RECOVERY OF MANGROVE HABITATS AT THE *VESTA BELLA* SPILL SITE

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National Oceanic and Atmospheric Administration
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THE *VESTA BELLA* SITE REVISITED:
CHEMISTRY AND MANGROVE OBSERVATIONS

INTRODUCTION

On March 6, 1991, the barge *Vesta Bella* sank about 30 miles southeast of Barbuda, Trinidad (Figure 1). The barge contained 560,000 gallons of a high aromatic #6 fuel oil that had been loaded at a refinery on St. Eustatius, Dutch Virgin Islands. U. S. Coast Guard overflights reported oil bubbling up from the barge and a slick containing sheen with some brown oil extending 15 by 5 nautical miles. The barge continued to leak oil for more than 20 days, feeding the slick. The actual amount of oil lost in the spill was never fully determined.

The oil slick moved about 170 miles west-northwest and contaminated the shoreline of St. John Island and, ultimately, Puerto Rico. On St. John, shoreline contamination was restricted to the north side of the island, with most of the oil accumulating in Haulover Bay and Newfound Bay on the island's eastern end (Figure 2). No oil confirmed as being from the *Vesta Bella* was reported on the south side of St. John or on any of the other U.S. Virgin Islands.

On March 23, National Oceanic and Atmospheric Administration personnel reported to St. John at the request of the Federal On-Scene Coordinator to help establish beach survey procedures and cleanup methods. Cleanup of the beaches and mangroves on St. John began March 27. Cleanup consisted of removing oiled debris, manually tilling and moving the oiled sediments into the low intertidal zone, and recovering the oil with oil snares. Mangrove roots were cleaned using oil snares to scrub the roots and as a passive cleanup tool (Figure 3). The snares were placed in the root system of the red mangroves and allowed to wash up and down the roots through a combination of wave and tidal action. The snares were removed after 24 hours. This procedure was used for both the red and white mangroves that had been oiled, but was effective only along the outer fringe on exposed sections where wave energy was sufficient to actively work the snares against the roots.

On April 4, 1992, one year after the *Vesta Bella* oil spill, St. John Island was revisited to assess the extent of residual hydrocarbon contamination and to observe the condition of mangroves in Newfound and Haulover bays that had been oiled and subsequently cleaned by wiping the roots of the trees with oil snares. The objective of the site revisit was twofold: to identify and characterize trends in oil weathering and to determine if wiping was an effective cleanup method that increased the long-term survival of the mangrove plants.

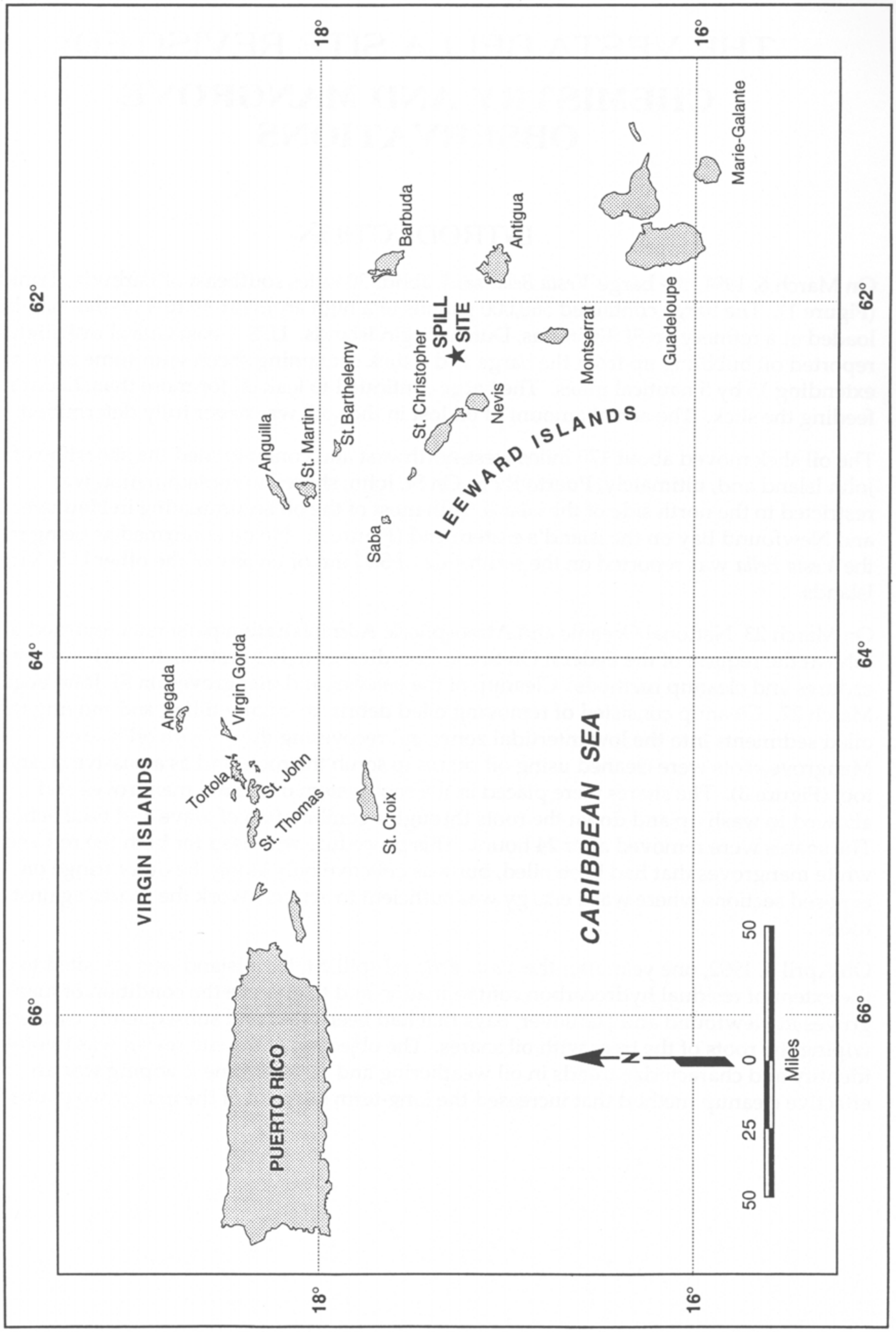


Figure 1. Location where the *Vesta Bella* sank, in relation to the Virgin Islands and Puerto Rico.

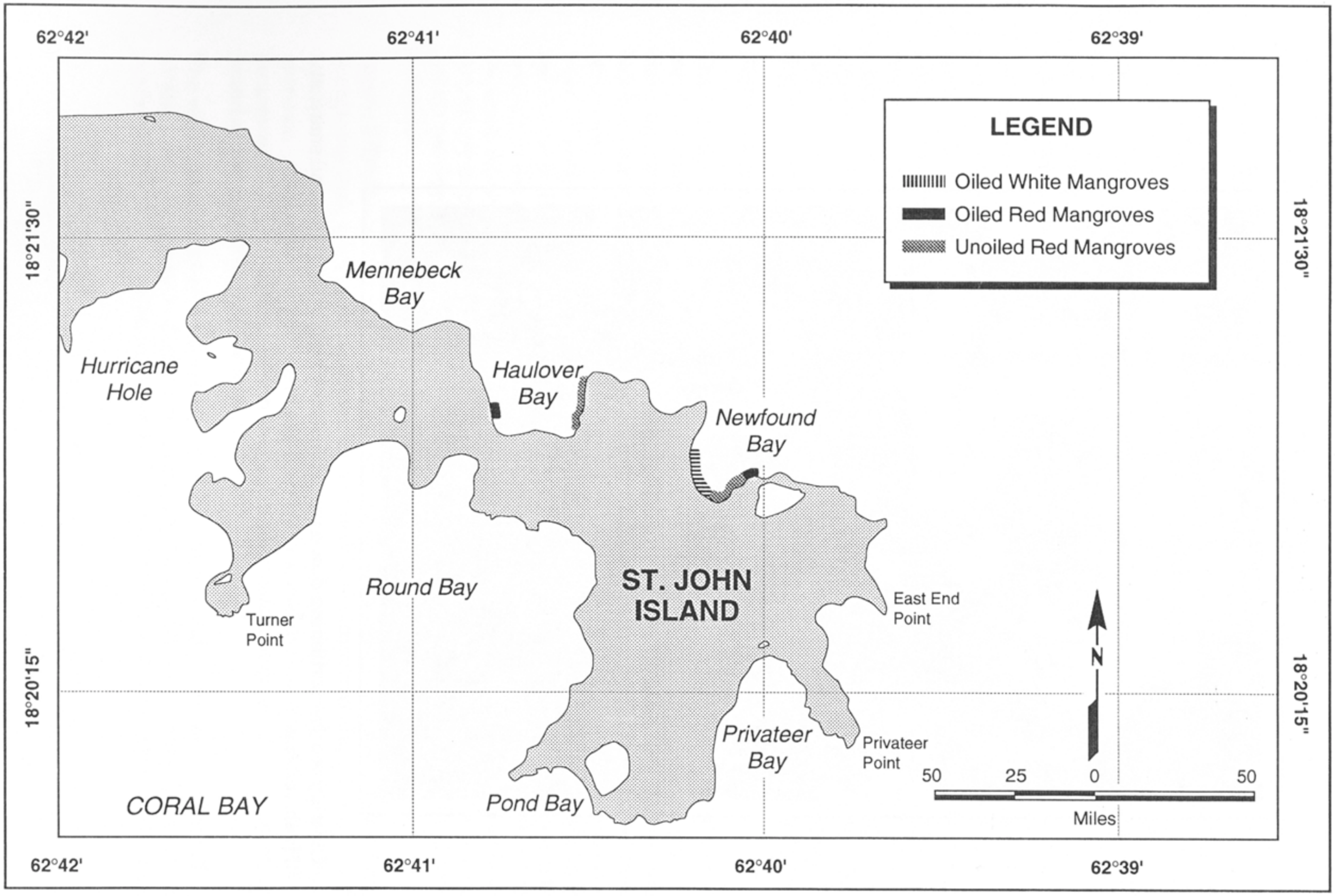


Figure 2. The areas of mangroves in Haulover and Newfound Bays where the oil came ashore on St. John Island.

Figure 3. Cleanup worker scrubbing down red mangrove prop roots with an oil snare at Haulover Bay.

CHEMICAL OBSERVATIONS

BACKGROUND

The intent of the field collections and laboratory analyses for chemistry was to characterize changes in the oil that had taken place after one year in a sand beach/fringing mangrove habitat. Discrete samples of oil were collected to provide trend information on oil weathering (evaporation and biodegradation) as determined by detailed gas chromatography/mass spectrometry (GC/MS) analysis. In addition, collected oil samples were source fingerprinted to confirm that they originated with the *Vesta Bella* barge or were derived from some other source, such as bilge pumping.

