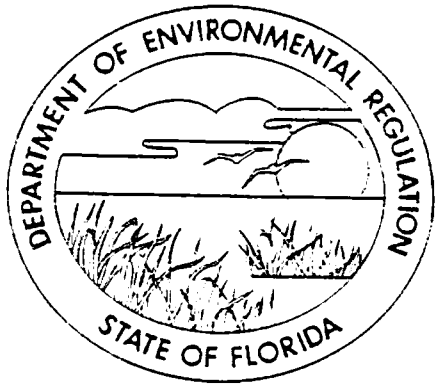


BIOSSAYS OF SEMINOLE REFINING, INC.

ST. MARKS, WAKULLA CO., FLORIDA

NPDES #FL0035220

Biological Section
Bureau of Water Analysis
December 3, 1980

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INTRODUCTION

Seminole Refining, Inc. is located in the City of St. Marks, Wakulla County, approximately 20 miles southeast of Tallahassee (Fig. 1). The plant is situated directly on the St. Marks River, 1.2 nautical miles upstream of the confluence of the St. Marks and Wakulla Rivers (Fig. 2).

The company processes up to 15,000 barrels per day of crude oil to produce military jet fuel (JP-4), #2 fuel oil, #5 fuel oil and asphalt. During the refining process, a crude topping unit and a vacuum unit are utilized to produce the desired products. Wastewater is generated from crude desalting, boiler blowdown, and miscellaneous minor sources including some cooling water.

A flow-through bioassay, and several static bioassays were performed by DER at this facility during early June 1979, to document the suspected toxicity of their wastewater. At that time, the discharge from NPDES outfall #001 was extremely toxic (Table 1). Since those tests, Seminole Refining, Inc, has implemented a large number of improvements in their wastewater treatment system (see attached letter from Kevin Songer to Craig Dye). To document any change in the toxicity of the Seminole discharge since the introduction of their new pollution control measures, the Biological Section conducted two 48 hour static bioassays beginning on 7 July 1980 on grab samples from outfall #001. The results of these tests are presented herein.

