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FINAL REPORT

Analysis of Water Samples from the Tampa Bay Area Following the August 10th Oil Spill

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INTRODUCTION

Significant quantities (5 to 9 thousand barrels) of number 6 fuel oil and an undetermined amount of jet fuel were spilled in the mouth of Tampa Bay following the August 10th collision of the freighter *Balsa 37* with the barges *Ocean 255* and *B155*. Shifting winds and current forces moved the majority of the spilled oil out of Tampa Bay and into the Gulf of Mexico in the days following the spill. Changes in wind direction several days later brought oil back to Gulf beaches and the inshore waters north of the mouth of Tampa Bay. In order to evaluate the extent of oil contamination and estimate it's potential for environmental impact we collected water samples in areas of potential or visible impact. Water samples were collected on August 12th from the waters around Mullet and Egmont Keys (the vicinity of the spill). And, on the 17th in the waters near John's Pass and Bunces Pass (areas of visible or potential impact by the shoreward moving oil). This report details the results of our analyses of these samples.

BACKGROUND

To provide a basis of discussion for the results of our hydrocarbon analyses in the waters of Tampa Bay, a brief review of some of the important environmental parameters which may affect the distribution and fate of spilled oil is we provided. The primary reference for the discussion which follows is the National Research Council's 1985 book on Oil in the Sea (NRC 1985). While research on the transport and fate of petroleum products has continued, this book provides a good general background which is still consistent with more current research.

The fate of oil entering the marine environment depends on both properties of the oil which is spilled (*i.e.*, density, vapor pressure, solubility, content of polar compounds), and on the state of the sea during and after the spill (temperature and the amount of mixing energy available). Advection and spreading of the oil cause an immediate increase in exposed surface area, both to the sea surface, and to the overlying atmosphere, thus enhancing the oil's susceptibility to weathering processes. These processes "include evaporation, dissolution, vertical dispersion, emulsification, and sedimentation" (NRC 1985). Evaporation of the low boiling ($<C_{20}$) components of a spilled oil begins immediately and can increase the density of the spilled oil. Low boiling components are also lost due to dissolution, with either subsequent evaporation or degradation. Surface turbulence can enhance both vertical dispersion of the oil (as small droplets) and formation of a water in oil emulsion (mousse formation). Once droplets have been separated from the slick they can be further transported through advection or by adsorption to suspended mineral matter. Both this process and that of mousse formation result in an increase in surface area exposed, resulting in increased biological and abiological (auto- and photo-) oxidation. Increases in an oil's density can cause it to sink below the surface, this and increased vertical dispersion as a result of mixing, can both contribute to transport through the water column and sedimentation of the oil.

Oil is a complex mixture of components, even refined oil products such as the number 6 fuel oil which was spilled in this accident consist of potentially thousands of different compounds. The complexity of petroleum products defies even the best chromatographic techniques to separate all of the individual components. In Figures 1 and 2 we show chromatograms of dilutions of two of the oil samples collected in this study.

The first, labeled Tarball, was from a surface slick sample collected August 12th just north of Egmont Key. The other, labeled Mousse, was collected in the shallow water off the beach about half-way up St Petersburg Beach (seaward of the Howard Johnson's) on August 17th. Several alkane peaks are labeled either as "Alkanes" or with their carbon chain length shown as a number (C 16 = hexadecane). The area below the chromatogram labeled UCM is an unresolved complex mixture of compounds. The UCM is composed of cyclic and branched hydrocarbons which have overlapping properties and thus cannot be resolved.

The similarity of these two oil samples suggests that the bulk of the oil which remained at the sea surface did not undergo significant alteration or weathering during the 5 days between the collection of these two samples. It is interesting to note that the *n*-alkanes in these two samples give essentially the same profile and are predominantly in the range of 13 to 30 carbons (C_{13}-C_{30}). The other facet to observe is that the alkanes do not show large differences in relative abundance of odd versus even carbon numbers (chain lengths). This latter fact is characteristic of petroleum products and facilitates the identification of oil related hydrocarbon contamination from other hydrocarbon signals of a more recent biogenic source. Biogenic hydrocarbons show a strong odd to even alkane chain length abundance (*i.e.*, odd chain lengths dominate biogenic hydrocarbons). The smaller peaks observed between the alkanes were determined to consist mostly of alkylated polycyclic aromatic hydrocarbons (PAH). These compounds are more toxic than the *n*-alkanes and also more difficult to biodegrade. All chromatograms presented here are drawn on the same scale and show the detector response from 10 to 60 minutes (GC program $45°C_{1\,min}$, 6°C/min to $285°C_{20\,min}$).

Degradation of oil begins once it is released into the environment. The relative importance of chemical versus biological degradation routes is likely to vary with type of oil and environmental factors. Our current discussion will focus only on changes in the hydrocarbon profile expected to result from degradation. Degradation of the entire mixture of compounds in an oil will occur simultaneously, however, because the different types of compounds have various degradation rates, the hydrocarbon profile will change with time. The *n*-alkanes are biodegraded rapidly, and within this group, compounds with greater solubility ($<C_{22}$) are degraded at a higher rate than are larger compounds which are only slightly soluble. Because of their branched and cyclic structures, the isoalkanes and cycloalkanes are not biodegraded as readily as the *n*-alkanes, and therefore remain in impacted sediments long after the *n*-alkanes have disappeared. Polycyclic aromatic hydrocarbons (PAH), even those with appreciable solubility, are biodegraded at a slower rate than are the alkanes.

The alterations one would expect to observe in the hydrocarbon profile as a result of all the processes which affect the oil's environmental distribution can be summarized as follows: loss of low boiling ($<C_{22}$) hydrocarbons (all types) through evaporation and dissolution (mostly $<C_{15}$), biodegradation of the *n*-alkanes with a proportional increase in the importance of the unresolved complex mixture and PAHs, followed by a subsequent shift in the relative abundance within the UCM towards higher molecular weights (as a result of both solubility and biodegradation of the lower molecular weight compounds).