Mass spectrometry has long been used by many researchers to study oil weathering processes such as evaporative loss, photolytic and biological degradation, and fate of oil spilled into the environment (e.g., Overton et al. 1980, 1981; Kennicutt 1988; Henry 1990; Michel et al. 1991). The method used for this investigation allowed for simultaneous source-fingerprinting and quantitative analysis of target analytes. Specifically, polynuclear aromatic hydrocarbons (PAHs), sulfur heterocyclic compounds, and related alkylated substituted homologues were monitored for quantitative analysis, while the decalins, steranes, hopanes, and alkanes were used to describe weathering trends and source fingerprinting. Table 1 details the target analytes and their respective quantitative ions.

FIELD SAMPLING

The chemical sampling plan concentrated on sampling visible oil residues within different microenvironments along the beach. In addition to the visibly oiled samples, apparently clean sand and shell fragments were collected to provide information on residual impacts to beach substrate from which the mangroves were growing. Numerous tar balls littered the study area, and a few (11 of hundreds observed) were collected for source fingerprinting. In total, 23 samples were collected and analyzed with reference oils from the *Vesta Bella* and a spill at the St. Eustatius Refinery that occurred in March 1992. Of particular interest in the analysis of the reference oils was whether the GC/MS method could differentiate between the same refined product produced on two different dates at the St. Eustatius Refinery that potentially impacted the same area. The ability to clearly discern between the two oils would provide further validation of the use of GC/MS as a primary source-fingerprinting technique.

Figure 2 illustrates the location of study sites on St. John Island. All three major species of mangroves (red, white, and black) were identified in the impacted area. Newfound Bay is a small embayment located on the northeast end of St. John with coral reefs bordering the entrance. A small stand of white mangroves was located in the intertidal zone of the innermost portion of the bay, which was unusual: white mangroves are not commonly found as the outer fringe in the intertidal zone.

The white mangroves showed very little visible surface oiling. However, removal of recently deposited sand and debris revealed weathered oil trapped between roots. A composite sample was collected from several locations of this kind and designated sample SJ-1.

Numerous tar balls varying in size from 1 to 15 centimeters (cm) were found along the beach at Newfound Bay. The source of these tarballs was unclear; the St. Eustatius Refinery spill on March 30, 1992, represented a potential candidate as did the *Vesta Bella*. Eleven individual tar balls (SJ-13 through SJ-23) were collected within a 2-meter radius at a single location on the beach near the grove of white mangroves.

Table 1. Target compounds.

Compound	Quantitative ion
alkanes (nC-10 through nC-31	85
decalin*	138
C-1 decalin	152
C-2 decalin	166
C-3 decalin	180
naphthalene	128
C-1 naphthalenes	142
C-2 naphthalenes	156
C-3 naphthalenes	170
C-4 naphthalenes	184
fluorene	166
C-1 fluorenes	180
C-2 fluorenes	194
C-3 fluorenes	208
dibenzothiophene	184
C-1 dibenzothiophene	198
C-2 dibenzothiophene	212
C-3 dibenzothiophene	226
phenanthrene	178
C-1 phenanthrene	192
C-2 phenanthrene	206
C-3 phenanthrene	220
naphthobenzothiophene	234
C-1 naphthobenzothiophene	248
C-2 naphthobenzothiophene	262
C-3 naphthobenzothiophene	276
fluoranthrene/pyrene	202
C-1 pyrenes	216
C-2 pyrenes	230
chrysene	228
C-1 chrysenes	242
C-2 chrysenes	256
hopanes (191 family)*	191
sterenes (217 family)*	217
benzo(b)fluoranthene	252
benzo(k)fluoranthene	252
benzo(c)pyrene	252
benzo(e)pyrene	252
benzo(a)pyrene	252
perylene	252
indeno(g,h,i)pyrene	276
dibenzo(a,h)anthracene	278
benzo(1,2,3-cd)perylene	276

* Used primarily for source-fingerprinting and generally not quantified.

Red mangroves in Newfound Bay showed visible evidence of oil remaining on prop roots. Oil samples were scraped from several red mangrove roots along the east side of the bay, and the composited sample was designated SJ-6.

Near the eastern edge of Newfound Bay, a small beach area exposed to higher energy wave conditions (as evidenced by the abundance of smooth cobbles) was designated as Outside Bay. At several locations along Outside Bay, samples of the beach substrate were collected by removing large surface cobbles and sampling the finer beach material trapped between and below. These areas contained some visible oil that appeared to be heavily weathered, and a composite sample (SJ-2) was collected. Small asphalt pavements were also discovered and sampled (SJ-3 and SJ-4). Oil "splatter" and stain were found on many of the beach cobbles. While samples of oil splatter were scraped off the substrate for analysis (SJ-5), no samples of oil stain were collected.

In Haulover Bay, located just west of Newfound Bay, infrequent patches of tar were found and sampled (SJ-7) along the beach, just above the high-tide mark. Thick oil splatter was found on several cobbles and a small amount was collected (SJ-8). The red mangroves within this area appeared to be more heavily oiled than those in Newfound Bay. Many of the prop roots were heavily oiled and had become soft and rotten. Some of the prop roots had rotted completely through and were no longer attached to the remainder of the mangrove plant. A sample of the oil on the red mangroves was collected as SJ-9. Small asphalt pavements were found at the base of many red mangrove prop roots and were sampled (SJ-10); a few were relatively substantial and one was sampled separately (SJ-11). Most of the beach substrate appeared to be clean, recently deposited sand and shell fragments. Samples of this apparently clean substrate were collected between prop roots and were composited as a single sample (SJ-12). Core samples were not collected; thus, subsurface penetration of the oil was not assessed.

In addition to the samples described above, three samples collected at Northeast Stevens Cay by the National Park Service were analyzed.

RESULTS AND DISCUSSION

Source-fingerprinting

Of the 12 samples collected as part of the one-year post-spill assessment on St. John, only 7 were a positive match to the original spill. The five non-match samples were each from different sources, and two of the samples matched sources also identified in the small number of tarballs analyzed. The 26 samples analyzed represented at least eight and possibly nine different spill sources. The composite samples collected from the white mangrove roots and the red mangrove prop root scrapings, SJ-1 and SJ-6, respectively, may represent a mixture of source oils and suggest effects from more than one spill. Given the abundance of tar balls observed on the beaches of Newfound Bay that were not sourced to the *Vesta Bella* spill, this seems a likely possibility. None of the samples analyzed, including those from Northeast Stevens Cay, were a positive match to oil from the recent St. Eustatius Refinery spill.

Table 2 provides a list of the collected samples as well as a description, match/nonmatch determination.

Table 2. List of collected samples.

Sample ID	LSU ID	Sample Description	M/NM*
SJ-1	N2129-01	oiled sediment between white mangrove roots	NM (A) †
SJ-2	N2129-02	oiled beach substrate	M
SJ-3	N2129-03	Outside Bay, asphalt pavement	M
SJ-4	N2129-04	Outside Bay, asphalt pavement	M
SJ-5	N2129-05	Outside Bay, oil splatter	NM (B)
SJ-6	N2129-06	root scrapings, red mangroves	NM (C)
SJ-7	N2129-07	tar, above high-tide mark	NM (D)
SJ-8	N2127-08	oil/tar on cobbles	NM (E)
SJ-9	N2127-09	root scrapings, red mangroves	M
SJ-10	N2127-10	asphalt pavement at base of prop roots	M
SJ-11	N2127-11	asphalt pavement, upper intertidal	M
SJ-12	N2127-12	“clean” sediment at base of red mangroves	M
SJ-13	N2127-13	tarball	NM (D)
SJ-14	N2127-14	tarball	NM (B)
SJ-15	N2127-15	tarball	NM (F)
SJ-16	N2127-16	tarball	NM (D)
SJ-17	N2127-17	tarball	NM (G)
SJ-18	N2127-18	tarball	NM (D)
SJ-19	N2127-19	tarball	NM (D)
SJ-20	N2127-20	tarball	NM (H)
SJ-21	N2127-21	tarball	NM (I)
SJ-22	N2127-22	tarball	NM (D)
SJ-23	N2127-23	tarball	NM (D)
NESCAY	N2127-24	tarball	NM (D)
NESCAY	N2127-25	tarball	NM (D)
NESCAY	N2127-26	tarball	NM (D)

*M/NM stands for Match/Nonmatch to *Vesta Bella* oil.

†The letter in parenthesis denotes different sources that are matches. Note sources A and C may represent not one, but a mixture of oils derived from several sources.

Figure 4 shows a cluster plot highlighting samples that were a positive match to the *Vesta Bella* spill. The scatter in values calculated from the positive-matched *Vesta Bella* stranded oil samples (i.e., the circled sample), is attributable to changes in the oil's composition due to weathering. The tar balls SJ-13, -19, -22, -24, and -25, are clustered very tightly; each is from the same source (unknown source D). All were relatively fresh tar balls derived from what appeared to be a tank sludge wash discharge. However, as spilled oil becomes highly degraded, the analytical ability to positively match it to its original source also declines.

In the standard source-fingerprinting method employed by LSU, many constituents of petroleum that are very slow to change as a result of weathering processes are targeted. One such group of compounds is the triterpanes and hopanes. Figure 5 shows a chromatographic comparison of the triterpanes and hopanes as monitored by ion m/e 191 for the undegraded *Vesta Bella* cargo oil and a heavily weathered tarmat sample, SJ-4. The compounds shown in Figure 5 have very low vapor pressures and very low water solubilities (i.e., they are not expected to evaporate or be lost from the bulk oil by dissolution, nor will they easily biodegrade). Because of their persistence, the hopanes are considered to be good source-fingerprinting compounds. In addition, they are also receiving a great deal of attention as potential oil-specific, integral "internal" standards (Peters, and Molfoesn 1991; Butler 1991; Prince et al. 1991).

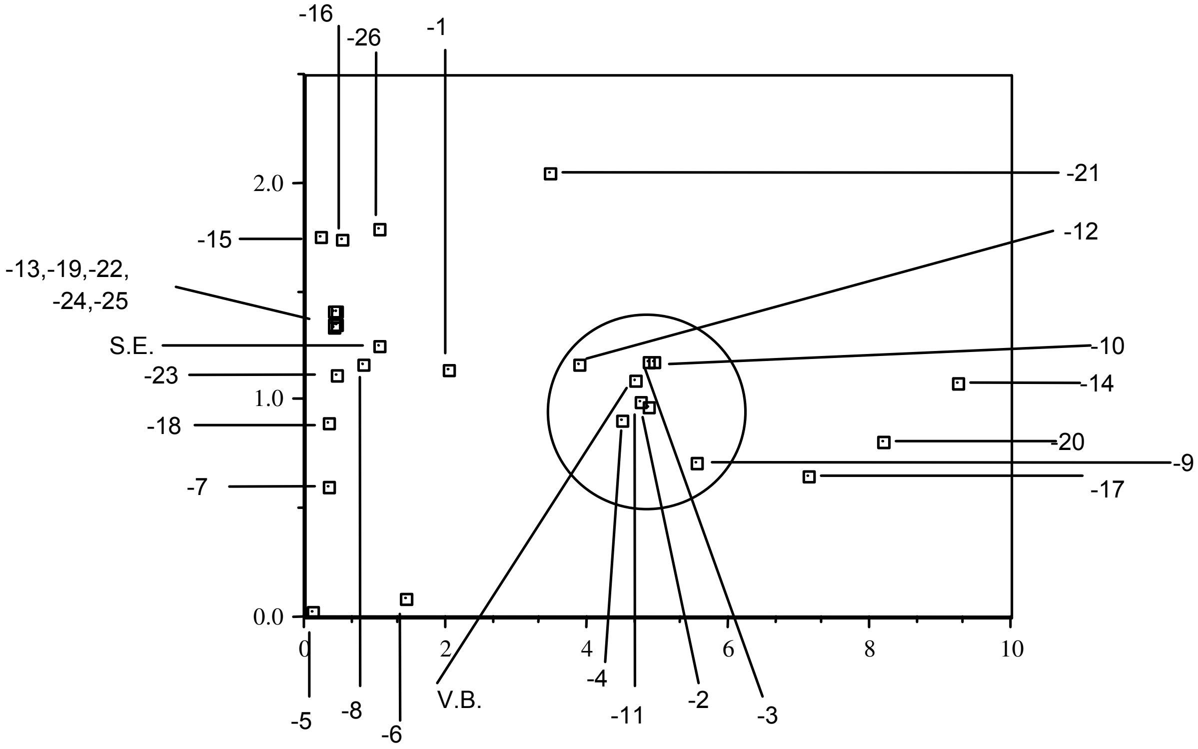


Figure 4. The cluster plot above is a ratio of two indexes, C-2 pyrenes/C-2 chrysene (x axis) vs. C-3 phenanthrenes/C-3 dibenzothiophenes (y-axis). The circled loci represent the samples that were positively identified as being sourced from the M/B Vista Bella. V.B. represents the M/B *Vesta Bella* reference oil and S.E. the St. Eustatius Refinery reference oil. The hyphened values are representative of their sample ID, e.g., -1 is SJ-1).