FIGURE 1

St. Marks River and Surrounding Area

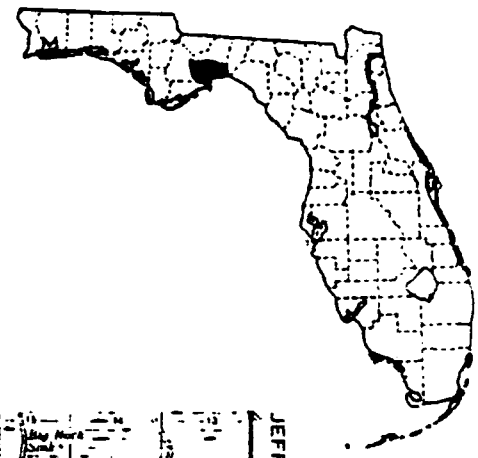
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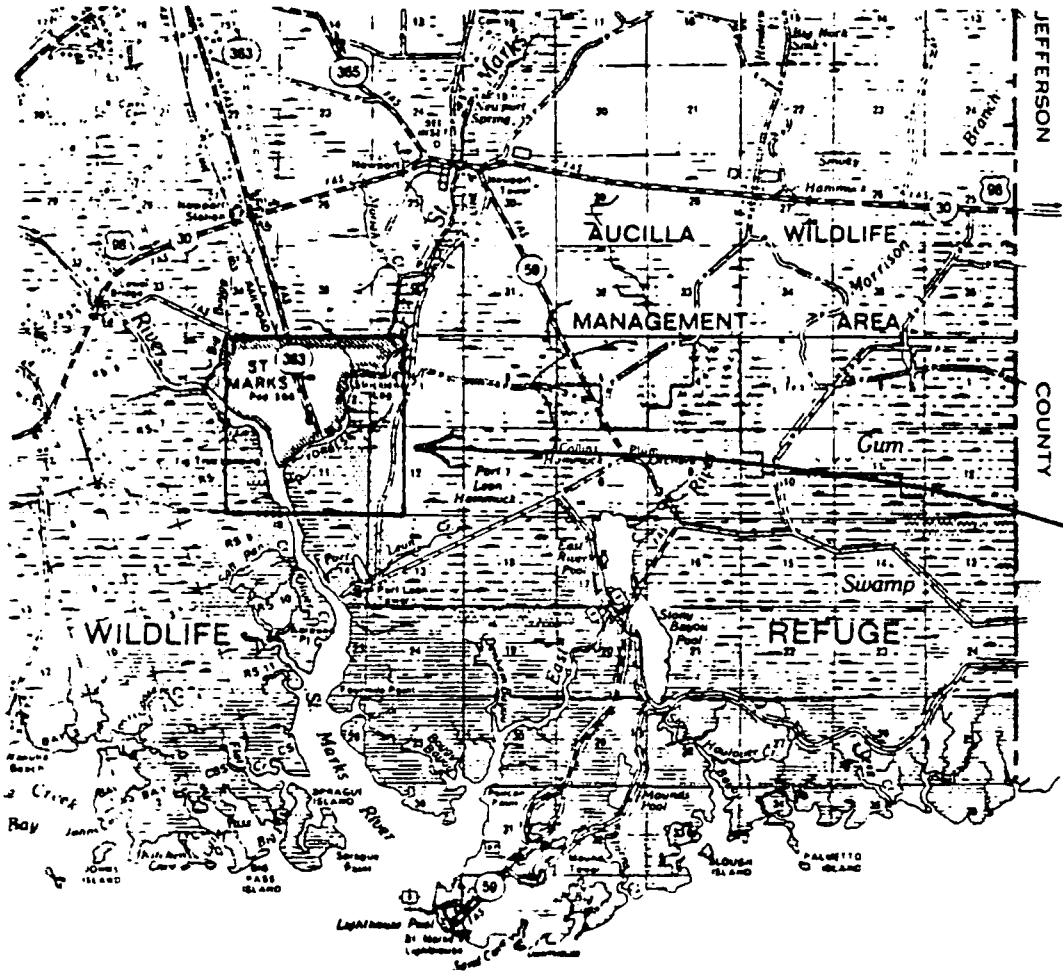
WAKULLA COUNTY

FLORIDA

PREPARED BY THE
PHOTOGRAMMETRIC DIVISION
FOR THE
TRAFFIC AND PLANNING DIVISION
FLORIDA STATE ROAD DEPARTMENT
IN COOPERATION WITH THE
U.S. DEPARTMENT OF COMMERCE
BUREAU OF PUBLIC ROADS

