Prince William Sound Regional Citizens' Advisory Council

Contract No. 611.98.1

Long Term Environmental Monitoring Program Data Analysis of Hydrocarbons in Intertidal Mussels and Marine Sediments, 1993-1996

Submitted by:

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Non-Technical Summary Report

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Prince William Sound Regional Citizens' Advisory Council Long Term Environmental Monitoring Program

Objective

The primary objective of the ongoing Long-Term Environmental Monitoring Program (LTEMP) is to collect data to monitor hydrocarbon pollution due to the oil transportation industry in Prince William Sound and the northern Gulf of Alaska.

Approach

To accomplish this objective, mussel tissues and sediments have been collected for detailed hydrocarbon (oil-fingerprint) analyses at nine stations (Figure 1) from March 1993 through July 1997¹¹. Samples include mussel tissues from intertidal habitats along with shallow (15 to 30 feet, 5 to 10 m) and deep (85 to 130 feet, 28 to 43 m) sediments. To support the interpretation of the hydrocarbon data, additional measurements, including fat content in mussel tissues, shell characteristics, and reproductive state, have been measured on the mussels. The sediment samples have also been characterized for total organic carbon and grain-size distribution.

In the laboratory, sensitive analytical techniques allow the identification of individual hydrocarbon compounds that are characteristic of naturally occurring biological hydrocarbons, Alaskan North Slope (ANS) crude oil, *Exxon Valdez* Oil Spill (EVOS) residues, and background signals from other sources (e.g., combustion products or the Katalla oil seeps and coal particles from east of Prince William Sound).

The sediment samples were analyzed for two classes of hydrocarbons: the relatively nontoxic aliphatic compounds (AHC) which are similar to fats and cooking oils, and the polynuclear aromatics (PAH), which are more toxic and significantly more persistent in the environment. The mussel tissues were initially analyzed for both classes of compounds, but because the natural fats and other components from the tissues themselves interfered with the aliphatic analyses, only the polynuclear aromatic hydrocarbons have been analyzed from later samples.

Most crude oils and other sources of PAH that have been introduced to Prince William Sound have specific compounds present in unique ratios relative to each other. This characteristic allows us to obtain relatively distinctive fingerprint patterns. Figure 2 shows the fingerprint representing the relative abundance of the 39 PAH constituents in fresh Alaskan North Slope/EVOS crude oil and three sediment samples that are generally representative of the range of patterns and concentrations observed throughout the program. Figure 3 shows the same reference oil contrasted to three mussel tissue samples

¹ The following table is a key relating cruise numbers to sampling periods.

	0			0					
Cruise No.	1	2	3	4	5	6	7	8	9
Period	3/93	7/93	3/94	7/94	3/95	7/95	3/96	7/96	3/97

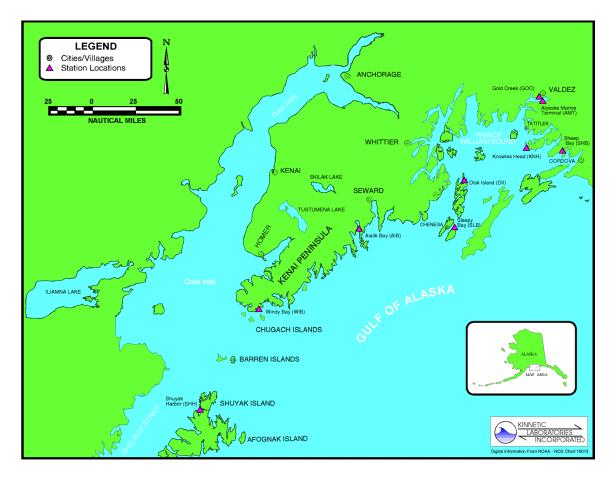


Figure 1. LTEMP Station Locations (Overall Study Area).

