BIOASSAY OF GARDINIER, INC., U.S. PHOSPHORIC PRODUCTS

TAMPA, HILLSBOROUGH COUNTY, FLORIDA

NPDES #FL0000761, OUTFALL 005

SAMPLED 6/29/87

SEPTEMBER 29, 1987

Biology Section
Division of Environmental Programs

BIOASSAY OF GARDINIER, INC., U.S. PHOSPHORIC PRODUCTS

TAMPA, HILLSBOROUGH COUNTY, FLORIDA

NPDES #FL0000761

Biology Section
Bureau of Laboratories and
Special Programs
September 29, 1987

EXECUTIVE SUMMARY

Gardinier, Inc., U.S. Phosphoric Products, Tampa, Hillsborough County, Florida, NPDES #FL0000761, 30 June to 2 July, 1987.

One 48 hour static screening bioassay was performed on a sample of effluent collected from Outfall #005 of Gardinier Inc., which discharges to the Alafia River. Results indicated chronic toxicity to the test organism, Mysidopsis bahia, with a 48 hour LC_{50} of 376.6%. The total and unionized ammonia (7.5 mg/l and 0.04 mg/l, respectively) may have contributed to the observed toxicity.

Chemical analyses indicated trace amounts of the metals antimony and chromium, as well as arsenic (13.0 ug/l), cadmium (2.5 ug/l), and selenium (49.0 ug/l). These metals may have contributed to the observed chronic toxicity to M. bahia.

