

BIOASSAYS OF SCHUYLKILL METALS CORPORATION PLANT CITY, HILLSBOROUGH COUNTY, FLORIDA

DER TEMPORARY OPERATING PERMIT #IT 29-29835

Biological Section
Bureau of Water Analysis
February 4, 1981

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INTRODUCTION

Schuylkill Metals Corporation is located at 402 S. Woodrow Wilson Street, Plant City, Hillsborough County, Florida (Fig. 1). According to the DER Temporary Operating Permit #IT 29-29835 issued 23 July 1981:

> This company is a battery breaking operation with secondary lead recovery. The acid from the batteries is captured and transported by PVC pipe to the treatment system. Ammonia is mixed with the sulfuric acid to neutralize it. Heavy metals are settled from the mixture. Treated water is held in the pond until recycled back for use in the plant battery sawing and clean-up operation.

Under the terms of the permit (appended), Schuylkill Metals Corporation has until 1 January 1982, to bring their facility into compliance with state water quality regulations.

Leachate from the holding pond enters a ditch that surrounds the pond (Fig. 2). This ditch drains to Pemberton Creek, a tributary of Lake Thonotosassa.

On 10 November 1980, a sample of leachate was taken from the ditch at Schuylkill Metals (Fig. 2) and a bioassay performed on it to determine the existence and extent of toxicity to the biota of the receiving water.