SCALE





General location of Study Area

FIGURE 2

Location of Point of Discharge from Seminole Asphalt

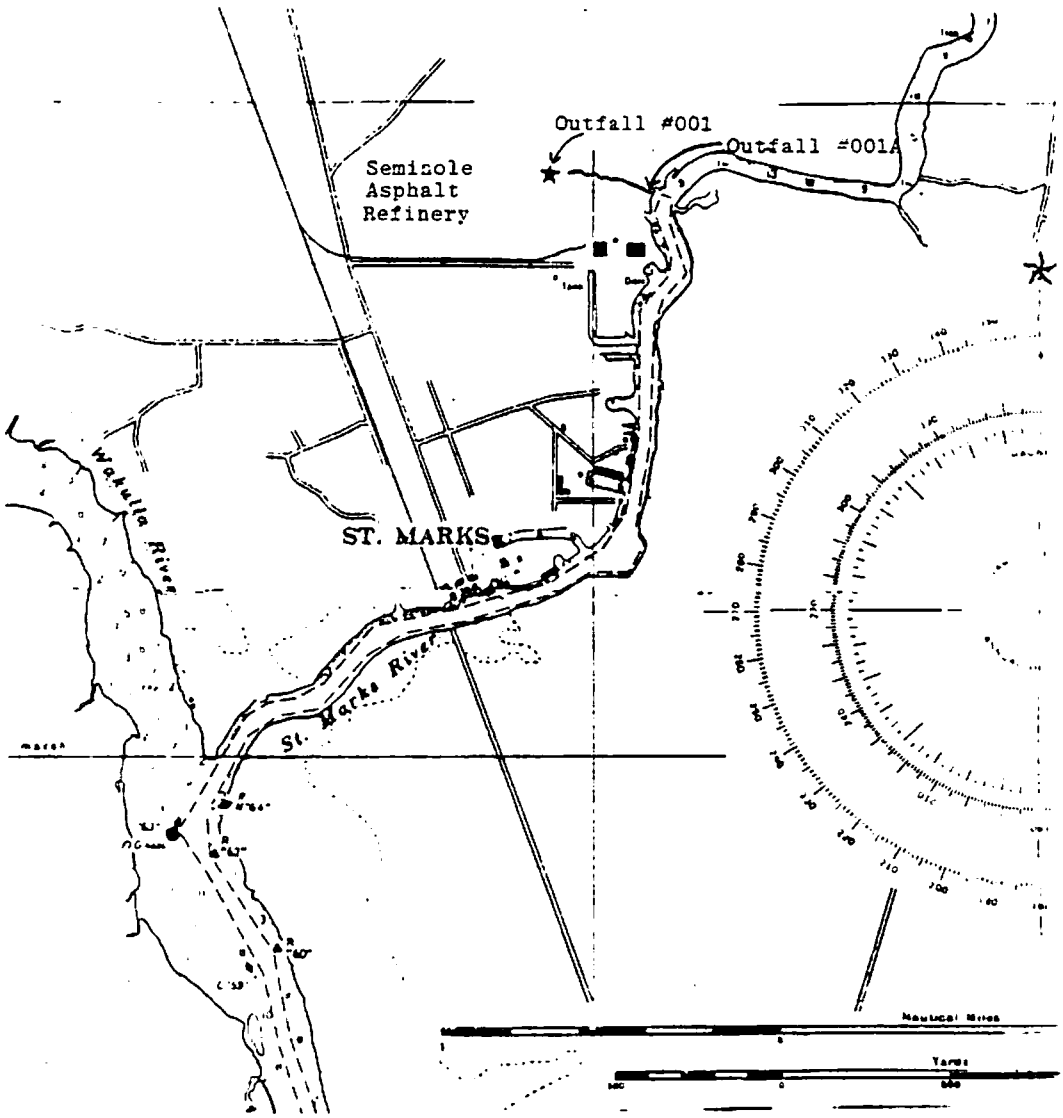


Table 1.

LC_{50} values for various organisms obtained during DER bioassay of Seminole Asphalt, Inc. June, 1979.

Type of Test	Organism	LC_{50}
96 hr. flow-through	Mysidopsis bahia (mysid shrimp)	0.65%
48 hr. static	Mysidopsis bahia	1.2%
96 hr. static	Pimephales promelas (fathead minnow)	5.02%
96 hr. static	Lepomis machrochirus (bluegill sunfish)	14.17%

METHODS AND MATERIALS

Test methods used to conduct these static bioassays are extensively described by Peltier (1978). The organisms selected for this study are among those recommended by Peltier (1978) and the U.S. EPA (1978). Life histories of these test organisms and maintenance procedures used to culture them are detailed below.

History and Maintenance of Bioassay Organisms

Daphnia pulex (water flea)

A breeding culture of Daphnia pulex was obtained from the EPA laboratory in Athens, Georgia on March 9, 1979. This culture has been maintained since its arrival, in 2½ gallon all glass aquaria using a 16:8 hour light-dark cycle. Organisms have been fed a liquified blend of Purina Trout Chow ® and Cerophyl ® twice daily.

