ENVIRONMENTAL PROTECTION AGENCY

OFFICE OF ENFORCEMENT

REPORT ON
EVALUATION OF INDUSTRIAL WASTE DISCHARGES
AT
W. R. GRACE AND COMPANY
DAVISON CHEMICAL DIVISION
LAKE CHARLES, LOUISIANA

Prepared By

VISION OF FIELD INVESTIGATIONS - DENVER CENTER

DENVER, COLORADO

AND

REGION VI DALLAS, TEXAS

CLEAN WATER

OCTOBER 1971

ENVIRONMENTAL PROTECTION AGENCY
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Report on

Evaluation of Industrial Waste Discharges at The Davison Chemical Division Plant W. R. Grace and Company Lake Charles, Louisiana

Prepared By
Division of Field Investigations-Denver Center
Denver Colorado
and
Region VI
Dallas, Texas
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INTRODUCTION

Louisiana's second largest industrialized area is located near Lake Charles in the Calcasieu River Basin in the southwestern corner of the State. Area industries are primarily involved in the production of chemical, petrochemical, and petroleum products.

These industries discharge waste waters into the Calcaseiu River or its tributaries - Bayou d'Inde, Bayou Verdine, Houston River, Mill Creek, and Palmetto Creek. The Rivers and Harbors Act of 1899,[1/*] the Water Quality Act of 1965, and the Water Quality Improvement Act of 1970[2/] are applicable to the Calcasieu River and its tributaries. [Water quality regulations established pursuant to the provisions of these Acts are presented in Appendix A.]

The Division of Field Investigations-Denver Center, Environmental Protection Agency (EPA), at the request of the Director, Water Quality Office, Region VI, EPA, undertook a study of the Calcasieu River Basin in March-April 1971. Specific objectives of the study were to:

1. Compile an up-to-date inventory of industrial waste sources discharging to the Calcasieu River and its tributaries.
2. Ascertain a) types of treatment presently provided and b) the quality and quantity of each industrial waste discharge.
3. Evaluate the individual and collective impacts of wastewater discharges on the beneficial water uses of the Calcasieu River and its tributaries.

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* Numbers in _/ refer to references.

4. Determine abatement proceedings necessary or warranted under the Rivers and Harbors Act of 1899, the Water Quality Act of 1965, and/or other applicable local, State and Federal laws.

This report summarizes information pertaining to raw materials, processes, waste loads, and treatment needs at the W. R. Grace Davison Chemical Division plant, Lake Charles, Louisiana, and recommends actions necessary to protect the quality of the receiving waters. Complete custodial records [Appendix C], for each sample taken during the course of this investigation, are on file in the Denver, Colorado, office of the Division of Field Investigations-Denver Center.

Assistance and support in the conduct of this investigation was provided by the following EPA entities:

Division of Field Investigations-Cincinnati Center

Enforcement Office, Region VI, Dallas, Texas

Southeast Water Laboratory, Athens, Georgia

The assistance of personnel of the Lake Charles Office, Louisiana Wildlife and Fisheries Commission, is gratefully acknowledged.

BACKGROUND INFORMATION

General

The total drainage area of the Calcasieu River and its tributaries equals about 4,000 square miles; measures approximately 120 miles in length and 55 miles in width; and includes portions of eight different parishes (population - about 230,000). [Figure 1] The Lower Calcasieu River encompasses the area downstream from a salt water barrier (located

