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FEDERAL/STATE NATURAL RESOURCE DAMAGE ASSESSMENT

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November 1990

Pre-spill and post-spill concentrations of hydrocarbons in sediments and mussels at intertidal sites within Prince William Sound and the Gulf of Alaska.

Coastal Habitat Study Number 1

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STUDY TITLE AND I.D. NUMBER

Pre-spill and post-spill concentrations of hydrocarbons in sediments and mussels at intertidal sites within Prince William Sound and the Gulf of Alaska. Coastal Habitat Study Number 1

EXECUTIVE SUMMARY

Only 24 selected pre-spill and post-spill sediment samples collected in 1989 have been analyzed and we report here the preliminary results of those analyses compared with the earlier baseline study. The 1989 pre-spill data from historical sites and sites established ahead of spill impact indicate values less than 1 ppm total aromatic hydrocarbons (AH) suggesting that hydrocarbon concentrations in Prince William Sound (PWS) at the time of the spill were not greatly elevated above historical baseline levels. Barnes Cove sediments, on the west side of Knight Island, showed AH concentrations on April 7 similar to Naked Island and Bay of Isles - 1 to 2 orders of magnitude less than the oil-contaminated samples collected the 0 ft tide level at several sites by Rice and O'Clair for Air/Water Study No. 2.

The limited samples (post EVOS impact) that have been analyzed and data returned indicate increases above pre-spill and historic levels. Two sites had AHs in sediments above historical levels. Aromatic hydrocarbons levels at Sleepy Bay in May were about 15 times historical levels. Our site at Elrington Island, which is near the southwest exit to the Sound and received weathered oil, showed mean AH in the sediment in May about 4 times greater than the historical levels at Naked Island.

Patterns of selected aromatic hydrocarbons (phenanthrenes, dibenzothiophenes, fluorenes, and chrysenes) in sediments appear to be similar for all sites and may be indicative of Prudhoe Bay crude. Patterns at Naked Island prior to the spill were very different; dibenzothiophenes, fluorenes, and chrysenes were absent and only a trace amount of phenanthrenes were present.

Odd/even ratios of alkanes are also indicative that petroleum was added to the sediments. Mean ratios were about 6 at Naked Island from 1977-79, but ratios ranged from 1 to 3 in 1989.

Abundance of mussels and other epifauna along sediment and mussel transects were photographically recorded during each sampling period. Analysis of these data show decreases in live mussels at one oiled site, Elrington Island. We are expecting results of tissue hydrocarbon analyses soon. These data will provide a basis for determining the cause of the observed differences.

OBJECTIVES

A. Sample and estimate hydrocarbon concentrations in mussels and sediment from 20 sites within 10% of the actual concentration 95% of the time, when total aromatic concentrations are greater than 200 ng/g dry wt.

B. Test the null hypotheses that hydrocarbon contamination of sediments and mussels is the same for the pre-spill and post-spill period.

C. Document changes in abundance and distribution of intertidal epifauna and test the null hypothesis that no differences occur at oiled and non-oiled sites.

INTRODUCTION

On 26 March 1989, we began resampling 10 historically established intertidal hydrocarbon baseline sites in Prince William Sound in response to the *EXXON VALDEZ* oil spill. We also established 10 additional sites (in PWS and the Kenai Peninsula) along the spill trajectory before oiling, and sampled after oiling to measure changes in hydrocarbon levels in sediments and mussels resulting from the spill. Baseline levels of hydrocarbons at 8 historic sites are very low; about 0.2 ppm or less. No significant increase in aromatic hydrocarbons in intertidal sediments at the 8 sites was apparent from 1977 to 1980.

The present study will eventually compare hydrocarbon levels in sediments and mussels at the historically established sites plus 6 additional sites established in advance of *EXXON VALDEZ* crude oil impact.

STUDY METHODS

Historically established baseline sites were resampled in March 1989 immediately before several of them were impacted by the *EXXON VALDEZ* oil spill, and additional sites were established to cover areas of special concern. Sediment and mussel samples were taken. Photos documented biota in quadrats every 4 m along both mussel and sediment transects. Selected sites were resampled post-spill in April, May, June and August 1989 and in April, June and August in 1990. Details of methodology are described in the study plan dated 27 September 1989.

