ENVIRONMENTAL PROTECTION AGENCY

OFFICE OF ENFORCEMENT

# REPORT ON
# EVALUATION OF INDUSTRIAL WASTE DISCHARGES
# AT
# CALCASIEU PAPER COMPANY
# ELIZABETH, LOUISIANA

Prepared By

DIVISION OF FIELD INVESTIGATIONS - DENVER CENTER
DENVER, COLORADO

AND

REGION VI DALLAS, TEXAS

OCTOBER 1971

CLEAN WATER

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENFORCEMENT

Report on

# Evaluation of Industrial Waste Discharges at Calcasieu Paper Company Plant Elizabeth, Louisiana

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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 on the Lower Calcasieu River are primarily involved in the production of chemical, petrochemical, and petroleum products. Significant industries in the Upper Calcasieu River area include a Kraft paper process mill and a tall oil processing plant.

These industries discharge waste waters into the Calcasieu 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 (DFI-DC), 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.

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 Calcasieu Paper Company plant, Elizabeth, Louisiana, and recommends actions necessary to protect the quality of the receiving waters. Complete custodial records [Appendix B], 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

Analytical Quality Control Laboratory, Cincinnati, Ohio

Enforcement Office, Region VI, Dallas, Texas

Southeast Water Laboratory, Athens, Georgia

## 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 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 up-

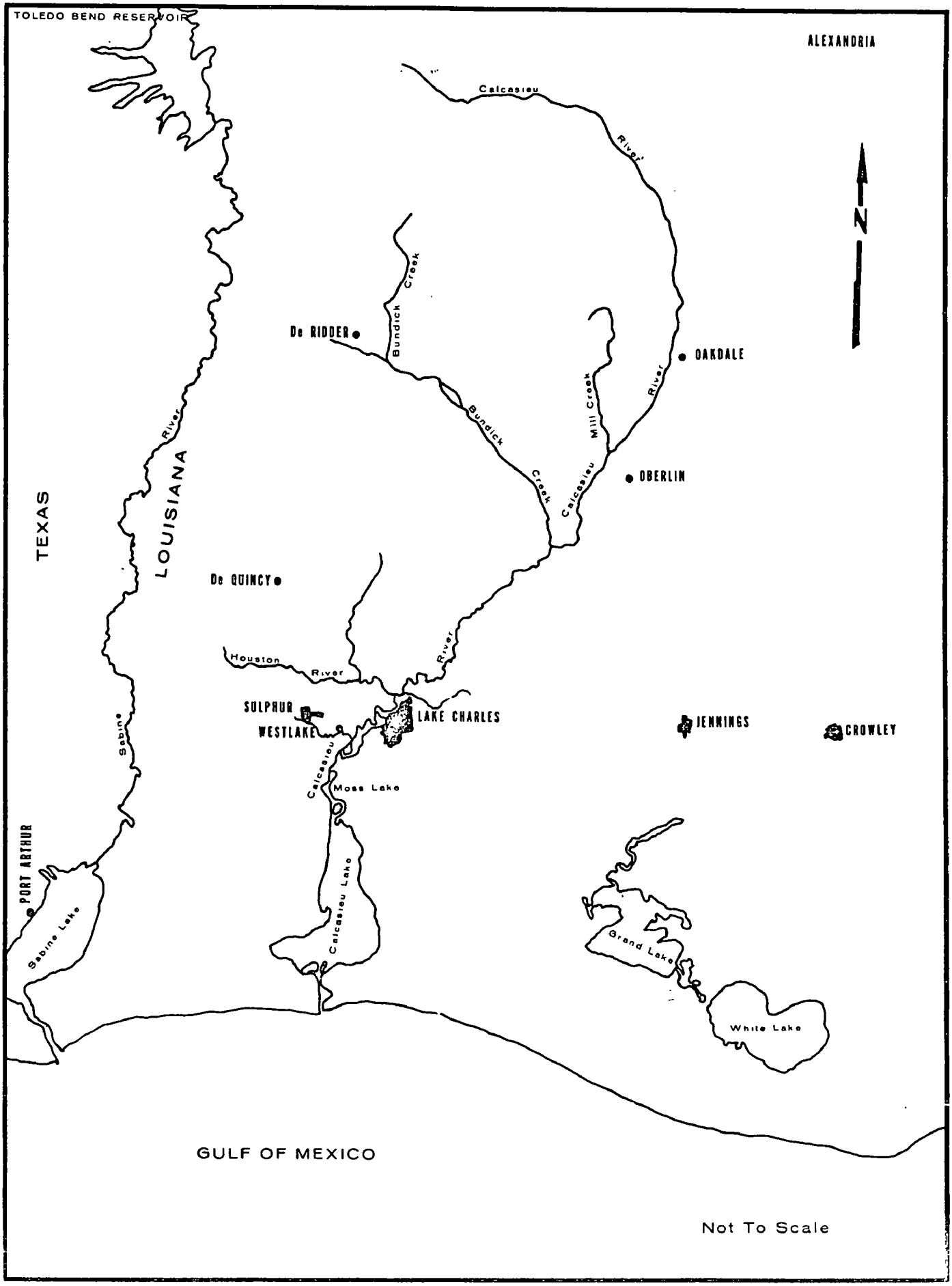


Figure 1. Location Map - Calcasieu River Drainage

stream from the salt water barrier to the headwaters of the basin.

The River is navigable from its mouth to Moss Bluff, Louisiana (about ten miles upstream from 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).

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.

The Calcasieu Paper Company, located between timber production areas and a seaport, contributes significantly to the economy of the area.

## Facility Description

The Calcasieu Paper Company (a Kraft process mill) and the Iron Kraft Bag Company (adjacent to the mill) are divisions of Unijax Corporation, West Bay annex, Jacksonville, Florida. At the paper company, whose capacity is 350 tons per day, there is no bleaching of pulp. The raw materials used are wood, salt, coke, lime, caustic soda, and sodium sulfate. (The product is converted to wrapping paper and bags by the adjacent bag company.)

About 850 people are employed at the two plants. The mill operates continuously, three shifts per day. During the visit of EPA personnel, this plant was not operating at full capacity. Two engineers, one chemist, and a laboratory technician are assigned full-time to water pollution control at the Kraft process mill.

Water Supply