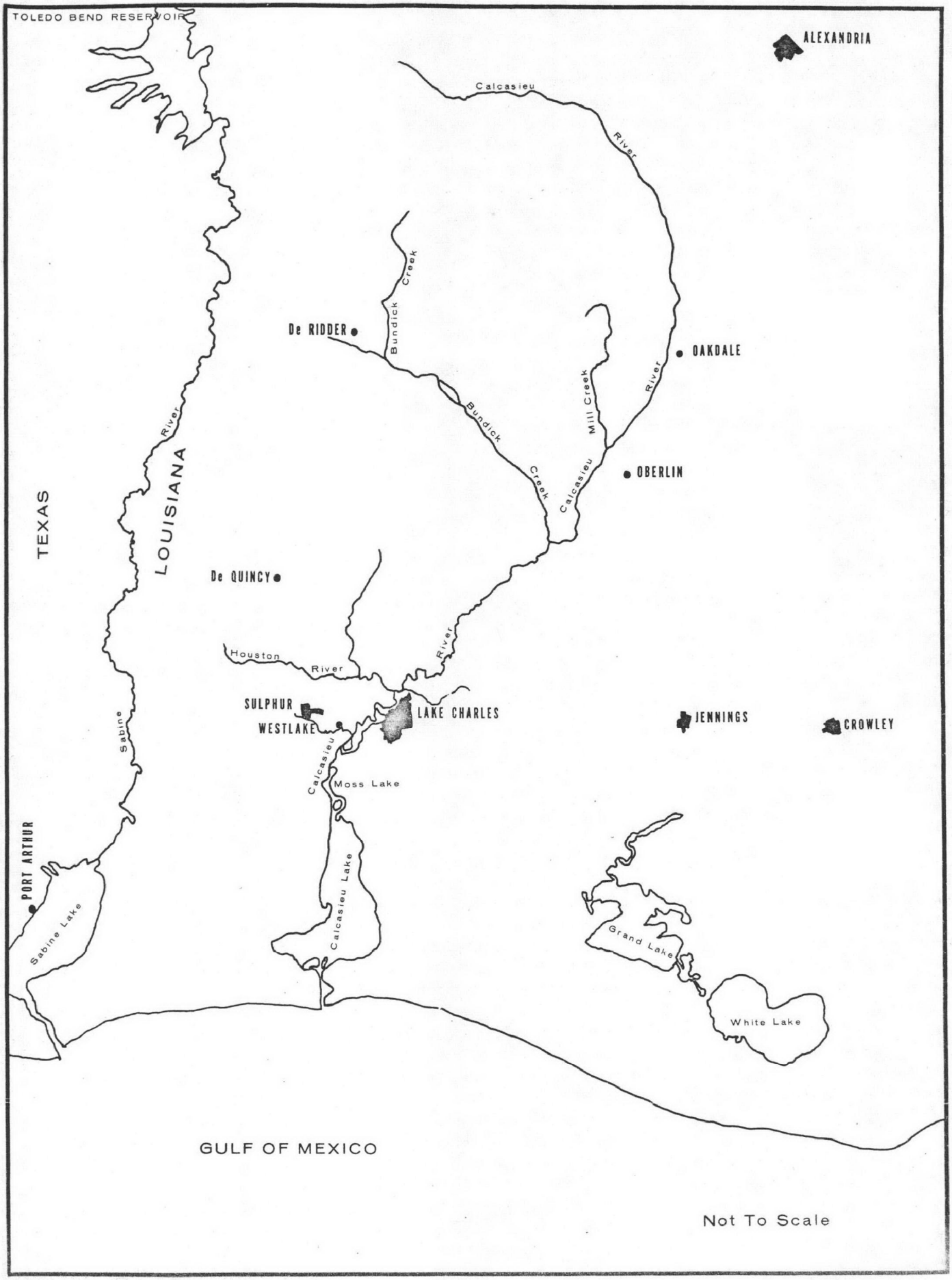

Figure 1. Location Map - Calcasieu River Drainage

just north of the city of Lake Charles) to the Gulf of Mexico. The Upper Calcasieu River consists of the fresh water portion of the watershed extending upstream from the salt water barrier to the basin headwaters.

The River is navigable upstream to Moss Bluffs, Louisiana (about ten miles upstream of Westlake).[3/] Barges and ships navigate a channel that has been dredged from the Gulf of Mexico northward along the west side of Calcasieu Lake to Devils Elbow, thereafter following the natural river channel, except for two cutoffs, to the Port of Lake Charles.

Thundersqualls and tropical storms with high wind velocities occasionally pass through the area. Prevailing winds are primarily from the north during months of November through January and from the south during the remainder of the year. Frosts are experienced from late November to late February. Average temperatures range from the low 50's (in January) to the 80's (in July).

The Lower Calcasieu River, Lake Calcasieu, Bayou d'Inde, Bayou Verdine, and Indian Marais are affected by lunar tides. Passage of a cold front or high winds may cause wind-dominated tides that produce flooding of low-lying areas and tributary streams and bayous. As a result of these events flow and mixing patterns may be highly irregular.

Brackish inland lakes and marshes that border the main River channel and the adjacent shallow offshore area support a large commercial and sport fishery. The area is an excellent spawning and rearing ground for shrimp, crabs, and various estuarine fish.

In addition to furnishing a location for the propagation of aquatic life, the waters of the Calcasieu River system and its tributary streams support other beneficial activities, including municipal and industrial water supplies, recreation, irrigation, and navigation.

In conjunction with other chemical plants and all the major petroleum refineries, the Davison Chemical plant provides much of the support of the economy in the Lower Calcasieu River area. This W. R. Grace operation is involved primarily in the production of catalysts.

Facility Description

The Davison Chemical Division manufactures synthetic cracking catalysts to supply various petrochemical complexes operating in the Lake Charles area. This plant operates on a year-round basis, 168 hours per week. One hundred fifty employees are involved in production and another fifty carry out management and administrative duties. The Company's director of environmental matters declined to answer EPA's question regarding the rated capacity of this plant.

The basic raw materials used in the production of catalysts at this facility are silica and aluminum. Intermediate compounds are sodium silicate, aluminum hydrate, aluminum sulfate, and ammonia. Various clays are added in the process also. The final step is a spray wash and drying. It is at this point that a portion of the product is lost and eventually finds its way into the industrial waste discharge.

Water Supply

Water is obtained from two wells, each rated at 1,250 gpm (1.8 mgd). Uses of this water are for process, boiler feed, sanitary service, and non-

contact cooling.

Existing Waste Treatment

Untreated process waste is discharged from a single outfall to an unnamed bayou that flows to the Calcasieu River [Figure 2].

The plant is currently operating under a permit from the Louisiana Stream Control Commission.

Chronology of Contacts

On March 26, 1971, J. L. Hatheway and M. R. Helton of the Division of Field Investigations-Denver Center, EPA, met with Henry E. Craven, Plant Manager, and Fred Henke, Director of Environmental Matters, in order to initiate an industrial waste inventory at this plant. The meeting had been arranged by E. D. Anthony, Jr., enforcement program specialist, Region VI Office, EPA, Dallas, Texas, on March 25, 1971.