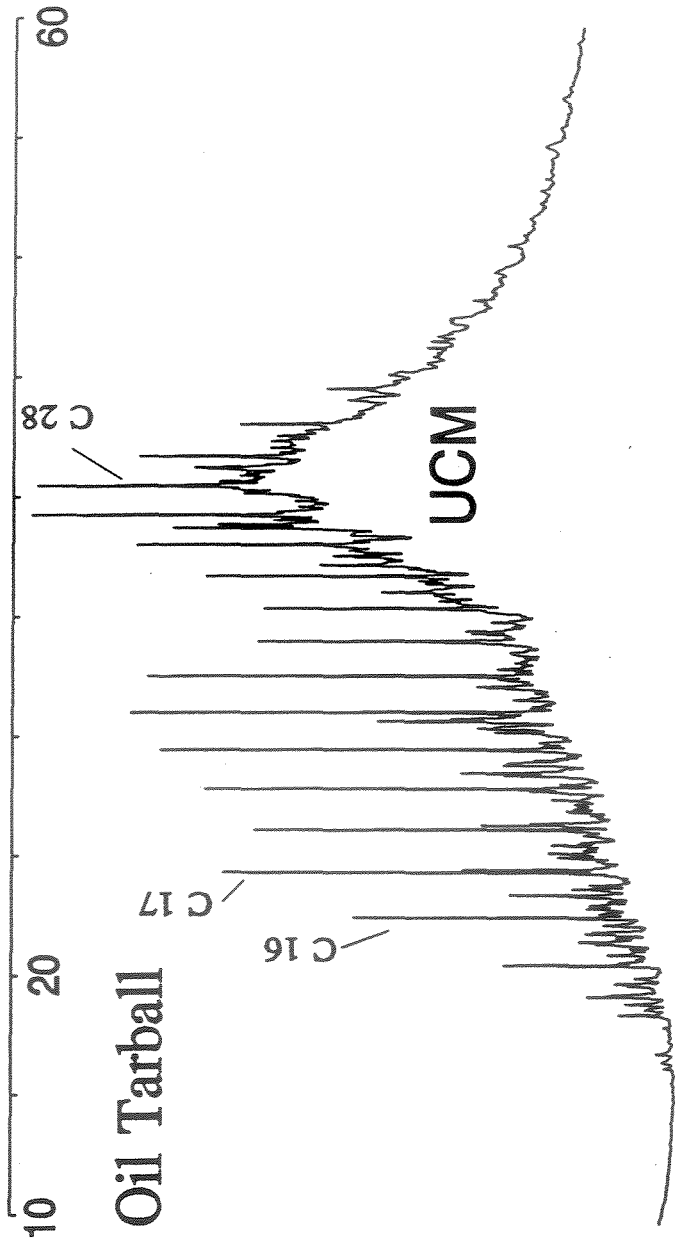

Figure 1. Chromatogram of a dilution of the oil sample collected August 12th. See text for details.

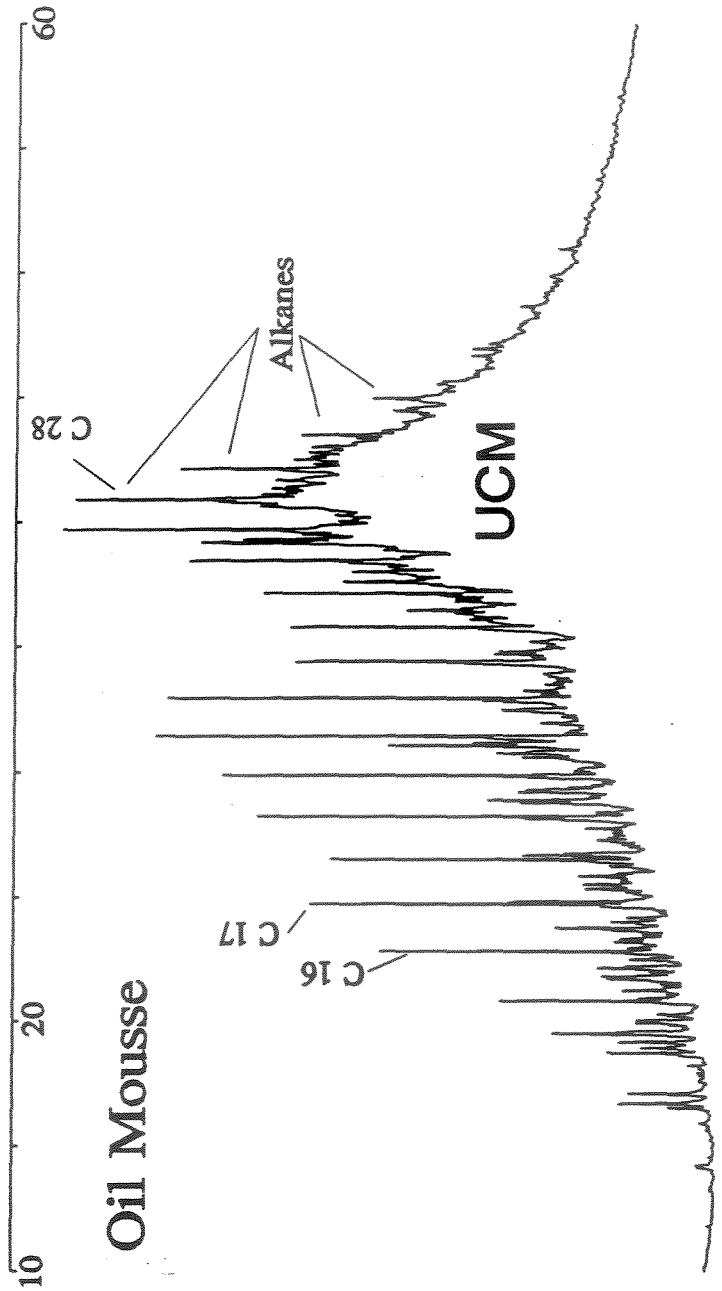

Figure 2. Chromatogram of a dilution of the oil sample collected August 17th. See text for detatils.

METHODS

Water samples were collected by siphoning through precleaned silicone (silastic) tubing from a depth of either 1 or 6 feet, into clean amber glass jars. Water and oil slick samples were also collected on each of the two sampling days. These samples were collected by submersing the sample jar through the oil slick to collect samples of the spilled oil. After sampling, the exterior of these jars were wiped clean and the jars were placed in plastic bags to minimize any potential for cross contamination with other samples being collected. All samples were stored over ice until return to the laboratory.

Upon return, water samples were spiked with recovery surrogates and stored under refrigeration until extraction. Storage time was less than 24 hours for all water samples except the two oil-water mixed samples, these were stored refrigerated until an opportunity arose to extract them. Prior to extracting the oil-water samples, the aqueous phase was separated from the overlying oil either by passing it through a precleaned glass wool plug (the August 12th sample), or by carefully pipetting the water into a separatory funnel (the 17th sample), avoiding the transfer of any visible oil droplets. The oil solutions were prepared by diluting a weighed amount of oil (4-6 mg) with hexane in a 10 ml volumetric flask. All water samples were extracted with dichloromethane (DCM, 3x). Extracts were reduced in volume using rotary evaporation, samples which still contained water after rotary evaporation were placed in a small separatory funnel and the aqueous phase was rinsed (3x) with DCM, which was collected and further reduced in volume. The concentrated extract was passed over anhydrous sodium sulfate, taken to just dryness under a stream of nitrogen (N_2) and redissolved in a solution of 5-α-Androstane for TEO analysis. This analysis provided a quick initial indication of the contaminant levels present in each of the samples.

