

DEPARTMENT OF NATURAL RESOURCE PROTECTION

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**A SURVEY OF PETROLEUM HYDROCARBONS
IN PORT EVERGLADES SURFACE WATERS**

ENVIRONMENTAL MONITORING DIVISION

JUNE 1998

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Executive Summary

In March 1998, a Nova-Southeastern University researcher reported that water drawn from Port Everglades surface waters smelled of diesel fuel and was killing shrimp he used in breeding experiments. The researcher suggested that ground water, contaminated as a result of decades of fuel importing activities, had seeped into Port surface waters. In April 1998, the Broward County Department of Natural Resource Protection launched a study to determine if (1) there is evidence of petroleum in Port surface waters, (2) if petroleum-contaminated ground water could be a source of the contamination and (3) if ambient concentrations of petroleum were high enough to be toxic to shrimp.

Nine sites located near the sea walls around the periphery of the Port were sampled and tested for both light and heavy-weight petroleum hydrocarbons. Sampling was conducted at low tide when the highest hydrocarbon concentrations would be expected to highest as ground water flows back into the Port.

The results of the testing suggested that there was no wide-spread petroleum contamination in Port surface waters. Although very low levels of seven different hydrocarbons were detected in the Port water samples, only two of these (benzene & methyltertbutylether) were associated with petroleum products and three others (trichlorofluoromethane, methylene chloride and chloroform) were thought to come from the laboratory atmosphere. Benzene was detected in one sample at 0.03 ug/l. Methyltertbutylether (MTBE), a water-soluble component of gasoline, was detected at part per billion levels throughout the Port. The lack of a clear MTBE concentration gradient originating at the sea walls, however, failed to support the contention that ground water migration was a source of the contamination. Although contaminated ground water cannot be ruled out, a more plausible explanation for the occurrence of MTBE in Port waters is the expulsion of unburned fuel from the many fuel-inefficient outboard motors that traverse the inland waterways.

None of the hydrocarbons were detected at levels that would be expected to be toxic to members of the crustacean family of which shrimp are members. An alternate explanation for the researcher's notice of diesel fuel odors in the water may be the sporadic release of fuel from vessels at the nearby docks. Lightweight petroleum hydrocarbons, responsible for the diesel fuel smell, are the first chemical components lost as petroleum ages in the environment. The ground water petroleum contamination is unlikely to contain high concentrations of these more volatile compounds.

1.0 INTRODUCTION

Port Everglades is the second largest petroleum distribution facility in the United States and the largest import, storage and distribution center for petroleum products in Florida. In 1993, 668 petroleum tankers/barges called at the Port delivering 98,236,000 tons of petroleum products (gasoline, jet fuel, diesel, residual fuel asphalt, crude oil propane and aviation gasoline). The petroleum is pumped through a maze of underground pipelines from ships and stored in 264 tanks at the Port. As a result of over 70 years of fuel importation activities, a lens of petroleum products has formed on the ground water beneath the Port. The Port Everglades Environmental Corporation (PEECO), a consortium of oil companies who are involved in the initial receipt, storage and handling of petroleum products from ship to storage area, completed an initial assessment of subsurface contamination in 1991. This assessment indicated that, of the 394 ground water monitoring wells, recovery wells and well points that were in existence at the time, approximately 62 wells contained measurable amounts of free phase petroleum hydrocarbon (FPPH). The thickness of the FPPH within the contaminated wells ranged from 0.1 to 7.95 feet (PEECO, 1991).

In March 1998, a researcher at the Nova-Southeastern University Oceanographic Laboratory in Port Everglades reported problems with keeping shrimp alive during breeding experiments at the Nova Oceanographic Laboratory near the mouth of Port Everglades. The intake for the breeding tanks was located near the mouth of the Port. He had noted the odor of diesel in the tanks shortly before the shrimp began to die and attributed the shrimp mortality to petroleum contamination of Port waters (Chabot, 1998).