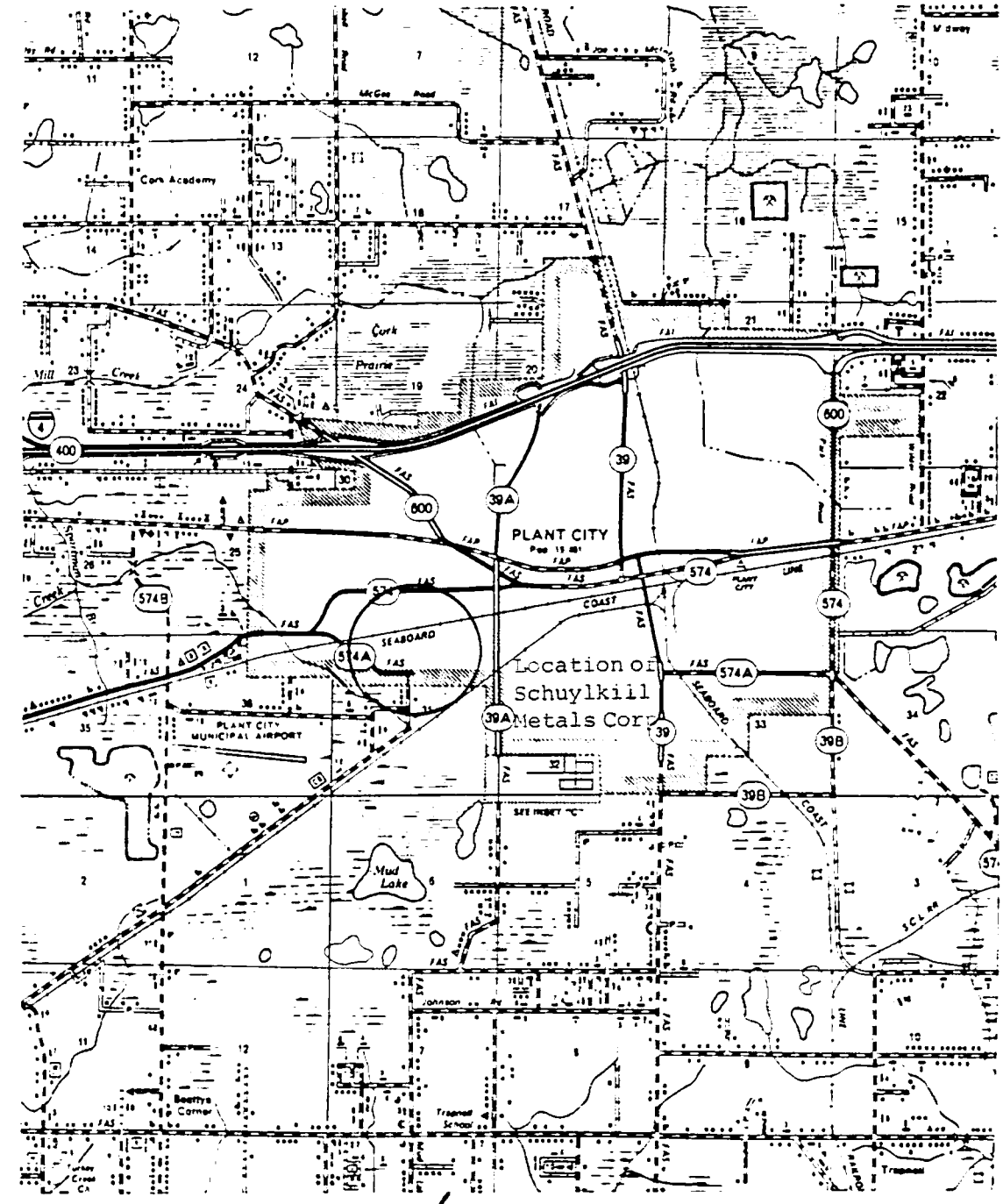


Figure 1. Portions of Hillsborough County including the Study Area

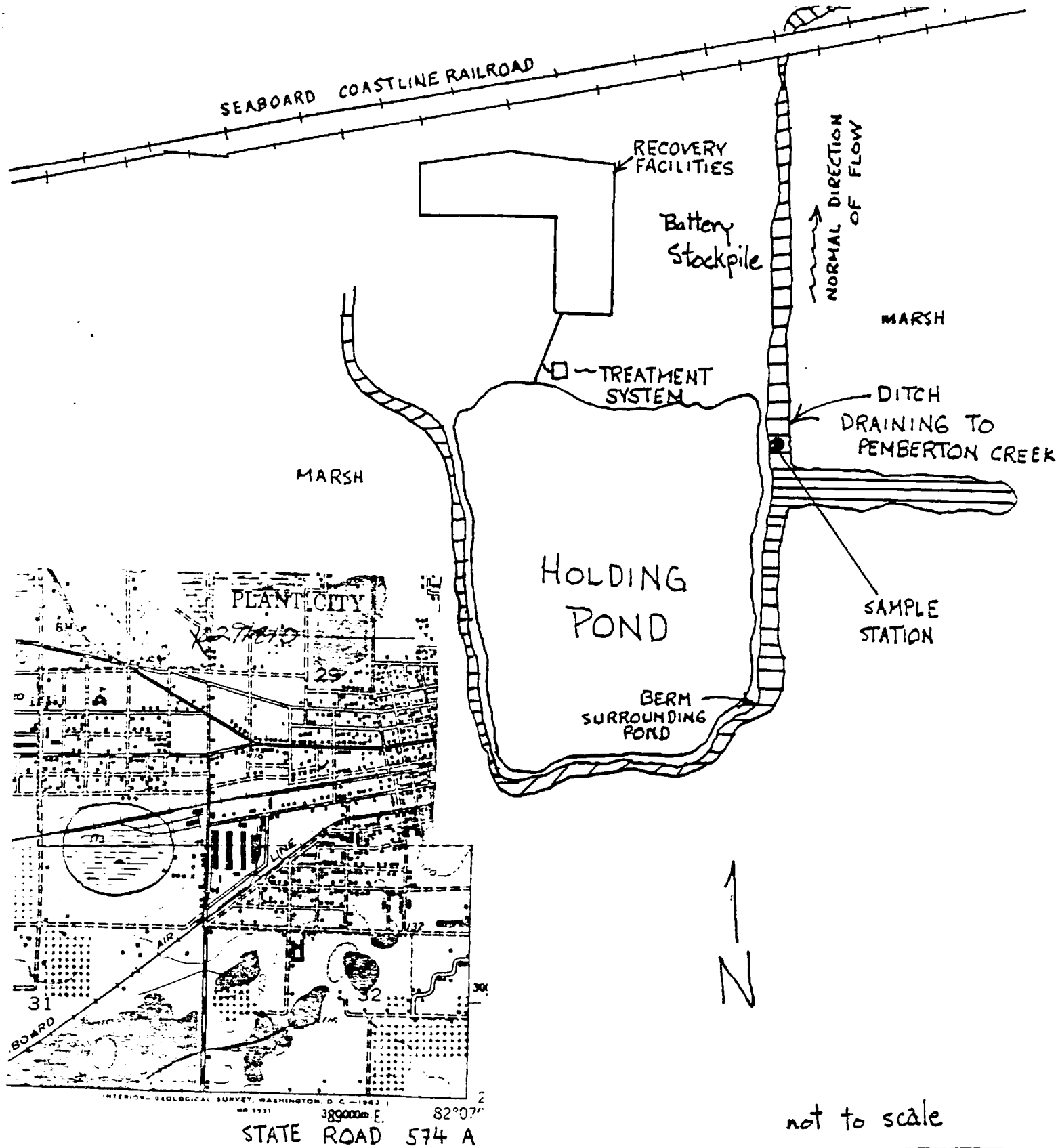


Figure 2. SCHUYLKILL METALS - PLANT CITY

METHODS AND MATERIALS

Test methods used to conduct these static bioassays are extensively described by Peltier (1978). The organisms selected for this study include species recommended by Peltier (1978) and the U.S. EPA (1978). Additionally, the Biological Section maintains cultures of several species of organisms indigenous to the State of Florida. 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 in March, 1979. This culture has been maintained since its arrival, in 2½ gallon all glass aquria filled with unchlorinated DER well water, using a 16:8 hour light-dark cycle. Organisms are fed a liquified blend of Purina Trout Chow ® and Cerophyl ® twice daily, and are kept at a constant temperature of $22^{\circ} \pm 1^{\circ}C$. The aquaria are cleaned weekly by siphoning off half the water along with the detritus and excess daphnids. They are then refilled with fresh aerated well water. Additional measures are taken and/or new cultures started in the event of abnormal circumstances such as: declining populations, ephippia formation, or excessive fungal or bacterial growth.

Simocephalus serrulatus (water flea) - An indigenous breeding population of S. serrulatus was collected from Lake Jackson, Leon County, Florida, in March, 1980, by personnel from DER's Biological Section. Positive identification of the organism was performed by Mr. Jeff Foran of the Department of Environmental Engineering Sciences, University of Florida in Gainesville. The cultures are maintained in 2½ gallon all glass aquaria, filled with unchlorinated DER well water, under a 16:8 hour light-dark cycle. The organisms are fed a liquified blend of Purina Trout Chow ® and Cerophyl ® twice daily, and are kept at a constant temperature of $22^{\circ} \pm 1^{\circ}C$. The aquaria are cleaned weekly by siphoning off half the water along with the detritus and excess population. They are then refilled with fresh aerated well water. Additional measures are taken and/or new cultures started in the event of abnormal circumstances.