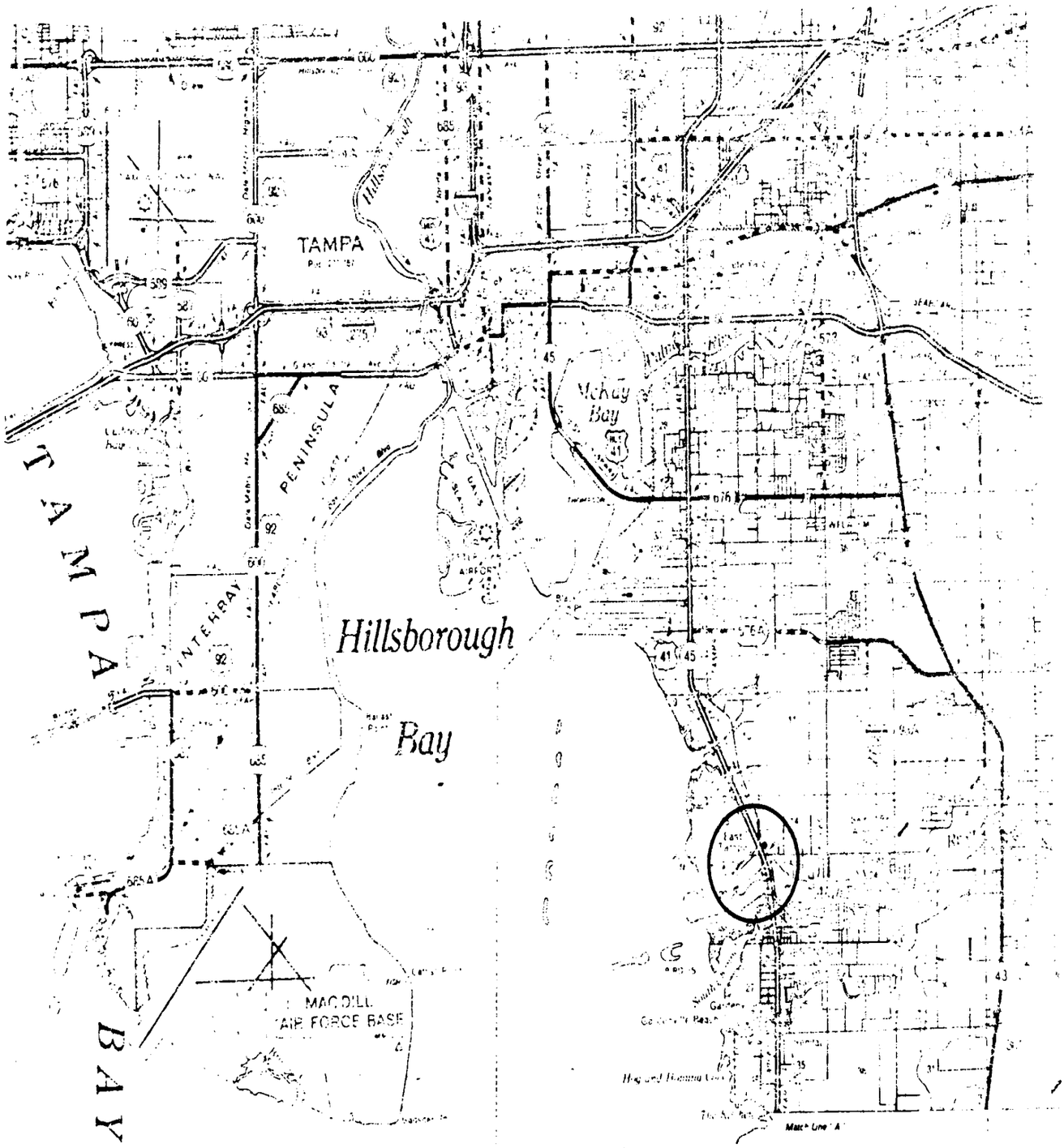
INTRODUTION

Gardinier, Inc., U.S. Phosphoric Products, is located at US 41 and Riverview Drive, just north of the mouth of the Alafia River on Hillsborough Bay, Tampa, Hillsborough County, Florida (Figure 1). This facility manufactures fertilizer and inorganic chemicals, including sulfuric, phosphoric fluosilicic acids (11567 tons per day), triple super and super phosphate (2600 tons per day), ammonium phosphate (1728 tons per day), anhydrous ammonia (385 tons per day), and gypsum (14320 tons per day). Wastewater from the various operations is treated by liming and retention in three sludge ponds. As many as six NPDES permitted outfalls are located on the site, three of which (#001, #005, and #012) discharge to surface waters. Outfalls #001 and #005 contain water from the sulfuric acid plant. They discharge to the Alafia River. Outfall #012 contains supernatant from the sludge ponds, and is discharged to Archie Creek, a tributary of Hillsborough Bay. A schematic of the facility and its wastewater outfalls is shown in Figure 2.

In 1973, Gardinier, Inc., was fined for damaging public lands (DER NPDES file). Since then major modifications were introduced in the manufacturing of phosphate chemicals, including a new gypsum disposal field (Figure 3). These modifications reduced energy consumption, and increased efficiency and production.

Since the various discharges from this manufacture of fertilizers and chemicals may adversely affect the aquatic community, the Biology Section performed 48 hour static acute toxicity bioassays on effluent from each of the three surface water outfalls #001, #005 and #012, on 22 to 24 September, 1981. Mysidopsis bahia was used as the test organism. Although some mortality occurred in the highest test concentrations, an insufficient number of organisms died for the calculation of LC_{50} values. Chemical analysis indicated that zinc and selenium were present in an effluent sample from Outfall #005. Unionized ammonia was detected in potentially toxic concentrations in effluent from Outfall #012. It was suggested that testing be repeated on samples from Outfall 012, because of the high concentration of ammonia found in the sample.

To further evaluate the potential toxicity of this effluent, the Biology Section performed a static screening bioassay on a sample collected from Outfall #005 in June, 1987. Results are presented in this report. Those involved in performing the test and in preparation of this report were: R. B. Frydenborg, K. M. Lurding, and M. L. Roll.



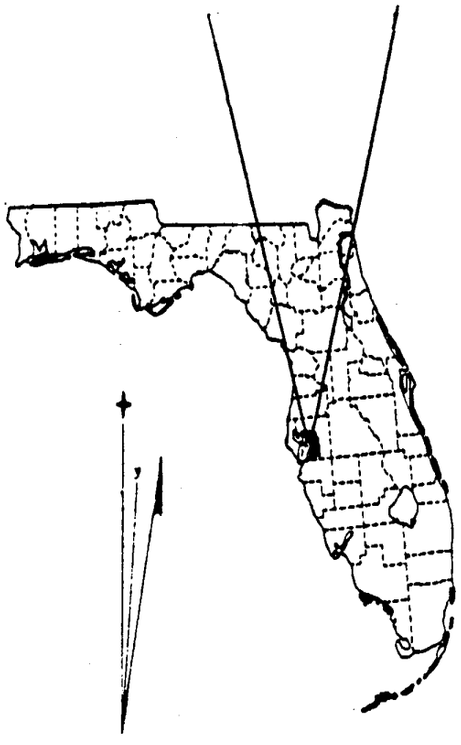


Figure 1. Portions of Tampa Hillsborough County, Florida, including study area.