The Total Extractable Organics (TEO) solution was analyzed by gas chromatography - flame ionization detection (GC/FID). Subsequent to this analysis, the hydrocarbon fraction was isolated from the TEO via column chromatography. The hydrocarbon fraction was isolated using combined silica gel - alumina columns. Stationary support materials were extensively cleaned *via* sonication in methanol, DCM and hexane, dried and then activated at 210°C. Upon cooling, the support materials were deactivated 5% with HPLC grade water and stored under hexane. Approximately 12 gm of silica and 6 gm of alumina were sequentially slurry packed into chromatography columns with gentle tapping to ensure uniform packing. The sample (in hexane) was applied to the column in a small volume (<0.5 ml) and the container sequentially rinsed (2x) with 0.25 ml hexane. The sample was eluted from this column using 10 ml of hexane and 30 ml of 20% DCM in hexane.

The hydrocarbon fraction was reduced to just dryness with N_2 and taken up in a solution of quantitation standard and analyzed by gas chromatography with flame ionization (GC/FID). All quantitations were performed against these standards which were added at known concentrations. Selected confirmatory analyses were performed using gas chromatography with mass spectral detection (GC/MS). GC/FID analyses were performed on a Varian 6000 GC with data being collected, stored and analyzed using a P.E./Nelson 2600 Chromatography Data System (DS) software and interfaces. Mass spectral confirmations were performed on a Varian Saturn II iontrap GC/MS/DS system.

RESULTS AND DISCUSSION

Total Extractable Organics

The preliminary TEO results of the water analyses are presented in Table 1. This table reproduces the one page report provided to DEP on September 24th, which provided a qualitative analysis of the distribution of the oil in the water samples collected. Because of the significant contributions by non-hydrocarbons to the TEO in these samples, these preliminary assessments of oil contamination did not always agree with the results obtained with the hydrocarbon analyses. In general, however, there is good agreement between the qualitative and the quantitative analyses.

Total Hydrocarbon Concentrations

The results of the hydrocarbon analyses are presented in Table 2. This table provides the sample number and collection coordinates, as well as the total hydrocarbon concentration determined for each sample. Also provided is a one letter code which indicates whether the hydrocarbon profile observed in a particular sample was indicative of a biogenic (B), oiled (O), or weathered oil (W) source. Two other abbreviations indicate a high molecular weight alkane (A) profile, and no identifiable hydrocarbon profile (N). These will be discussed further below.

Total hydrocarbon concentrations in various parts of the Gulf of Mexico have been reported in the range of 0.1 to 76 μg/L (NRC 1985). Background hydrocarbon values fall on the low end of this range, whereas the higher values represent areas which are impacted by shipping traffic and other local sources. The results from the small number of samples analyzed in this study suggest that background hydrocarbon values for the areas sampled in this study would be in the range of <0.5 to 15 μg/L, and stations with higher levels than this are at least partially impacted by oil related hydrocarbons.

There was no region sampled on either sampling date, which could be said to be wholly non-impacted by the oil spill. The hydrocarbons observed at individual stations ranged from those of a purely biogenic source, to an overwhelming predominance of oil spill related hydrocarbons. The waters collected from north of Mullet Key on August 12th (stations 1-5) showed variable concentrations of spill related hydrocarbons (0.8 to 22 μg/L). The samples collected in the vicinity of the ship channel (stations 8-18) also exhibit an extreme range of hydrocarbon concentrations (from <0.5 to 46 μg/L). The waters collected on August 17th gave a wide range of hydrocarbon concentrations (from <0.5 to 39 μg/L) as well. Both the John's Pass area, which was visibly oiled, and the Bunces Pass samples, an area which had no visible oil contamination, had stations which showed hydrocarbon concentrations and profiles indicating contamination by suspended oil.

Table 1. Preliminary results from analysis of total extractable organics (TEO) of water samples collected after the Tampa Bay oil spill of 8-10-93. Initially reported 9-24-93.

Samples collected 8-12-93 at 1 foot depth unless otherwise noted

	TB-1	TEO shows little or no oil signature.
	TB-2	TEO dominated by non-oil peaks, may have trace of oil.
	TB-3	TEO dominated by non-oil peaks, shows some oil impact.
	TB-4	TEO dominated by non-oil peaks, shows some oil impact.
	TB-5	TEO dominated by non-oil peaks, shows some oil impact.
	TB-6	TEO shows moderate loading - mostly FAs trace of oil.
	TB-7	TEO shows moderate loading - mostly FAs trace of oil.
	TB-8	TEO shows no oil signature.
	TB-9	TEO dominated by non-oil peaks, may have trace of oil.
	TB-10	TEO dominated by non-oil peaks, shows some oil impact.
	TB-11	TEO shows no oil signature.
	TB-12	TEO dominated by non-oil peaks, shows some oil impact.
	TB-13	TEO dominated by non-oil peaks, shows some oil impact.
6 ft	TB-13	TEO dominated by non-oil peaks, shows some oil impact - more than 1 ft.
	TB-14	TEO dominated by non-oil peaks, shows some oil impact.
	TB-15	TEO dominated by non-oil peaks, shows some oil impact.
6 ft	TB-15	TEO dominated by non-oil peaks, shows some oil impact.
	TB-16	TEO dominated by non-oil peaks, shows definite oil impact.
	TB-17	TEO dominated by non-oil peaks, shows definite oil impact.
	TB-18	TEO dominated by non-oil peaks, shows some oil impact.
	TB-8/9	TEO dominated by non-oil peaks, shows some oil impact.
	Oil slick	TEO is mix of oil and non-oil peaks.

Samples collected 8-17-93 at 1 foot depth

2056	Johns Pass South	TEO shows no oil signature.
2055	Mangrove Island	TEO shows little or no oil signature.
1863	Mangrove Island	TEO shows trace of oil.
2052	East of Elinor	TEO shows trace of oil.
2054	Johns Pass North	TEO shows no oil signature.
2053	Elinor Island	TEO shows definite oil signature.
1864	Bunces Pass	TEO shows little or no oil signature.
1868	Bunces Pass	TEO shows no oil signature.
1871	Bunces Pass	TEO dominated by non-oil peaks, shows oil impact.
1873	Bunces Pass	TEO dominated by non-oil peaks, shows possible oil impact.
2051	Bunces Pass	TEO dominated by non-oil peaks, shows possible oil impact.
1872	Bunces Pass	TEO dominated by non-oil peaks, shows oil impact.