Seven wells, each rated at 900 gpm, provide a total of 9 mgd of water. This water is used for processing, cooling, boiler feed, fire control, and sanitary purposes.

Existing Waste Treatment

Major sources of wastewater are the white water from the paper machines and the black liquor (spent cooking liquor) from the pulp process. White water and cooling water blowdown are released, without treatment, to Mill Creek, which flows for 14 miles through West Bay Wildlife Management Area before discharging to the Upper Calcasieu River. The black liquor is treated in the oxidation ponds that overflow to Mill Creek. During an EPA tour of the mill (April 2, 1971) black liquor was being discharged, along with the the white water, directly to Mill Creek. Company officials stated that this was not a routine occurrence, but was due to a breakdown in the pulp process. The resulting effluent was black in appearance and ranged in temperature from 36° to 42°C.

Chronology of Contacts

On April 2, 1971, M. R. Helton and R. D. Harp of EPA's DFI-DC met with J. E. Mailhaus, the Calcasieu Paper Company plant manager, to collect information on wastewater disposal practices at the plant. E. D. Anthony, Jr.,

enforcement program specialist, Region VI, EPA, Dallas, Texas, had arranged for the meeting on March 31.

Subsequent to the April 2 meeting (about a week later) the Plant Manager was contacted by DFI-DC representatives and a request was made to sample the plant discharges. Mr. Mailhaus was informed that effluent sampling was in conjunction with a water quality survey of the Calcasieu River Basin that was being conducted 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;

(5) Abatement proceedings 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. Mailhaus objected to the planned sampling regime that included sampling of the plant effluent at the outfall, at the Company's property fence. He asserted that the waste receives additional treatment while flowing in Mill Creek and claimed it was the Company's right to use the stream for treatment purposes. The investigating team explained to Mr. Mailhaus that the Refuse Act applies to waste discharges at the point of discharge to the naturally occurring waterways that are classified as navigable or as tributaries to navigable streams. Permission was granted

to sample at the point of discharge (MC-2). Mill Creek was also sampled at the mouth (MC-1).

## SAMPLING PROGRAM AND RESULTS

Samples (125 ml. aliquots) were composited every two hours, for a 24-hour period, commencing at 6:25 a.m., April 19. A grab sample for oil and grease analyses was taken at 8:25 a.m., April 19. Eight days later, water quality and sediment samples were collected from Mill Creek and from the Calcasieu River upstream and downstream from the mouth of Mill Creek. [Descriptions of the sampling stations and their locations are shown in Table 1 and Figure 2, respectively. Analytical results from the sampling program are listed in Table 2.]