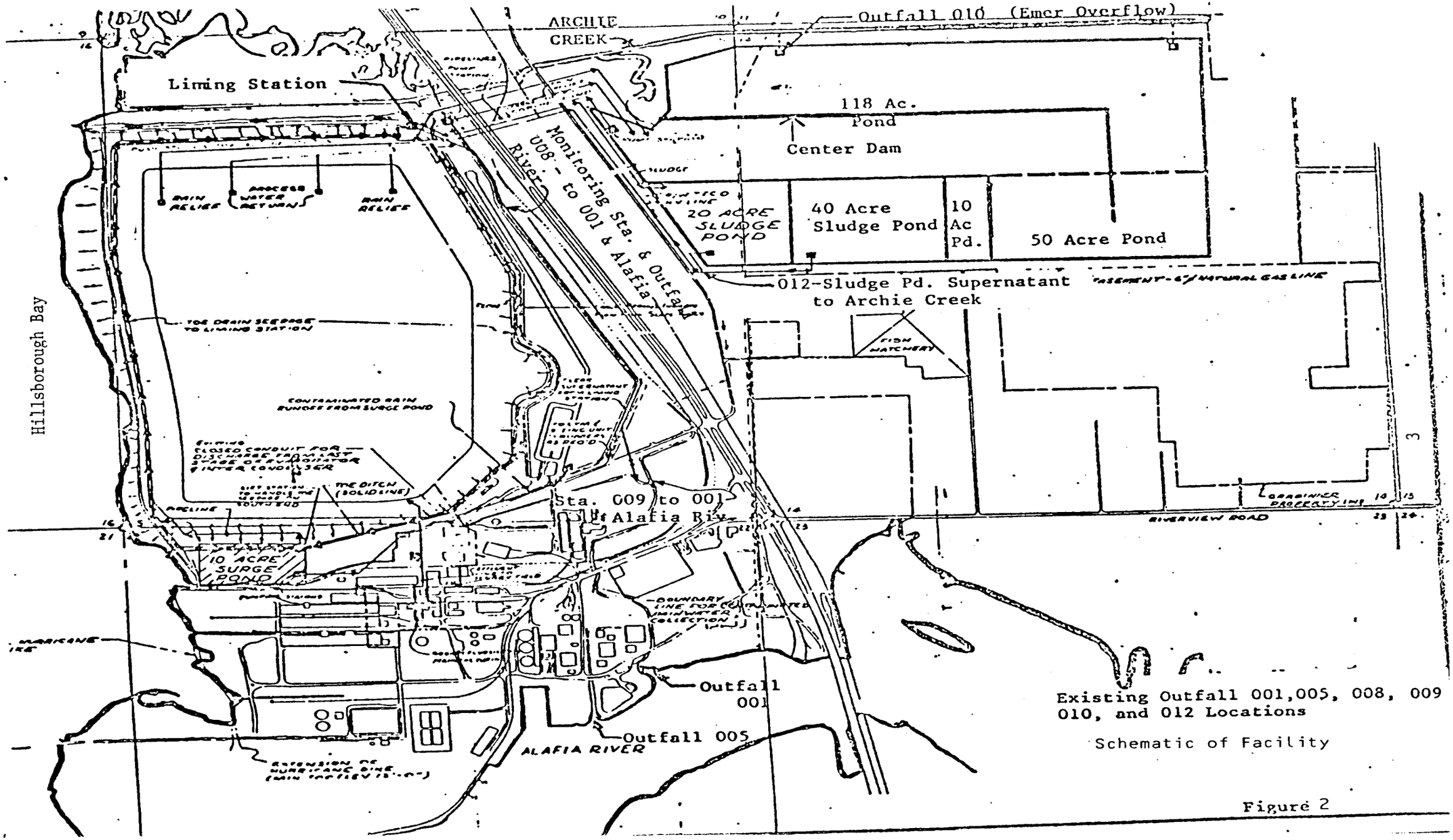

Outfall 010 (Emer Overflow)
ARCHIE CREEK
Liming Station
118 Ac. Pond
Center Dam
Monitoring Sta. & Outfall U08 - to 001 & Alafia River
20 ACRE SLUDGE POND
40 Acre Sludge Pond
10 Ac Pd.
50 Acre Pond
012-Sludge Pd. Supernatant to Archie Creek
Hillsborough Bay
FISH HATCHERY
Sta. G09 to 001 Alafia Riv
10 ACRE SURGE POND
Outfall 001
Outfall 005
ALAFIA RIVER
RIVERVIEW ROAD
Existing Outfall 001,005, 008, 009 010, and 012 Locations
Schematic of Facility