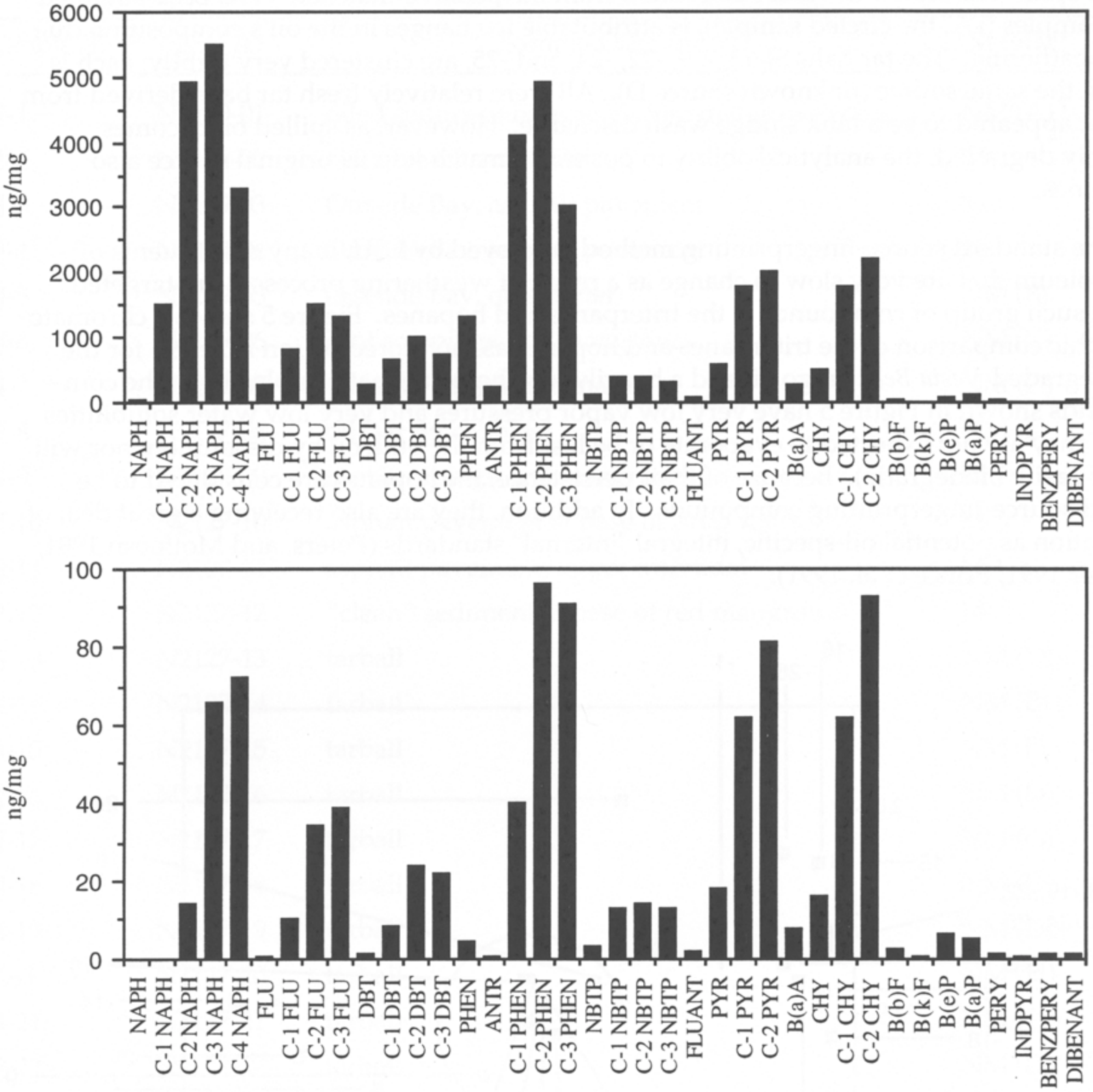


Figure 5. Histogram comparison of the unweathered M/B *Vesta Bella* cargo oil (top) to oil extracted from a tar mat in Outside Bay (SJ-3). This oil is the least weathered of the M/B *Vesta Bella* samples.

Quantitative Results

Quantitative GC/MS analysis of the *Vesta Bella* reference oil indicated that the PAHs targeted for analysis account for only 4.6 percent of the spilled oil by weight. These compounds, while constituting only a minor fraction of the bulk oil composition, include the constituents generally associated with chronic toxicity of weathered crude and bunker oils. The samples of residual oil identified as being a positive match to the *Vesta Bella* spill ranged in concentration of TPAH from less than 1 nanogram per milligram (ng/mg) or parts per million, for the "clean" beach substrate to a high of 950 ng/mg for one of the asphalt pavements sampled at Outside Bay.

Weathering

Weathering is a term that encompasses the physical and chemical changes that spilled oil undergoes as a result of its interaction with the environment. Factors affecting the fate and transport of spilled oil include evaporation, dissolution, emulsification, adsorption, and photochemical and microbial degradation. The ultimate fate of petroleum spilled in the marine environment is degradation by a chemical process: primarily biological- and photolytic-degradation. The rate at which these processes occur is controlled by many factors, including the physical and chemical composition of the oil, physical processes the oil is exposed to, abiotic environmental factors, and the presence or absence of hydrocarbon degrading microorganisms (bacteria, molds, fungus, and yeast). Emulsification or mousse formation slows biodegradation because the stable "water-in-oil emulsion" formed has a smaller surface area of exposed oil compared to, for example, very thin sheens. The spilled oil from the *Vesta Bella* was a #6 fuel oil. The chemical composition of this oil was initially similar to a weathered crude oil in that the lighter fractions (compounds lighter than nC-12) that would be lost in the initial evaporation and dissolution phase were not present.

Most chemical actions affecting whole oil occur at the interface between either the oil/water or oil/atmosphere. Biodegradation and photolytic degradation are surface active processes; therefore, we generally expect oil that has been spread thin or broken up into small droplets or fragments (examples include samples SJ-2 and SJ-6) to weather at faster rates than thick residue, such as that found in asphalt pavements (SJ-3, SJ-4, SJ-10, and SJ-11).

Temperature and nutrient availability are factors that affect microbial activity. Temperature is probably less of a limiting factor in the tropics due to the consistently moderate temperatures that encourage microbial activity as well as enhance evaporative processes. The microbes utilize the oil as a carbon source in much the same way that humans metabolize food: that is, oil is converted into energy, biomass, CO_2 and H_2O. Often, the limiting factor for further microbial degradation of stranded oil is the availability of the oil to a microbial population. Physical processes such as high-energy storms increase the dispersion of oil (i.e., greater oil surface exposure) and generally reduce the persistence of oil spilled in the environment. Continued degradation will be slow unless the stabilized oil formations (i.e., thick tar on prop roots and asphalt pavements) are broken up, exposing the oil for additional chemical processes to occur.

The quantitative results for two of the samples analyzed are shown as histogram plots that highlight changes in oil composition due to weathering (see Figures 6 through 9. For samples derived from the same source, differences in the histogram plots reflect changes in oil composition resulting from weathering processes. For non-match samples, the histogram plots highlight compositional differences.