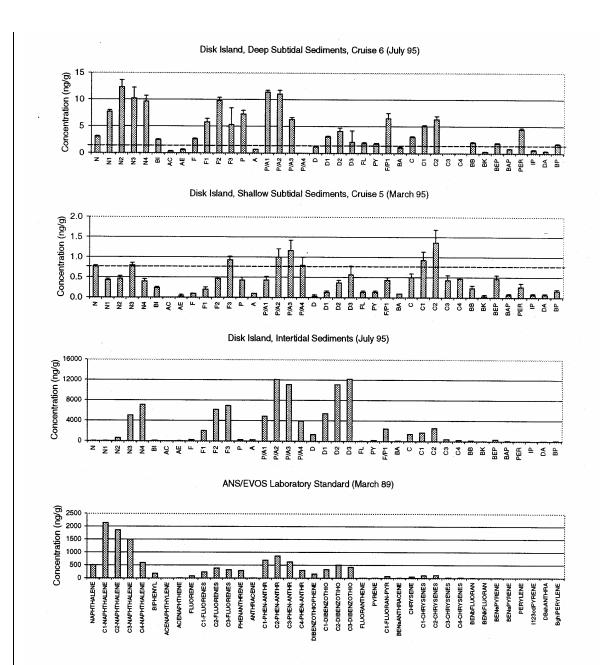


Figure 2. Aromatic hydrocarbon fingerprint (histogram plots) showing the observed distribution of target PAH constituents in representative sediment samples and fresh ANS/EVOS oil. Concentrations for individual components are in nanograms per gram of sediment or oil extracted (note the different scales). The histograms for the deep and shallow sediment samples represent the average of three replicate analyses, and the "error bars" shown above each component represent the variability associated with each measurement. The dashed horizontal line in the plots represents the average method detection limit (MDL) for the individual PAH in a sample. Differences among the profiles due to different hydrocarbon sources and weathering behavior are discussed in the text.

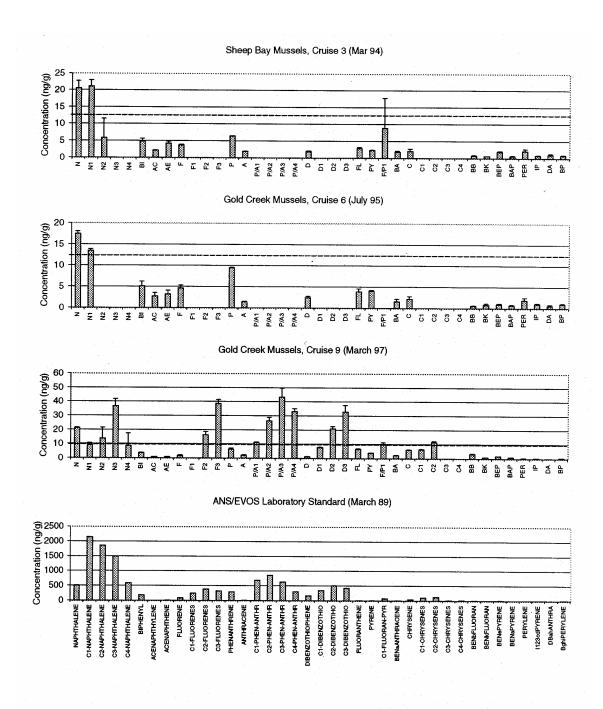


Figure 3. Histogram plots showing the observed distribution of target PAH constituents in representative mussel tissue samples and fresh ANS/EVOS oil. Concentrations for individual components are in nanograms per gram of tissue or oil extracted (note the different scales). The histograms for the mussel tissue samples represent the average of three replicate analyses, and the "error bars" shown above each component represent the variability associated with each measurement. The dashed horizontal line in the plots represents the average method detection limit (MDL) for the individual PAH in a sample. Differences among the profiles due to different hydrocarbon sources and weathering behavior are discussed in the text.

peaks are noted, and each individual bar represents the absolute concentration of a given component (or group of similar-weight components). These different constituents weather (evaporate and dissolve) to different degrees after oil is released to the environment. Knowledge of how these patterns change with time and exposure conditions, is also important in identifying contaminants in the different samples examined.