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	TB-4	TEO dominated by non-oil peaks, shows some oil impact.
	TB-5	TEO dominated by non-oil peaks, shows some oil impact.
	TB-6	TEO shows moderate loading - mostly FAs trace of oil.
	TB-7	TEO shows moderate loading - mostly FAs trace of oil.
	TB-8	TEO shows no oil signature.
	TB-9	TEO dominated by non-oil peaks, may have trace of oil.
	TB-10	TEO dominated by non-oil peaks, shows some oil impact.
	TB-11	TEO shows no oil signature.
	TB-12	TEO dominated by non-oil peaks, shows some oil impact.
	TB-13	TEO dominated by non-oil peaks, shows some oil impact.
6 ft	TB-13	TEO dominated by non-oil peaks, shows some oil impact - more than 1 ft.
	TB-14	TEO dominated by non-oil peaks, shows some oil impact.
	TB-15	TEO dominated by non-oil peaks, shows some oil impact.
6 ft	TB-15	TEO dominated by non-oil peaks, shows some oil impact.
	TB-16	TEO dominated by non-oil peaks, shows definite oil impact.
	TB-17	TEO dominated by non-oil peaks, shows definite oil impact.
	TB-18	TEO dominated by non-oil peaks, shows some oil impact.
	TB-8/9	TEO dominated by non-oil peaks, shows some oil impact.
	Oil slick	TEO is mix of oil and non-oil peaks.

Samples collected 8-17-93 at 1 foot depth

2056	Johns Pass South	TEO shows no oil signature.
2055	Mangrove Island	TEO shows little or no oil signature.
1863	Mangrove Island	TEO shows trace of oil.
2052	East of Elinor	TEO shows trace of oil.
2054	Johns Pass North	TEO shows no oil signature.
2053	Elinor Island	TEO shows definite oil signature.
1864	Bunces Pass	TEO shows little or no oil signature.
1868	Bunces Pass	TEO shows no oil signature.
1871	Bunces Pass	TEO dominated by non-oil peaks, shows oil impact.
1873	Bunces Pass	TEO dominated by non-oil peaks, shows possible oil impact.
2051	Bunces Pass	TEO dominated by non-oil peaks, shows possible oil impact.
1872	Bunces Pass	TEO dominated by non-oil peaks, shows oil impact.

Table 2. Hydrocarbon concentrations determined in water samples collected in Tampa Bay.

Samples collected August 12, 1993.

Sample #	Latitude (N)	Longitude (W)	Total Hydrocarbons µg / L	Hydrocarbon Profile Type[1]
TB-1 1839	27°44'2"	82°46'03"	0.8	B
TB-2 1840	27°40'6"	82°45'90"	7.2	O
TB-3 1841	27°39'01"	82°45'86"	12.4	O
TB-4 1842	27°41'54"	82°41'15"	22.4	O
TB-5 1844	27°39'68"	82°40'93"	15.1	O
TB-6 1845	27°32'17"	82°39'88"	16.9	O
TB-7 1846	27°32'05"	82°42'13"	3.3	B/O
TB-8 1859	27°33'21"	82°42'78"	BLQ[2]	N
TB-8/9 1843	27°37'27"	82°40'04"	BLQ	N
TB-9 1857	27°37'13"	82°39'87"	5.9	B/O
TB-10 1853	27°38'40"	82°41'50"	3.2	B
TB11 1861A	27°36'62"	82°50'66"	8.8	O
TB11 1861B	27°36'62"	82°50'66"	13.6	A
TB-12 1851	27°36'06"	82°46'11"	2.6	B
TB13-1ft 1847	27°35'97"	82°45'33"	2.1	B/O
TB13-6ft 1850	27°35'97"	82°45'33"	10.7	O
TB-14 1858	27°36'60"	82°41'89"	9.2	O
TB15-1ft 1856A	27°37'58"	82°42'06"	BLQ[3]	N
TB15-1ft 1856B	27°37'58"	82°42'06"	18.7	W
TB15-6ft 1855	27°37'58"	82°42'06"	1.1	B
TB-16 1848	27°36'96"	82°43'29"	11.2	B/O
TB17-1ft 1854	27°37'27"	82°44'83"	0.8	N
TB17-6ft 1849	27°37'27"	82°44'83"	46.2	O
TB-18 1860	27°37'03"	82°47'26"	BLQ	N
Spill 1ft 1866	27°37'13"	82°45'10"	46.4	O

Samples collected August 17, 1993.

Sample #	Latitude	Longitude	Hydrocarbons µg / L	
1863 Bunces Pass	27°39'27"	82°40'04"	3.0	B/O
1864 Bunces Pass	27°39'20"	82°44'95"	BLQ	B
1868 Bunces Pass	27°39'06"	82°44'11"	BLQ	N
1871 Bunces Pass	27°39'22"	82°44'00"	10.6	B/O
1872 Bunces Pass	27°39'04"	82°43'24"	12.8	A/O
1873 Bunces Pass	27°39'32"	82°43'71"	35.5	O/B
2051 Bunces Pass	27°39'13"	82°43'35"	14.7	O/B
2052 East Elinor	27°47'30"	82°46'28"	BLQ	N
2053 Elinor Island	27°47'24"	82°46'55"	39.4	W
2054 North John Pass	27°48'31"	82°47'01"	0.5	N
2055 Mangrove Island	27°47'54"	82°46'44"	12.2	W
2056 South John Pass	27°47'21"	82°45'63"	10.8	W

[1]Hydrocarbon Profile Type and abbreviations are explained in the text.
[2]BLQ indicates hydrocarbon concentrations are at or below the limit of quantitation (0.5 µg/L).
[3]Potential reasons for the concentration differences between these two duplicates will be discussed in Appendix 1.

In our August 12th sampling we collected samples from both 1 foot and 6 foot water depths at 3 of the stations sampled. While it is difficult to generalize from a small number of samples, they may provide information regarding hydrocarbon transport following the spill. Comparison of the 1 foot hydrocarbon data with that from 6 foot depths at each station reveals that at one of these stations the 1 foot station had a higher hydrocarbon concentration, whereas the other two stations showed higher concentrations at depth. These deeper samples had hydrocarbon profiles which demonstrated the deeper waters were also impacted by oil. The profiles observed at these stations (oil and weathered oil) indicated that both oil, and related hydrocarbons were well dispersed into the water column following the spill. This was graphically evident on the 17th when oil globules could be seen floating just above the bottom.