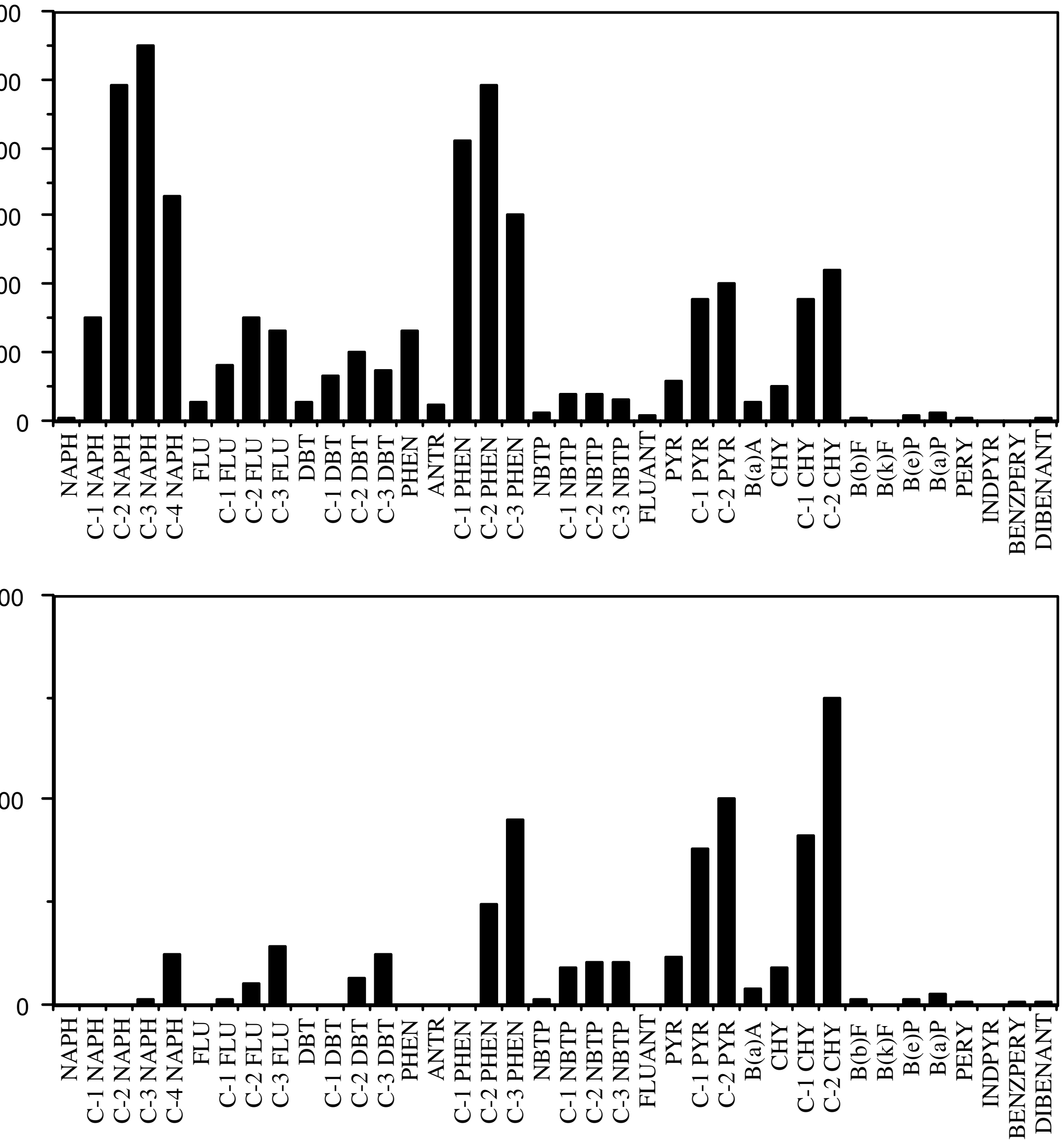


Figure 6. Histogram comparison of the *Vesta Bella* cargo oil (top) to oil extracted from a composite sample of sediments collected between the partially exposed white mangrove roots (bottom; sample SJ-1). This composite sample is suspected of containing oil from another source in addition to that from the *Vesta Bella*.

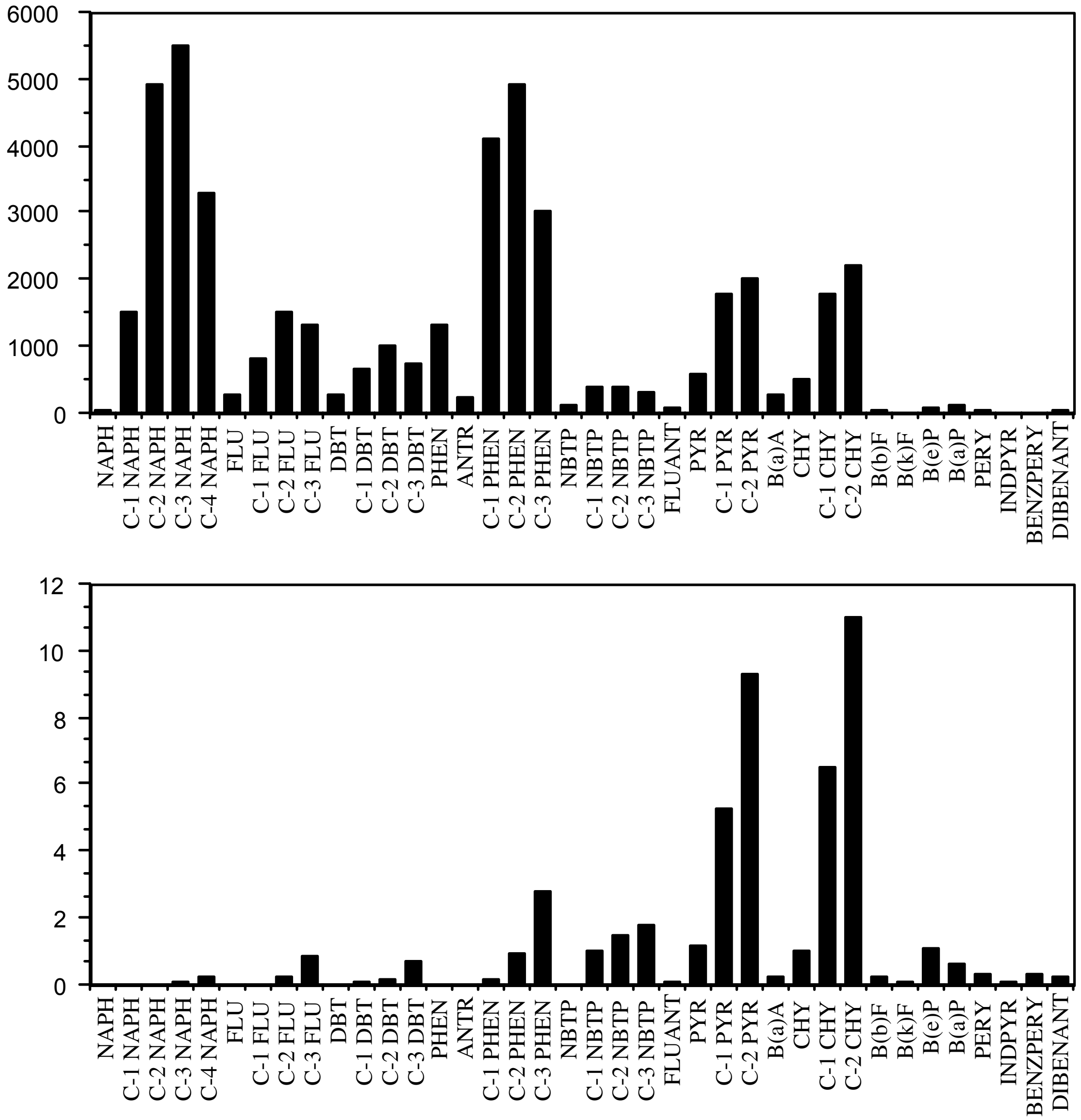


Figure 7. Histogram comparison of the unweathered *Vesta Bella* cargo oil (top) to oil extracted from slightly oiled beach substrate (SJ-2). The changes in the PAH distribution are the result of weathering.

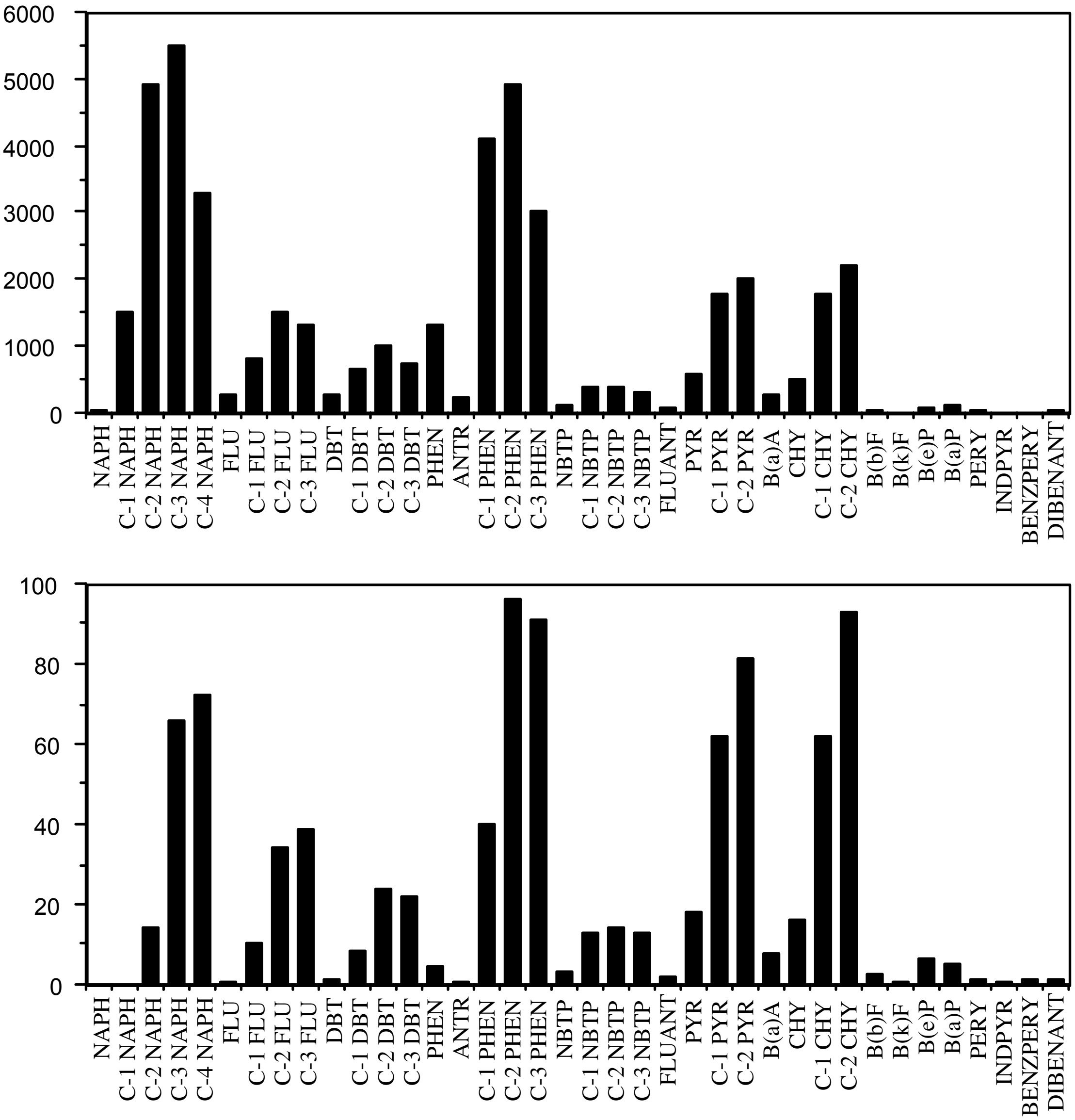
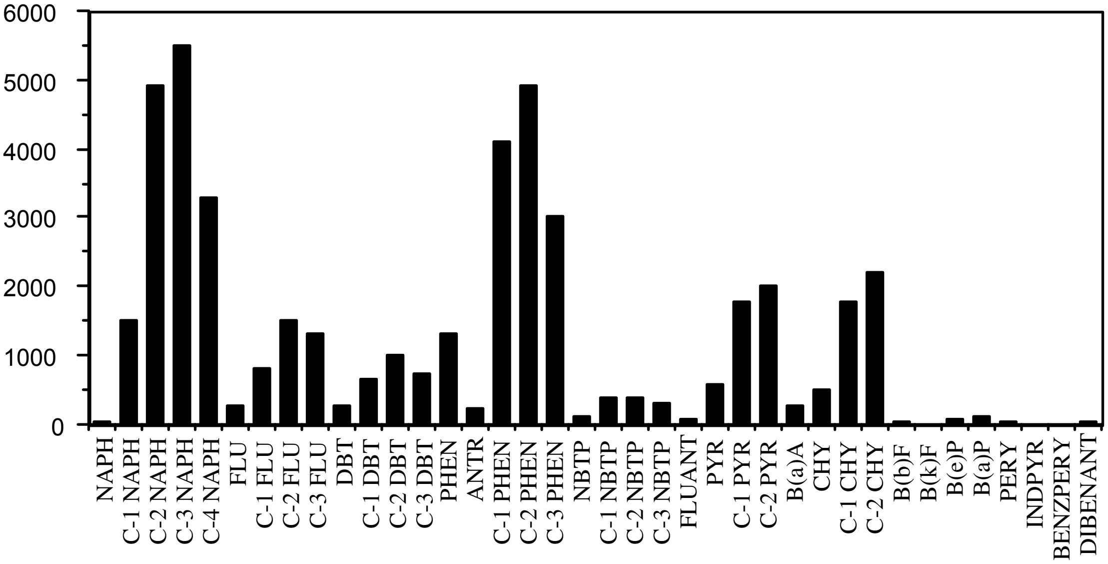


Figure 8. Histogram comparison of unweathered *Vesta Bella* cargo oil (top) to oil extracted from an asphalt pavement in Outside Bay (SJ-3). This oil is the least weathered of the *Vesta Bella* samples.