Results

Overall concentrations and general sources

In the 4½ years of data collection during this program, there have been some changes in the sampling design regarding station coverage. As a result, sediment data were not always collected from all stations at both deep and shallow depths in winter and summer seasons. Mussel tissue collections, however, have been essentially continuous for the March and July samplings at all stations for the entire period. Between the sediment and mussel tissue collections, sample coverage is sufficient to identify time trends and sources of individual hydrocarbons at the different stations.

All hydrocarbon levels in both sediments and tissues are generally very low. Average PAH concentrations in the cleaner sites for deep sediments range from less than 30 nanograms² per gram (ng/g) dry weight of sediment at Aialik Bay to over 500 ng/g dry weight at Sleepy Bay. Shallow sediments have generally even lower PAH levels, ranging from less than 10 ng/g dry weight at Knowles Head to approximately 400 ng/g dry weight at Sleepy Bay. Average PAH hydrocarbon burdens in the mussel tissues ranged from less than 130 ng/g dry weight at Aialik Bay to over 510 ng/g dry weight at Alyeska Marine Terminal in the Port of Valdez.

The PAH patterns in the sediments and tissues examined in this program reflect several "background" sources, including the Katalla oil seeps and coal particles from east of Prince William Sound, as well as oil-transportation activities associated with the Alyeska Marine Terminal in the Port of Valdez. At this time, there is a debate in the scientific literature as to whether the natural "background" hydrocarbons are actually derived from oil seeps or from coal particles. However, for the purposes of this program, it is sufficient that these fingerprints can be distinguished from the pattern generated from Alaskan North Slope crude oil introduced from present-day activities or weathered EVOS residues that are still present at a few locations.

The histograms for the Disk Island deep and shallow subtidal sediments shown in Figure 2 are representative of the pattern classified as being from sources such as coal or seep oil from outside Prince William Sound. The histogram for the Disk Island intertidal sediment is representative of the classic weathered PAH pattern associated with EVOS residues. In comparison, the fresh ANS/EVOS oil standard shows the naphthalene group to be the most prominent, with lower relative levels of the other PAH constituents. With evaporation and dissolution weathering, most of the lighter and more water-soluble

² a nanogram is 0.000,000,001 gram or approximately 0.3 trillionth of an ounce

naphthalene components are removed, leaving only the heavier PAH compounds at very characteristic ratios in the remaining oil residues.

In the histograms for the mussel tissue extracts shown in Figure 3, most of the individual analytes are below the average individual component MDLs for both the Sheep Bay cruise 3 (March 94) and the Gold Creek cruise 6 (July 96) samples. This pattern is characteristic of most of the mussel samples obtained from cleaner areas throughout the program where few PAHs derived from more common oil sources are observed. Many of the constituents observed in the upper two profiles if Figure 3 have been identified as either combustion-derived PAH by-products from burning oil or as "procedural artifacts." In any event, the point to be emphasized is that the levels are extremely low, and that when a pulse of oil is released, it is easily detected as shown by the histogram obtained from the Gold Creek mussels collected during cruise 9 (March 97). In this instance the characteristic pattern of relatively fresh ANS oil can be observed and potentially traced back to the Alyeska Ballast Water Treatment Plant spill that occurred in January 1997.

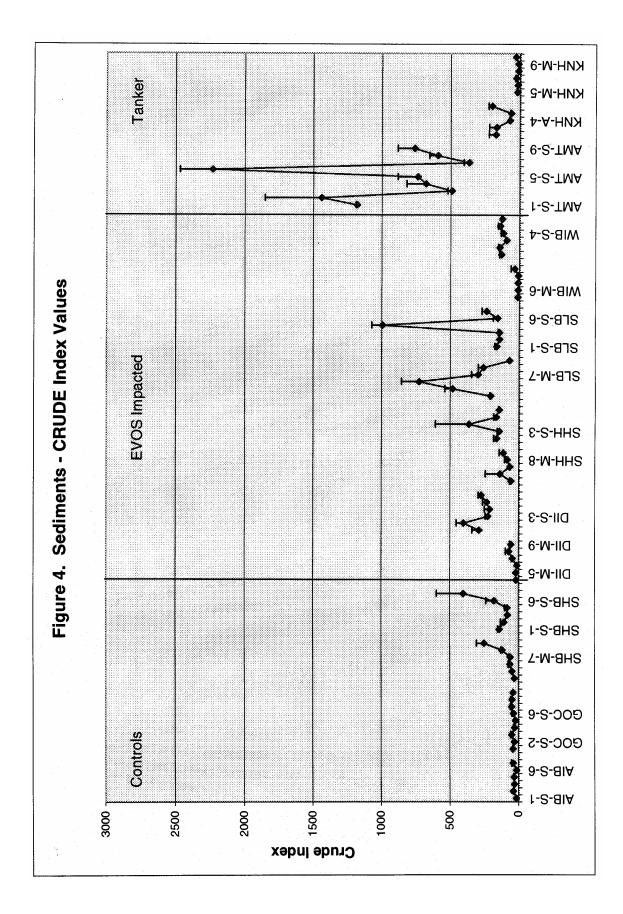
Analysis of geographical and time trends