The hydrocarbon concentrations in the 1 foot depth samples show an areal distribution of oil related hydrocarbons indicating a patchy distribution. As with the deeper stations, the distribution of hydrocarbons in the 1 foot reflects tidal flux and water movement independent of the surface slick. The hydrocarbon profiles (discussed below) suggested that these hydrocarbons consisted of both dissolved and colloidal oil mixed into the water column over the course of time. The oil which became thus dispersed into the water column would be transported with that water. Subsurface currents often transverse or even flow in the opposite direction of the surface current, leading to separation between the surface oil slick and hydrocarbons transported lower in the water column. This resulted in a wider distribution of hydrocarbon contamination than could be observed by following the movement of the surface slick. The contrary is also true, water movement under the surface slick would bring water with low hydrocarbon content into areas which were visibly impacted by the surface slick. This also means that an area which was bathed in low hydrocarbon content water when we sampled that location would not necessarily avoid exposure during a different tidal cycle.

Hydrocarbon Profiles: Aqueous Phases from Oil Samples

In order to better understand the hydrocarbon profiles observed in the water column samples we examined the profiles of two aqueous phases which had been collected with their overlying oil. Figures 3 and 4 show the hydrocarbon profiles of the aqueous phases collected with oil samples taken on August 12th and 17th (shown in Figures 1 and 2 respectively). These two chromatograms show completely different hydrocarbon profiles, both from the overlying oils, and between the two aqueous samples. The sample collected on the 12th of August (Figure 3) has low concentrations of the alkanes and other resolved components, with a relatively larger proportion of this sample being comprised of the UCM. This chromatogram may represent a combination of dissolution from the overlying oil with rapid biodegradation or evaporation of these lighter components and advection of the underlying water before significant concentrations can be achieved. Comparison of this sample with the aqueous phase from under the oil sample collected on August 17th (Figure 4) suggests that these samples represent somewhat different conditions. The August 17th sample shows both higher relative concentrations and a higher molecular weight distribution of the alkanes and the UCM. Degradation/evaporation could explain the loss of the lower molecular weight material in both these water samples. The cause of the observed difference in the higher molecular weight alkanes and UCM might be that they could reach higher concentrations in the

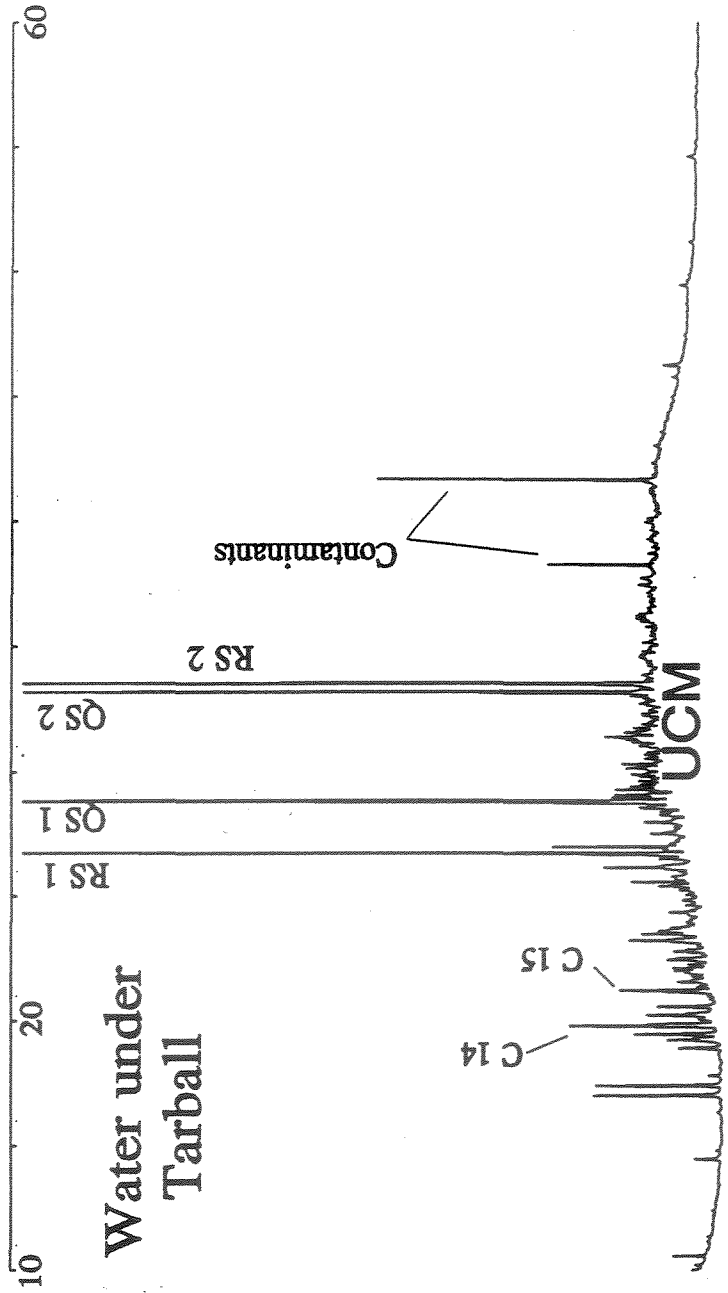

Figure 3. Chromatogram of the hydrocarbons isolated from the water collected with the oil (Tarball) sample collected on August 12th. See text for details.