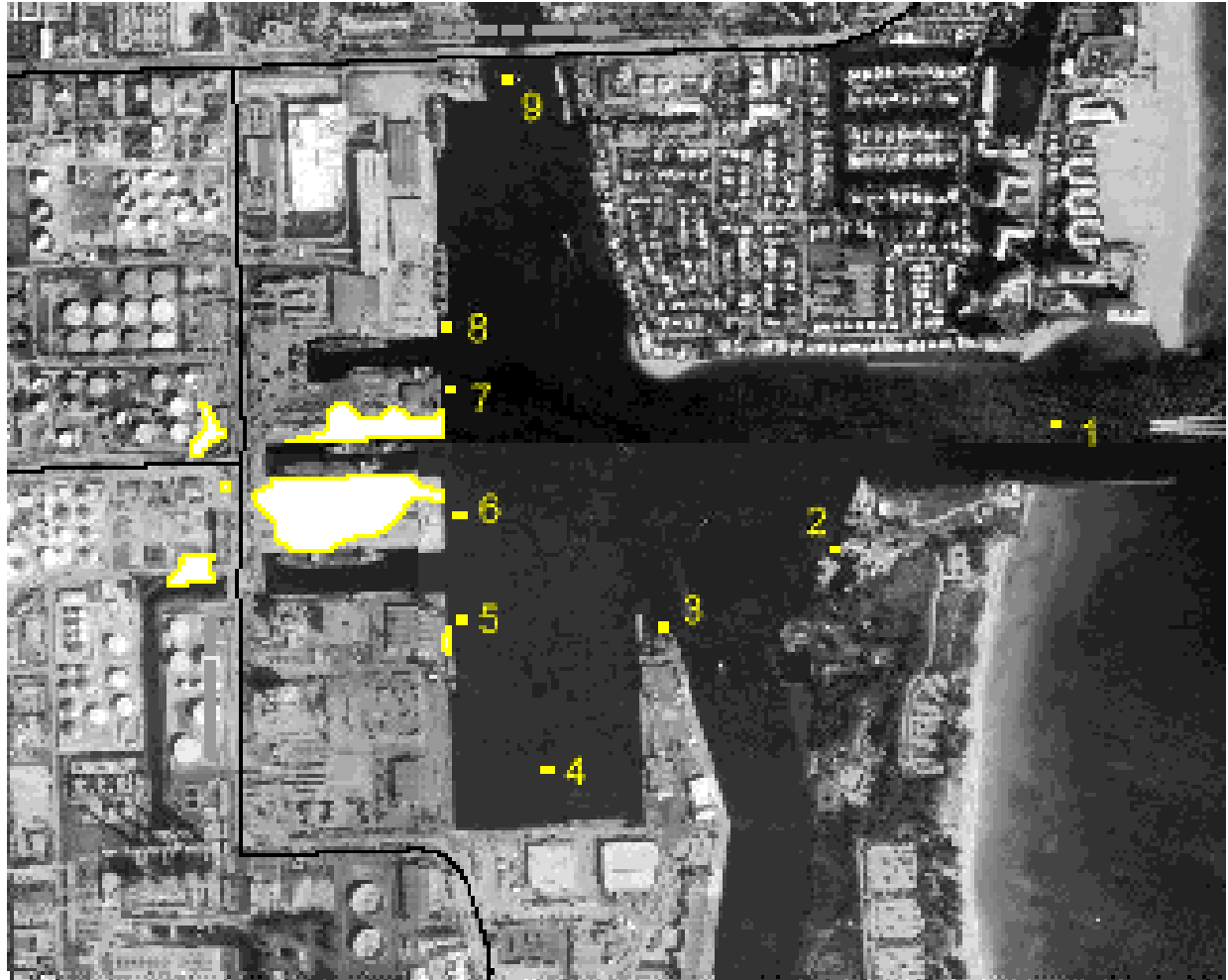
In April 1998, the Broward County Department of Natural Resource Protection conducted a study to determine if (1) there is evidence of petroleum in Port surface waters (2) if contaminated ground water could be a source of surface water contamination and (3) if any hydrocarbons detected in surface waters were at levels that could be toxic to shrimp.