Because there is natural variability or scatter at every site, the LTEMP program collected three replicates of sediment or tissue at each sampling. The results from each type of sample were averaged to generate a total aliphatic hydrocarbon (TAHC) and/or total aromatic hydrocarbon (TPAH) concentration for each station, at each time. In addition, as described in the previous section, histogram plots for the individual aliphatic and aromatic compounds were generated for all the samples for the project chemist to evaluate. On every sample plot, each chemical compound is represented by a bar with another line (a standard error bar) projecting from it showing how much scatter there was among the three replicate measurements. Although there is generally a fair amount of natural variability among the replicates from a single sampling event, the data generated in this program are quite precise. The high precision allows evaluations of geographic and time trends among the stations or over time at a single station.

To aid in analyzing all of the available data from this program, a new empirical value, we named the "CRUDE" index, was developed to emphasize the crude oil fraction (rather than biological or combustion-product hydrocarbons) in the chemical results. The CRUDE index³ approach combines into a single value many of the individual parameters and ratios that are used to identify patterns within the data. By combining many of these parameters into a single unit, it is now possible to plot the value of this single index for each station and sample type over time, and thereby, show where trends occur within a station and identify significant differences among stations.

Figure 4 presents the CRUDE index values obtained from the sediment samples collected in the control sites at Aialik Bay, Gold Creek, and Sheep Bay; the EVOS-impacted sites at Disk Island, Shuyak Harbor, Sleepy Bay, and Windy Bay; and sites associated with tanker activities, Alyeska Marine Terminal and Knowles Head anchorage. Standard

³ The CRUDE index is a summation of TPAH, TAHC and UCM (unresolved complex mixture from AHC analysis) weighted to assess the petrogenic fraction.



error bars reflecting the scatter associated with each triplicate measurement appear on top of each sample. This allows an easy evaluation of apparent trends over time or among stations, with the scatter associated with each measurement easily factored into the visual analysis. As noted earlier, sediment samples were collected at deep and shallow stations. Therefore, in the figure, station identifications are denoted as DII-M-2 or DII-S-3, etc. DII-M-2 stands for <u>DIsk Island, Mid-depth sediment, cruise 2</u>, and DII-S-3 represents <u>DIsk Island, deep Sediment, cruise 3</u>, etc.

As shown by Figure 4, relatively flat and extremely low-level CRUDE index values are obtained for the deep sediments at Aialik Bay and Gold Creek (control stations); the mid-depth sediments within Windy Bay and Disk Island (EVOS-impacted stations); and finally in the mid-depth sediments at Knowles Head (tanker-affected area). At these stations, there was very little change observed in the absolute hydrocarbon concentrations and little apparent change in the patterns associated with the plots generated for each station over time. Likewise, these stations exhibited little or no evidence of ANS or EVOS crude-derived oil, and only extremely low-level background hydrocarbons from the petrogenic or coal patterns were noted.

Some changes in sediment hydrocarbon burdens were suggested over time by the increases in the CRUDE index values at Sheep Bay (mid-depth and deep), at Disk Island (deep), and at Sleepy Bay (mid-depth and deep). Likewise, very high variability and much higher absolute concentrations of petroleum-derived hydrocarbons were noted in the deep sediments at the Alyeska Marine Terminal.

