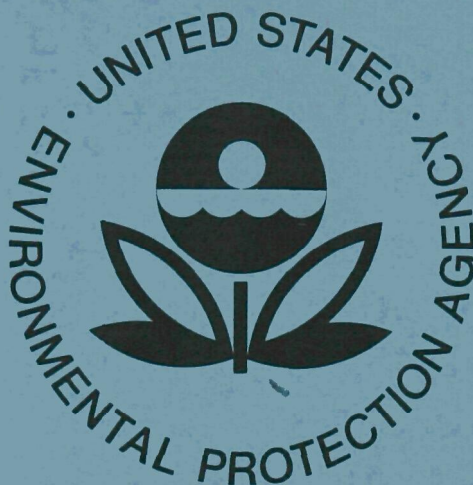


INDUSTRIAL POLLUTION OF THE LOWER MISSISSIPPI RIVER IN LOUISIANA



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Region VI **Dallas, Texas**

SURVEILLANCE AND ANALYSIS DIVISION

April 1972

INDUSTRIAL POLLUTION
OF THE
LOWER MISSISSIPPI RIVER IN LOUISIANA

ABSTRACT

Waste waters from 60 industries discharging to the Mississippi River from the Baton Rouge area to its mouth have been analyzed and found to contain organic chemicals and toxic metals in high concentrations. Municipal water supplies were found to contain organic compounds in trace amounts which are believed to be the cause of the off-flavors in these supplies, and which may present a potential threat to the health and wellbeing of the consumers. Fish exposed to the river water developed objectionable tastes within seventy-two hours. Violations of taste and odor criteria in the river and in fish flesh were identified.

United States
Environmental Protection Agency
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FOREWORD

In 1967, at the time this study was requested by the State of Louisiana, concern had developed over the quality of the Mississippi River water as a drinking water supply. Complaints of off-flavors - variously described as "oily" or "chemical" - in the drinking water of New Orleans and nearby communities were occurring with increasing frequency. Fishermen were finding that fish caught in the reach of the river below Baton Rouge were no longer saleable because of these same bad tastes.

The deterioration of the water quality in the river closely paralleled the explosive development of a petrochemical industrial complex which began in the middle 1950's and which by the end of the 1960's had resulted in the location of over 60 major industries from Baton Rouge to the mouth of the river. Most of the industries discharged their partially treated or untreated wastes to the river.

As this investigation progressed from 1969 through 1971, results of the findings were made available to industry. This factor, coupled with a complete review of all industrial waste permits by the State of Louisiana and the initiation of the Refuse Act Permit Program jointly by the Environmental Protection Agency and the Corps of Engineers, resulted in the beginning of an active program by industry to reduce the waste discharges to the River. Some of the immediate improvements are reflected in the data in this report. Further substantial improvements in the quality of the waste discharges are expected within the next two to three years as the ongoing waste abatement programs are developed and completed.

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INTRODUCTION

In the spring of 1964, a conference on pollution of interstate waterways of the Lower Mississippi River and its tributaries was called by the Secretary of Health, Education, and Welfare. The Secretary, "...having reason to believe that pollution of the Mississippi River was responsible for recent (1963-64) fish kills and was endangering the health and welfare of persons in States other than those in which the discharges originate" caused a conference to be convened on May 5 in the Federal Office Building, New Orleans, Louisiana. The conferees, representing the states of Louisiana, Mississippi, Arkansas, Tennessee, and the Federal Government met for two days to review evidence related to the alleged pollution. The conference adjourned after adopting a set of conclusions and recommendations which have been reported elsewhere (65). Of principal interest here is Recommendation No. 3 which says, "A technical committee composed of the conferees or their designees be established to direct and advise in the identification and abatement of all sources of pollution affecting the main stream of the Lower Mississippi. The Department of Health, Education, and Welfare will participate and aid in the investigation project."

On March 23, 1967, Dr. Leslie L. Glasgow, Chairman of the Louisiana Stream Control Commission, wrote to Mr. James M. Quigley, Commissioner, Federal Water Pollution Control Administration, U. S. Department of the Interior, requesting technical assistance (see Appendix, Exhibit A). In response to this request, and in compliance with Recommendation No. 3 of the 1964 Enforcement Conference, a project plan was prepared, approved and field work started in early 1969. This report presents the results of this study and is considered to respond both to Recommendation No. 3 of the 1964 Conference insofar as it pertains to Louisiana and to Dr. Glasgow's request of 1967.

AUTHORITY

The study reported herein is authorized by the Federal Water Pollution Control Act, as amended, Section 5(b) and Section 10(d).