Heterandria formosa (least killifish) - Approximately 100 adult killifish were obtained from a wild population in the St. Marks Wildlife Refuge (Wakulla County, Florida) during August, 1980. The fish have been maintained in 2½ to 5 gallon all glass aquaria equipped with a flow-through water exchange system. Water for this system is unchlorinated and is pumped from a deep well near the DER laboratory. The fish have been reared at $22^{\circ} \pm 2^{\circ}C$ under a 16:8 hour light-dark cycle and fed freshly hatched Artemia (brine shrimp) twice daily. New born fish are initially maintained in the adult tanks, but are removed at weekly intervals, thereby segregating fish into even age groups. The fish used in this test were ≤ 4 weeks old.

To ensure the uniform sensitivity of these test organisms to toxic substances, the Biological Section conducts monthly Standard Reference Toxicant Bioassays using sodium lauryl sulfate as the reference toxicant.

Test Methods

Three separate 48 hour static bioassays were conducted from 1100 hours 11 November 1980 to 1100 hours 13 November 1980, on a grab sample of leachate from the ditch surrounding the holding pond. The sample was collected by Charles Biedermann of DER's Biological Section at 1100 hours on 10 November 1980 using standard wastewater sampling procedures. Separate samples were obtained for chemical and biological testing. Samples for metal analysis were preserved with HNO_3. Samples 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 DER well that is used to culture the test organisms. The concentration series selected for this study (Table 1) is that recommended by APHA (1976).

Two replicates, each with six concentrations and a control, were used to test with Daphnia pulex and Simocephalus serrulatus. 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 and Simocephalus were siphoned into large culture dishes 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 per chamber, resulting in 20 per test concentration.

Two replicates, of six concentrations and a control, were used for the Heterandria bioassay. The fish were transferred individually or by twos, by net, into wide mouth quart jars containing 500 ml each of the appropriate test concentration. The killifish were loaded 5 per chamber resulting in 10 per 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 Tables 3, 4 and 5. Organisms were not fed during these tests.