Figure 2

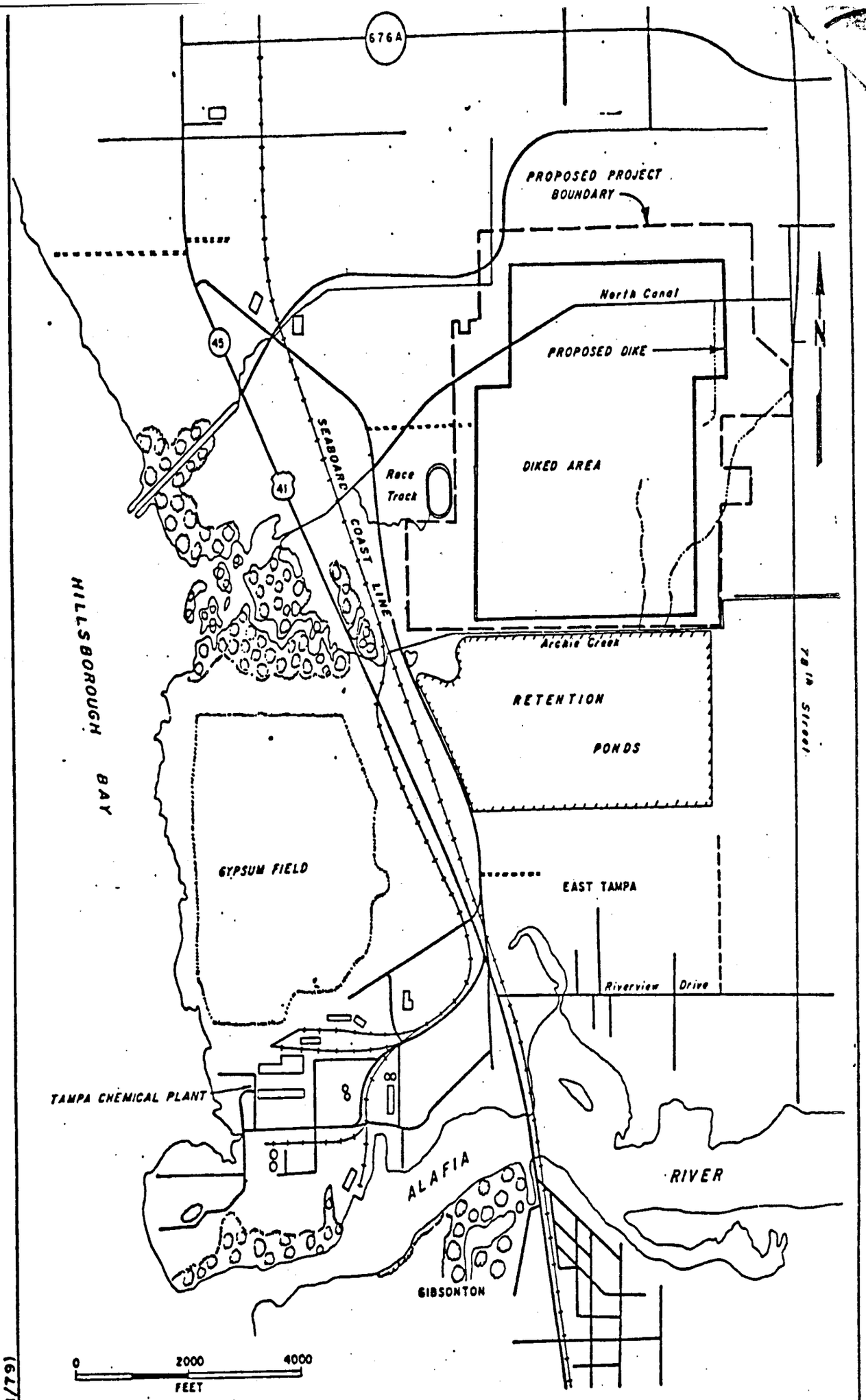


FIGURE 3 GYPSUM DISPOSAL FIELD **LOCATION MAP**

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METHODS AND MATERIALS

Test methods used to conduct this static bioassay are extensively described by Peltier and Weber (1985) and the FDER Biology Section (1985). The organism selected for this study is among those recommended by Peltier and Weber (1985), the U.S. EPA (1978), and the FDER Biology Section (1985). The life history and maintenance procedures used to culture the organism are detailed below.

History and Maintenance of Bioassay Organisms

Mysidopsis bahia (mysid shrimp) - In June, 1987, approximately 300 adult mysid shrimp were obtained from the laboratory of Cosper Environmental Services in New York. The mysids are cultured under a 16:8 hour light-dark cycle in 10 and 15 gallon all-glass aquaria equipped with undergravel filtration and aeration. The mysid shrimp are cultured at a salinity of approximately 20 ppt. Seawater, used for culturing the test organisms and as diluent in the bioassays, is prepared by mixing artificial sea salts (Forty Fathoms®) and deionized water to obtain a final salinity of 20-30 ppt. Deionized water is also used for dilution of the seawater as necessary. The mysids are fed twice daily and once daily on weekends with freshly hatched Artemia (brine shrimp) and are kept at a constant temperature of 23° ± 2°C. Adult or large juvenile mysids were used in this test.

To ensure the uniform sensitivity of these test organisms to toxic substances, the Biology Section conducts monthly standard reference toxicant bioassays using sodium lauryl sulfate as the reference toxicant.

Test Methods

Methods used to perform acute toxicity bioassays are described by Peltier and Weber (1985) and the FDER Biology Section (1985). Some of the methods described below are more specific than those of Peltier and Weber. These will be noted in more detail.

Sampling Methods and Test Dates

One static acute toxicity screening bioassay was performed on a sample of effluent collected from Outfall #005 of Gardinier, Inc. The test was performed from 1030 hours on 30 June to 1030 hours on 2 July, 1987.