SCOPE

The study area comprises the main stem of the Lower Mississippi River from St. Francisville, Louisiana, near the Mississippi-Louisiana state line, downstream to Venice, Louisiana (see Appendix, Exhibit B). The period covered extends from January 1969 through June 1971.

OBJECTIVES

The general objective of the study is to determine water quality degradation in the Lower Mississippi River Basin through the identification of hazardous industrial wastewaters which endanger human health and the health of the aquatic biota and cause off-flavors in food fish and drinking water supplies.

Specific objectives are to:

1. Evaluate the pollution potential of industrial discharges from St. Francisville, Louisiana, to Venice, Louisiana.
2. Identify drinking and stream water quality standards violations.
3. Support - by providing technical data - state action, and subsequent federal action, if necessary, to stop violations of standards and abate pollution.

ACKNOWLEDGEMENTS

Special appreciation is expressed to Dr. A. A. Rosen and his staff at the Federal Water Quality Laboratory in Cincinnati for consultation, guidance, staff training, and the loan of equipment. The cooperation and assistance of the Executive Secretary of the Louisiana Stream Control Commission and his staff contributed greatly to the success of this study. Assistance was also provided by The Dow Chemical Company, Midland, Michigan, in the analysis of special samples and by the managers and environmental engineers of the industries discharging to the Lower Mississippi River. Consultation, advice, and analytical support were provided by personnel of the Robert S. Kerr Water Research Center, Ada, Oklahoma, the Analytical Quality Control Laboratory, the Robert A. Taft Engineering Center, and National Field Investigation Center, all in Cincinnati, Ohio, and the Southeast Water Laboratory in Athens, Georgia, and the Bureau of Sport Fisheries and Wildlife, Denver, Colorado. To all of these and to all others who participated in this study we extend our sincere thanks.

SUMMARY OF FINDINGS

1. Liquid wastes from sixty major industries discharge to the Lower Mississippi River in Louisiana in a two hundred and fifty-eight mile stretch between St. Francisville and Venice.
2. The Mississippi River in this reach serves as the source of raw water for forty water utilities that provide water for approximately 1.5 million people.
3. Cyanides, phenols, arsenic, lead, cadmium, copper, chromium, mercury and zinc were present in samples of industrial wastes.
4. Forty-two industrial plants each contributed over five pounds per day of at least one heavy metal each to the river.
5. Twenty-two plants each discharged wastes containing five or more pounds per day of lead each to the river.
6. Twenty-nine plants each discharged wastes containing five or more pounds of chromium per day.
7. Twenty-nine plants each discharged wastes containing five or more pounds of zinc per day to the river.
8. Eight plants each discharged wastes containing five or more pounds per day of cadmium to the river.
9. Five plants each discharged wastes containing five or more pounds per day of arsenic to the river.
10. Five plants discharged wastes containing measurable amounts of cyanide to the river.
11. Seventeen plants each discharged wastes containing ten or more pounds per day of phenolics to the river.

12. Forty-six organic chemicals in trace amounts were present in the raw or treated water supplies from three water plants - the U. S. Public Health Service Hospital at Carville, the Carrollton plant of the City of New Orleans and the Jefferson Parish #2 Water Plant at Marrero. Thirteen of these were present in wastes from seven industrial plants.

13. An additional forty-four organic chemicals were present in the wastes from ten industrial plants. These chemicals were not found in the finished water of the three municipal water plants.

14. Fifteen plants each discharged wastes with 40,000 pounds or more per day of chemical oxygen demand and ten discharged 20,000 pounds per day or more of total organic carbon.

15. Thirty-two plants each discharged 50,000 pounds per day or more of total solids and twenty-six discharged 25,000 pounds or more of volatile solids.

16. The average threshold odor in the raw water at six water treatment plants increased from 7.3 at river mile 260 to 12.0 at river mile 99.

17. The characterization of the river water odor varies from "earthy" or "musty" upstream to "chemical" or "petrochemical" downstream.

18. All of the sixty industrial plant discharges were found to have discernible odors. Each was capable of causing detectable odors in flows ranging from 758 billion gallons per day to 50 thousand gallons per day. The average flow of the Mississippi River at New Orleans is considered to be 500,000 cubic feet per second or 323 billion gallons per day.

19. Threshold odor numbers at the intake of downstream water utilities indicate that odor contributions from upstream industries are still present when the waters are taken in for treatment to become potable water.

20. A survey of fishermen and wholesale fish dealers revealed that fish caught in the reach of the river below Baton Rouge were not saleable because off-flavors in the fish made them unacceptable to the public.

21. Experimental fish placed downriver from major industrial complexes developed pronounced off-flavor after 72 hours of exposure to the river water.