STUDY RESULTS

Site Locations and Field Sampling. The locations of 20 sites sampled in the summer of 1989 and 1990 are given in Table 1. Site name, general location, latitude, longitude and the data base abbreviation for each intertidal sample location are listed. Ten of these sites were established as hydrocarbon baseline sites in 1977-81 in a pre-spill study to monitor possible changes in hydrocarbon contamination following the initiation of tanker traffic. The ten sites, four in Port Valdez and six in Prince William Sound, were chosen to bracket the tanker traffic lanes. Sites at Siwash Bay and Olsen Bay were control sites as little incidental introduction of hydrocarbons were expected at these sites. The remaining sites were Dayville, Mineral Creek, Gold Creek, and Sawmill Creek in Port Valdez; and West Bay, Outside Bay, Rocky Bay, and Constantine Harbor in PWS. Six additional sites were established in PWS (see Figure 1) and 4 along the Kenai Peninsula.

Three trips to Prince William Sound and two trips to the Kenai Peninsula were made in the summer of 1990 to collect samples; (1) April 23-28 (Kenai and PWS), (2) June 20-26 (Kenai and PWS) and (3) August 4-10 (PWS). A total of 285 samples were collected; 54 blanks, 165 sediments and 166 mussels.

Historical Baseline Results, 1977-1982. Sediments, mussels, water and fish samples were collected from 8-10 intertidal sites in the summers of 1977-81 and analyzed for aliphatic and aromatic hydrocarbons. Selected sites were sampled in 1982. These data are in a manuscript in preparation (Karinen et al.).

Mean concentrations for selected aromatic hydrocarbons in sediments from samples collected at 8 sites in 1977-79 are compared with aromatic hydrocarbon levels measured in 1980 (Table 2). Concentrations of total selected aromatic hydrocarbons in sediments were very low at all 8 sites; usually less than 0.2 ppm. Highest concentrations in Prince William Sound sites (Constantine Harbor and Rocky Bay) were about 68 times less than concentrations reported for the Auke Bay Marina and 600 times less than moderately polluted harbors in Puget Sound (Karinen 1988). Control sites (Olsen Bay and Siwash Bay) had 1,360 to 12,000 less total aromatic hydrocarbons than the indicated marina sites. The higher concentrations of hydrocarbons at Constantine Harbor and Rocky Bay are probably the result of the large numbers of boats which use these bays for anchorages. Rocky Bay was also the site of one or more boat groundings from 1977 to 1982 as it was used as an anchorage for pilot boats accompanying the tankers from Hinchinbrook Entrance to Port Valdez in the early days of oil shipment from Port Valdez. Although several of the locations show increases in total aromatic hydrocarbons from mean levels (1977-79) compared to 1980; the concentrations are so low and near the

detection limit of the method that these changes cannot be regarded as significant. Statistical comparisons will be applied to these data and data for later years where possible to determine if a significant change of aromatic hydrocarbons concentrations occurred at these locations prior to the *EXXON VALDEZ* oil spill.

Composition of the aromatic hydrocarbons at Constantine Harbor and Rocky Bay (Table 2) does not match that reported for the ballast effluent, suspended particulates, or sediments in Port Valdez (Karinen 1988) indicating that these hydrocarbons are probably not the result of the ballast effluent introduced to Port Valdez and Prince William Sound. Comparisons with the composition of Prudhoe Bay crude oil suggest some similarity with patterns of aromatics at Rocky Bay.

Analysis of 1989 Sediment Samples. Results of hydrocarbon analyses (aromatics and aliphatics) were received late last week for only 24 sediment samples collected just prior to oil impact from the spill and at various times after the spill. The small number of samples analyzed precludes a statistical analysis of these data and allows us to make only preliminary conclusions. Sediments from five sites (Naked Island, Bay of Isles, Barnes Cove, Sleepy Bay, and Elrington Island) and four time periods (late March ,early April, early May, and mid-August) were analyzed: Naked Island- 2 samples- 3/28/89, 3 samples- 4/08/89, 2 samples- 5/08/89, and 3 samples- 8/15/89 ; Bay of Isles- 2 samples- 3/30/89, and 3 samples- 4/08/89; Barnes Cove- 2 samples- 4/07/89; Sleepy Bay-2 samples- 5/07/89, and 1 sample - 8/17/89; and Elrington Island - 2 samples -5/10/89, and 2 samples -8/17/89.

Mean total aromatic hydrocarbons in sediments from most sites were very low (<0.2-0.3 ppm/dry wt.); only about two to three times historical levels. Lack of data from reference sites (Siwash Bay and Olsen Bay) makes it impossible to say with certainty that this small increase above historical levels is the result of oil from the *Exxon Valdez* or from a gradual input of hydrocarbons over the last nine years.

Two sites (Sleepy Bay and Elrington Island) had mean aromatic concentrations in sediments that were about 15 and 4 times historical levels (1.5 and 0.4 ppm). These two sites were impacted by oil from the spill and had fresh oil layered over much of the upper half of the intertidal zone (Sleepy Bay) or scattered patches of weathered black tarry oil on rocks in the high intertidal zone at the time of sampling.