Table 1. Concentration Series and Volumes Used for These Static Bioassays

Water fleas (Daphnia pulex and Simocephalus serrulatus)

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

Least killifish (Heterandria formosa)

Concentration	Dilution Water	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 2 Data recorded during 48 hour, Daphnia pulex, static acute toxicity bioassay performed on the Schuylkill Metals Corporation, Plant City, Hillsborough County, Florida. 1100 hours 11 November 1980 to 1100 hours 13 November 1980.

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)
		0	8.5	24	0	24	0	24	0	24	0	24	0
Control	A	10	10	7	8.3	8.3	7.6	7.9	110	128	123	125	205
Control	B	10	10	10	8.3	8.4	7.6	7.9					
5.6%	A	10	0	--	8.3	8.6	7.7	7.7					1450
5.6%	B	10	0	--	8.3	8.6	7.7	7.7					
10.0%	A	10	0	--	8.3	8.7	7.8	7.7					2150
10.0%	B	10	0	--	8.3	8.7	7.8	7.8					
18.0%	A	10	0	--	8.4	8.6	7.9	7.7					3550
18.0%	B	10	0	--	8.3	8.6	7.9	7.7					
32.0%	A	10	0	--	8.2	8.5	8.0	7.7					6000
32.0%	B	10	0	--	8.1	8.5	8.0	7.7					
56.0%	A	10	0	--	7.7	8.5	8.1	7.7					9750
56.0%	B	10	0	--	7.8	8.5	8.1	7.7					
100%	A	10	0	--	7.2	8.3	8.2	7.9	347	117	1130	1170	16,000
100%	B	10	0	--	7.3	8.3	8.2	7.9					

Remarks:
a. Test temperature range 19.2° to 20.2 °C.
b. Since all test organisms, except for the controls, were dead within 24 hours, the test was discontinued and 48 hour parameters are not reported.

Table 3 Data recorded during 48 hour, *Simocephalus serrulatus*, static acute toxicity bioassay performed on the Schuylkill Metals Corporation, Plant City, Hillsborough County, Florida. 1100 hours 11 November 1980 to 1100 hours 13 November 1980.

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)
		0	8.5	24	0	24	0	24	0	0	0
Control	A	10	10	9	8.5	8.4	7.6	7.7	110	123	205
Control	B	10	10	9	8.5	8.5	7.7	7.8			
5.6%	A	10	0	--	8.6	8.6	7.8	7.7			1450
5.6%	B	10	0	--	8.6	8.6	7.8	7.7			
10.0%	A	10	0	--	8.6	8.7	7.8	8.0			2150
10.0%	B	10	0	--	8.5	8.7	7.8	8.0			
18.0%	A	10	0	--	8.6	8.7	7.9	7.9			3550
18.0%	B	10	0	--	8.5	8.6	7.9	7.9			
32.0%	A	10	0	--	8.4	8.7	8.0	7.8			6000
32.0%	B	10	0	--	8.4	8.6	8.0	7.8			
56.0%	A	10	0	--	8.5	8.6	8.1	7.8			9750
56.0%	B	10	0	--	8.2	8.5	8.1	7.8			
100%	A	10	0	--	7.6	8.3	8.2	8.0	347	1130	16,000
100%	B	10	0	--	7.5	8.3	8.2	8.0			

Remarks a. Test temperature range 19.8° to 20.5 °C.
b. Since all test organisms, except for the controls, were dead within 24 hours, the test was discontinued and 48 hour parameters are not reported.

Table 4 Data recorded during 48 hour, *Heterandria formosa*, static acute toxicity bioassay performed on the Schuylkill Metals Corporation, Plant City, Hillsborough County, Florida. 1100 hours 11 November 1980 to 1100 hours 13 November 1980.

Conc. of %	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)
		0	8.5	24	0	8.5	24	0	24	0	0	0
Control	A	5	5	5	8.6	8.2	8.4	7.7	7.9	123	123	205
Control	B	5	5	5	8.7	8.1	8.4	7.7	7.8			
5.6%	A	5	0	--	8.7	8.3	--	7.8	7.8			1450
5.6%	B	5	0	--	8.7	8.4	--	7.8	7.8			
10.0%	A	5	0	--	8.6	8.4	--	7.9	7.8			2150
10.0%	B	5	0	--	8.6	8.2	--	7.9	7.8			
18.0%	A	5	0	--	8.6	8.4	--	8.0	7.8			3550
18.0%	B	5	0	--	8.5	8.3	--	8.0	7.8			
32.0%	A	5	0	--	8.4	8.1	--	8.0	7.8			6000
32.0%	B	5	0	--	8.4	8.1	--	8.0	7.8			
56.0%	A	5	0	--	8.2	7.9	--	8.1	7.8			9750
56.0%	B	5	0	--	8.2	8.0	--	8.1	7.9			
100%	A	5	0	--	7.5	7.7	--	8.2	7.9	347	1130	16,000
100%	B	5	0	--	7.3	7.7	--	8.2	7.8			