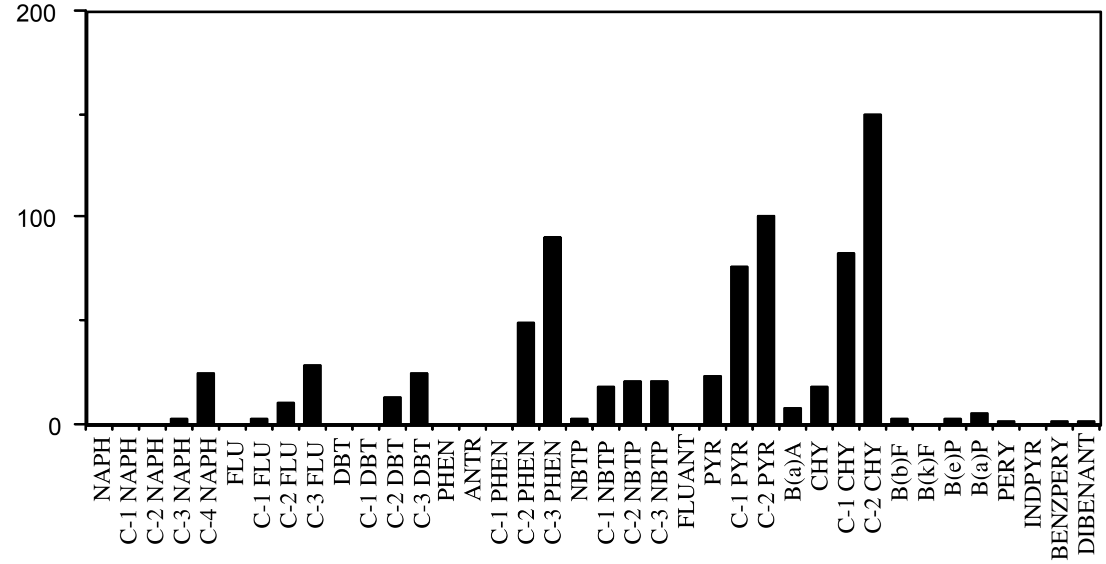


Figure 9. Histogram comparison of unweathered*Vesta Bella* cargo oil (top) to oil extracted from a tarmat in Outside Bay (SJ-5).

Overall, the samples analyzed, which were sourced from the *Vesta Bella*, showed a significant degree of weathering due to evaporative loss and microbial degradation. The composition of the spilled cargo oil was highly enriched with aromatic hydrocarbons; the normal alkanes were a minor compositional element for this fuel oil (this is typical of many residual fuel oils). Only two of the samples showed any evidence of a normal paraffinic hydrocarbon profile and both exhibited evidence of microbial degradation. Changes in the histogram plots reflect a change in the oil composition, and for the samples analyzed in the study, can be generally summarized as follows:

- ❐ General shift from the dominance of the 2- and 3-ring aromatic hydrocarbons (naphthalenes and phenanthrenes) to the larger, 4-ring-plus compounds (pyrenes and chrysenes).
- ❐ A shift in the normal homologue distribution pattern as demonstrated by the apparent enrichment of the higher alkylated compounds (C-2 and C-3) and a reduction in the parent and C-1 compounds. The higher molecular weight aromatic hydrocarbons such as the chrysenes are less affected than the lower molecular weight hydrocarbons such as the naphthalenes.
- ❐ The naphthobenzothiophenes appear very resistant to degradation.

If the quantitative data for the unweathered cargo oil and a weathered sample are processed so that the quantitative values are normalized relative to 17 α (H), 21 β (H) hopane, and then these normalized values are portrayed as a histogram plot, it can be shown that the stranded oil has changed in direct relation to the unweathered cargo oil. Table 3 shows the relative percent change in the target compounds detected in the tarmat sample SJ-4 compared to the unweathered *Vesta Bella* oil. Essentially 100 percent of many of the target compounds are lost from the residual oil. Many of the more persistent aromatic hydrocarbons, such as the C-2 chrysenes, were only slightly affected by the weathering process (only a 4.5 percent change was detected in the sample shown). Overall, the loss of target analytes was 76.3 percent, relative to the spilled oil (Figure 9).

Table 3. Hopane normalization of sample NFB04.

MS File	HP2147C ref. oil	HP1249J N2129-04	ref. oil	N2129-04	Percent Loss
EDL*	2.00	0.20			
GC/MS target analyte	ng/mg	ng/mg**	NORM****	NORM****	
Naphthalene	24.00	0.00	0.11	0.00	100.0
C-1 Naphthalene	1500.00	0.00	7.14	0.00	100.0
C-2 Naphthalene	4900.00	0.00	23.33	0.00	100.0
C-3 Naphthalene	5500.00	3.00	26.19	0.20	99.2
C-4 Naphthalene	3300.00	24.00	15.71	1.60	89.8
Fluorene	260.00	0.00	1.24	0.00	100.0
C-1 Fluorene	830.00	2.60	3.95	0.17	95.6
C-2 Fluorene	1500.00	10.00	7.14	0.67	90.7
C-3 Fluorene	1300.00	29.00	6.19	1.93	68.8
Dibenzothiophene	260.00	0.00	1.24	0.00	100.0
C-1 Dibenzothiophene	660.00	0.00	3.14	0.00	100.0
C-2 Dibenzothiophene	1000.00	13.00	4.76	0.87	81.8
C-3 Dibenzothiophene	720.00	24.00	3.43	1.60	53.3
Phenanthrene	1300.00	0.00	6.19	0.00	100.0
Anthracene	230.00	0.00	1.10	0.00	100.0
C-1 Phenanthrene	4100.00	0.00	19.52	0.00	100.0
C-2 Phenanthrene	4900.00	49.00	23.33	3.27	86.0
C-3 Phenanthrene	3000.00	90.00	14.29	6.00	58.0
Naphthobenzothiophenes	110.00	3.00	0.52	0.20	61.8
C-1 Naphthobenzothiophenes	400.00	18.00	1.90	1.20	37.0
C-2 Naphthobenzothiophenes	380.00	21.00	1.81	1.40	22.6
C-3 Naphthobenzothiophenes	320.00	20.00	1.52	1.33	12.5
Fluoranthene	86.00	0.00	0.41	0.00	100.0
Pyrene	570.00	23.00	2.71	1.53	43.5
C-1 Pyrene	1800.00	76.00	8.57	5.07	40.9
C-2 Pyrene	2000.00	100.00	9.52	6.67	30.0
Benzo(a)anthracene	290.00	7.10	1.38	0.47	65.7
Chrysene	510.00	18.00	2.43	1.20	50.6
C-1 Chrysene	1800.00	83.00	8.57	5.53	35.4
C-2 Chrysene	2200.00	150.00	10.48	10.00	4.5
Benxo(b)fluorant	57.00	3.10	0.27	0.21	23.9
Benzo(k)fluorant	17.00	0.63	0.08	0.04	48.1
Benzo(e)pyrene	94.00	3.00	0.45	0.20	55.3
Benzo(a)pyrene	110.00	5.00	0.52	0.33	36.4
Perylene	31.00	0.83	0.15	0.06	62.5
Indeno(1,2,3-cd)Pyrene	4.50	0.22	0.02	0.01	31.6
Benzo(g,h,i)perylene	0.00	0.00	0.00	0.00	0.00
Benzo(g,h,i)perylene	17.00	0.78	0.08	0.05	35.8
Dibenzo(a,h)anthracene	30.00	1.80	0.14	0.12	16.0
Hopane***	210.00	15.00			
Total PAH	46,000.00	780.00	219.05	52.00	76.3

* estimated detection limit (EDL)

** ng/mg wet weight. Values valid to two significant figures only.

*** semiquantitative only

**** Relative concentration to hopane

CHEMISTRY CONCLUSIONS

The field observations at Newfound Bay and Haulover Bay, St. John Island, confirmed that remnants of stranded oil in the form of tar on mangrove prop roots and small asphalt pavements were easily found. However, chemical analyses of residual oil samples collected at the sites revealed evidence of oiling from additional sources in addition to impacts from the *Vesta Bella*. The morphology of the tar balls and the detailed chemical data suggested that most of the stranded oil was residual fuel oils. Excluding the *Vesta Bella,* as many as nine different sources were differentiated from a small number of samples. Based on this, it is our hypotheses that most of these tar balls (identified as unknown sources A, B, C, E, F, G, H, and I) were from small, unrelated transportation spillages. Also, a significant number of tar balls were related and matched to unknown source D, which may represent a "mystery spill" of tens to as much as thousands of gallons of oil. From this limited survey, it is impossible to provide a better estimate. However, the use of source-fingerprinting to investigate chronic shoreline oiling is of utility in the identification and future management of marine oil pollution studies.

All samples identified as being sourced from the *Vesta Bella* were moderately to heavily degraded. The persistent compounds remaining in the residual oil include the higher molecular weight, higher alkylated aromatic hydrocarbons such as the C-1 and C-2 chrysenes and the alklyated naphthobenzothiophenes. The asphaltene fraction represented a major portion of the residual oil; this fraction was not quantified. The asphaltenes are very persistent and tend to stabilize the oil in clumps that impede the normal weathering processes.

The aquatic and human health toxicity of the weathered *Vesta Bella* #6 fuel oil would be extremely difficult to assess, even if the toxicity of each component was known. This difficulty arises from the additive, synergistic, and/or antagonistic effects of various components of these mixtures. In addition, the toxicity of these mixtures can vary with composition because different chemical components have varying effects on different organs as well as different organisms. The differences in toxic effects are due not only to qualitative compositional differences but also the concentration differences of various chemical constituents as a result of weathering (oil degradation).

The diaromatic compounds such as naphthalenes in the unweathered *Vesta Bella* oil are generally considered acutely toxic. Weathered oil samples analyzed in this study showed relatively low levels of naphthalenes still present; therefore, the residual oil was considered to be significantly less acutely toxic than oil mixtures with higher naphthalene composition. However, they remained "toxic" in that the high molecular weight PAHs, many of which have been identified as being mutagenic (including at least one that is a known human carcinogen, benzo(a)pyrene), were still present and may actually have been comparatively enriched in the bulk oil remaining due to the loss of the lighter compounds. Nevertheless, for a toxic response to occur, there must be a route of exposure. The residual, weathered oil was composed of relatively water-insoluble compounds; therefore, the most likely route of exposure to biota, if any, would have been through ingestion of oil.