Figure 5 presents the data generated for the *Mytilus* Petrogenic index, which is derived from the sums of individual compounds that are particularly characteristic of PAHs associated with petroleum as opposed to combustion sources. As with the CRUDE index plot presented above, standard error bars reflecting the scatter associated with each triplicate measurement appear on top of each sample. In this case, there are time changes and patterns noted for the mussel samples collected at essentially every station. The relative magnitude of the error bars associated with each triplicate measurement is very small when compared to the overall change in *Mytilus* Petrogenic index values observed for each station over time. Therefore, the observed trends are believed to reflect real changes in the field, and not artifacts of the analytical method or collection procedures. The patterns observed at several of these stations can, in fact, be correlated with spill events or clean-up activities that have occurred in Port Valdez or Prince William Sound since 1993 (see below).

Hot spots and areas of high variability

Table 1 presents the major observations from the 4½ years of the program. This table was generated after detailed examination of every aliphatic and aromatic hydrocarbon histogram plot for every sample, the trends from the CRUDE and *Mytilus* Petrogenic indices, and the fingerprint ratios that are characteristic of different oil sources. From the data summary, highly variable stations or so-called "hot spots," indicating higher oil

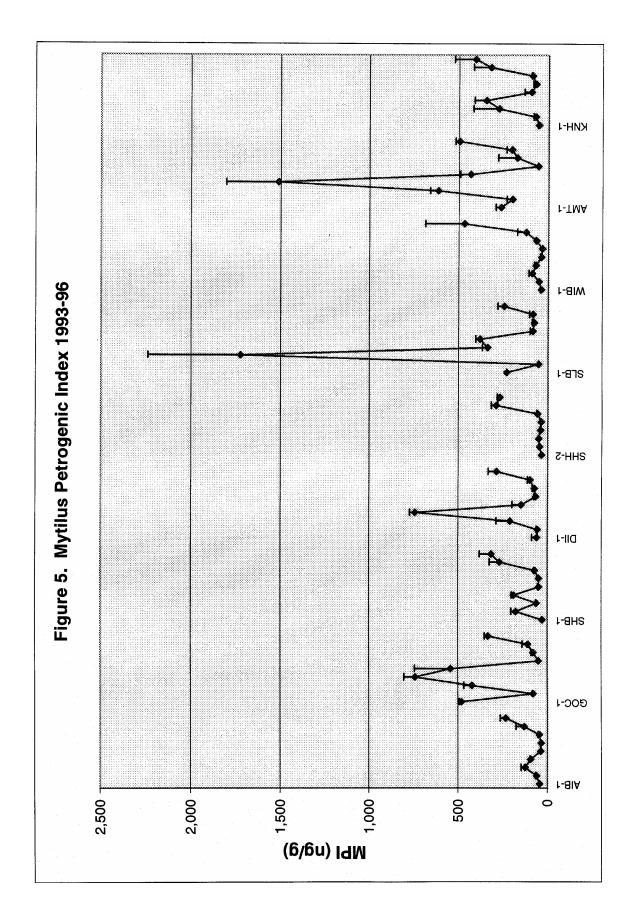


Table 1. Summary of Sediment and Mussel Tissue Hits and Percent ANS / EVOS Crude Contributions for Highly Variable and High Oil Concentration Samples -- LTEMP Cruises 1-9, March 93 - March 97.

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concentrations, were noted. A subset of those hot spots was then examined for evidence of ANS or EVOS oil, and identified in the table. From these analyses, the following distribution of ANS or EVOS-related oil were observed:

- Alaska Marine Terminal ANS oil was detected in deep sediments for all nine cruises; mussels showed evidence of ANS oil for cruises 1, 3, 4, 5, 7, 8, and 9.
- Disk Island No ANS or EVOS oil was detected in any deep sediment samples; mussels exhibited evidence of EVOS oil in cruises 3, 4, 5, 8, and 9; intertidal sediments (opportunistically collected when weathered oil was observed on the beach during mussel collection) showed significant quantities of EVOS oil in cruises 6 and 8.
- Gold Creek ANS oil was observed only once in deep sediments during cruise 4; mussels showed ANS oil in cruises 1, 3, 5, and 9.
- Knowles Head -- no evidence of ANS crude was noted in either the anchorage or shallow sediment locations; however, ANS crude was detected in the mussel samples collected during cruise 8.
- Sheep Bay -- no samples showed any evidence of ANS or EVOS oil for either sediments or mussel tissue.
- Shuyak Harbor -- ANS or EVOS oil was noted in the deep sediment for cruise 3 only; mussel tissue showed no contamination from ANS or EVOS oil.
- Sleepy Bay -- there was no evidence of ANS or EVOS oil in the deep sediment samples; however, the shallow sediments showed positive hits for ANS or EVOS-derived oil during cruises 4, 6, and 7. Mussel samples showed evidence of ANS or EVOS oil in cruises 1, 3, 4, 5, and 9.
- Windy Bay -- ANS or EVOS-derived oil was observed in the deep sediments during cruises 3, 4, 6, and 8, but not in any of the shallow sediments. ANS or EVOS oil was detected in the mussel samples only during cruise 9.

Table 1 also lists the range of values obtained for the relative percent ANS or EVOS contribution to the total aromatic hydrocarbon burdens in the different sample matrices at the different stations. The relative percent contributions range from nondetect to upwards of 60 or 70 percent of the total PAH measured. It should be remembered, however, that the total PAH levels in most of these samples were extremely low. Therefore, although the relative percent ANS or EVOS oil for any given station may have been high, the absolute value for the concentration of residual oil itself was extremely low.

Correlation of mussel hydrocarbon values with known events

On initial examination, the mussel hydrocarbon patterns may appear wildly variable with no apparent trend or explanation. However, the trends observed in Figure 5 can be correlated with a chronology of documented events that have occurred within Port Valdez and Prince William Sound since 1993. In May of 1994, the *Eastern Lion* oil spill occurred at the Alyeska Marine Terminal during loading operations. Mussel samples collected at the time of the spill showed extremely high levels of hydrocarbons at the Alyeska Marine Terminal station, which is located near berth 5, the site of the spill.

Elevated levels were still noted in the mussel tissues at Alyeska Marine Terminal during cruise 4 (July 1994), and a strong signal was observed in the Gold Creek samples at the same time.

A similar spike in the mussel contamination from a weathered ANS source was also noted in the samples collected at Disk Island during July of 1994, and at first it might seem plausible to speculate that it too might be from the *Eastern Lion* oil spill. However, sheens released from mussel bed cleaning operations at Disk Island just prior to the RCAC samplings are a much more likely source.

After the July 1994 events, hydrocarbon levels in the mussels at all stations dropped to uniformly low values by July 1995. The PAH histogram pattern for the mussels collected from Gold Creek in July 1995 (Figure 3) is indicative of the extremely low background signal observed in mussel samples throughout Prince William Sound at that time. As noted earlier, this pattern is identified as either being characteristic of the by-products associated with the combustion of oil or as a low-level procedural artifact of the sampling and measurement program. It also shows up consistently at low-level sites in other monitoring efforts, such as the NOAA Status and Trends program.

Examination of the *Mytilus* Petrogenic index plot shows another increase at all stations during the period of July 1996 to March 1997. The profiles obtained in these samples are again consistent with that observed for ANS crude oil at Alyeska Marine Terminal, Gold Creek, and Disk Island. The cruise 9 profiles for the increase observed at Sleepy Bay and Knowles Head, however, are not consistent with the source being ANS crude oil. One possible source for a newly arising signal observed in the March 1997 sampling interval (at least for Alyeska Marine Terminal and Gold Creek), would be from the Alyeska Ballast Water Treatment Plant (BWTP) spill, which occurred in January of 1997.

The increases in hydrocarbon concentrations at Sleepy Bay during cruises 3, 4, and 5 show that the source is consistent with EVOS or more recent releases of Alaskan North Slope crude oil.