Mysidopsis bahia (mysid shrimp)

On 19 September 1978 approximately 300 adult mysid shrimp (Mysidopsis bahia) were obtained from the Gulf Breeze EPA Laboratory in Pensacola, Florida. The mysids were cultured under continuous lighting in two 15 gallon and two 10 gallon aquaria equipped with undergravel filtration. Sea water was obtained from the FSU Marine Laboratory located at Turkey Point, Florida (salinity range 17-31 0/00). The mysids were fed twice daily with freshly hatched Artemia salina (brine shrimp) and kept at a constant temperature of $22^{o} \pm 1^{o}C$.

Test Methods

Two separate 48 hour static bioassays were conducted from 1315 hours 7 July to 1330 hours 9 July 1980, on a grab sample of effluent from outfall #001. The sample was collected by Mr. Charles Biedermann of DER's Biological Section using standard wastewater sampling procedures. Separate samples were obtained for chemical and biological testing. Samples for organic chemical analysis and for the bioassays were unpreserved. The samples were iced and transported to the DER laboratory in Tallahassee within 24 hours of collection.

Freshwater for dilution of the effluent sample was obtained from the same unchlorinated DER well that is used to culture the test organisms. The concentration series selected for this study (Table 2) is that recommended by APHA (1976).

Two replicates, each with six concentrations and a control, were used to test with Daphnia pulex. Flint glass jars of 250 ml capacity were used as test chambers, and 200 ml of the appropriate test concentration was placed in each chamber. Daphnia were siphoned into a large culture dish through a series of nested stainless steel screens to isolate the proper size and age organisms (neonates). These neonates were then transferred individually by glass pipette and were loaded 10 to 11 per chamber, resulting in 20 to 22 per test concentration.

Dissolved oxygen, pH, and the number of live organisms were recorded for each test chamber at 0 hours, 24 hours, and 48 hours. Total alkalinity, total hardness, and conductivity were recorded at the beginning of the test for the controls and the 100% effluent concentration. These values were recorded on the bioassay data forms and are presented in Table 3 and organisms were not fed during these test.

Saltwater for dilution of the effluent sample was obtained from the FSU marine laboratory at Turkey Point (Salinity = 22 o/oo). To minimize salinity differences between the various concentrations, freshly autoclaved artificial sea salt (Marinemix®) was added to the effluent sample and mixed with a magnetic stirrer until the dry salt mix dissolved and a salinity of 20-22 o/oo was achieved.

Two replicates, each of six concentrations of effluent and a control were used in this static test (Table 2). Individual mysid shrimp were siphoned or pipetted via glass tube, carefully examined for injury and randomly transferred to wide mouth quart jars, each containing 500 ml of the appropriate concentration. The concentration series selected for this study (Table 2) are those recommended by APHA (1976).

Five organisms were loaded per test chamber giving 10 per concentration (Table 4). Temperature, pH, dissolved oxygen and the number of live organisms were recorded at 0, 24, and 48 hours (Table 4). "Although it is generally undesirable to feed most fish and macroinvertebrates during static toxicity tests, an exception is necessary for M. bahia" (EPA 1978). Therefore, mysids were fed bring shrimp (Artemia) nauplii daily at a rate of approximately 10-20 per mysid to minimize cannibalism among the mysids.

Table 2.

Concentration Series and Volumes used for these Static Bioassays.