2.0 METHODOLOGY

Figure 1 depicts Port Everglades surface waters, the 9 sampling sites of this study, and approximate contours defining the extent of FPPH as determined by the PEECO study. The sampling sites, located on the periphery of the Port, were selected to determine hydrocarbon concentrations in surface water near the sea walls where hydrocarbon concentrations would be expected to be highest if contaminated ground water was migrating to the surrounding surface waters. One of the sites was sampled in duplicate to assess sampling reproducibility. Sampling was conducted on April 22, 1998 from noon to 1 pm. A light rain was falling during the sampling (0.06" recorded at Peele-Dixie water plant located 5 miles west of the Port). No other rainfall had been recorded in the previous 7 days. The sampling was done near low tide (11:20 am at the turning basin) because surface water hydrocarbon concentrations would be expected to be highest at this time if hydrocarbon-contaminated ground water was moving into the Port during the outgoing tide. A site near the shrimp tank water intake was also sampled. A laboratory blank made from organic-free water was analyzed to check for laboratory contamination.

Samples were collected by hand at the surface, packed in ice and transported to the DNRP laboratory for analyses. Since petroleum hydrocarbons are generally insoluble in water, surface samples would be expected to contain the highest levels of any contamination. Two analytical methods were used to measure petroleum hydrocarbons in the samples. EPA method 8260 (USEPA, 1985) was used to measure light-weight hydrocarbons typical of gasoline such as benzene, toluene and xylene. Method FL-PRO (FDEP, 1995) was used to measure heavier-weight aromatic and aliphatic hydrocarbons characteristic of diesel fuel and crude oil.

FIGURE 1
LOCATION OF SAMPLE COLLECTION SITES



500 0 500 Feet



3.0 RESULTS

No detectable levels (<0.1 ppb) of the heavier-weight hydrocarbons were found using method FL-PRO.

Low levels (<1 ppb) of seven volatile hydrocarbons were detected in the samples. Methyltertbutylether, an anti-knock compound added to gasoline was also detected in all samples. Several trihalomethane (THM) compounds, which are common in chlorinated drinking water, were detected at very low levels. One of the THMs, chloroform, was detected in every sample. Trichlorofluoromethane, a refrigerant gas, was detected in 4 samples, also at sub-ppb levels. Methylene chloride, a solvent and ingredient in paint stripper, was detected in 4 samples at levels near the detection limit. Chloroform and methylene chloride, are solvents commonly used in the laboratory. A “blank” water sample, analyzed at the same time as the samples, showed evidence of contamination with chloroform, trichlorofluoromethane and methylene chloride. This observation suggests that the laboratory is the source of these compounds. Benzene, a component of gasoline, was detected in only one sample at a level near the method detection limit. Table 1 summarizes the results of the EPA method 8260 tests.

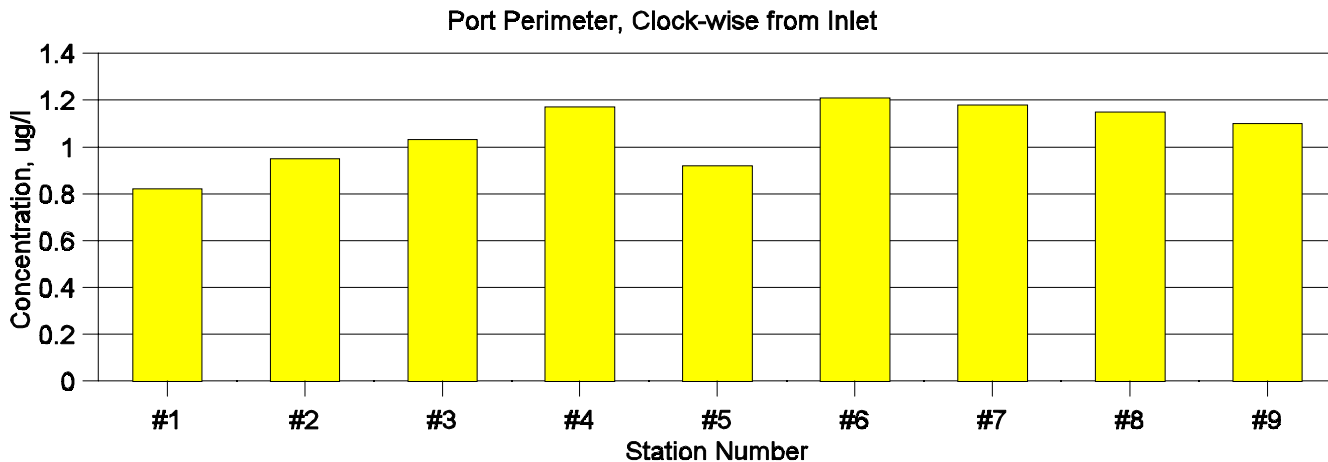
TABLE 1
Results of EPA Method 8260 Tests for Light-weight Hydrocarbons