Separate samples were obtained for chemical and biological testing. Samples for metal analyses were preserved with HNO_3. Samples for organic chemical analyses and for the bioassays were unpreserved. The sample was collected by Mr. David Demmi of DER's Southwest District Office at 1315 hours on 29 June, 1987, using standard wastewater sampling procedures. The samples were iced and transported to the DER laboratory in Tallahassee for analyses within 24 hours of collection.

Test Temperature

Upon arrival of the iced (4°C) bioassay sample in the Tallahassee laboratory, the containers were placed in warm water and the temperature of the sample allowed to rise to 20° ± 2°C. Although this temperature may be different than the temperature of the sample during collection, it is the temperature range to which the test organisms are acclimatized and is the range recommended in the above referenced bioassay protocols. This avoids stressful effects caused by exposure to unusually cold or warm samples.

Saltwater Test

Saltwater for dilution of the effluent sample and for use as the control was prepared from artificial sea salts (Forty Fathoms®), and adjusted with DER well water until a salinity of approximately 20 ppt was achieved. For the 50% test concentration, this diluent was mixed directly with the effluent, achieving a final salinity of 20 ppt. The 100% effluent contained an ambient salinity of 20.0 ppt.

The concentration series selected for this study is presented in Table 1. Two replicates of each test concentration and of the control were used to test with Mysidopsis bahia. Immediately prior to the bioassay, a suitable number of mysids were transferred by net from the appropriate salinity aquarium to a culture dish for observation and selection of individuals for the test. Individual mysid shrimp were siphoned using a glass tube, carefully examined for injury, and transferred to wide mouth quart jars, each containing 500 ml of the appropriate concentration. For each concentration, the mysid shrimp were pre-acclimated to within 2 ppt salinity. Five organisms were loaded per test chamber, giving ten per concentration. Based on the recommendations of EPA (1978), the mysids were fed brine shrimp (Artemia) nauplii at the rate of approximately 10 to 20 nauplii per mysid per day to minimize cannibalism.