The interpretation of the *Mytilus* Petrogenic index pattern at Windy Bay is somewhat more complicated. A mixed source is indicated, including contributions from aromatics that look like they could be derived from Bunker C or No. 6 fuel oil. In addition, the contributions from biogenic hydrocarbons (plant waxes and natural oils), as measured in the sediments, are higher at Windy Bay than at any other site. This site also contains traces of ANS or EVOS-related oil that were detected in the deep sediments during cruises 3, 4, 6, and 8. No hydrocarbons were associated with EVOS oil in the shallow sediments, however, and of all the mussel samples collected at Windy Bay, evidence of EVOS oil was only indicated in cruise 9. Kinnetic Laboratory personnel (the field samplers) suggest the logging operations in the area may be a possible new source of hydrocarbons.

Conclusions and Recommendations

After intensive examination of the rationale, methods, and results of the LTEMP program during the preparation of this report, we offer the following assessments and recommendations to RCAC to better tune the program.

Program Strategy

The following table summarizes our general assessments of the monitoring program.

Sample Type	Program Assessment	
Deep sediments	Working well, sampling is consistent and detection levels are good, but samples are only detecting background hydrocarbons (i.e., non-ANS).	
Shallow sediments	Generally working well, but there are problems with detection limits and sampling depths.	
Mussel tissues	Hydrocarbon detection is working very well, but the morphometric and lipid data being collected are unnecessary.	

Overall, the program is working well although the station coverage is a somewhat sparse. The use of mussels as a sentinel organism within Prince William Sound is successful. Although the measured hydrocarbon levels are low, and there are potential problems with interferences due to background contaminants associated with field and laboratory procedures (particularly at very clean sites), these low-level concentrations will allow a very minor increase in hydrocarbon concentrations to be detected. While such detection is difficult to do on a statistically significant basis, the utilization of characteristic patterns (such as those shown in the histogram plots presented in this report) makes it easier to identify trends and changes in sources, even when absolute total hydrocarbon loadings may not be changing that much. As such, the overall TPAH or TAHC concentration value at a site may not change that much, but the influence of a new source can be readily identified by a change in the histogram pattern for constituent compounds.

We were able to assess sources, track patterns, correlate with events, and detect a few statistically significant differences within the existing data, but there were definite constraints due to small sample size (i.e., number of sites and sampling intervals). It may be possible to monitor larger reaches of the Sound on a limited budget by reducing the sampling efforts, for example, by sampling during one season rather than two or by changing to biennial samplings at "stable" sites. If, under this looser but broader-focus sampling, an acute change were detected or a catastrophic event occurred, the program could still respond with increased intensity of monitoring in an affected locale.

Sample Types

Several options are available for restructuring the monitoring program. The following table assesses the pros and cons of continuing the three types of samples currently being collected and addresses the option of initiating sampling of intertidal sediments, an option that has been suggested.

	Sample Type	Advantages	Disadvantages	
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The depositional sodiment regime	The hydrocarbons measured are			
1 0	almost exclusively background			
	• •			
0	from seeps or coal transported into the Sound. There is little			
nyurocarbons.				
	correlation between deep and			
	shallow sediment hydrocarbons.			
	Thus, it is unlikely that a surface			
	spill will be detected in significant			
	amounts in deep sediments.			
•	Subtidal sediments don't acquire			
	the dissolved water-soluble			
in shallow sediments.	fractions from oil as mussels do.			
	Relative to sampling the shallow			
	sediments, the risk of sampling			
	failure due to inclement weather,			
	equipment malfunction, sample			
	handling, or station keeping is			
	higher.			
Hydrocarbons from intertidal spills	Shallow sediments are exposed to a			
are transported relatively rapidly	higher energy regime relative to			
to the shallow subtidal sediments.	deeper sediments. Thus, the			
	coarser sediment matrix rapidly			
	loses its hydrocarbon loads either			
	through dispersion or weathering.			
Diver sampling is tedious and at	Subtidal sediments don't acquire			
risk to being weathered out but	the dissolved water-soluble			
less liable to failure than deep	fractions from oil as mussels do.			
sediment grab sampling.				
	There is little apparent correlation			
	between shallow subtidal sediment			
	hydrocarbons and mussel tissue			
	loads and, presumably, intertidal			
	sediments.			
	to the shallow subtidal sediments. Diver sampling is tedious and at risk to being weathered out but less liable to failure than deep			