Mr. Henke commented that none of the local employees devote significant time to water pollution control. There are, however, two employees at the corporate home office [P.O. Box 2117, Baltimore, Maryland] who are assigned principal duties in water pollution and/or air pollution control for all operating subdivisions. These employees were present and accompanied the EPA investigators on the initial tour of the plant. Mr. Henke and the EPA investigators on the initial tour of the plant. Mr. Henke and the others present indicated that no heavy metals are used in any of the processes, and added that heavy metals cannot be permitted to be present in the finished product. The Company representatives were cooperative, attempted to answer all the questions posed by the investigating team, and conducted the team on a tour of the plant.

On April 16, 1971, R. D. Harp, R. L. King, and Mr. Hatheway (all EPA

representatives) met with Mr. Henke to discuss the industrial wastewater sampling program. He was informed that waste source evaluations and water quality investigations were being conducted by EPA in the Calcasieu River Basin to provide the basis for:

(1) Evaluation of Corps of Engineers permits as required under the Rivers and Harbors Act of 1899;

(2) Determination of present water quality conditions in the Calcasieu River and its tributaries;

(3) Evaluation of the individual and collective impacts of wastewater discharges on the beneficial water uses of the Calcasieu River and its tributaries;

(4) Determination of water pollution control needs within the area; and

(5) Abatement measures as necessary or warranted under the Rivers and Harbors Act of 1899, the Water Quality Act of 1965, and/or other applicable local, State and Federal laws.

Mr. Henke consented to sampling of the W. R. Grace and Company Davison Chemical effluent.

SAMPLING PROGRAM AND RESULTS

Wastewater effluent samples [as illustrated in Figure 2] were collected from the discharge channel at a point about 200 feet outside the southeast corner of the property (Station WRG-1). Shrimp survival studies were conducted on the Lower Calcasieu River upstream and downstream from the W. R. Grace discharge. Sediment samples were collected from the Lower Calcasieu River at the point of the discharge (Station CR-2). [In Table 1