Test Parameters

Dissolved oxygen (YSI Model 57 oxygen meter), pH (Corning Model 7 pH meter with Orion Ross® combination electrode), temperature (NBS calibrated glass thermometer), and the number of live organisms were recorded for each test concentration at 0 hours, 24 hours, and 48 hours. Total alkalinity and total hardness (measured as $CaCO_3$ using HACH Chemical Company reagents) were recorded at the beginning of the test for the control and the 100% effluent concentration. The salinity (YSI Model 33 S-C-T meter) of each test concentration was recorded at the beginning and end of the test. All instruments were calibrated daily according to manufacturer's recommendations. Ammonia concentrations, including the total and unionized fraction (expressed in mg/l as N and as NH_3, respectively), were recorded in the control and the 100% effluent test concentration at the beginning of the test. Total ammonia concentrations were determined using an Orion® specific ion probe and an Orion Ionalyzer®. The unionized fraction was then calculated based on the total ammonia concentration, and the pH, temperature, and salinity of the sample. These values were recorded on the bioassay data form and are presented in Table 2.

RESULTS AND DISCUSSION

One 48 hour static acute toxicity bioassay was performed on a sample of effluent collected from Outfall #005 of Gardinier, Inc., which manufactures fertilizers and organic chemicals. Results of this bioassay using Mysidopsis bahia as the test organism indicated a 48 hour LC_{50} of 376.6%. This concentration is considered chronically toxic in the absence of a mixing zone. The total and unionized ammonia (7.5 mg/l and 0.04 mg/l, respectively) may have contributed to the observed toxicity.

Chemical analyses (Table 4) indicated the presence of the following metals: antimony (< 200.0 ug/l), arsenic (13.0 ug/l), cadmium (2.5 ug/l), chromium (< 100.0 ug/l), and selenium (49.0 ug/l). These metals may have contributed to the observed toxicity to M. bahia.

Table 1. Concentration Series and Volumes Used for This Static Bioassay.

Mysidopsis bahia (mysid shrimp)

Concentration	Dilution Water	Sample	Total Volume
Control	500 ml	--------	500 ml
50.0%	250 ml	250 ml	500 ml
100.0%	------	500 ml	500 ml

Table 2. Data recorded during 48 hour, Mysidopsis bahia, static acute toxicity bioassay of Gardinier, Inc., NPDES #FL0000761, 30 June to 2 July, 1987.

Concentration or %	Number of Live Organisms			Dissolved Oxygen (mg/l)			pH			Temperature (°C)			Salinity (ppt)	
	0	24	48	0	24	48	0	24	48	0	24	48	0	48
Mysidopsis bahia														
Control	5	5	5	9.5	8.0	7.3	8.7	8.5	8.4	20.3	19.8	18.2		
Control	5	5	5	9.5	8.0	7.3	8.7	8.5	8.4				21.2	19.3
50%	5	5	5	8.3	7.7	7.5	8.2	8.2	8.2	20.3	19.7	18.1		
50%	5	5	4	8.3	7.7	7.5	8.2	8.2	8.2				20.8	19.9
100%	5	4	4	6.3	7.6	7.6	7.1	7.8	8.0	20.4	19.5	18.2		
100%	5	4	4	6.3	7.6	7.6	7.1	7.8	8.0				20.0	19.3

Control Water

NH_3(as NH_3)(mg/l) 0

Total ammonia (as N)(mg/l) 0

Total Alkalinity 108 (mg/l $CaOO_3$)

Total Hardness 116 (mg/l $CaOO_3$)

100% Effluent

NH_3(as NH_3)(mg/l) 0.04

Total ammonia (as N)(mg/l) 7.5

Total Alkalinity 137 (mg/l $CaOO_3$)

Total Hardness — (mg/l $CaOO_3$)

Table 3. LC_{50} Data for Bioassay of Gardinier, Inc., NPDES #FL0000761, 30 June to 2 July, 1987.