During the sampling period, the Calcasieu Paper Company was discharging 8.7 mgd, carrying a load of 10,900 lbs of total organic carbon (TOC); 36,700 lbs of chemical oxygen demand (COD); 26,200 lbs of suspended solids; and 290 lbs of oil and grease. Samples collected at MC-1 and at the CR-20 and CR-21 stations indicated that the wastes carried by Mill Creek increased the TOC and suspended solids concentrations in the Calcasieu River from 11 mg/l to 15 mg/l, and from 18 mg/l to 49 mg/l (35 percent and 170 percent, respectively).

Bottom sediments from MC-2 near the point of discharge contained 25 percent volatile materials, while the sediments from MC-1 near the mouth of Mill Creek contained 3.8 percent volatiles [Table 3]. The differential confirms that substantial decomposition of discharged solids from the Calcasieu Paper Company takes place in Mill Creek.

TABLE 1

DESCRIPTION OF EFFLUENT AND RECEIVING WATER SAMPLING POINTS

| Station Number | Description and Remarks |
|---|---|
| CAL-1 | Sample taken 20 yards downstream from the point where the "Front Ditch" and "Back Ditch" combine at the headwaters of Mill Creek. Mill Creek is a tributary to the Calcasieu River. |
| CR-20 | Calcasieu River at Highway 26 bridge (USGS 135) downstream from the mouth of Mill Creek. |
| CR-21 | Calcasieu River at bridge in Sec 15, T4 and R4W upstream from the mouth of Mill Creek. |
| MC-1 | Mill Creek near mouth at USGS 134.5. |
| MC-2 | Mill Creek south of Elizabeth, Louisiana. |