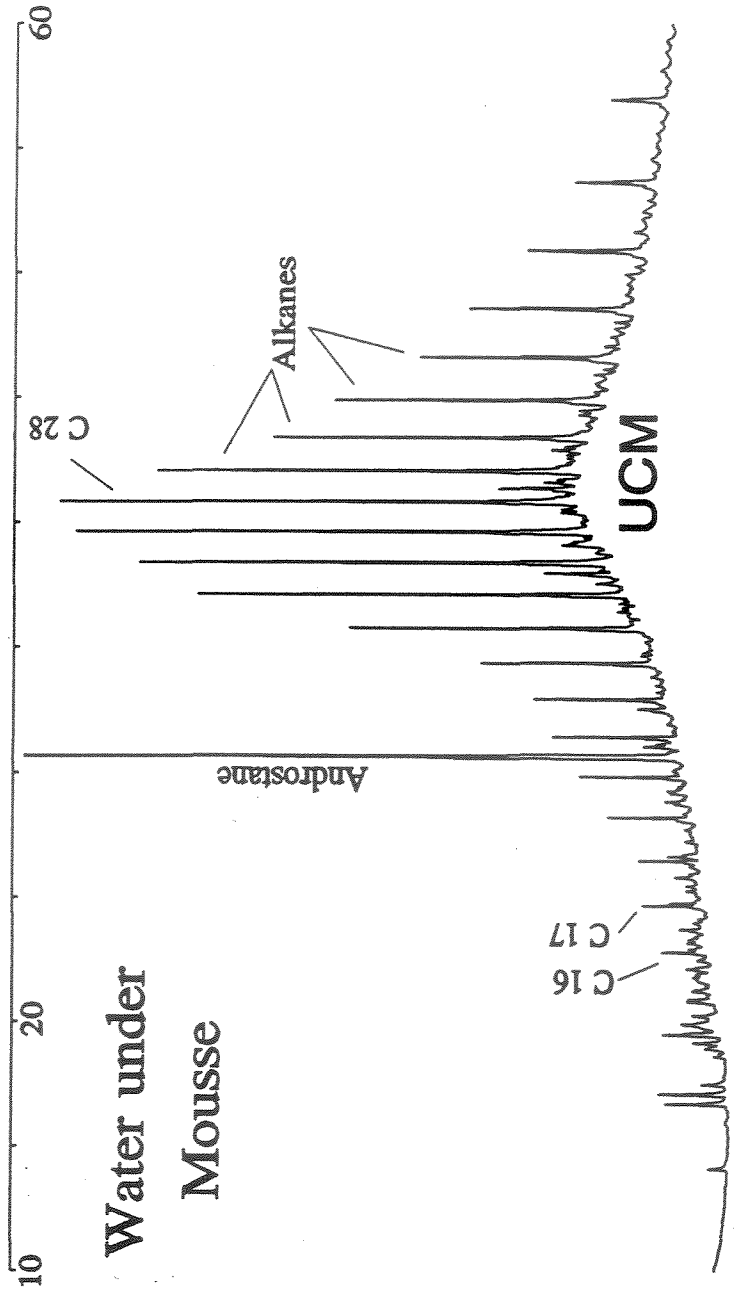

Figure 4. Chromatogram of the hydrocarbons isolated from under the oil mousse sample shown in Figure 2. See text for details.

sample collected off the beach because they degrade more slowly and the water under the oil sample collected on the 17th was not subjected to the same transport processes as the sample taken near the mouth of Tampa Bay on the 12th.

Comparison of the August 17th aqueous phase hydrocarbons with the overlying oil reveals that a number of components of the oil were present in the water in contact with it, however, the profiles are sufficiently different to indicate that droplets or colloidal particles of oil were not included in the aqueous phase to any great extent. The interesting and important factors to note are the relative abundances of different components found in these samples. The alkane profile observed in the oil is one of similar peak heights from C_{16} to C_{28}, with perhaps a maximum around C_{21} and C_{22}. The alkane profile observed in the water is quite different, this sample shows a concentration peak centered around C_{27}-C_{28}, and the alkane series appears to extend at least to C_{36} in the water sample whereas it drops off rapidly above C_{28} in the oil. This is puzzling because the aqueous phase concentration of hydrophobic compounds is dependant not only on their solubility but also on their concentration in the hydrocarbon phase. Given the low concentration of the alkanes above C_{32} in the oil, and their low aqueous solubility, we would expect that these compounds would not be present in the aqueous phase in the concentrations at which they are observed. Also, in our initial discussion of the oil profile, we noted that the smaller peaks between the alkanes were comprised mostly of alkyl-PAH. It was also stated that the low molecular weight PAH are both more soluble, and more resistant to biodegradation than are the alkanes. Given this combination of facts, one would expect the alkyl-PAH to be more significant components in the lower molecular weight range of the August 17th aqueous phase than they were determined to have been.

Hydrocarbon Profiles: Water Column Samples

The hydrocarbon profiles for these samples can be characterized as being one of three types. The first type are stations which have low total hydrocarbon content, or which have hydrocarbon abundances reflective of biogenic (marine or terrestrial) inputs (N & B). The second type is represented by stations with hydrocarbon profiles similar to the tarball or mousse samples shown in Figures 1 and 2, or which indicate a more weathered version of this (O & W). The third type of hydrocarbon profile found in these water samples is dominated by high molecular weight alkanes (C_{23}-C_{35}, A). This is an unexpected pattern to observe since, as was mentioned before, the oil samples have higher and relatively uniform *n*-alkane concentrations in the lower molecular weight range (C_{13}-C_{28}), with no visible *n*-alkanes beyond C_{31}. The alkane profile observed in these samples is similar to that found in the aqueous phase taken from under the August 17th oil sample (Figure 4), except there is no visible UCM in these water sample hydrocarbon profiles.

Examples of the latter two types of observed hydrocarbon profiles are illustrated in Figures 5 and 6. The peak labels in these chromatograms indicate the following compounds: RS 1: 1-Octadecene; QS 1: orthoTerphenyl; QS 2: 1-Docosene; RS 2: paraTerphenyl-D14. Peaks labeled contaminants are phthalates which were inadvertently introduced to the sample extracts during the extraction and workup of these samples. Comparison of these chromatograms clearly shows the differences between these two types of hydrocarbon signatures in the water samples. Figure 5 presents the hydrocarbon fraction of a water sample collected on August 12th (TB-11). Figure 6 illustrates the

hydrocarbon profile of a water sample collected on the 17th of August and is likely to represent a weathered oil signature.

SUMMARY

Water samples from various areas of Tampa Bay were sampled twice after the August 10th oil spill. The first samples were collected two days after the spill from areas which were observed to be impacted as well as areas which appeared not to be impacted by the oil spill. The second sampling 7 days after the spill also sampled areas which showed visible and no visible impacts from the surface slick. Hydrocarbon concentrations on both sampling dates and in both visibly impacted and non-impacted areas were determined to range from background levels (<0.5 μg/L) to a maximum of roughly 46 μg/L. Hydrocarbon profiles of samples with higher concentrations show significant contributions from the spilled oil.

Of the 25 samples collected from 20 sites on the 12th of August, 9 samples were found to be free of oil related hydrocarbons, 14 showed low to moderate levels of oil contamination (3 to 22 μg/L) and the remaining 2 were found to contain high levels (46 μg/L) of oil related hydrocarbons. Similar results were determined for the 12 stations sampled on August 17th, 4 samples were free of oil contamination, 6 contained low to moderate levels (3 to 15 μg/L) and 2 had high concentrations (35 & 39 μg/L) of oil hydrocarbons.

