30-meter transect. Samples in 16 oz. jars will be cooled, transported and frozen in the same manner as the sediment samples.

Quality assurance and quality control (QA/QC) plans. In the matter of data collection and analysis, sample collection (with labeling), and chain-of-custody procedures, we will adhere to guidelines as developed by the NRDA Hydrocarbon Technical Committee and implemented by NOAA/Auke Bay Laboratory.

DATA ANALYSES

Random sample and subsample collection up to the analysis procedure should assure that hydrocarbons present in the sample represent the average concentration at each site. "Hot spots" of hydrocarbon concentration over the 30 meter transects should be cancelled out by this procedure.

All hydrocarbon level data among sites will be analyzed by ANOVA. For comparison over time, a repeated ANOVA will be used. Further

multiple (Scheffe) or paired (Tukey) methods may be used to test differences at selected sites and will be tested at p=.05.

Sources of the hydrocarbons over time (natural or anthropogenic) will be determined by examining the relative composition of various components of aromatics and alkanes, i.e. odd/even ratios of alkanes, pristane/phytane ratio, 1 and 2 ring aromatic abundance versus 4 and 5 ring compounds, relative numbers of substituted aromatic compounds versus parent compounds, comparison of hydrocarbon patterns with those of Prudhoe Bay crude oil, etc.

All data will be presented in tabular and graphic forms, and selected data will be mapped.

SCHEDULES AND PLANNING

Data and report submission schedule. This proposal is for sediment and mussel sampling during the lowest tide series in August 1991. Covering all 16 sites during this short period (7 days), requires transportation of the field team by helicopter. The team will probably be based out of Valdez, Alaska.

Data compilation, analyses timetable and report writing will be accomplished according to a schedule to be set by the Restoration Planning Work Group and the Trustee Council. Issuing of reports will necessarily be controlled by completion of chemical analyses of the samples collected. Interim status reports will be written as required.

Sample and data archives. Study Plans (with revisions), QA/QC plans, data sets, log books, etc. will be stored under secured conditions as prescribed by the Trustees and implemented by NOAA.

Management plan. This one field trip will be conducted by the two Principal Investigators, John Karinen and Malin Babcock, plus 1 field party member (as yet, unidentified).

Logistics. See first paragraph under this heading.

PERSONAL QUALIFICATIONS

JOHN F. KARINEN

Professional Address

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Education

1957	B.S., Biological and Physical Science, Black Hills State College, Spearfish, South Dakota
1958	B.S., Education, Black Hills State College, Spearfish, South Dakota
1965	M.S., Biological Oceanography, Oregon State University, Corvallis, Oregon
1965-91	Various graduate and training courses: OSU, University of Alaska, Federal government

Professional Positions

1989-present: Habitat Investigations, ABL - Fishery Research Biologist; Principal Investigator, *Exxon Valdez* Natural Resource Damage Assessment Study "Pre-Spill and Post-Spill Concentrations of Hydrocarbons in Sediments and Mussels at Intertidal Sites in Prince William Sound." General consultant in patterns and implication of hydrocarbons in sediments and fauna. Member, Technical Advisory Group for the Alyeska Ballast Effluent Facility.

1985-1989: Marine Investigations, ABL - Supervisory Oceanographer, Groundfish: Included resource assessment and prediction of stock abundance, distribution and recruitment with emphasis on demersal fish in eastern Gulf of Alaska.

1972-1985: Habitat Investigations, ABL - Task Leader, Oil effects studies: Laboratory and field-oriented oil effects studies (established historical baseline sites for hydrocarbon levels in sediments and biota in Prince William Sound); supervised staff of 10 scientists; general consultant - environmental impacts (mining, oil and marina development).

Selected Publications

Karinen, John F. 1988. Sublethal effects of petroleum on biota. Pp. 294-328 in Shaw, D. G. and M. J. Hameedi (eds.), Environmental Studies in Port Valdez, Alaska: A Basis for Management. Lecture Notes on Coastal and Estuarine Studies 24. Springer-Verlag. New York.

Karinen, John F. 1985. Occurrence of juvenile king crabs, *Paralithodes camtschatica* (Tilesius), in Auke Bay, Alaska, on sediments with relatively high concentrations of aromatic hydrocarbons. Pp. 377-387 in Proc. Int. King Crab Symp. Jan. 1985, Anchorage, Alaska. Alaska Sea Grant Report No. 85-12.