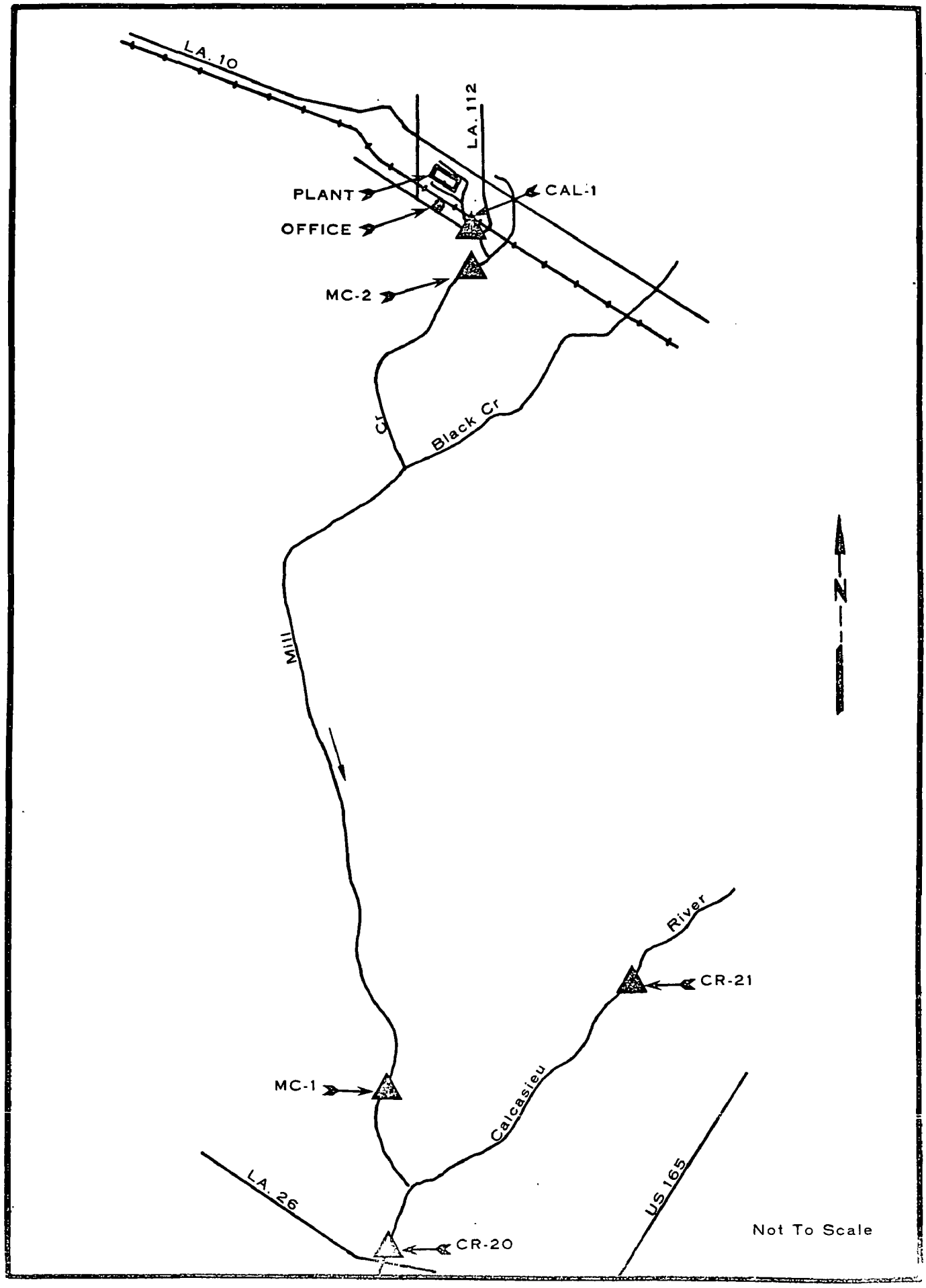


Figure 2. Effluent & Receiving Water Sampling Locations for Calcasieu Paper Company

TABLE 2

SUMMARY OF ANALYTICAL RESULTS AND FIELD MEASUREMENTS[a/]

| Sta | Flow mgd | pH range | Conductivity umhos/cm range | Conductivity umhos/cm composite | Temp °C range | TOC mg/l | TOC lbs/day | COD[b/] mg/l | COD[b/] lbs/day | Solids total mg/l | Solids total lbs/day | Solids susp mg/l | Solids susp lbs/day |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CAL-1 | 8.71 | 7.2-11.2 | 320-5,000 | 750 | 36-42 | 150 | 10,900 | 504 | 36,700 | 918 | 66,800 | 360 | 26,200 |
| CR-20 | | 6.5- 7.3 | | 117 | 23 | 15 | | | | 182 | | 49 | |
| CR-21 | | 7.4- 8.0 | | 75.5 | 20-22 | 11 | | | | 116 | | 18 | |
| MC-1 | | 6.4- 6.6 | | 2,000 | 22 | 48 | | 200 | | 451 | | | |
| MC-2 | | 7.6- 9.3 | | 12,800 | 36-37 | 390 | | 560 | | 1,810 | | | |

| Sta | Oil & Grease mg/l | Oil & Grease lbs/day | Cadmium mg/l | Chromium mg/l | Chromium lbs/day | Mercury µg/l | Copper mg/l | Lead[c/] mg/l | Aluminum mg/l |
|---|---|---|---|---|---|---|---|---|---|
| CAL-1 | 4 | 290 | <0.05 | 0.10 | 7 | <0.1 | | | |
| CR-20 | | | <0.05 | <0.02 | | <0.1 | <0.02 | <0.1 | 1.5 |
| CR-21 | | | <0.05 | <0.02 | | <0.1 | <0.02 | <0.1 | 2.4 |
| MC-1 | | | | | | <0.1 | | | |
| MC-2 | | | | | | <0.1 | | | |

a/ Analytical procedures are outlined in Appendix C.
b/ COD analyses were performed when TOC values exceeded 20 mg/l.
c/ No interference from calcium detected.

TABLE 3

ANALYTICAL RESULTS OF BOTTOM SEDIMENT SAMPLES

| Station | Date | Nitrogen % | Organic Sediment Index | Sediment Type | Mercury[a/] µg/g | Volatiles % | Organic Carbon % |
|---|---|---|---|---|---|---|---|
| MC-1 | 4/27/71 | 3.78 | 4.1 | III | 0.2 | 3.8 | 1.08 |
| MC-2 | 4/27/71 | | | | <0.1 | 25.0 | |

a/ Results based on dry weight. Samples dried at 35°C for two days.