HYDROCARBON	# of detection s	mean ug/l	std dev ug/l	maximum ug/l	detection limit ug/l	Present in Blank?
benzene	1	0.03	NA	0.03	0.01	No
bromoform	1	0.06	NA	0.06	0.04	No
bromodichloromethane	2	0.03	0.00	0.03	0.02	No
trichlorofluoromethane	4	0.05	0.00	0.06	0.01	Yes
methylene chloride	4	0.19	0.02	0.21	0.10	Yes
chloroform	10	0.12	0.06	0.28	0.10	Yes
MTBE	10	1.08	0.16	1.37	0.29	No

Figure 2 depicts MTBE concentrations found in Port waters. MTBE appeared to exhibit a very slight concentration gradient; higher levels in the western and southern areas of the Port, decreasing to the north and east.

FIGURE 2

MTBE Concentrations in Port Everglades



4.0 DISCUSSION

A lens of free-phase petroleum hydrocarbons (FPPHs) from years of fuel delivery and storage floats on the ground water under Port Everglades. A recent article in a weekly magazine suggested that seepage was occurring into the surface water of the Port and questioned the impact of the contamination on aquatic organisms. This study was undertaken to determine if the petroleum hydrocarbons were present in the surface water surrounding the Port.

Heavy-weight hydrocarbons, characteristic of diesel and crude oil were not found at any of the nine sample sites in the Port. The absence of these compounds suggests that FPPHs in the ground water are not leaking into the Port surface waters at detectable levels. Their relatively low toxicity and scarcity in the samples suggests that these heavier hydrocarbons do not appear to be an immediate threat to local aquatic flora and fauna.

The toxicity of petroleum products is more often associated with low molecular weight volatile components like toluene and benzene. A number of these compounds were found albeit at very low concentrations in the Port samples. Methyltertbutylether and chloroform were detected in all the samples while trichlorofluoromethane was found at four of the nine sites. With the exception of these three compounds, all other detected hydrocarbons were present at levels too low to reliably measure. Other than noting their detection, no significance can be associated with their presence in surface waters. The presence of chloroform, trichlorofluoromethane, and methylene chloride in the laboratory blank suggest that these compounds were not actually present in the surface waters but came from the laboratory.

MTBE levels were fairly uniform (0.82-1.37 ug/l). A slight concentration gradient was apparent; higher levels in the western and southern areas of the Port, decreasing to the north and east. The variability of the results for MTBE evident from the duplicate samples collected at Site 6 (1.37 & 1.06 ug/l), however, suggest that there may not be any significance to the apparent gradient. MTBE is unique among the petroleum hydrocarbons detected in this study in that it is much more soluble in water (51 g/l) than the others (e.g., benzene, 0.62 g/l) . This solubility, together with the plethora of gasoline-powered vessels plying the waters of the Port and surrounding waterways, may explain its occurrence at the relatively high levels seen in this survey although contaminated ground water cannot be ruled out as the source of the MTBE. Outboard motors are notorious for their inefficient use of fuel; unburned, insoluble hydrocarbon fuel components would be expected to float on the surface and quickly evaporate while the water-soluble MTBE would remain in the water column.

Chloroform was detected in all of the surface water samples. The observation of chloroform in the laboratory blank, however, suggests that the source of the chloroform is the laboratory atmosphere.

Trichlorofluoromethane was detected in samples collected at stations 3, 4, 5 and 6a, in the general vicinity of the turning basin. The measured levels were very low and uniform for this compound and no center of contamination was evident. This compound was also found in the laboratory blank. Trichlorofluoromethane is not normally associated with petroleum products. This compound is a common laboratory atmosphere contaminant and is likely to have gotten into the samples during storage.

Methylene chloride was detected in four samples. Traces of this compound were also detected in the laboratory blank. The origin of these compounds is also believed to be the laboratory atmosphere.