Water flea (Daphnia pulex)

Concentration	Dilution Water	Effluent	Total Vol.
Control	200 ml	-	200 ml
5.6%	188.8 ml	11.2 ml	200 ml
10.0%	180 ml	20 ml	200 ml
18.0%	164 ml	36 ml	200 ml
32.0%	136 ml	64 ml	200 ml
56.0%	88 ml	112 ml	200 ml
100%	-	200 ml	200 ml

Mysid shrimp (Mysidopsis bahia)

	Seawater diluent	Effluent	Total Vol.
Control	500 ml	-	500 ml
5.6%	472 ml	28 ml	500 ml
10.0%	450 ml	50 ml	500 ml
18.0%	410 ml	90 ml	500 ml
32.0%	340 ml	160 ml	500 ml
56.0%	220 ml	280 ml	500 ml
100%	-	500 ml	500 ml

Table 3 . Data recorded during 48 hour, Daphnia pulex, static acute toxicity bioassay of Seminole Refining, Inc., St. Marks, Wakulla Co., Florida. [illegible] 9 July 1980. NPDES Permit #FL0035225

Conc. or %	Test Container Number	Number of Live Organisms			Dissolved Oxygen (mg/l)			pH			Total Alkalinity (mg/l as $CaCO_3$)			Total Hardness (mg/l as $CaCO_3$)			Conductivity (umhos/cm)		
		0	24	48	0	24	48	0	24	48	0	24	48	0	24	48	0	24	48
Control	A	10	9	8	8.2	8.0	8.6	7.0	7.9	7.6	130			120			370		
Control	B	10	9	8	8.1	8.2	8.6	7.0	7.8	7.6									
5.6%	A	11	11	9	8.2	8.3	8.7	7.1	7.8	7.5									
5.6%	B	10	10	10	8.1	8.2	8.7	7.2	7.8	7.5									
10.0%	A	11	11	10	8.1	7.9	8.6	7.2	7.8	7.6									
10.0%	B	11	11	11	8.1	7.8	8.7	7.2	7.8	7.7									
18.0%	A	11	11	11	8.0	8.1	8.7	7.3	7.8	7.8									
18.0%	B	11	11	11	7.9	7.9	8.8	7.3	7.8	7.8									
32.0%	A	11	10	10	7.9	7.9	8.9	7.3	7.8	7.8									
32.0%	B	11	11	11	7.4	7.8	8.8	7.4	7.8	7.9									
56.0%	A	11	11	11	6.4	7.8	9.0	7.3	7.8	7.7									
56.0%	B	10	10	10	6.4	7.9	8.9	7.4	7.8	7.8									
100%	A	10	10	8	6.4	7.9	9.1	7.3	7.8	7.9									
100%	B	10	10	8	5.4	8.1	8.9	7.3	7.8	7.9	145			275			2000		

Remarks: 1. Test temperature range 22± 1°C.

Table 4 . Data recorded during 48 hour, Mysidopsis bahia, static acute toxicity bioassay of Seminole Refining Inc., St. Marks., Wakulla Co., Florida. 7-9 July, 1980. NPDES Permit # FL0035220.

Conc. or %	Test Container Number	Number of Live Organisms			Dissolved Oxygen (mg/l)			pH			Total Alkalinity (mg/l as $CaCO_3$)			Total Hardness (mg/l as $CaCO_3$)			Salinity (0/00)		
		0	24	48	0	24	48	0	24	48	0	24	48	0	24	48	0	24	48
Control	A*	5	5	5	8.3	6.6	7.0	8.8	8.4	8.3							22		
Control	B*	5	5	2[3]	8.3	6.4	6.4	8.8	8.5	8.4									
Control	C*	5	5	5	8.2	5.9	6.7	7.5	8.2	7.5							20		
Control	D*	5	5	5	8.2	6.0	6.7	7.5	8.3	7.5									
5.6%	A	5	5	5	8.1	6.3	6.7	8.0	7.7	7.5									
5.6%	B	5	5	5	8.1	6.2	6.3	7.9	7.6	7.5									
10.0%	A	5	5	5	8.1	5.9	6.2	8.0	7.6	7.5									
10.0%	B	5	5	5	8.1	6.0	6.5	8.0	7.7	7.6									
18.0%	A	5	5	5	7.9	5.5	6.4	8.1	7.7	7.6									
18.0%	B	5	4[3]	4	7.9	4.9	5.8	8.1	7.7	7.6									
32.0%	A	5	5	5	8.0	5.4	6.1	8.3	7.9	7.8									
32.0%	B	5	5	5	7.9	5.5	6.5	8.3	8.0	7.8									
56.0%	A	5	5	5	7.5	4.7	5.2	8.5	8.1	8.1									
56.0%	B	5	5	5	7.5	5.6	6.6	8.5	8.2	8.1									
100%	A	5	3	3	6.8	5.2	6.0	8.8	8.4	8.3							20		
100%	B	5	4	4	6.9	5.5	6.1	8.8	8.4	8.3									