It is likely that the removal of much of the thick, stranded oil by manual cleanup facilitated higher rates of natural degradation. Microbial degradation can occur only on exposed oil surfaces where microbes are not excluded from water, oxygen, and nutrients. Physical breakdown of the oil into small fragments enhances the rate at which spilled oil is broken down and assimilated into the environment as a source of energy and biomass.

MANGROVE OBSERVATIONS

BACKGROUND

The type of oil plays a major role in determining the impacts from a spill on mangroves. Light fuel spills often result in tree mortality, with indications of stress obvious within several weeks. For example, a jet fuel spill in Puerto Rico killed six hectares of mangroves, with yellowing of the leaves obvious within 10 days (Research Planning Institute 1987). Mortality results from uptake of the light aromatic fractions. In contrast, heavy oils coat and smother and then interfere with respiration through the lenticels. Oiled mangroves may exhibit one or more of the following symptoms:

- ☐ Yellowing of leaves (chlorosis)
- ☐ Partial to complete defoliation
- ☐ Leaf deformities
- ☐ Reduced leaf size and flower production
- ☐ Increased insect infestation
- ☐ Death of the individual plant

There have been no studies quantifying the amount of oil on the prop roots or pneumatophores (in terms of percent coverage of the root area) likely to result in these symptoms. Partially oiled trees have been known to survive. Heavy oils such as #6 fuel oil are known to have lower overall toxicities (Getter et al. 1984) and result in higher tree survival. Recent work by Teas et al. (1993) has shown that removal of heavy oil coating on lenticels a few days after the initial oiling could restore oxygen delivery to the subsurface roots and increase the chance of tree survival.

OILED MANGROVES ON ST. JOHN

The mangroves that were oiled on St. John were located on the north side of the island near the east end (Figure 2). Oil was originally expected to come ashore on the south side of the island, which had extensive mangrove forests in sheltered lagoons. However, oil was not reported on the south side of the island. The constant trade winds usually create 2- to 4-foot seas in Sir Francis Drake Channel outside the bays on the north side of the island. The shoreline in this area is composed of gravel beaches, rocky/carbonate platforms, rocky shores, and some sand or sand and gravel beaches. The mangroves have managed to grow in this environment, with most of the red mangroves found on the gravel beaches or carbonate platforms. The white mangroves are located on an erosional sand beach. This environment does not provide an ideal substrate for the trees, so they are stressed without any external sources affecting them.

Two species of mangroves were oiled during the *Vesta Bella* spill: red (*Rhizophora mangle*) and white (*Laguncularia racemosa*). The red mangroves formed the outer fringe, in the intertidal zone. Most of the red mangroves were on the east sides of the bays, which had escaped heavy oiling because of the east and northeast trade winds. (This effect was noted after Hurricane Hugo hit the south side of St. John Island in September 1989 destroying a large percentage of the mangroves. The north side of the island, being leeward of the winds, was protected so little hurricane damage was seen on oiled trees.) Thus, oiling of red mangroves occurred as an individual tree or a solitary stand of two or three trees (Figure 10) rather than extensive stretches of vegetation. The oiled mangrove trees had moderate to heavy oiling of the prop roots with little or no oil in the sediments (Figure 10A). The extent of oiling of the prop roots was patchy. Some roots on the tree had a continuous heavy coating, while others had only a patchy, light coating. The height of oil was 30 to 45 cm, whereas the roots were up to 1-meter high (Figure 11A); therefore, only a small percentage of the root surface area of a tree was covered. Based on laboratory and field studies on red mangroves, mortality would not be expected for the lightly oiled trees. Heavily oiled trees typically die as a result of the oiling. Some stress, manifested by leaf deformities, discoloration, and loss, would be expected on all the oiled trees, with the amount of stress being proportional to the amount of oil on the roots. The cleaning procedure worked very well on the red mangroves along the outer fringe because they were relatively exposed, with enough wave energy to work the snares.

The white mangroves typically grow in the supratidal zone. However, because of beach erosion, the roots of white mangroves at Newfound Bay were exposed at the high tide line (Figure 12A). The band of exposed roots, approximately 15 cm high, was coated with oil from the spill. The mangroves were stressed before the spill, because of root exposure resulting from the beach erosion. Although there are few studies of oiled white mangroves (Getter et al. 1981), oiling of exposed roots is expected to have the same smothering effects as oiling of prop roots and pneumatophores. Oiled mangroves would be heavily stressed and possibly die as a result of the oil. Root cleanup was conducted by a select group of workers who carefully wiped the roots with oil snares. A line of snare was also strung in front of the roots to allow natural tide and wave action to further scrub the roots. This method was not very successful for the white mangroves, since the roots were at the high-tide line. There was little wave energy and the water was at a level high enough to float the snares for only a very short period (Figure 13A).

Figure 10. An individual red mangrove at Haulover Bay, typical of the type of red mangroves oiled at St. John Island. This tree had been cleaned with snares. Photograph taken April 4, 1992, one year after the spill.

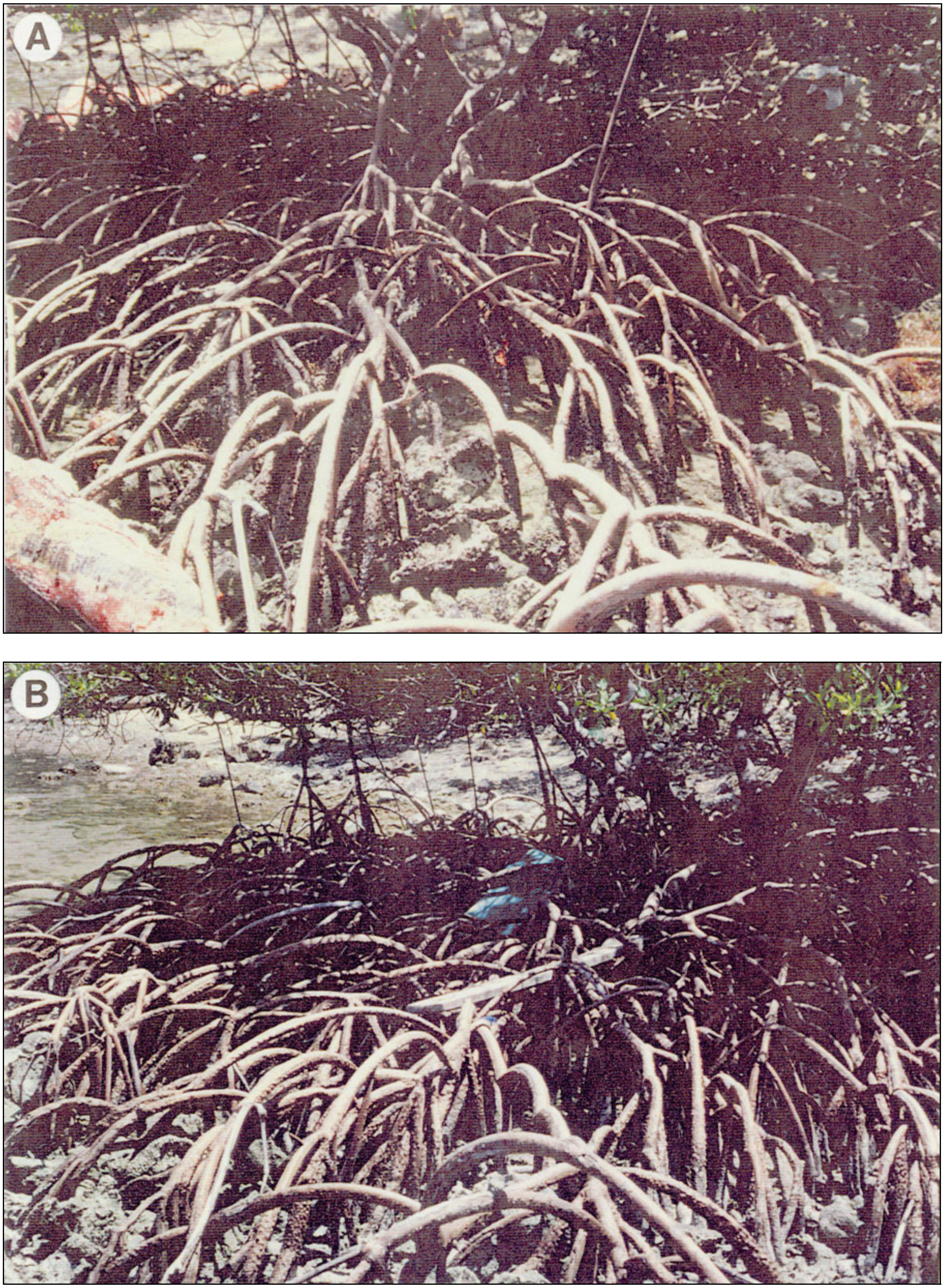


Figure 11. Oiled red mangrove roots at Haulover Bay. (A) March 1991. Note the rocky rubble substrate and paucity of sediments. (B) April 1992. There was little evidence of oil on the roots.