Organism	Method of Data Analysis	24 Hour LC_{50} and 95% Confidence Intervals	48 Hour LC_{50} and 95% Confidence Intervals
Mysidopsis bahia	Binomial	a	a
	Moving Average	a	a
	Probit	a	376.6% (97.7% and ∞)

[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.

Table 4. Results of chemical analyses performed on effluent from Gardinier, Inc., NPDES #FL0000761, collected on 29 June, 1987.

Organics

Acid Extractables	N.D.
Base Neutral Extractables	N.D.
Pesticide Extractables	N.D.

Metals

Antimony	<200.0 ug/l[a]
Arsenic	13.0 ug/l
Beryllium	N.D.
Cadmium	2.5 ug/l
Chromium	<100.0 ug/l[a]
Copper	N.D.
Lead	___[b]
Mercury	N.D.
Nickel	N.D.
Selenium	49.0 ug/l
Silver	___[b]
Thallium	N.D.
Zinc	___[b]

N.D. = None Detected

[a] Actual value is known to be less than value given.

[b] Results for zinc, silver and lead were invalidated due to contaminated field blank.

Discussion of the Toxicity Criteria

The toxicity standards of Chapters 17-3 and 17-4, F.A.C., are complex. Because of this complexity, they will be briefly reviewed here so that these test results may be more readily compared with the standards. For legal purposes, however, the language of the Florida Administrative Code should be consulted directly.

The two basic concepts utilized in the standards are acute and chronic toxicity (defined in 17-3.021(1) and (4), respectively). Simplifying the actual F.A.C. language somewhat, acute toxicity is defined as the presence of a substance in a concentration one-third as great as that concentration which kills one-half of the test organisms in 96 hours, i.e., one-third of the 96 hour LC_{50}. Chronic toxicity is similarly defined as onetwentieth of the 96 hour LC_{50}. Therefore, if a test solution kills one- half or more of a group of test organisms in 96 hours, it must contain at least three times the defined "acutely toxic" concentration and at least twenty times the "chronically toxic" concentration of some substance or substances. If a test solution causes that same mortality in less than 96 hours, (for example, in 24 or 48 hours), it is at least as toxic as the example given above, and actually is probably considerably more toxic.

The particular restrictions applied to a given discharger depend upon the existence of a mixing zone, whetheras a specific part of the permit or based on the existence of a currently valid permit predating the language in Chapter 17-4 requiring mixing zone designation. In the absence of a mixing zone, the general criteria for surface waters [17-3.061] are applicable at all points, beginning at the point of discharge. This section prohibits the discharge of substances in concentrations which are chronically toxic [17-3.061(2)(p)]; that is, the concentrations cannot exceed one-twentieth of the 96 hour LC_{50} as discussed above. If a mixing zone does exist, then this chronic toxicity standard is only applicable from the edge of the mixing zone and beyond. Within the mixing zone, the less stringent acute toxicity standard of the minimum criteria for all waters [17-3.051(1)(d)] applies: one-third of the 96 hour LC_{50}. The acute toxicity standard does not apply, however, to each point within a mixing zone not designated for dredge and fill permitting, but rather to the average of a number of points within such a mixing zone, based on the provisions of the surface water mixing zones section of Chapter 17-4 [17-4.244(4)]. At the same time, though, this same rule prohibits waste concentrations within such a mixing zone (i.e., at any point within the mixing zone), from exceeding the 96 hour LC_{50}. Therefore, at any point within such a mixing zone, including the point of discharge, one-half of the test organisms cannot be killed in 96 hours. Within a mixing zone designated for dredge and fill permitting, the acute toxicity standard (one-third of the 96 hour LC_{50}) applies at all points, including the point of discharge.

From the above discussion, it should be clear that if the least stringent toxicity standard, the 96 hour LC_{50}, is exceeded at any point, from the point of discharge outwards, by any discharger, then a violation of the standards has occurred. This is an important consideration since the test procedure here reported involves the measurement of the 50% lethal concentration, and not some fraction of that concentration. Any discharger required to meet the one-twentieth of the 96 hour LC_{50} standard is therefore being tested very leniently. Any reduction in the test period from 96 hours provides an added degree of leniency to a discharger.