Karinen, John F., Stanley D. Rice, and Malin M. Babcock. 1985. Reproductive success in Dungeness crab (*Cancer magister*) during long-term exposures to oil-contaminated sediments. U. S. Dep. Commer., NOAA, OCSEAP Final Rep. 67:435-461.

Rice, Stanley D., D. Adam Moles, John F. Karinen, Sid Korn, Mark G. Carls, Christine C. Brodersen, Jessica A. Gharrett, and Malin M. Babcock. 1984. Effects of petroleum hydrocarbons on Alaskan aquatic organisms: A comprehensive review of all oil-effects research on Alaskan fish and invertebrates conducted by the Auke Bay Laboratory, 1970-81. NOAA Tech. Memo. NMFS F/NWC-67. 128 p.

Karinen, J. F. 1983. Distribution of heavy metals and hydrocarbons in Auke Bay sediments and in biota near active marinas. Final Report to State of Alaska Dept. Trans. and Pub. Fac. - Project # K78180, Northwest and Alaska Fisheries Center, Auke Bay Lab. 52 p.

Karinen, J. F. 1980. Petroleum in the deep sea environment: Potential for damage to biota. Environ. Int. 3(2):135-144.

PERSONAL QUALIFICATIONS

MALIN MARIE BABCOCK

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Education

1962	B.S. Zoology, Oregon State University, Corvallis, Oregon
1962-1964	Graduate course work in Zoology, Oceanography Oregon State University, Corvallis, Oregon
1969	M.S. Zoology (Fisheries), University of Alaska, Fairbanks (UAF)
1969-Present	Continuing education in professional field, supervision, management, personal growth and writing areas through workshops, short courses and classes.

PROFESSIONAL HISTORY:

1987 - Present: Habitat Investigations, ABL - Task Leader and Supervisory Fishery Research Biologist: conduct and supervise research on critical habitat and physiological requirements in juvenile king crabs. Co-Principal Investigator (P.I.), *Exxon Valdez* Natural Resource Damage Assessment (NRDA) Study "Pre-Spill and Post-Spill Concentrations of Hydrocarbons in Sediments and Mussels at Intertidal Sites in Prince William Sound." One of ABL staff scientists to consult with ADF&G biologists in establishing experimental designs and study plans for their many NRDA projects. Supervise staff whose responsibilities include NRDA database management, QA/QC for sample collection and handling, and P.I.'s on other NRDA studies.

1973 - 1987. Habitat Investigations, ABL - Fishery Research Biologist: Research during this period was mainly laboratory oriented and concerned effects of hydrocarbon exposures to aquatic organisms. Assisted (1979 to 1981) in establishing base line hydrocarbons levels in sediments and selected organisms of subtidal and intertidal areas of Prince William Sound.

Selected Publications

Thomas, Robert E., Stanley D. Rice, Malin M. Babcock, and Adam Moles. 1989. Differences in hydrocarbon uptake and mixed function oxidase activity between juvenile and spawning adult

coho salmon (*Oncorhynchus kisutch*) exposed to Cook Inlet crude oil. Comp. Biochem. Physiol. 93C(1):155-159.

Moles, Adam, Malin M. Babcock, and Stanley D. Rice. 1987. Effects of oil exposure on pink salmon, *Oncorhynchus gorbuscha*, alevins in a simulated intertidal environment. Mar. Environ. Res. 21(1):49-58.

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Karinen, John F., Stanley D. Rice, and Malin M. Babcock. 1985. Reproductive success in Dungeness crab (*Cancer magister*) during long-term exposures to oil-contaminated sediments. U. S. Dep. Commer., NOAA, OCSEAP Final Rep. 67:435-461.

BUDGET

Line Item		Amount (Thousands)
Labor		8.0
Travel		6.0
Contracts:	Helicopter	13.5
	Sample Analysis*	55.9
Supplies & Equipment		0.5
TOTAL		**83.9**

*16 sites x 2 (sediment, mussels) x 3 (triplicate) = 96 samples
96 x $582 (current analytical cost, ABL) = $55,872.00

SELECTED LITERATURE

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Krahn, M. M., C. A. Wigren, R. W. Pearch, L. K. Morre, R. G. Bogar, W. D. MacLeod, Jr., S. Chan, and D. W. Brown. 1988. Standard analytical procedures of the NOAA National Analytical Facility, 1988, New HPLC cleanup and revised extraction procedures for organic contaminants. NOAA Tech. Memor. NMFS F/NWC-153. 52 pp.

Warner, J. S. 1976. Determination of aliphatic and aromatic hydrocarbons in marine organisms. Anal. Chem. 48:578-583.