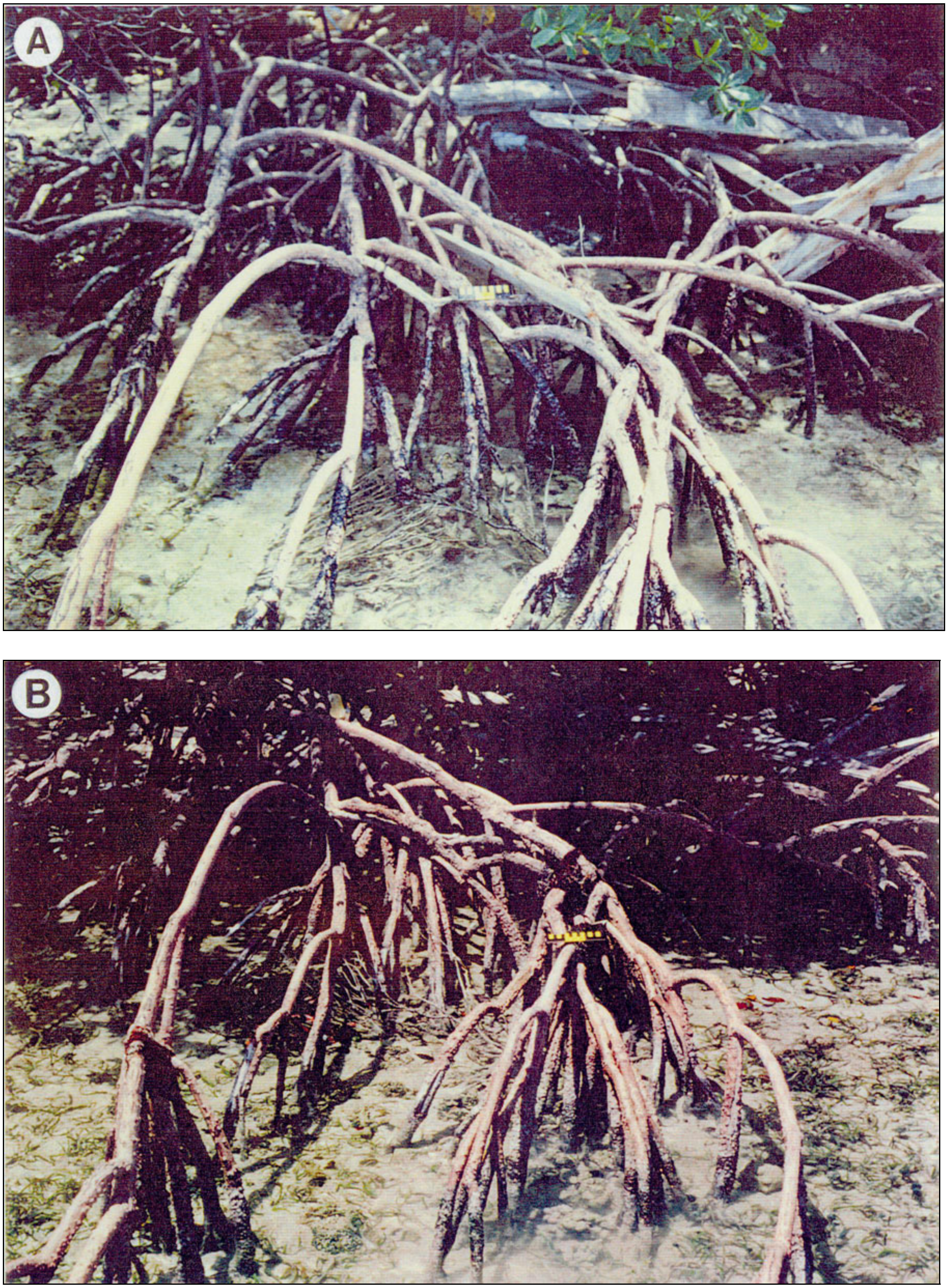


Figure 12. Oiled red mangrove roots at Newfound Bay. (A) March 1991. Note the height and coverage of oil on the roots. (B) April 1992. No *Vesta Bella* oil was observed.

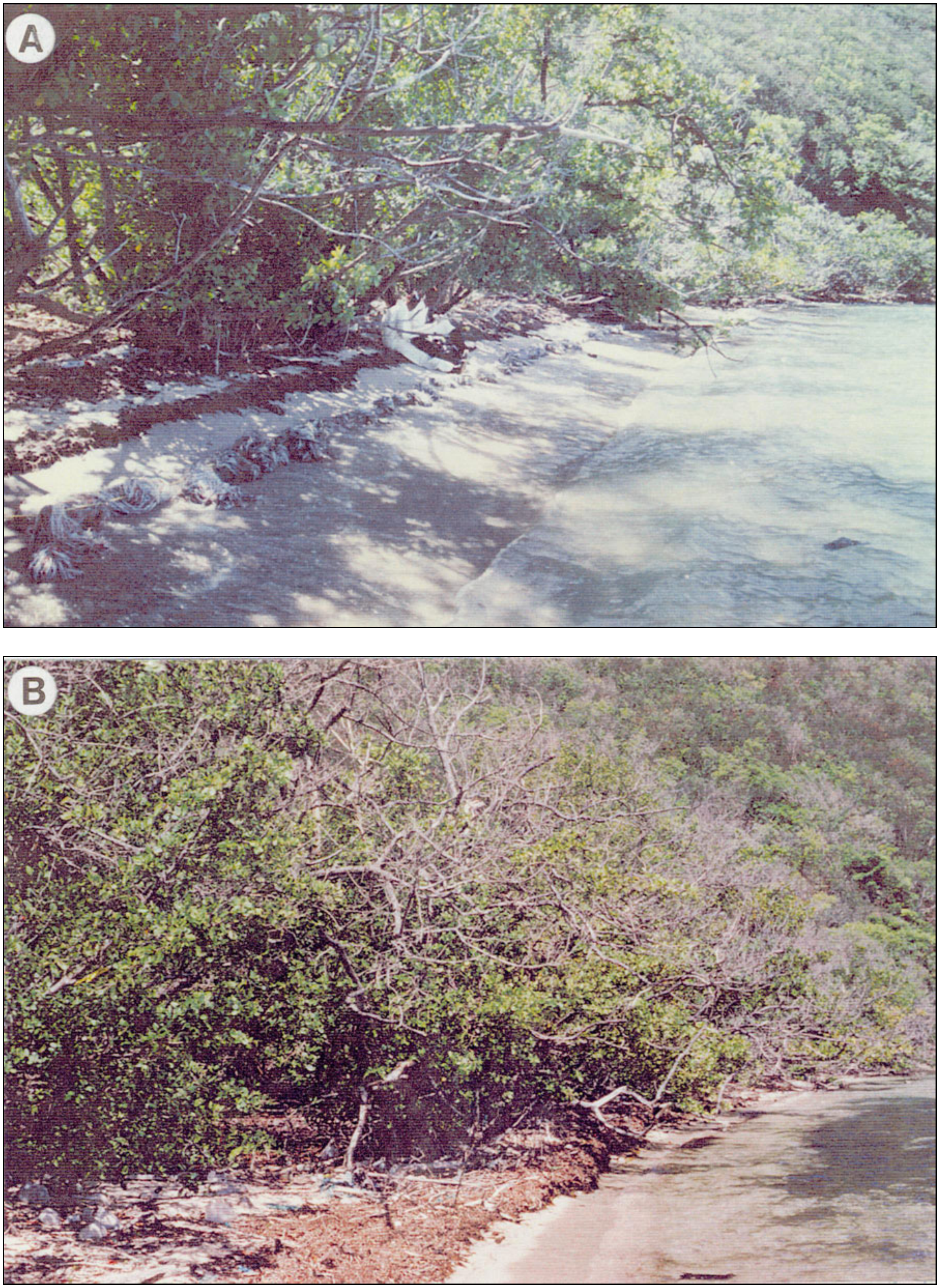


Figure 13. White mangroves at Newfound Bay. (A) March 1991. The workers are sitting on the exposed root band. (B) April 1992. Note the extensive defoliation that has occurred.

ONE-YEAR POST-SPILL OBSERVATIONS

METHODS

The site revisit on April 4, 1992, was designed primarily to obtain observational data. Color photographs were taken from the same locations as during the spill to show the changes in oiling and vegetation after one year. Color infrared photographs were also taken as a time series from shortly after the spill to one-year post spill, to identify stress in the mangroves. The revisit also involved careful visual observations of the plants and estimates of canopy coverage. Visual observations included looking for oiled roots, oiled sediments, new leaf growth, stressed leaves, and dead trees.

Canopy coverage estimates where made using a spherical densiometer. Three readings were taken in each group (oiled whites, unoiled whites, oiled reds, and unoiled reds). However, with the small area of oiled trees and the relatively small size of the trees it was not possible to get accurate or statistically significant readings. It was difficult to find a location under the mangrove canopy where the canopy completely filled the viewing area. Also, it was not possible to find a true control site for the oiled mangroves. All the oiled white mangroves were cleaned and the only unoiled white mangroves were in the supratidal zone and not subject to erosion.

RESULTS AND DISCUSSION

Based on visual examination of the mangrove environments, no completely dead trees were observed; there appeared to be a 100 percent survival as of one year post spill. However, there were signs of increased stress to the trees, probably as a result of the oil spill.

The white mangroves at Newfound Pass showed extensive defoliation (Figure 14B). While there was some defoliation at the time of the spill, the amount of defoliation at one-year post spill was considerably higher than at the time of the spill. Close inspection of the trees showed there was extensive new growth on many of the branches. There were no indications of new growth from the visit made three- and six-month post-spill observations of the National Park Service personnel on the island. Based on visual observations, comparisons between the oiled and unoiled trees showed that the unoiled trees had much denser foliage. The readings from the spherical densiometer supported these observations with a mean canopy cover of 80 percent at the oiled site and 91 percent at the control. The new growth on both the oiled and unoiled trees appeared to be about the same. This would indicate that the regrowth potential at one-year post spill was not being inhibited by the oil.

Most of the leaves that remained on the oiled white mangroves were healthy. Mangrove leaves show stress by chlorosis, necrosis, and gross deformities (Getter et al. 1985). There did not appear to be more signs of stress on oiled trees than on unoiled trees. Most of the stressed leaves had probably fallen off, as indicated by the reduced foliage. The abundance of new growth would indicate the oiled trees were recovering from the oiling and starting to regrow.

There were no signs of oil on the roots of the plants or in the substrate. The root scarp was still very evident (Figure 14B) but no oil was seen on any portion of these exposed roots. There was also no oil visible on the beach in front of the mangroves, or on the sediments at the base of the trees.

Red mangroves were oiled in both Haulover and Newfound bays. The oiled red mangroves in Haulover Bay were only a small clump of two or three trees (Figure 12). The trees had trace amounts of oil on the roots at the time of the revisit (Figure 12). Chemical analysis of this oil indicated a positive match to the *Vesta Bella* oil (Henry and Roberts 1992). Close observation of the foliage did not reveal any indications of stress; the trees appeared to be fully foliated. All the leaves were healthy without signs of yellowing, leaf loss, or necrosis (Figure 12). The densiometer readings showed a 94 percent canopy cover in the oiled red mangroves and 98 percent canopy cover in the unoiled red mangroves. Visual observations also indicated a denser canopy in the unoiled areas; this difference is because there were fewer trees. The unoiled areas had a large band of red mangroves resulting in canopy cover. The oiled trees were solitary stands (Figure 12) and there was greater chance of open canopy since there were not as many branches.

Only one red mangrove at Newfound Bay was significantly oiled and cleaned using the passive snare method. This tree, on the east side of Newfound Bay, was similar to the trees in Haulover Bay. The oil on the roots of this tree was from a different spill, based on fingerprint analysis (see previous discussion). After one year there were no visible signs of impact from the oil on any of these red mangroves (Figure 14B). The canopy of this tree was as lush one year after the spill as at the time of the spill. This tree was at the end of a healthy stand of mangroves and not isolated like the oiled mangroves in Haulover Bay. No readings were taken at this location but visual observations indicated that there was no difference in the health of this tree and the adjacent trees.

CONCLUSIONS

Since there were no oiled, untreated sites (set asides), it was not possible to determine if the cleanup methods employed enhanced recovery or survival of the trees. Based on the observations made, however, the cleanup methods did not cause any mortality to the trees, and may have saved some of the white mangroves.

In red mangroves, the cleanup did not appear to hinder recovery since observations showed that all red mangroves had recovered fully. This particular cleanup technique appears to be a viable method for cleaning the mangroves since it does not appear to cause additional harm. Unfortunately, it is not possible to determine whether the cleanup method is better than others that have been used because all oiled mangroves were cleaned in this manner and they all survived.

It should be noted that cleanup was conducted in areas where the substrate was very firm, either rocky rubble or sand. The substrates could readily support foot traffic without disrupting the soils and roots. Also, there was very little contamination of sediments, so there was no risk of mixing surface oil deeper by foot traffic. The cleanup techniques used on St. John Island would not be appropriate for soft or heavily oiled substrates.