The few number of samples analyzed to date and the absence of an analysis from a control site far removed from the spill area (Siwash Bay or Olsen Bay) makes it difficult to ascertain the source of the increased aromatic content in the sediments. Two observations seem to implicate the *Exxon Valdez* spill as the

source. The pattern of selected aromatic hydrocarbons (phenanthrenes, dibenzothiophenes, fluorenes, and chrysenes) in the sediments and oil from the Exxon Valdez shows some similarity. Oil from the tanker has the following composition for these groups of compounds; phenanthrenes - 16.1%, dibenzothiophenes - 9.2%, fluorenes - 3.5%, and chrysenes - 0.9%. Sediments at Naked Island on May 8, 1989 had 19.8% phenanthrenes, 5.9% dibenzothiophenes, 9.0 % fluorenes, and 12.0% chrysenes. Differences from the parent oil may reflect differences in rates of movement to the sediment by the various groups of compounds. The pre-spill distribution of these aromatic compounds in sediments at Naked Island (1977-79) was very different. No dibenzothiophenes, fluorenes, or chrysenes were present, and phenanthrenes constituted only about 1% of the total aromatic compounds. The second observation that implicates oil from the tanker as the source are the odd/even ratios of alkanes in the tanker oil and that found in the sediments. The tanker oil has an odd/even ratio of .82. The mean ratio in sediment at Naked Island on May 8 was 1.19 - much different than the mean value of 6.09 in sediments at this site from 1977-79. Addition of alkanes from the tanker oil may be responsible for this change. Statistical analyses of these and additional data, hopefully, will determine the source of these hydrocarbon compositional changes.

Based on baseline analyses we expect that even lightly oiled and some beaches with no visible oil will show the presence oil from the spill when samples are analyzed. The early baseline data will provide a firm basis for evaluating injury from the spill.

Photographs of Transect Quadrats. Quadrat slides from mussel transects were analyzed, for May and August 1989, for six sites - Bligh Island, Bay of Isles, Olsen Bay, Elrington Island, Barnes Cove, and Naked Island. Barnacles and mussels and the presence of dead mussels were counted using the 100-random dot method as outlined in the detailed study plan. Differences in abundance of biota were compared among May and August estimates.

The only site which showed significant differences ($P<.05$, Tukey comparison) in live (decrease) and dead (increase) mussels was Elrington Island, an oiled site. This needs to be confirmed with further statistical review and analyses of 1990 photos. There were no significant differences in abundance of barnacles between May and August at any of the sites analyzed.

STATUS OF INJURY ASSESSMENT

Sediments

Only a few of the pre- and post-spill samples from 1989 have been analyzed.

Mussels

None of the 1989 and 1990 samples have been analyzed.

Photographic Quadrats

While significant differences in abundance in live and dead mussels were found at Elrington Island (between May and August 1989), this needs to be confirmed with further statistical review and analyses of 1990 quadrat photos.

CITATIONS

Karinen, John F., L. Scott Ramos, Patty G. Prohaska, William D. MacLeod, Jr. In Preparation. Hydrocarbon Distribution in the Marine Environment of Port Valdez and Prince William Sound, Alaska.

Karinen, John F. 1988. Sublethal effects of petroleum on biota, Pp 293-328 in Shaw, David G. and Mohammad J. Hammeedi (Eds.), Lecture Notes on Coastal and Estuarine Studies, Environmental Studies in Port Valdez, Alaska. Springer-Verlag, New York.

Table 1. Site Locations and abbreviated names for intertidal baseline sites sampled in 1989 and 1990.