## DATA REPORTED TO LOUISIANA STREAM CONTROL COMMISSION

The Louisiana Stream Control Commission recently approved the discharge levels of certain materials based on data submitted them by Calcasieu Paper Company. A summary of the information from the Commission is as follows:

| | |
|---|---|
| Date of Application: | August 20, 1970 |
| Quantity of Discharge: | 11 cfs |
| Temperature: | Equivalent to stream temperature |
| Turbidity: | 80 |
| True Color: | 135 |
| Organic Materials: | 8,883 lbs/day, equivalent to 150 ppm |
| Inorganic Materials: | 11,843 lbs/day, equivalent to 200 ppm |

No toxic materials were listed in the application. Discharge is to the Upper Calcasieu River.

## PROPOSED WASTE TREATMENT

According to Company officials, a new waste treatment facility has been designed and is scheduled to be completed within the next year. The major portion of the present wastewater flow will be recirculated. The proposed system is designed to reduce BOD to 25 mg/1, suspended solids to 25 mg/1, and color to 100 APHA units. The "treatment" afforded by Mill Creek will, according to Company estimates, reduce the BOD by an additional 75 percent at the mouth of Mill Creek. The Company officials contend, further, that the constituents in the wastewater will be reduced correspondingly by treatment in Mill Creek, thus causing a negligible effect on the Calcasieu River.

## CONCLUSIONS

1. Because Mill Creek flows, for its entire length downstream from the point of discharge, through the West Bay Wildlife Management Area, using the stream as a treatment facility is unacceptable.

2. The Calcasieu Paper Company has indicated intent to claim use of Mill Creek as part of the treatment process subsequent to the installation of new treatment facilities. Use of a tributary to a navigable stream for waste treatment or disposal is a violation of the Refuse Act and, in the case of Mill Creek, constitutes a violation of Louisiana law.

3. Present treatment permits the daily discharge to a tributary of a navigable stream of 10,900 lbs of carbonaceous materials; 26,200 lbs, suspended solids; and 290 lbs of oil and grease, thus constituting violations of Section 407, Rivers and Harbors Act of 1899 (33 USC: 401-413).

## RECOMMENDATIONS

It is recommended that:

1. The Office of Enforcement, EPA, monitor progress toward initiation of suitable treatment by July 1, 1972, and evaluate the effectiveness of treatment by January 1, 1973, to ascertain that effluent quality at the point of discharge is adequate for release into a wildlife refuge.

2. The Office of Enforcement, EPA, notify the Louisiana Stream Control Commission that:

a) The Calcasieu Paper Company claims the right to use Mill Creek for waste treatment, is presently doing so, and intends to continue the practice subsequent to construction of new treatment facilities and that,

b) Mill Creek is the property of the State of Louisiana, by virtue of LSA - R.S. 9:51 Section 1101, and the statute gives specific guidance in the control of pollution "... injurious to ....aquatic life or wild or domestic animals or fowls."

3. If the implementation of this treatment program is not carried out according to schedule, or if treatment is not adequate, consideration be given to initiating appropriate abatement actions against the Company.

4. The discharge permit to be issued by the Corps of Engineers limit discharges of BOD, COD, TOC, suspended solids, color, and toxic materials to levels consistent with applicable water quality standards and best available treatment.

## 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 $TLM_{48/10}$. |
| 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 $TLM_{48/10}$. |
| 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 $TLM_{48/10}$. |
| 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

## CUSTODY OF SAMPLES

# APPENDIX B

## CUSTODY OF SAMPLES

Special procedures were employed during the field investigations of waste sources in the Calcasieu River Basin to insure that a chain of custody was documented for water quality samples potentially useful as evidence for enforcement actions. This documentation was designed to maintain a record of the collection and source of each sample, as well as of the personnel involved in the handling, preparation, and disposition of each.

A unique "custody" number was assigned to each of the Company's waste effluent samples collected. This number was recorded on the sample tag, the corresponding "custody" information sheet, and on the laboratory receipt log.

As each sample was collected, a labeled tag was attached to each bottle or container. The tray information recorded on the tag included the "custody" number; the sampling station number and description; the time and date of collection; the types of analyses to be performed on the sample by the laboratory; the types of preservatives added [see Appendix C, Analytical Procedures]; and the personnel collecting the sample and performing the sample preservation. Sample containers were placed in plastic bags and the bags sealed with paper tape bearing the initials of the individual packaging the sample. The intact seal and bag guaranteed the integrity of the sample during shipment.

A special "custody" information sheet was prepared for each "custody" number assigned. In addition to information being recorded on the sample

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 for 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 C

# 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,

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 air-freight 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 developed 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-Hitachi 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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