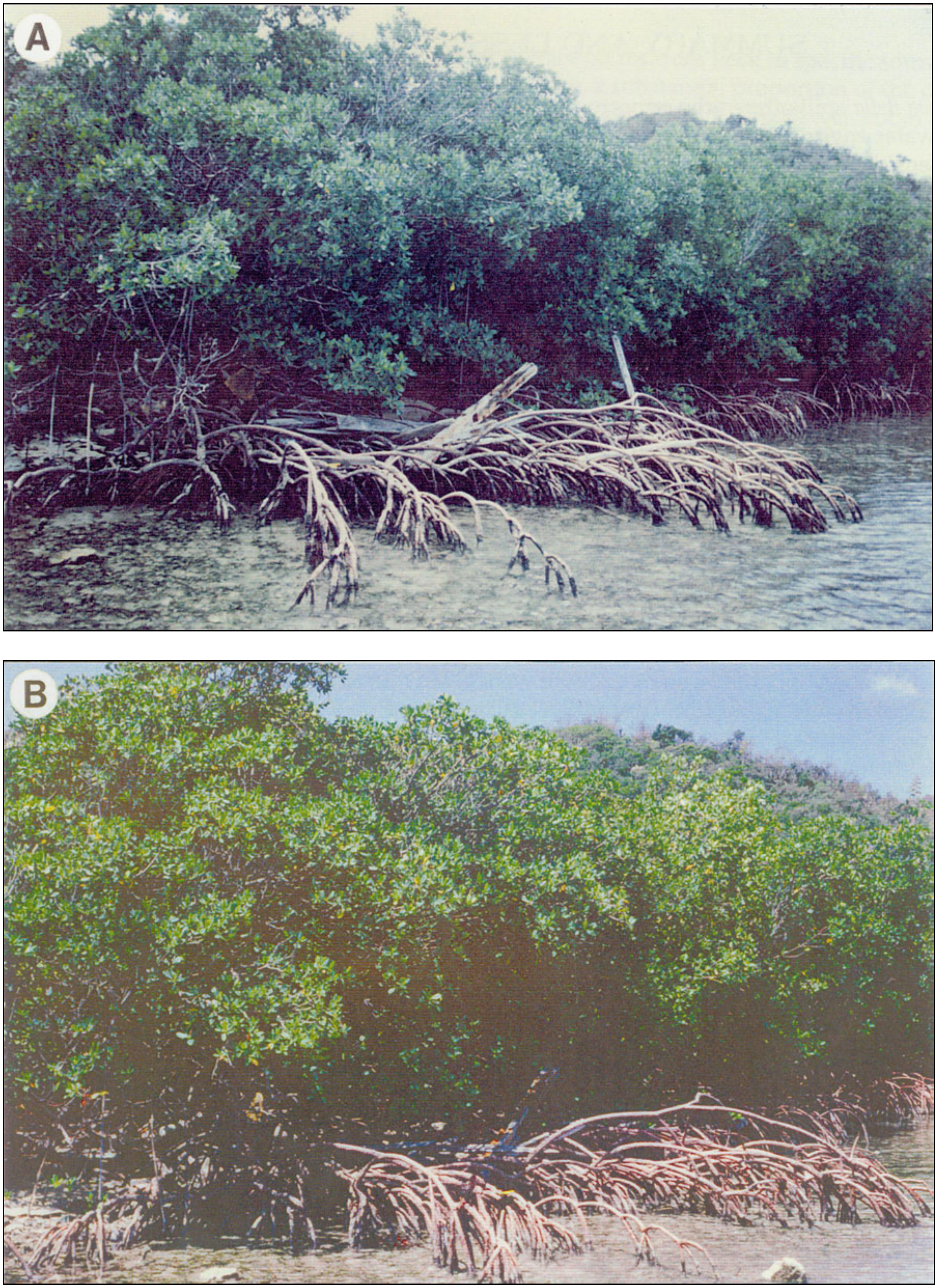


Figure 14. Red mangrove at Newfound Bay that was oiled during the spill. (A) March 1991. (B) April 1992. There has been little change in the canopy.

SUMMARY AND LESSONS LEARNED

The *Vesta Bella* spill offered the opportunity to revisit an oiled mangrove shoreline in a warm-water environment to study the persistence of oil and longer-term effects on relatively sensitive resources. It was hoped that the visit would yield both qualitative and quantitative results to increase our understanding of oil and cleanup effects in mangroves, and help improve the nature of spill response there.

Several different forms of oil were readily found at Newfound and Haulover bays one year after the *Vesta Bella* spill. The chemistry results showed that the study area on St. John had been subjected to a number of different oil sources, of which the *Vesta Bella* spill was but one. Although more than half of the samples collected were attributable to the *Vesta Bella*, the fact that seven other sources could be characterized suggests that the assessment of effects from the spill of interest would be a complex and difficult task.

As would be expected one year after the spill event, the samples for which the *Vesta Bella* was identified as the source showed a significant degree of weathering due to evaporative loss and microbial degradation. Detailed GC/MS analysis of the original source oil and the residues collected one year later indicated that the levels of the PAH compounds targeted declined about 76 percent over the intervening period.

Observations of white and red mangroves in oiled areas one year after the spill gave mixed results. Although apparently no mangroves were killed outright as a result of the *Vesta Bella* spill, and there were signs of new growth in both oiled and unoiled stands, there were also indications of increased stress in oiled stands. In particular, unoiled white mangrove trees appeared to have much denser foliage than oiled trees, a visual observation that was supported by readings from the spherical densiometer. However, other signs of continued stress to the plants, such as morphological deformities, chlorosis, or necrosis, were no more prevalent in oiled mangroves than unoiled.

Comparisons between oiled and unoiled red mangroves in Newfound and Haulover bays failed to elicit any significant indication of oiling effects. However, the comparison was complicated by differences in tree densities in the areas.

Unfortunately, no "set-aside" areas (oiled and uncleaned) were established during this spill; it was not possible to evaluate the effects that the cleanup methods themselves may have had on accelerating or inhibiting recovery of the mangroves. Neither the oiling nor the cleanup procedures caused direct mortalities, however. If it is assumed that the physical removal reduced the bulk amount of oil present and its environmental persistence by increasing exposure to weathering processes, it is a reasonable conclusion that there was an environmental benefit gained by performing the cleanup. It is likely that the firm substrate characteristics of the affected area contributed significantly to the apparently low-impact nature of the cleanup by minimizing effects of foot traffic; this kind of approach may not be appropriate in soft substrate areas or where substrate oiling was heavier.

The follow-up visit to St. John resulted in several lessons learned that may be of use in future incidents, in the Caribbean and elsewhere. These include but are not limited to:

❐ The value of chemical fingerprinting to trace oil residues back to specific sources or to differentiate between sources. In this case, a substantial proportion of the oil found one year later on the shorelines oiled by the *Vesta Bella* spill was not in fact attributable to that spill.

❐ The rapidity with which exposed oil weathers in a tropical mangrove environment, where relatively warm temperatures, sunlight, and the availability of nutrients contribute to degradation of residues.

❐ Observations after one year indicate that oil spills in mangrove stands do not by definition translate into certain death for the trees. Carefully selected and implemented non-intrusive physical cleanup methods may contribute to survival of oiled mangroves

❐ The importance of defining oiled and untreated set-aside sites during the early stages of a response for use as reference areas to evaluate effects of cleanup techniques independent from the effects of oiling.

REFERENCES

Butler, E. L., G. S. Douglas, W. G. Steinhauer, R. C. Prince, T. Aczel, C. S. Hsu, M.T. Bronson, J. R. Clark, and J. E. Lindstrom. 1991. Hopane, a new chemical tool for measuring oil biodegradation. In: *On-Site Bioreclamation*. Stonehan, MA: Butterworth-Heinemann Publishers. pp 515-521.

Getter, C. D., G. I. Scott, and J. Michel. 1981. The effects of oil spills on mangrove forests: A comparison of five oil spill sites in the Gulf of Mexico and the Caribbean Sea. *1981 Oil Spill Conference, (Prevention, Behavior, Control, Cleanup)*, Atlanta, GA, March 2-5, 1981, Washington, D.C., American Petroleum Institute, pp 535-540.

Getter, C. D., G. Cintron, B. Dicks, R. R. Lewis, III, and E. D. Seneca. 1984. The recovery and restoration of salt marshes and mangroves following an oil spill. In: *Restoration of Habitats Impacted by Oil Spills.* J. Cairns, Jr. and A. L. Buidema, Jr. (eds) Boston: Butterworth Publishers. pp 65-113.

Getter, C.D., T. G. Ballou, and C. B. Koons. 1985. Effects of dispersed oil on mangroves: synthesis of a seven year study. *Marine Pollution Bulletin 16*(8): 318-324.

Kennicutt, M. C. 1988. The effects of biodegradation on crude oil bulk and molecular composition. *Oil & Chemical Pollution 4*:89-112.

Michel, J., M. O. Hayes, W. J. Sexton, J. C. Gibeaut, and C. B. Henry. 1991. Trends in natural removal of the *Exxon Valdez* oil spill in Prince William Sound from September 1989 to May 1990, *Proceedings of the 1991 Oil Spill Conference, (Prevention, Behavior, Control, Cleanup)*, San Diego, March 4-7, 1991, Washington, D.C., American Petroleum Institute, pp 181-187.

Overton, E. B., L. V. McCarthy, S. W. Marcaella, S. R. Antoine, J. L. Laseter, and J. W. Farrington. 1980. Detailed chemical analysis of Ixtoc I crude oil and selected environmental samples from the *Researcher* and *Pierce* cruises. *Symposium on Preliminary results from the September 1979 Researcher/Pierce Ixtoc 1 Cruise,* Key Biscayne, FL, June 9-10, 1980, Boulder, CO, Office of Marine Pollution Assessment, NOAA, pp 439-498.

Overton, E.B., S. W. Mascarella, J. A. McFall, S. A. Antoine, C. F. Steele, I. R. Politzer, and J. L. Laseter. 1981. Identification of pertroleum residues sources after a fire and oil spill, *1981 Oil Spill Conference (Prevention, Behavior, Control, Cleanup)*, Atlanta, GA, March 2-5, 1981, Washington, D.C., American Petroleum Institute, pp 541-546.

Peters, K. E. and J. M. Moldowan. 1991. Effects of source, thermal maturity, and biodegradation on the distribution and isomerization of hopanes in petroleum. *Organic Geochemistry Vol 17, No. 1*:47-61.

Prince, R. C., D. L. Elmendorf, J. R. Lute, C. S. Hsu, C. E. Haith, J. D. Senlus, G. J. Dechert, G. S. Douglas, E. L. Butler. 1994. 17α(H), 21 β(H), hopane as a conserved internal marker for estimating the biodegradation of crude oil. *Environmental Science and Technology 23*: 124-145.

Research Planning Institute. 1987. Environmental assessment and restoration recommendations for a mangrove forest affected by jet fuel. RPI/R/87-10, Columbia, SC: Research Planning Institute. 32 pp.

Teas, H. J., R. R. Lessard, G. P. Canevari, C. D. Brown, and R. Glenn. 1993. Saving oiled mangroves using a new non-dispersing shoreline cleaner, *1993 International Oil Spill Conference. Prevention, Preparedness, Response*, Tampa, Florida, March 29-April 1, 1993, Washington, D. C.: American Petroleum Institute, pp 147-151.