The final question to be answered by this study is whether the levels of hydrocarbons found in Port surface waters are at levels that could be toxic to shrimp. Table 2 provides some information on toxicity of certain volatile organic compounds (VOC) to members of the crustacean family. It should be noted that toxicity data specific for shrimp were not available and some of the crustaceans listed in the table are fresh water species.

TABLE 2

Toxicity of Hydrocarbons to Crustaceans*

Compound	Species	Toxicity Test	24 hr	96 hr	Maximum Study Concentration
Benzene	<i>Daphnia magna</i>	LC ₅₀		20 ug/l	0.03 ug/l
Bromoform	<i>Crangon septemspinosa</i>				0.06 ug/l
Chloroform	<i>Daphnia magna</i>	LC ₅₀	290 ug/l		0.28 ug/l
Methylene chloride	<i>Daphnia magna</i>	LC ₅₀		220 ug/l	0.21 ug/l
MTBE	<i>Alburnus alburnus</i>	LC ₅₀	1,700 ug/l		1.37 ug/l
Naphthalene	<i>Calanus finmaricus</i>	LC ₅₀		3.8 ug/l	<0.1 ug/l

* (Ramamoorthy and Baddaloo, 1995)

The data in Table 2 indicates that the levels of petroleum hydrocarbons that are toxic to common test species of the crustacean family are many times higher than the levels found in Port surface waters. For this reason, ambient hydrocarbon concentrations were an unlikely cause of the shrimp mortality seen at the Nova laboratory. Since the intake for the shrimp farm was near the docks of the laboratory, a release of gasoline, diesel fuel or fuel-contaminated bilge water from one of the docked boats could have contaminated the surrounding waters to levels toxic to the shrimp. By extending the tank intakes to well below the water's surface, the contamination risk to the shrimp tanks by this mechanism could be greatly reduced.

5.0 CONCLUSIONS

The absence of detectable levels of heavy-weight petroleum hydrocarbons in Port surface waters suggest diesel or crude oil type hydrocarbons are not migrating from contaminated Port ground waters.

Although the presence of an apparent MTBE concentration gradient showing higher concentrations in the vicinity of the petroleum off-loading area suggests the possibility of petroleum-contaminated ground water flowing into Port surface waters during the outgoing tide, the precision of the measurements minimizes the significance of the observed gradient. The large number of fuel-inefficient outboard motor-powered vessels is a more plausible source of the MTBE. The absence of other light-weight petroleum products, however, suggests that these highly water-insoluble compounds are not migrating with the ground water and thus not contributing to surface water contamination.

In any event, remediation and removal of the free product petroleum hydrocarbon should be encouraged and expedited to reduce any future threat by it to the Port surface waters.

The ambient levels of petroleum hydrocarbons in Port surface waters is far below that shown to be toxic to members of the crustacean family. Shrimp mortality seen at the Nova laboratory is not due to ambient hydrocarbon levels but could be due to the sporadic release of fuels (e.g., contaminated bilge water, careless

fueling, leaks, etc.) from boats moored near the shrimp tank intake. Extension of the water intake deeper into the water column may alleviate this concern.

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APPENDIX

SURFACE WATER QUALITY DATA
All Results in Micrograms/liter

STATION #	1	2	3	4	5	6A	6B	7	8	9	Blank
Petroleum Range Organics	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzene	0.030	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoform	0.060	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloro-methane	ND	ND	ND	ND	ND	ND	ND	0.025	ND	0.030	ND
Chloroform	0.060	0.080	0.090	0.100	0.110	0.130	0.120	0.130	0.130	0.280	0.09
Methylene Chloride	ND	ND	0.190	0.210	0.160	0.200	ND	ND	ND	ND	0.39
MTBE	0.820	0.950	1.030	1.170	0.920	1.370	1.060	1.180	1.150	1.100	ND
Trichlorofluoro-methane	ND	ND	0.050	0.050	0.050	0.060	ND	ND	ND	ND	0.06