Sample Type	Advantages	Disadvantages
Intertidal	Intertidal sediments receive the	Hydrocarbons are patchily
sediments	bulk of deposited hydrocarbons	distributed both horizontally and
	following an oil spill.	vertically within the sediments and
	All forms of hydrocarbons (e.g.,	along the intertidal slope. This is a
	gross contamination by fresh crude	function of beach exposure,
	containing water-soluble fractions	sediment type, and the chance
	and heavier constituents) may be	involved in grounding of wave-
	represented in intertidal sediments.	deposited hydrocarbons. It is
		difficult to select a single sampling
	Identification of sampling stations	location that is representative of a
	is straightforward, and accurate	contaminated beach.
	resampling is facilitated by the use	
	of landmarks, flagged markers	
	(rebar), or other prominent	
	geographical features.	
	Mussel tis sue loads correlate better	
	with intertidal than subtidal	
	sediments.	
	The risk of sampling failure is	
	much lower than for subtidal	
	sediments.	
Mussel	Mussels are very sensitive	Depuration and metabolism create
tissues	indicators of contamination by	a limited temporal window for
	both water-soluble fractions and	detection of low-level events.
	discrete oil droplets (very fine	
	particulate hydrocarbons).	
	The risk of sampling failure is	Body loads vary with body size.
	much lower than for subtidal	Sampling consistency is
	sediments.	paramount.

Field Sampling, Statistical Methods and Analytical Techniques

We have several specific technical recommendations regarding field, statistical and laboratory procedures. Refer to section 6 of the full report for details.

Seasons

Based on the mussel and sediment data analyses, it is conceivable that the seasonal samples could be reduced to one season. PAH concentrations appear to be higher for mussel samples in winter so this should improve the detection limit issues. Moreover, spikes were more common in winter samples. However, variability is marginally lower in summer and the risk and cost associated with sampling is definitely lower in summer. If cost reductions are obtained by eliminating an entire sampling season, it may be possible to add other sampling sites for more complete coverage of the Sound.

Sampling Locations

If RCAC were able to cut back on seasonal samplings, we would recommend adding additional sites to expand the area of coverage and monitor hydrocarbon exposure from background sources and human activities.

- Based on other recent studies, the deep stations are continuously exposed to background hydrocarbons transported either from oil seeps or coal deposits outside of PWS. We saw very little evidence of significant quantities of ANS/EVOS residues in any at the deep stations. EVOS oil apparently becomes widely dispersed or highly weathered once it leaves the shallow depths. If sampling at deep stations is continued, we recommend that a new sampling site be established in Hinchinbrook Entrance, either in Constantine Harbor, the entrance to Port Etches, or Zaikof Bay, to provide insight into the signatures, concentrations, and flux of the background hydrocarbons entering Prince William Sound. Alternatively, even if deep sediment sampling is dropped, we would recommend at least sampling sediments and potential hydrocarbon sources (Katalla crude and coal) from outside the Sound that could be used to tightly identify the deep sediment background signature.
- We recommend that the station network be expanded to other regions of the Sound, e.g., the eastern, north central, and northwestern Sound. In the event that another catastrophic spill like EVOS causes exposure to ANS crude in other regions in the Sound beyond the monitoring area, little information regarding current hydrocarbon loading in sediments or mussel tissues exists.
- All hydrocarbon studies conducted in the Sound find miscellaneous residues of petroleum hydrocarbons, typically from diesel fuels, bunker fuel, and combustion products. In 1991, NOAA contractors observed substantially higher concentrations of PAHs in mussel tissue from the vicinity of the cannery in Seward than from sites in Prince William Sound that previously had been grossly contaminated by EVOS. In 1995, other NOAA contractors reported that the highest PAH levels from their limited sampling of mussels were found in the harbor at Whittier. It seems obvious to expect inputs from the currently unmonitored human activities near towns and villages, marinas, hatcheries, ferry docks, airports, and logging operations throughout the Sound. A few screening samples from areas near human activities would help assess the needs for additional sites and provide helpful insights.