There were several features of the hydrocarbon distribution which indicated that the surface slick and subsurface hydrocarbons were transported independently of each other. These included both the finding of reasonable high hydrocarbon concentrations in areas which were not visibly oiled on the surface, and the hydrocarbon profiles observed in samples showing these higher concentrations. The independence of the subsurface hydrocarbon distribution from that of the oil slick most likely resulted from differences in flow direction of the surface and subsurface waters. This vertical mixing of the hydrocarbon contamination most likely resulted in a wider distribution of oil related hydrocarbons than was evidenced by the movement of the surface slick.

REFERENCE

National Research Council 1985. Oil in the Sea: Inputs, Fates, and Effects. Steering Committee for the Petroleum in the Marine Environment Update. Board on Ocean Science and Policy. Ocean Sciences Board. Commission on Physical Sciences, Mathematics, and Resources. National Research Council. National Academy Press. Washington, D.C. 601 pg.

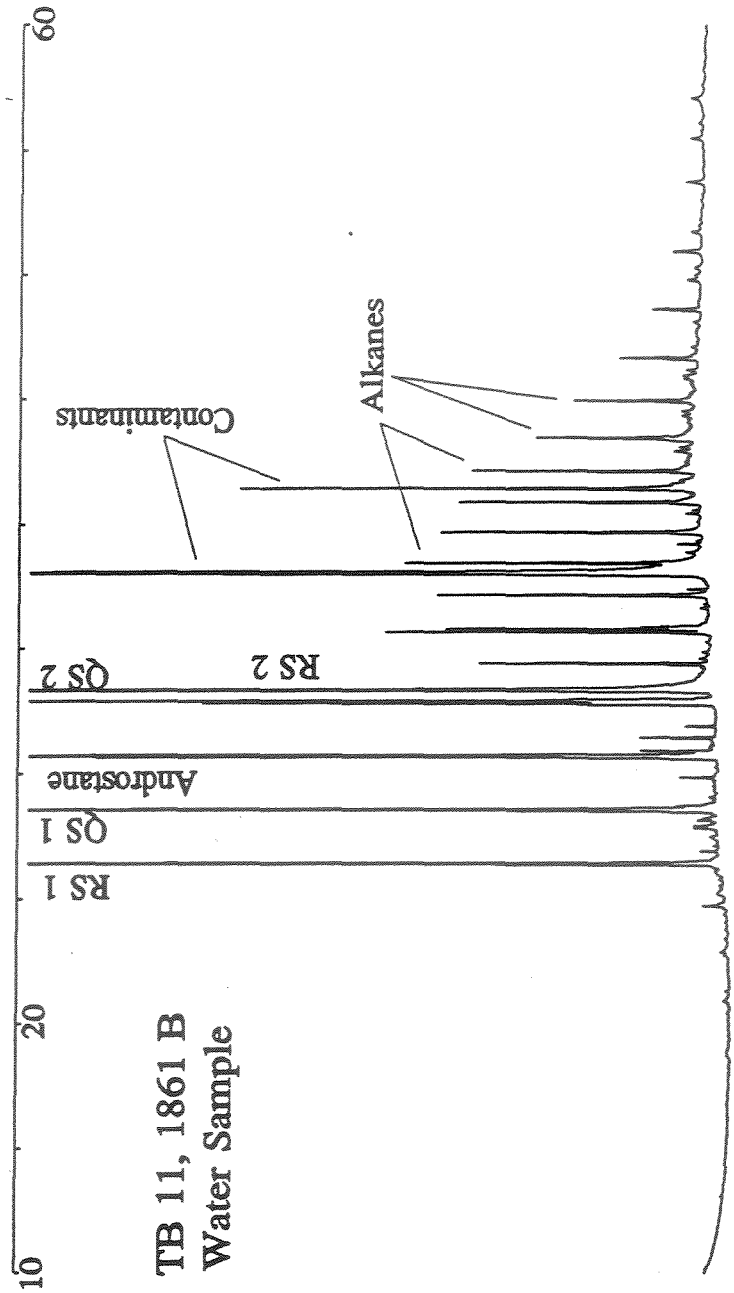

Figure 5. Chromatogram of the hydrocarbon fraction isolated from the water sample collected August 12th at station TB-11, see text for discussion.