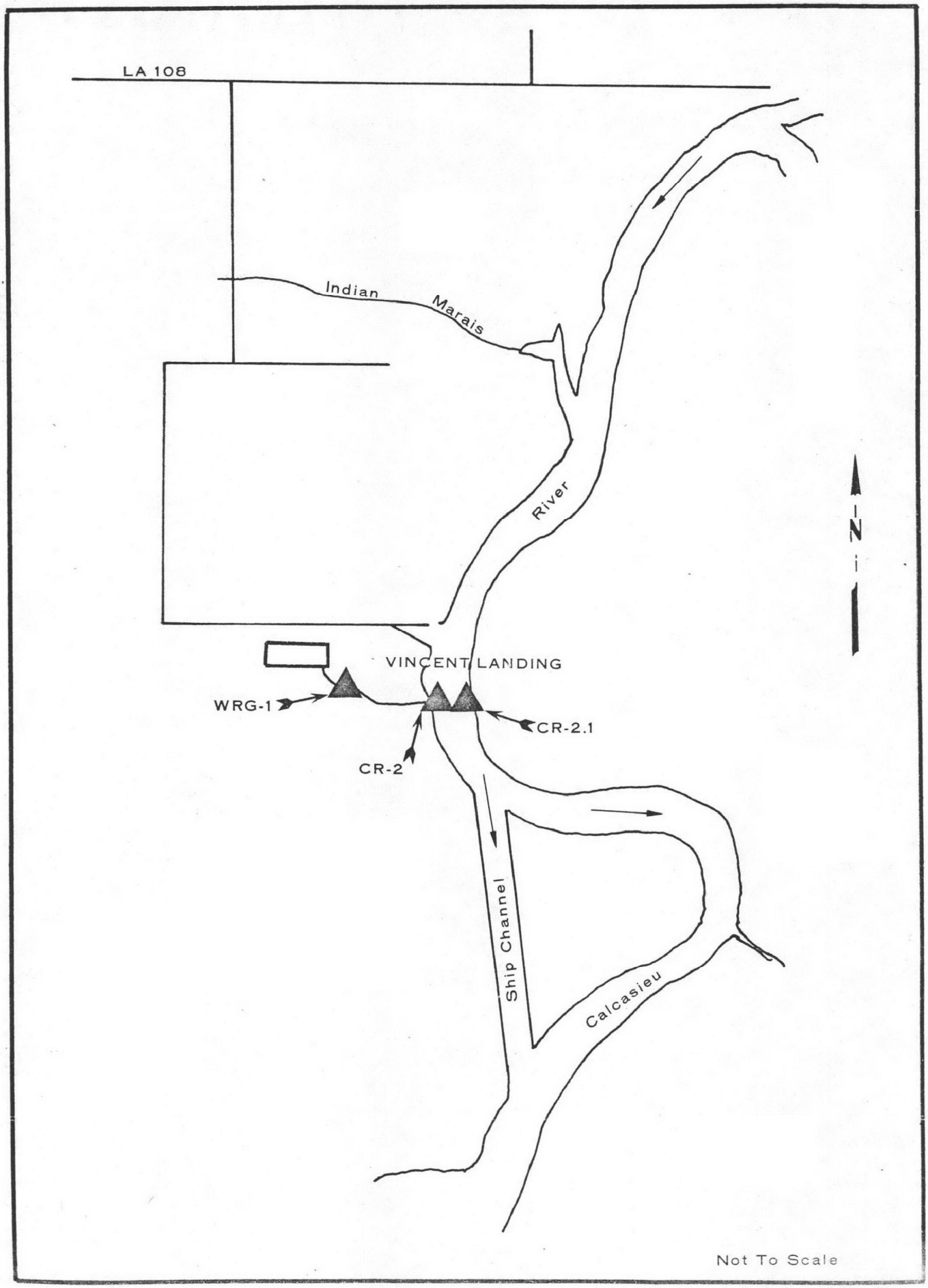

Figure 2. Effluent & Receiving Water Sampling Locations for W. R. Grace & Company

TABLE 1

DESCRIPTION OF EFFLUENT AND RECEIVING WATER SAMPLING POINTS

Station Number	Description and Remarks
WRG-1	Samples collected of the effluent from the drainage ditch at a point about 200 ft outside the southeast corner of the property. The ditch drains into the Lower Calcasieu River through an unnamed Bayou.
CR-1	Calcasieu River near Calcasieu Landing (upstream from intracoastal waterway) near Channel Marker 92 (control station).
CR-2	Lower Calcasieu River near Vincent's Landing, at the discharge from W. R. Grace and Company.
CR-2.1	Lower Calcasieu River, next to the east bank, opposite W. R. Grace and Company discharge.
CR-11.2	Calcasieu River, south shore, south of Clooney Island just west of Lake Charles (control station).

is a description of the stations where the effluent and the Lower Calcasieu River were sampled.]

Effluent samples (125 ml aliquots) were composited every two hours, for 24 hours, beginning at 6:15 a.m., April 23. [The results of the sampling are shown in Table 2.]

During the period of the sampling, Grace's Davison Chemical Division discharged each day loads of at least 910 lbs of aluminum; 3,870 lbs, chemical oxygen demand (COD); 290 lbs, total organic carbon (TOC); and 11,700 lbs of suspended solids into the Lower Calcasieu River.

Survival studies were made with shrimp at Station CR-2, CR-2.1 and at the control stations following methods outlined in Appendix B [Table 3]. These studies indicated that total shrimp mortality occurred within six hours. Near the east bank of the Lower Calcasieu River, opposite the discharge point (station CR-2.1), a total shrimp mortality occurred within two hours. Total mortality during the 6-hour test precluded taste and odor evaluation.

At control Stations CR-1 and CR-11.2 there were no mortalities during this time span. These stations [Table 1] are located in the Lower Calcasieu River so as to have the least possible contamination from industrial wastes. Station CR-1 is located downstream from industrial discharges and closer to the Gulf of Mexico than are all the other stations. Station CR-11.2 is located upstream of most industrial discharges and has water with lower salinity levels than has Station 1.

A sample of the bottom sediments, taken downstream from the industrial discharge of W. R. Grace and Company, was composed of grayish-white particulate

TABLE 2

SUMMARY OF ANALYTICAL RESULTS AND FIELD MEASUREMENTS[a/]

Sta	Flow mgd	pH range	Conductivity µ mhos/cm range	Conductivity µ mhos/cm composite	Temp range °C	TOC mg/l	TOC lb/day	COD mg/l	COD lb/day	Solids total mg/l	Solids total lb/day	Solids susp mg/l	Solids susp lb/day
WRG-1	1.81	4.1-8.6	19,500-40,000	28,000	37-42	19	290	256	3,870	22,900	346,000	772	11,700
CR-2		7.6-8.9		14,500	23-26	9.1, 11[b/]				8,950		16	

Sta	Cadmium mg/l	Chromium mg/l	Mercury µg/l	Mercury lb/day	Aluminum mg/l	Aluminum lb/day	Copper mg/l	Lead mg/l
WRG-1	<0.05	<0.01	0.8	0.0121	60	910		
CR-2	<0.05	<0.02	3.2		<0.5		<0.02	<0.1

a/ Analytical procedures are outlined in Appendix D.
b/ Two samples taken (morning and afternoon).

TABLE 3

IN SITU STUDIES OF WHITE SHRIMP
IN THE LOWER CALCASIEU RIVER, LOUISIANA

	96-Hour In Situ Study[a/]			
Station	Exposure Time	Alive	Dead	Percent Survival
CR-11.2 (Control)	Initial	10	0	100
	24-hour	9	1	90
	48-hour	8	2	80
	72-hour	8	2	80
	96-hour	5	5	50.
CR-2.1	Initial	10	0	100
	24-hour	0	10	0
CR-2	Initial	10	0	100
	24-hour	0	10	0
CR-1 (Control)	Initial	10	0	100
	24-hour	8	2	80
	48-hour	8	2	80
	72-hour	8	2	80
	96-hour	5	5	50

a/ April 20, 1971

material. A low organic sediment index of 0.25 indicates that the waste material discharged is primarily of inorganic character [Table 4].