Site	General Location	Latitude	Longitude	DatabaseAbbr.
		Port Valdez		
Dayville		61°05'13"	146°16'40"	DAYVI
Mineral Creek		61°07'40"	146°24'55"	MINEC
Gold Creek		61°07'59"	146°27'47"	GOLDC
Sawmill Creek		61°05'05"	146°26'12"	SAWMC
		PRINCE WILLIAM SOUND		
Siwash Bay	Unakwik Inlet	60°57'15"	147°40'50"	SIWAB
West Bay	Bligh Island	60°52'02"	146°45'20"	BLIGI
Olsen Bay	Port Gravina	60°44'22"	146°11'53"	OLSEN
Outside Bay	Naked Island	60°39'03"	147°26'14"	NAKEI
South Bay	Perry Island	60°41'00"	147°55'55"	PERRI
		60°40'43"	147°55'00"	PERRI
Bay of Isles	Knight Island	60°21'48"	147°41'30"	BOISL
Rocky Bay	Montague Isl.	60°20'06"	147°07'43"	ROCKB
Constantine Hbr.	Hinchinbrook	60°21'06"	146°39'38"	CONST
Barnes Cove	Drier, Knight	60°18'31"	147°45'43"	BARNC
Sleepy Bay	Latouche Isl.	60°04'00"	147°50'02"	SLEEB
Crab Bay	Sawmill, Evans	60°04'20"	147°59'48"	CRABB
Fox Farm	Elrington I.	59°58'15"	148°08'31"	ELRII
		KENAI PENINSULA		
Quicksand Cove	Aialik Bay	59°47'10"	149°47'12"	QUICC
Verdant Cove 1	Aialik Bay	59°41'48"	149°44'20"	VERDC
Verdant Cove 2		59°41'49"	149*44'19"	VERDC
Harris Bay		59°44'12"	149°53'30"	HARRB
Petrof Point	Nuka Passage	59°22'25"	150°60'00"	PETRP

Table 2. Mean concentrations (ng/g dry weight) for selected aromatic hydrocarbons found in intertidal sediments from 8 Prince William Sound Locations, 1977-1979 and 1980 (). * indicate values <0.1 ng/g (<0.1 ppb).

COMPOUND/ SITE	Constantine	Rocky Bay	Naked Isl.	Olsen Bay	Bligh Isl.	Siwash Bay	Dayville	Mineral Cr
i-Propylbenzene	0.3(*)	0.5(.2)	.2(*)	.2(*)	.2(*)	.2(*)	.2(*)	.1(*)
n-Propylbenzene	0.7(*)	0.8(.4)	.1(*)	.4(*)	.1(*)	1.0(*)	.2(*)	*(*)
Indane	0.1(*)	0.5(*)	*(*)	*(*)	*(*)	.1(*)	*(*)	.1(*)
Naphthalene	5.0(3)	4.0(6)	.5(*)	.4(*)	.2(.3)	.6(2)	1.0(2)	2(4)
Benzothiophene	0.1(*)	0.1(*)	*(*)	*(*)	*(*)	*(*)	*(*)	*(*)
2-Methylnaphthalene	15.0(14)	7.0(13)	.3(*)	.3(*)	.3(*)	.1(.7)	1.0(3)	2(4)
1-Methylnaphthalene	12.0(12)	2.0(6)	.1(*)	.3(*)	.1(*)	.1(*)	.4(1)	1(2)
Biphenyl	9.0(9)	3.0(6)	*(*)	*(*)	*(*)	.2(*)	*(*)	*(*)
2-6-Dimethylnaphthalene	9.0(10)	4.0(7)	.3(*)	*(*)	.1(*)	.1(*)	.1(.8)	.6(2)
2,3,5-Trimethylnaphthalene	7.0(7)	*(*)	*(*)	*(*)	*(*)	*(*)	*(*)	*(*)
Fluorene	3.0(4)	10(10)	*(*)	.1(*)	*(*)	*(*)	*(.5)	1(3)
Dibenzothiophene	3.0(*)	2(*)	*(*)	*(*)	*(*)	*(*)	*(.1)	.6(.7)
Phenanthrene	34.0(34)	35(60)	.9(*)	.4(*)	.5(2)	.4(4)	.8(5)	7(15)
Anthracene	0.1(*)	2(4)	*(.7)	*(*)	*(*)	.4(*)	*(*)	*(.4)
Fluoranthene	4.0(*)	9(17)	.4(3)	*(*)	*(*)	.1(*)	*(*)	6(12)
Pyrene	7.0(7)	11(21)	82(2)	*(*)	*(*)	.2(*)	*(*)	2(6)
Benz(a)anthracene	2.0(3)	1(.3)	*(*)	*(*)	*(*)	*(*)	*(*)	*(*)
Chrysene	8.0(13)	12(19)	*(*)	*(*)	*(*)	*(*)	*(*)	*(*)
Benzo(e)pyrene	3.0(4)	5(13)	*(*)	*(*)	*(*)	*(*)	*(*)	*(*)
Benzo(a)pyrene	3.0(*)	4(*)	*(*)	*(*)	*(*)	1(*)	*(*)	*(*)
Perylene	81.0(69)	31(56)	14(24)	8(*)	5(10)	4(7)	*(*)	*(*)
TOTAL AROMATICS	206(189)	144(248)	99(35)	10(*)	6(12)	9(19)	4(12)	22(49)

Figure 1. Intertidal baseline sampling sites.

▲ - historical sites■ - established in 1989.