Remarks:

a. Test temperature range 19.0° to 20.3 °C

b. Two age groups of fish were used in this test, one week old killifish weighed an average of 0.007 g each and four week old fish weighed 0.055 g each.

c. Since all test organisms, except for the controls, were dead within 24 hours, the test was discontinued and 48 hour parameters are not reported.

RESULTS AND DISCUSSION

This particular sample of leachate was toxic to all test organisms at all concentrations used in this bioassay (Tables 3, 4 and 5). All organisms, except the controls, were dead within 8.5 hours. Since all test animals were killed in the lowest concentration of effluent used (5.6%), it is obvious that the 8.5 hour LC_{50} is <5.6%. The 96 hour LC_{50} would, therefore, also be <5.6%.

Since this facility uses ammonia in the wastewater treatment process, we made determinations of ammonium and ammonia concentrations in the effluent sample. Results of these tests as well as some additional field parameters are presented in Table 5. According to U.S. EPA (1977), unionized ammonia is highly toxic to many aquatic organisms. "Levels of unionized ammonia in the range of 0.20 to 2 mg/l have been shown toxic to some species of fresh water aquatic life." (U.S. EPA 1976). The toxicity observed in these bioassays may, therefore, be attributed to the high concentration of unionized ammonia (27.5 mg/l) in the Schuylkill leachate. Additionally, the high salinity noted in Table 5 (10.5 $^{o}/_{oo}$) may also be responsible for the observed mortality as a result of osmotic shock. Other suspected toxicants may include heavy metals such as lead, copper, antimony, chromium, cadmium, and nickel which are associated with acid storage battery recycling operations. Chemistry data on this leachate sample will be available through DER's Chemistry Section in Tallahassee. These results were not available at the time of this report.

Chapter 17-3.051, Florida Administrative Code, indicates that "all waters of the State shall at all places and at all times be free from...components of discharges which...are acutely toxic." "Acute toxicity" is defined in Chapter 17-3.021(1) to mean "the presence of one or more substances...in amounts which are greater than one-third (1/3) of the amount lethal to 50% of the test organisms in 96 hours (96 hour LC_{50})...". In the absence of a mixing zone, this 1/3 of the 96 hour LC_{50} applies at the point of discharge. Chapter 17-4.244(4) states that "in no event shall the maximum concentration of wastes in the mixing zone exceed the amount lethal to 50% of the test organisms in 96 hours (96 hour LC_{50}) for a species significant to the indigenous aquatic community..." This criterion applies at the point of discharge if there is a mixing zone. The distinction between presence or absence of a mixing zone is not relevant here, however, since the testing procedure used does not involve effluent concentration. The 1/3 of the 96 hour LC_{50} criterion is three times as stringent as the 96 hour LC_{50} criterion, and, therefore, in the absence of a mixing zone, the procedure used is very lenient. The procedure followed is also lenient in that testing is only done for 48 hours. The 96 hour LC_{50} derived from this testing is, therefore, reported as "less than or equal to" the 48 hour measurement. The value found after 48 hours can never be more restrictive than the value found after 96 hours. It must be noted that all organisms used in these tests are significant to the indigenous aquatic community since they are sinsitive to toxic substances which may be expected to impact the indigenous community.

The toxicity reported here is in excess of allowable limits.

Table 5. Results of some chemical/physical measurements performed on a grab sample of leachate from Schuylkill Metals Corporation.

Parameter	Results
Temperature[1]	25°C
pH[1]	8.1
Dissolved Oxygen[1]	8.1 mg/l
Conductivity[1]	16000 umhos
Salinity[2]	10.5 °/oo
Unionized Ammonia	27.6 mg/l (as NH_3)
Total Ammonia[3]	476 mg/l (as N)

[1]Field measurements

[2]Laboratory measurements

[3]Laboratory measurements using a Orion Ion Analyzer electrode

[4]Calculated from Total Ammonia

LITERATURE CITED

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