DATA REPORTED TO LOUISIANA STREAM CONTROL COMMISSION

The Louisiana Stream Control Commission extended (December 16, 1970) the discharge permit of W. R. Grace and Company. A summary of information from the Commission files as to allowable levels of materials discharged is as follows:

Date of Application:	August 13, 1970
Quantity of Discharge:	3.09 cfs
Temperature:	Ambient
Turbidity:	50 to 800 ppm
True Color:	None
Inorganic Materials:	332,000 lbs/day equivalent to 19,500 ppm discharged to the Calcasieu River.

PROPOSED WASTE TREATMENT

Construction of a new wastewater treatment facility is underway with an estimated completion date of December 1972. This new facility consists of clarification and pH control. If properly designed and operated, this facility should provide adequate treatment to protect the quality of the receiving waters.

CONCLUSIONS

1. Present discharge of carbonaceous materials, aluminum, and suspended solids, by the Lake Charles Plant of W. R. Grace and Company (Davison Chemical Division) constitutes a violation of Section 407, Rivers and Harbors Act of 1899 (33 USC: 401-413).

2. The Company appears to be making suitable progress toward instal-

TABLE 4

ANALYTICAL RESULTS OF BOTTOM SEDIMENT SAMPLES

Station	Date	Time	Water Depth, Feet	Type[a/] of bottom	Odor[a/] of bottom	Volatiles %	Organic Carbon %
CR-1	4/22/71	1145	2.0	Soft mud	None	7.6	2.76
CR-2	4/22/71	1310	3.0	Greyish-white sediment	None	7.7	1.20

Station	Nitrogen %	Organic Sediment Index	Sediment Type	Mercury[b/] ppm
CR-1	0.189	0.52	II	<0.2
CR-2	0.209	0.25	I	0.9

a/ General appearance and odor at time of collection.
b/ Results based on dry weight. Samples dried at 35°C for two days.

lation of treatment facilities.

3. The Company should be permitted a reasonable time to complete the planned facilities and to attain routine operation thereof.

RECOMMENDATIONS

1. Progress toward implementation of planned treatment should be monitored by the Office of Enforcement, EPA;

2. If new treatment facilities are not in operation by January 1, 1973, appropriate abatement actions should be initiated against the Company.

3. If new treatment facilities are in operation by January 1, 1973, effluent quality should be examined; if the quality is found to be inadequate, appropriate abatement actions should be initiated against the Company.

4. The permit to be issued to W. R. Grace and Company limit discharges of BOD, COD, TOC, heavy metals, and aluminum to be consistent with best available treatment and the water quality standards for the Lower Calcasieu River.

REFERENCES

1/ Rivers and Harbors Act of 1899, 33 U.S.C. 401-413, Section 407 referred to as Refuse Act of 1899.

2/ Federal Water Pollution Control Act, 33 U.S.C. 466 et seq, as amended by the Federal Water Pollution Control Act Amendments of 1961-(PL 87-88), the Water Quality Act of 1965-(PL 89-234), the Clean Water Restoration Act of 1966-(PL 89-753), and the Water Quality Improvement Act of 1970-(PL 91-224).

3/ U. S. Department of Commerce, Environmental Science Service Administration Coast and Geodectic Survey, *Atlantic Coast Sixth (1967) Edition* 163-165.

APPENDIX A

APPLICABLE WATER QUALITY REGULATIONS

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APPLICABLE WATER QUALITY REGULATIONS

General

The Calcasieu River is a navigable waterway in law and in fact.[1/] Large ocean-going vessels travel up the Calcasieu River to Westlake, Louisiana. The remainder of the Calcasieu River upstream of Westlake is also used for navigation. Similarly, the lower portion of the Calcasieu River complex can be classified as a coastal water in that tidal influences are felt for significant distances upstream of the point where the Calcasieu joins the Gulf of Mexico. In compliance with the Federal Water Pollution Control Act, as amended, the State of Louisiana established water quality standards for interstate streams, coastal waters, and streams discharging into coastal waters. These standards were approved by the Secretary of the Interior. The Calcasieu River is also subject to the provisions of Section 407 of the 1899 Rivers and Harbors Act (the Refuse Act), and the oil discharge regulations established pursuant to the Water Quality Improvement Act of 1970.

Water Quality Standards

The State of Louisiana divided the Calcasieu River from the Gulf of Mexico to its origin into three distinct zones for the purpose of establishing water quality standards: (1) Zone 1, the Calcasieu River from its origin to the Salt Water Barrier; (2) Zone 2, the Calcasieu River from the Salt Water Barrier to the upper end of Moss Lake; and (3) Zone 3, that portion of the Calcasieu River from the upper end of Moss Lake to the Gulf of Mexico. Louisiana State Water Quality Standards for the Calcasieu River

describe a series of present uses of that river. They are industrial supply, primarily cooling water in the Lake Charles area; propagation of aquatic life for commercial fishing, including shellfish; irrigation water for considerable acreage of river; recreational use, including water contact sports; navigational use from the Lake Charles area to the Gulf of Mexico; and finally, carriage of municipal and industrial wastes.

Conditionally, the State indicated that they expected changes in the usage of this water with the progression of time. Primarily, these changes will take the form of municipal water supply in the upper reaches, carriage of treated municipal and industrial wastes in the lower area, and increased use for industrial supply.