*A and B are artificial seawater, C and D are natural seawater.

REMARKS:
1. Test temperature range 22 ± 1°C.
2. 3/4 adult size shrimp (≥ 10 daysold) used
3. missing shrimp cannibalized

RESULTS AND DISCUSSION

Results of these bioassays indicated a remarkable improvement in the quality of the Seminole Refining wastewater discharge. It was not possible to calculate a statistically sound LC_{50} for either 24 or 48 hours (Table 5) because of the small number of organisms which died (Table 3 and 4). The efforts that Seminole Refining, Inc. have made to improve the quality of their effluent appear to be responsible for the absence of toxicity. Additionally, the results of chemical tests to detect the presence of phenolic compounds in the grab samples were negative.

Table 5. LC_{50} Data for Bioassay of Seminole Refining, Inc.
7 July to 9 July 1980.

Organism	Method of Data Analysis	24 hour LC_{50} and 95% confidence intervals	48 hour LC_{50} and 95% confidence intervals
Daphnia pulex	Binomial	A	A
	Moving average	A	A
	Probit	A	>100%
Mysidopsis bahia	Binomial	A	A
	Moving average	A	A
	Probit	A	A

A. Due to an insufficient number of dead organisms, or to the irregular distribution of mortality, an LC_{50} value cannot be calculated using this method of statistical analysis.

LITERATURE CITED

American Public Health Association. 1976. Standard Methods for the Examination of Water and Wastewater. 14th ed. pp. 1193.

Peltier, William. 1978. Methods for measuring the acute toxicity of effluents to aquatic organisms. Environmental Research Laboratory. Athens, Georgia. EPA-600/4-78-012 (Revised July 1978) 51p.

U.S. Environmental Protection Agency. 1978. Bioassay procedures for the Ocean Disposal Permit Program. Environmental Research Laboratory. Gulf Breeze, Florida. EPA-600/9-78-010.

Attached Letter

SEMINOLE REFINING, INC.
P.O. Box 128 *St. Marks, Florida 32355*

July 21, 1980

Mr. Craig Dye
Biology Division
Department of Environmental Regulation
Twin Towers Office Building - Blairstone Road
Tallahassee, Florida 32301

Dear Craig:

Following is a brief list of improvements made in the process unit and wastewater treating system which resulted in the excellent effluent water quality characteristics exhibited in the recent DER bioassay results:

1. installation of a vacuum condensing system
2. initiation of an intense water hyacinth/bio-degredation program developed and designed by Seminole's Environmental Division in cooperation with the DNR
3. installation of two 7½ HP aireation units
4. construction and modification of three API seperators
5. installation of two additional oil skimmers
6. construction of an oily water sewer system
7. dredging of holding ponds
8. relocating hydrocarbon lines on above ground brackets
9. construction of dikes, berms
10. purchase and installation of a wastewater analysis lab

The above, which represent only a part of continuing improvements, total well over two million dollars in cost and countless man-hours.

If I can be of any further help, please contact me.

Yours very truly,

SEMINOLE REFINING, INC.

Kevin S. Songer

Kevin S. Songer
Environmental, Quality and
Safety Manager

KSS/ff

cc: H. Carl Vaught
Baxter M. Nichols

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