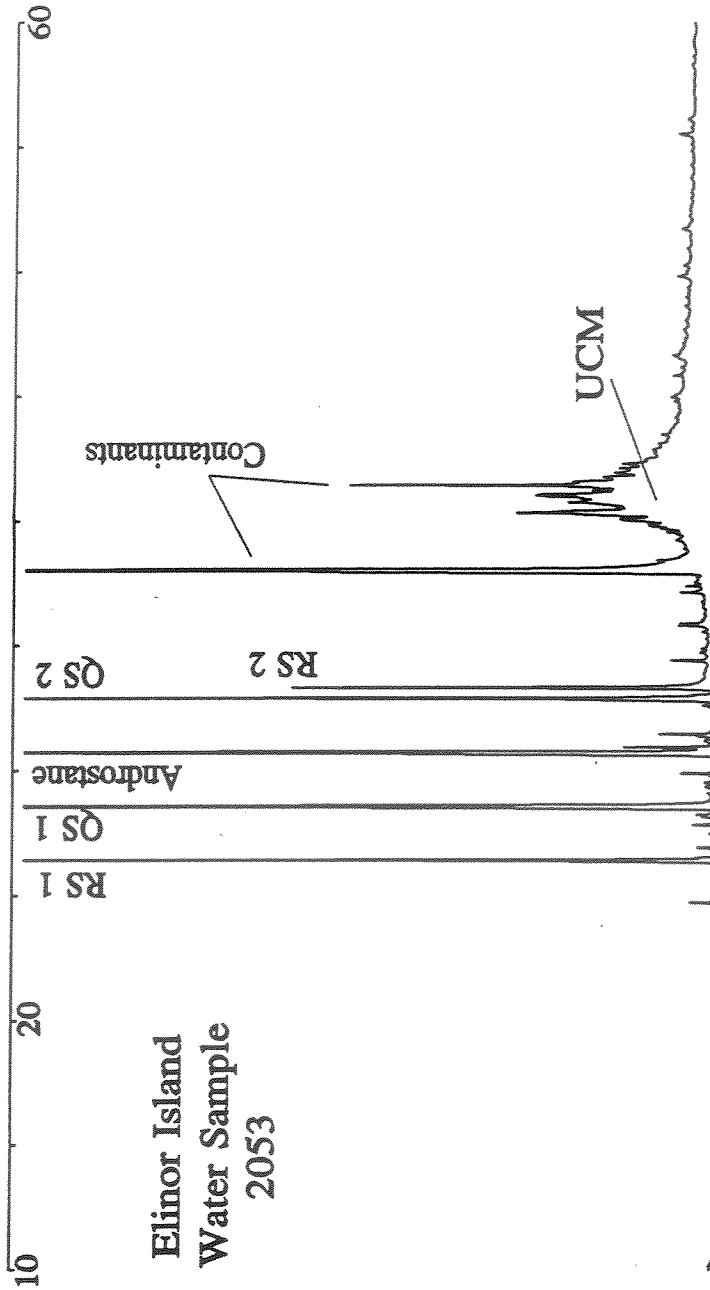

Figure 6. Chromatogram of the hydrocarbon fraction isolated from the water sample collected off Elinor Island on August 17th, see text for details.

APPENDIX 1. Quality Control/Quality Assurance Procedures

Precision and accuracy of analyses were meant to be assessed by analysis of duplicate and spiked samples. Extraction efficiency and potential loss of analytes during sample processing were assessed through the use of recovery surrogates added to the sample prior to extraction. There were two recovery surrogates used, one to simulate alkane recovery (C18:1) and one to simulate PAH recovery (p-terphenyl-d14). Results have not been corrected for recovery. Samples designated as spiked samples were amended with a solution of a crude oil spilled in Panama in 1986, this solution had already been prepared for analysis and was available prior to the dilutions of the number 6 fuel oil which was spilled. As discussed above, crude oil is composed of many types of compounds other than just the hydrocarbons, in fact it was later determined that the components isolated in our total hydrocarbon fraction comprised only about 30% (by weight) of the total mass of oil diluted for analysis. Thus, the amount of material spiked into these samples contained insufficient quantities of hydrocarbons for analysis using the analytical technique which was used for these samples. The resulting hydrocarbon contents of these samples were below the limit of quantitation and thus could not be used to evaluate our analytical accuracy.

None of the 3 procedural blanks analyzed contained quantifiable amounts of any hydrocarbons. The procedural blanks did contain the phthalates which are shown in some of the chromatograms, it is believed that these compounds contaminated the samples either during the column separation or subsequent to this step in the analysis.

One set of the 3 sample sets intended for duplicate analysis were accidently combined during the sample concentration step. This accident leaves us with only two duplicates to evaluate. The data for the remaining two duplicates show fairly variable results. Sample TB-11 (1861 A+B), gave the closer values (8.8 and 13.6 μg/L), but even these suggest inhomogeneity of the water samples (perhaps colloidal oil). The other duplicate (TB-15, 1856 A+B) is extremely divergent. One sample was found to be below the limit of quantitation, whereas the other yields a value of 18.7 μg/L. Given the low recovery of the paraTerphenyl in the BLQ sample there is the possibility that the column chromatographic separation of the compound classes in this sample was problematic, leading to a portion of the hydrocarbon fraction not being collected, causing the low recovery as well as low concentration. If an error such as this were combined with the concentration differences found in the TB-11 sample it may explain a majority of the differences between these two duplicates.

Table 3 presents the hydrocarbon data presented in Table 2 along with the data for the percent recovery of the surrogates in each of the samples analyzed. Occasional co-elution of what appears to be an alkene with the paraTerphenyl caused the recovery data for this compound to be erratic and unreliable without mass spectral confirmation.

Table 3. Hydrocarbon concentrations and recovery of surrogates (RS) in the water samples collected.

Sample #	Hydrocarbons µg / L	Percent Recovery[1] C18:1	Percent Recovery[1] p-Terphenyl
August 12 Collection			
TB-1 1839	0.8	66.9	124.7
TB-2 1840	7.2	63.3	77.6
TB-3 1841	12.4	86.3	137.8
TB-4 1842	22.4	70.2	82.6
TB-5 1844	15.1	73.7	84.4
TB-6 1845	16.9	79.4	85.1
TB-7 1846	3.3	77.4	127.3
TB-8 1859	BLQ	73.1	103.5
TB-8/9 1843	BLQ	83.0	72.2
TB-9 1857	5.9	83.5	89.1
TB-10 1853	3.2	73.1	78.5
TB11 1861A	8.8	58.1	69.9
TB11 1861B	13.6	62.3	76.5
TB-12 1851	2.6	58.8	121.4
TB13-1ft 1847 2.1		76.6	73.1
TB13-6ft 1850 10.7		88.2	99.6
TB-14 1858	9.2	84.4	90.8
TB15-1ft 1856A BLQ		89.4	97.2
TB15-1ft 1856B 18.7		70.7	74.7
TB15-6ft 1855 1.1		77.8	86.1
TB-16 1848	11.2	66.5	71.1
TB17-1ft 1854 0.8		75.8	82.6
TB17-6ft 1849 46.2		102.0	96.9
TB-18 1860	BLQ	84.2	94.3
Spill 1ft 1866 46.4		124.0	92.2
August 17 Collection			
1863 Bunces Pass	3.0	77.9	91.5
1864 Bunces Pass	BLQ	64.3	74.2
1868 Bunces Pass	BLQ	60.8	70.7
1871 Bunces Pass	10.6	80.5	88.3
1872 Bunces Pass	12.8	77.3	91.3
1873 Bunces Pass	35.5	95.5	141.9
2051 Bunces Pass	14.7	106.3	106.6
2052 East Elinor BLQ		82.9	84.8
2053 Elinor Island	39.4	80.0	78.3
2054 North John	0.5	71.1	54.5
2055 Mangrove Island	12.2	89.5	111.7
2056 South John	10.8	58.6	68.8
1851 Bottle Rinse		99.2	77.4
1856 Bottle Rinse		86.6	43.1
1861 Bottle Rinse		86.0	100.0
Blank 1		88.9	105.3
Blank 2		104.5	170.2
Blank 3		88.2	120.2
Spike 1[2]		107.2	100.7
Spike 2		79.0	144.2
Spike 3		72.4	134.2

[1]Hydrocarbon results are not adjusted for recovery of the surrogates, it is apparent that there was occasional interference (co-elution) with the para-terphenyl peak, leading to significantly greater than 100% recoveries.
[2]These water samples were spiked with a solution of crude oil, however, the concentration was inappropriate for the analytical procedure decided upon. Spiked concentrations were all below the limit of quantitation.