No water quality standards have been established for the following tributaries: Bayou d'Inde, Bayou Verdine, Contraband Bayou, English Bayou, Houston River, Mill Creek and Palmetto Creek, all intrastate waters. The Standards established for the Calcasieu River follow.

Zone 1 - The River from Its Origin to the Salt Water Barrier

General criteria were established in Zone 1 by the Louisiana State Stream Control Commission in 1968. These criteria state that no discharge to Zone 1 shall result in conditions in the stream that will adversely affect the public health or use of the water (i.e. municipal and industrial supplies, recreation, propagation of aquatic life, etc.).

Specific criteria are as follows:

pH	From 6.0 to 8.5
Dissolved Oxygen	Not less than 50 percent saturation at existing water temperature.

Temperature	Not to be raised more than 3°C above normal ambient water temperature nor to exceed an absolute maximum of 36°C.
Oil and Grease	No oil slicks of free or floating oil are present in sufficient quantities to interfere with the designated uses nor shall emulsified oils be present in the same quantity.
Toxic Materials	None present in quantities that alone or in combination will be toxic to animals or plant life, but in all cases the level shall not exceed a $TLM_{48/10}$. ($TLM_{48/10}$ remains undefined).
No foaming or frothing materials	
Coliform Density	1600/100 ml, calculated as the most probable number, as a monthly mean. However, 10 percent of the samples may exceed the previous number up to 5420/100 ml in any one month.
Other Materials	Limits on other substances not heretofore specified shall be in accordance with recommendations set by the Louisiana Stream Control Commission and/or by the Louisiana State Board of Health for municipal raw water sources.

Zone 2 - The Calcasieu River from the Salt Water Barrier to the Upper End of Moss Lake

General criteria for this zone indicate that, at present, the water is suitable for propagation of aquatic life, recreation, navigation, and low grade industrial supply when necessary adaptations are made by industry. No discharge is to be permitted that will result in stream conditions that will adversely affect public health, propagation and harvesting of aquatic life, recreation and navigation, or impose additional burdens of adaptation on industrial use.

Specific criteria for Zone 2 are shown in the following table:

pH	6.0 to 8.5
Dissolved Oxygen	Not less than 50 percent saturation at the existing temperature.
Temperature	Not to be raised more than 3°C above normal ambient water temperature nor to exceed an absolute maximum of 36°C.
Oil and Grease	There shall be no slicks of free or floating oil present in sufficient quantities to interfere with the designated uses nor shall emulsified oils be present in the same quantity.
Toxic Materials	None present in quantities that alone or in combination will be toxic to animals or plant life, but in all cases the level shall not exceed a $TLM_{48/10}$, ($TLM_{48/10}$ remains unidentified).
No foaming or frothing materials	
Coliforms	The monthly median for coliform density shall not exceed 542/100 ml (MPN) nor shall this count exceed 1750/100 ml in more than 10 percent of the samples in any one month.

Zone 3 - The Calcasieu River from the Upper End of Moss Lake to the Gulf of Mexico

The general criteria for this zone indicate that during periods of low flow the high mineral content of the water approaches that of the marine water itself. This mineral content is caused by tidal intrusion. Therefore, no discharge shall produce conditions in the stream adversely affecting public health or the use of waters for propagation and harvesting of aquatic life, recreation, or navigation.

Specific criteria for this zone are as follows:

pH	From 6.0 to 8.5
Dissolved Oxygen	Not less than 60 percent saturation at existing water temperature.
Temperature	Not to be raised more than 3°C above normal ambient water temperature nor to exceed an absolute maximum of 36°C.
Oil and Grease	No oil slicks of free or floating oil are present in sufficient quantities to interfere with the designated uses nor shall emulsified oils be present in the same quantity.
Toxic Materials	None present in quantities that alone or in combination will be toxic to animals or plant life, but in all cases a level shall not exceed a $TLM_{48/10}$ ($TLM_{48/10}$ remains undefined).
No foaming or frothing materials	
Coliforms	The monthly median shall not exceed 70/100 ml nor shall this count exceed 230/100 ml in more than 10 percent of the samples in any one month.

The Rivers and Harbors Act of 1899 (Refuse Act)

The Rivers and Harbors Act of 1899 prohibits the discharge of industrial wastes to navigable waters without a permit from the U. S. Army Corps of Engineers. Section 407 of the Act (referred to as the Refuse Act) makes it unlawful to discharge from any "... manufacturing establishment, or mill or any kind, any refuse matter of any kind or description whatever, other than that flowing from streets and sewers and passing therefrom in a liquid state, into any navigable water of the United States, or into any tributary of any navigable water from which the same shall float or be

washed into such navigable water ..." provided that a discharge may be permitted under certain conditions specified by the Corps of Engineers.

Executive Order No. 11574, Administration of the Refuse Act Permit Program, signed by President Nixon on December 23, 1970, tightens enforcement of the Refuse Act of 1899 by requiring that all sources of industrial wastes discharging to navigable waters or their tributaries must apply to the Corps of Engineers for permits to continue such discharges. All sources of industrial wastes investigated during this study will thus need to apply for such permits.