QUALITY ASSURANCE OBJECTIVES

METHOD	ANALYTE	PRECISION % Rel. Dif.	ACCURACY % Range	MDL	CONC UNITS
FL-PRO	PETROLEUM RANGE ORGANICS	0-20	41-101	0.100	UG/L
EPA 8260	DICHLORODIFLUOROMETHANE	0-14.8	69.3-110.7	0.054	UG/L
EPA 8260	CHLOROMETHANE	0-6.4	68.1-117.9	0.101	UG/L
EPA 8260	VINYL CHLORIDE	0-7.0	78.5-117.5	0.109	UG/L
EPA 8260	BROMOMETHANE	0-6.0	71.6-118.4	0.072	UG/L
EPA 8260	CHLOROETHANE	0-10.4	65.0-113.0	0.053	UG/L
EPA 8260	TRICHLOROFLUOROMETHANE	0-14.5	67.4-110.6	0.012	UG/L
EPA 8260	1,1-DICHLOROETHENE	0-7.1	75.1-112.9	0.022	UG/L
EPA 8260	METHYLENE CHLORIDE	0-8.9	80.0-110.0	0.099	UG/L
EPA 8260	T-1,2-DICHLOROETHENE	0-8.4	77.4-108.6	0.017	UG/L
EPA 8260	METHYLTERTBUTYLETHER	0-11.1	76.7-115.3	0.288	UG/L
EPA 8260	1,1-DICHLOROETHANE	0-10.7	30.8-142.9	0.024	UG/L
EPA 8260	2,2-DICHLOROPROPANE	0-4.8	56.0-115.0	0.043	UG/L
EPA 8260	C-1,2-DICHLOROETHENE	0-5.2	80.9-121.1	0.028	UG/L
EPA 8260	BROMOCHLOROMETHANE	0-7.2	72.9-107.1	0.031	UG/L
EPA 8260	CHLOROFORM	0-1.77	73.5-106.5	0.017	UG/L
EPA 8260	1,1,1-TRICHLOROETHANE	0-7.0	74.3-121.7	0.054	UG/L
EPA 8260	CARBON TETRACHLORIDE	0-23.5	61.8-106.2	0.087	UG/L
EPA 8260	1,1-DICHLOROPROPENE	0-7.85	71.9-124.1	0.069	UG/L
EPA 8260	2-CHLOROETHYL VINYL ETHER	0-12.4	94.4-107.6	0.024	UG/L
EPA 8260	BENZENE	0-10.5	87.1-110.9	0.010	UG/L
EPA 8260	1,2-DICHLOROETHANE	0-9.6	89.8-107.9	0.038	UG/L
EPA 8260	TRICHLOROETHENE	0-4.1	70.5-109.5	0.015	UG/L
EPA 8260	1,2-DICHLOROPROPANE	0-7.3	79.3-114.7	0.024	UG/L
EPA 8260	DIBROMOMETHANE	0-7.8	83.2-116.8	0.030	UG/L
EPA 8260	BROMODICHLOROMETHANE	0-12.9	86.3-103.7	0.022	UG/L
EPA 8260	C-1,3-DICHLOROPROPENE	0-6.00	89.0-106.9	0.041	UG/L
EPA 8260	TOLUENE	0-8.0	77.7-126.3	0.022	UG/L
EPA 8260	T-1,3-DICHLOROPROPENE	0-7.1	89.4-106.2	0.031	UG/L
EPA 8260	1,1,2-TRICHLOROETHANE	0-7.25	81.2-126.8	0.035	UG/L
EPA 8260	TETRACHLOROETHENE	0-5.60	71.0-107.0	0.024	UG/L
EPA 8260	1,3-DICHLOROPROPANE	0-12.8	78.9-113.1	0.031	UG/L
EPA 8260	DIBROMOCHLOROMETHANE	0-9.80	72.5-111.5	0.030	UG/L
EPA 8260	1,2-DIBROMOETHANE (EDB)	0-7.60	90.0-114.0	0.024	UG/L
EPA 8260	CHLOROBENZENE	0-6.30	80.6-115.4	0.024	UG/L
EPA 8260	1,1,1,2 TETRACHLOROETHANE	0-7.1	71.7-128.3	0.022	UG/L
EPA 8260	ETHYLBENZENE	0-8.0	73.8-124.2	0.025	UG/L
EPA 8260	ETA/PARA XYLENE	0-37.7	80.0-128.0	0.038	UG/L
EPA 8260	ORTHO XYLENE	0-8.4	80.8-125.2	0.017	UG/L
EPA 8260	STYRENE	0-6.1	80.1-123.9	0.028	UG/L
EPA 8260	BROMOFORM	0-8.9	81.8-120.2	0.042	UG/L
EPA 8260	ISOPROPYL BENZENE	0-16.8	78.9-119.1	0.034	UG/L
EPA 8260	BROMOBENZENE	0-9.9	83.5-116.5	0.035	UG/L
EPA 8260	1,1,2,2 TETRACHLOROETHANE	0-10.8	73.9-108.1	0.035	UG/L
EPA 8260	1,2,3-TRICHLOROPROPANE	0-8.8	78.0-138.0	0.114	UG/L
EPA 8260	N-PROPYLBENZENE	0-15.9	82.6-117.4	0.028	UG/L
EPA 8260	2-CHLOROTOLUENE	0-11.8	73.2-106.8	0.047	UG/L
EPA 8260	4-CHLOROTOLUENE	0-8.2	74.4-123.6	0.035	UG/L
EPA 8260	1,3,5-TRIMETHYLBENZENE	0-15.3	71.6-120.4	0.031	UG/L
EPA 8260	TERT-BUTYLBENZENE	0-15.7	79.8-124.2	0.031	UG/L
EPA 8260	1,2,4-TRIMETHYLBENZENE	0-14.7	75.0-123.0	0.040	UG/L
EPA 8260	SEC-BUTYLBENZENE	0-5.30	77.2-122.8	0.035	UG/L
EPA 8260	1,3-DICHLOROBENZENE	0-15.1	78.6-119.4	0.042	UG/L
EPA 8260	1,4-DICHLOROBENZENE	0-8.9	83.2-122.8	0.188	UG/L
EPA 8260	PARA-ISOPROPYL TOLUENE	0-9.3	78.9-119.1	0.040	UG/L
EPA 8260	1,2-DICHLOROBENZENE	0-8.5	75.6-110.4	0.040	UG/L
EPA 8260	N-BUTYL BENZENE	0-14.4	77.2-122.8	0.054	UG/L
EPA 8260	1,2,4-TRICHLOROBENZENE	0-7.2	81.0-135.0	0.112	UG/L
EPA 8260	HEXACHLOROBUTADIENE	0-15.9	79.6-120.4	0.113	UG/L
EPA 8260	NAPHTHALENE	0-11.1	78.2-129.8	0.116	UG/L
EPA 8260	1,2,3-TRICHLOROBENZENE	0-12.7	80.8-137.2	0.171	UG/L