A number of different dilutions were examined in order to determine by how much, if any, the discharge exceeds the 96 hour LC_{50}. For example, if the sample, after two-fold dilution with diluent (a 33% concentration), kills one-half of the test organisms after 96 hours, then the sample is three times as toxic as is allowed by that standard. Similarly, if a 5% solution of the sample kills 50% of the organisms, the sample is twenty times as toxic as is allowed. Toxicities are reported here in that manner, i.e., in terms of the percentage dilution of the test sample. The smaller the percentage which is reported means a correspondingly greater toxicity.

Note that even if a discharger receives a very large mixing zone not designated for dredge and fill permitting, the regulations require that the maximum toxicity at any point within the mixing zone be restricted to the 96 hour LC_{50}. The results here reported are based on actual discharge samples, representative of the concentration which enters waters of the state at the point of discharge. If it is demonstrated that, under the conditions existing at the point of discharge, concentrations will be less than at the actual sampling point (if the two points are different), the reported bioassay results will reflect the reduced discharge concentration.

With respect to the species of organisms used in these tests, the language of the F.A.C. indicates that they should be "significant to the indigenous aquatic community". All species used in these tests are significant to the indigenous aquatic community since they are sensitive to toxic substances which may be expected to impact the indigenous community.

The toxicity reported here is in excess of allowable limits.

LITERATURE CITED

Florida Department of Environmental Regulation, Biology Section. 1985. Quality Assurance Manual for Performing Acute Toxicity Tests (Second Edition). FDER.

Peltier, W. and C. I. Weber. 1985. Methods for measuring the acute toxicity of effluents to aquatic organisms (Third Edition). Environmental Research Laboratory. Athens, Georgia. EPA-600/4-85-012. 217 p.

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. 121 p.

BIOASSAY DATA FORM

Facility/Toxicant Gardinier — Test # 1 — Sample Collected: Date 5/29/87 Time 1315

Address Hwy U.S. 41 Gibsonton — Type Screen — Test Beginning: Date 5/30/87 Time 1030

NPDES Number FL0000761 — Organism M. bahia — Test Ending: Date 2 JN/87 Time 1030

Outfall Number 005

Test Concentration	Chamber Number	Live Organisms 0	24	48		Dissolved Oxygen (mg/L) 0	24	48	pH 0	24	48	48	Temperature °C 0	24	48	Salinity 0	48	Ammonia Total 0	48	Unionized 0	48
Control	76	5	5	5		9.5	8.0	7.3	8.7	8.5		8.4	20.3	14.8	13.2			0		0	
Control	3	5	5	5		9.5	8.0	7.3	8.7	8.5		8.4				21.2	14.3				
50%	44	5	5	5		8.3	7.7	7.5	8.2	8.2		8.2	20.3	14.7	13.1						
50%	65	5	5	4		8.3	7.7	7.5	8.2	8.2		8.2				20.8	14.1				
100%	—	5	4	4	(4)	6.3	7.6	7.6	7.1	7.8		8.0	20.4	14.5	13.2						
100%	66	5	4	4	(4)	6.3	7.6	7.6	7.1	7.8		8.0				20.0	14.3	7.5		.04	
		MLR	CBA	MLR		MLR	MLR	MLR	MLR	MLR	MLR		MLR	MLR	MLR	MLR	MLR	MLR		MLR	

NOTES

Control Water

Total Alkalinity (mg/l $CaCO_3$) 108

Total Hardness (mg/l $CaCO_3$) 116

100% Sample

Total Alkalinity (mg/l $CaCO_3$) 137

Total Hardness (mg/l $CaCO_3$) [redacted]

Age of Test Organisms juveniles < 2 weeks

Weight ____

Instrument Calibrations

	pH Meter:	D.O. Meter:	S-C-T Meter:
0 Hours	7.0 at 7, 9.0 at 9	9.2 at 20°C	11 at 10 28.5 at 30
24 Hours	7.0 at 7, 9.0 at 9	9.1 at 20.5°C	[illegible] at 30
48 Hours	7.0 at 7, 9.0 at 9	9.3 at 19.7	[illegible] at 30

* Several shrimp near death in 100% at 48 hrs

Reviewed by: [signature]

Date: 8/15/87