Water Quality Improvement Act of 1970

On September 11, 1970, Federal regulations regarding the discharge of oil to navigable waters were established pursuant to the provisions of Section 11(b)(3) of the Federal Water Pollution Control Act, as amended by the Water Quality Improvement Act of 1970. This legislation required the President to publish, in the Federal Register, rules regarding the allowable discharge of oil to navigable water from any source. Subsequently, the President published rules which specifically stated:

(1) That discharges of oil shall not occur in amounts which violate applicable water quality standards, or;

(2) That discharges of oil shall not occur in amounts to cause a film or sheen upon or discoloration of the surface of the water or adjoining shorelines or cause a sludge or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines.

APPENDIX B

BIOLOGICAL STUDY METHODS FOR PALATABILITY AND SURVIVAL STUDIES

Lower Calcasieu River
Louisiana
(April 20-24, 1971)

APPENDIX B

STUDY METHODS

Common white, or lake, shrimp (*Penaeus setiferus*), sized from 90-110 mm,* were used for survival and palatability studies in the Lower Calcasieu River. Shrimp were captured by bottom seining at 5-minute intervals in Lake Calcasieu near Turner's Bay. The catch was released from the seining net into a holding tub. These test shrimp were transferred, with extreme care, employing a nylon dipnet, or by hand, from the tub to an aerated acclimation tank filled with clean water from Lake Prein. Shrimp exposure out of the water was kept to a minimum.

After a 24-hour acclimation period in the tank, less than ten percent of the shrimp were found in distress or dead because of the previous day's netting and handling. These were culled from the tank. Live, healthy shrimp were taken from the holding tank, decapitated, wrapped in foil, and frozen with dry ice for use as a taste and odor reference sample. The remaining live, healthy shrimp were used for survival and palatability tests.

At selected stations, wire, minnow baskets were attached to floats and suspended at 1-foot depths in the River. Cloth net bags, measuring 12 by 24 inches and having a mesh opening of one-quarter inch, were placed inside the baskets. Live shrimp were carefully transferred from the holding tank to cloth net bags inside the wire baskets. This basket apparatus permitted free circulation of River water through the cages, retained the test shrimp, and reduced predation by crabs.

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* Determined by measuring from the tip of the rostrum to the end of the telson.

Flavor and Odor Evaluation (Field and Laboratory Procedures)

Baskets, each containing six shrimp, were placed at control stations and near the Company's effluents in the Lower Calcasieu River and its tributaries. After a 6-hour River exposure near the Company's discharge, the shrimp were retrieved and examined. Survivors were decapitated, wrapped, in foil, and frozen with dry ice. These frozen shrimp were shipped to the Department of Food Science and Technology at Oregon State University, Corvallis, Oregon, for flavor and odor evaluations by a panel of experienced judges.

Odor Test -- At the Oregon State University facility, the wrapped, frozen shrimp were transferred from the shipping container to a -10°F freezer. Later, the shrimp were removed from the freezer and placed at 40°F. until defrosted, then cooked in eight ounces of unsalted boiling water for five minutes. The cooked shrimp were quickly peeled and then tightly wrapped with plastic film. The cooking water was poured into 100 ml beakers and the beaker then tightly covered with aluminum foil. Each respective sample of shrimp and cooking water was placed on a plate coded with a 3-digit random number.

The reference sample* was divided into four portions, two of which were placed on coded plates and the other two on plates marked "Ref." These shrimp were then alloted to two groups and placed on opposite counters for odor testing, with the first sample in each group being a "Ref" sample. Half of the judges smelled one group first and then smelled the other,

* Shrimp that were kept in aerated Lake Prien water and not exposed to River water near industrial discharges.

with a 3- to 5-minute wait between groups. The judges were asked to sniff both the shrimp and the cooking water and score the intensity of "off-odor" as related to the reference sample. Re-sniffing the reference sample was allowed. Thirty minutes after the first odor test was completed, the plates were recoded with new 3-digit random numbers, the order changed, and a second test conducted by the same ten judges.

Flavor Test -- Each shrimp was cut into four pieces and each respective sample mixed, then served in paper cups coded with 3-digit random numbers. The coded cups were randomly placed on two serving trays, each of which contained a labeled and a coded "Ref" sample. The trays were served in balanced order to the judges seated in individual testing booths lighted with yellow-orange light. The judges were asked to score the degree of "off-flavor" and the overall desirability of the samples on a 7-point scale. (0=extreme "off-flavor" and 7=no "off-flavor.") Because the sample size varied from one to six shrimp, only five judges were served on the flavor panel. Because there was only one shrimp in four of the 96-hour exposure samples, only two judges received these samples.

Survival Tests

Baskets, each containing ten shrimp, were placed at "flavor evaluation test" stations and elsewhere. These shrimp were used as test animals for 96-hour survival studies. At the termination of each 24-hour exposure period, mortalities were recorded and the surface water near each basket was tested for pH, temperature, and salinity.

Shrimp that survived the 96-hour exposure were tested for flavor in the manner described above.

APPENDIX C

CUSTODY OF SAMPLES

tag, the information sheet recorded the laboratory to which the sample was sent, the time and method of shipment, and the carrier. Federal Government Bills-of-Lading provided additional records of the shipments made.