MDL=Method Detection Limit

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10. SUPPLEMENTARY NOTES			
11. ABSTRACT <i>THIS REPORT DESCRIBES A STUDY OF SURFACE WATERS IN PORT EVERGLADES, LOCATED IN FORT LAUDERDALE, FLORIDA (1) TO DETERMINE AMBIENT CONCENTRATIONS OF PETROLEUM HYDROCARBONS, (2) TO EVALUATE THE POSSIBILITY OF SURFACE WATER CONTAMINATION RESULTING FROM THE MIGRATION OF PETROLEUM CONTAMINATED GROUND WATER, AND (3) TO ASSESS THE POTENTIAL FOR HARM TO SHRIMP BEING BRED IN PORT SURFACE WATERS.</i> <i>NINE SITES ON THE PERIPHERY OF PORT SURFACE WATERS WERE SAMPLED AND TESTED FOR LIGHT AND HEAVY WEIGHT HYDROCARBONS. SEVEN COMPOUNDS WERE DETECTED; THREE WERE AT LEVELS ABOVE THE PRACTICAL QUANTITATION LIMIT. CHLOROFORM AND METHYL TERT BUTYLETHER (MTBE) WERE FOUND IN ALL SAMPLES. THE MTBE WAS ATTRIBUTED TO UNBURNED FUEL FROM OUTBOARD MOTORS. THE CHLOROFORM MAY HAVE BEEN A LABORATORY CONTAMINANT.</i> <i>WIDE-SPREAD CONTAMINATION OF PORT SURFACE WATERS WAS NOT EVIDENT. CLEAR EVIDENCE OF CONTAMINATION FROM GROUND WATER WAS NOT FOUND. THE LEVELS OF THOSE HYDROCARBONS THAT WERE DETECTED WAS WELL BELOW CRUSTACEAN TOXICITY LEVELS.</i>			
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