Upon arrival of each shipment at its destination, laboratory personnel recorded the time and date of receipt; the number and type of samples received; and the analyses to be performed. This documentation procedure maintained a "custody" record from the field-to-the-laboratory transit. Each analytical laboratory involved (Division of Field Investigations - Denver Center; Division of Field Investigations-Cincinnati Center; Analytical Quality Control Laboratory, Cincinnati, Ohio; and the Southeast Water Laboratory, Athens, Georgia) then maintained custody of each sample, using procedures and records standard for the specific laboratory.

This special "custody" documentation was employed for industrial waste effluent samples only. No "custody" numbers were assigned for water and sediment samples collected from streams. Normal documentation procedures including tagging of samples, as discussed above, and logging of field measurements were followed.

APPENDIX D

ANALYTICAL PROCEDURES

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ANALYTICAL PROCEDURES

Grab, or 24-hour composite, samples of water, industrial waste, and bottom sediments were collected in the Lake Charles area by DFI-DC personnel. Samples were preserved when collected as outlined in the Federal Water Quality Administration's Manual for the Chemical Analysis of Water and Wastes.[1/]*

One-liter grab samples were collected in glass containers from each Company's effluent suspected of containing oil and grease. The samples were preserved with 2 ml concentrated H_2SO_4/l and shipped on ice to the Division of Field Investigation-Denver Center. Within 24 hours after collection, the samples were tested for oil and grease, according to the procedure outlined in Standard Methods for the Examination of Water and Waste Water[2/] - *with the exception that n-hexane was used as the extraction solvent instead of petroleum ether.* Because only single grab samples were taken from each effluent, the results may not be representative of the composite daily discharge.

Twenty-four-hour composite samples were collected at each of the Company's effluents. One liter of the sample was preserved with 2 ml concentrated H_2SO_4 for total organic carbon (TOC), chemical oxygen demand (COD), ammonia nitrogen (NH_3-N), and organic nitrogen (org.-N) analyses. One liter was preserved with 5 ml concentrated HNO_3 for metals analyses and one liter was left untreated for total and suspended solids analyses.

Water and effluent samples specified for metals analyses were shipped,

* Numbers in _/ refer to listing in References.

air-freight, to the Division of Field Investigations-Cincinnati Center. These samples were analyzed for cadmium (Cd), copper (Cu), Lead (Pb), chromium (Cr), zinc (Zn), aluminum (Al), and nickel (Ni) by atomic absorption spectrophotometry. All samples were analyzed for total mercury (Hg) according to the flameless AA procedure of Hatch and Ott.[3/]

Other samples were shipped, air-freight, to the Analytical Quality Control (AQC) Laboratory in Cincinnati where they were analyzed, by DFI-DC personnel, according to procedures described in the FWQA Manual.[1/]

These samples were tested for TOC by injection of homogenized 100 µl aliquots into a Beckman Model 915 Carbon Analyzer after having been purged with nitrogen gas for five to ten minutes. Injections were made in duplicate and triplicate; the average peak height was taken for comparison to a standard curve. In general, reproducibility was within five percent. Industrial waste samples with more than 20 mg/l TOC were also analyzed for COD. These determinations were made according to the procedure for "high level COD," (i.e., digestion with 0.25N $K_2Cr_2O_7$). For this analysis sufficient mercuric sulfate was added to each sample to tie up the chloride ions -- as determined by titration with mercuric nitrate. In general, each sample was tested only once, although one duplicate analysis was reproducible within eight percent. Both NH_3-N and org.-N were determined using the micro-Kjeldahl apparatus. Consequently, all reagent concentrations were scaled down to one-tenth of the level of the regular Kjeldahl procedure. Several duplicate analyses were performed with reproducibilities of four and six percent.

Total and suspended solids were determined on the unpreserved samples.

The residues were dried at 105°C.

Bottom sediment samples were collected with an Eckman Grab Sampler at selected sites along the Calcasieu River and in the vicinity of waste discharges. The muds were packed in Whirlpack bags, frozen, and shipped airfreight to the AQC Laboratory in Cincinnati.

Samples, when thawed, were air-dried at 35°C for two days under a stream of clean, dry air. The percent volatiles were calculated from the weight loss after heating the dried sample at 600°C for one hour. The percent carbon and organic nitrogen were determined by the procedures outlined by Ballinger and McKee.[4/] The organic sediment index (OSI) was calculated as the product of the percent carbon and percent organic nitrogen.

Mercury in the dried sediments was determined by an adaptation of the "wet digestion/flameless AA procedure" for mercury in fish development by Uthe, et al.[5/] Standard additions using mercuric chloride or methyl mercuric chloride were made on each sample; recoveries ranged from 87 to 122 percent throughout the 20 samples.

One-liter grab samples were collected from the Company's effluents for organic characterization. Immediately after collection, the samples were frozen and shipped, air mail-special delivery, to the Southeast Water Laboratory, Athens, Georgia. The samples were thawed, then extracted with chloroform. Chloroform extracts were concentrated to one ml or less and injected into a Perkin Elmer Model 900 gas chromatograph. Conditions were adjusted to obtain the best resolved chromatogram by using open tabular columns of Carbowax 20 M or SE-30. Once the conditions were selected, the

column effluent was directed into a Perkin Elmer-Hatachi Mass Spectrometer Model RMU-7. Mass scans were made of all major peaks. Identity of the extract components was confirmed by injecting known compounds under the same conditions and comparing both the retention time and the mass spectrum.

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