22. Six organic chemicals found in trace quantities in the finished water supplies at either the U.S. Public Health Service Hospital at Carville or the New Orleans Carrollton Plant, or both, have been shown by others to induce histopathological changes in animals in chronic toxicity studies.

23. Three of the organic compounds found in trace quantities in the finished water supplies of the U.S. Public Health Service Hospital at Carville and the Carrollton plant at New Orleans have been shown by others to be carcinogenic.

24. Many of the industries investigated in this study have initiated waste abatement programs as required by the State of Louisiana and/or by the Refuse Act Permit Program of the Corps of Engineers and the Environmental Protection Agency.

CONCLUSIONS

1. This report fulfills the request for technical assistance from the Louisiana Stream Control Commission dated March 23, 1967 and Recommendation No. 3 of the 1962 Lower Mississippi Enforcement Conference.
2. Industrial waste discharges are contributing significant quantities of hazardous and/or undesirable pollutants to the Mississippi River in Louisiana.
3. The industrial waste discharges are the principal cause of the persistent "oily-petrochemical" odor in the public water supplies downstream from Baton Rouge.
4. The industrial waste discharges are the principal cause of the tainted flesh of fish caught in the Mississippi River downriver from Baton Rouge.
5. The trace organics in the Mississippi River drinking water supplies are a potential threat to the health of the 1.5 million people who consume this water, particularly the elderly, those that are ill and children.
6. The water quality standards of the State of Louisiana and the Federal Government relating to taste and odor producing substances are being violated by industrial waste discharges to the Lower Mississippi River in Louisiana.
7. Past industrial waste abatement practices of Mississippi River industries were not adequate to control the discharges of heavy metals or organics.
8. Ongoing industrial waste abatement programs should remove and/or reduce many of the hazardous discharges to the river.

RECOMMENDATIONS

Based on the findings and conclusions contained in this Report, and in order to protect and enhance the suitability of the Lower Mississippi River as a source of raw water supply, it is recommended that:

1. The State of Louisiana in cooperation with the Environmental Protection Agency review the proposed waste abatement programs of all industries identified in this Report as having excessive discharges of odorous components, organics and heavy metals to insure that each waste abatement program will adequately reduce the discharge of these components to an acceptable level.

2. The Environmental Protection Agency, through appropriate Federal permit programs review all industrial permit applications to insure that all existing and planned waste treatment facilities are designed for maximum reduction of halogenated compounds, complex organics and heavy metals. The effluent concentrations and consequent loadings of heavy metals, complex organics and halogenated compounds should be consistent with information contained in Water Quality Criteria Data Book, Volumes 1 and 3 and other appropriate toxicological summaries and subsequent rules and regulations that from time to time may be promulgated.

3. The State of Louisiana take action to insure that all future industrial expansion is accompanied by best available waste treatment practices.

4. Municipal water treatment plants install treatment facilities designed to (a) obtain optimum removal of organic contaminants and heavy metals, and to (b) provide increased protection of the water supplies from accidental spills of chemicals and oil upstream from the municipality's raw water supply intake structure.

5. Municipalities using the Mississippi River as a source of drinking water expand their finished water monitoring programs to include organic and heavy metals analyses on a weekly basis.

6. The United States Public Health Service consider modifying the water treatment plant at their Carville, Louisiana hospital to include the addition of facilities designed to remove organic contaminants.

7. Appropriate medical agencies or foundations undertake epidemiological investigations to determine the chronic effects on humans of low level intakes of combinations of organic contaminants such as those found in the Mississippi River water supplies as described in this report.

8. The State of Louisiana take appropriate action to insure that:

a. The State Board of Health has adequate legal authority to cause (1) immediate cessation or impoundment of discharges which contain noxious, poisonous, or otherwise objectionable substances into any source of water supply, (2) immediate revocation of any permit for a discharge containing objectionable substances where such substances adversely affect in any manner the public water supply, or are noxious, poisonous or carcinogenic, or otherwise threaten the public health and welfare or enjoyment of the public water supply; and

b. State and local prosecutors have adequate legal authority, acting on requests from any agency, department or commission of the State to secure such relief as may be necessary to abate the presence of objectionable substances present in a public water supply before or after treatment for potable water.

9. An investigation be undertaken of the Mississippi River estuary to determine the extent of heavy metal, complex organic, halogenated compound and other pollution upon shrimp, fish, shellfish and other biota in the food chain.

10. A continuing assessment be made of the water quality of the Lower Mississippi River to determine the effectiveness of abatement practice schedules.

CHAPTER I

DESCRIPTION OF STUDY AREA AND PERTINENT PROBLEMS

The Mississippi River rises in Minnesota and flows southward 2,350 miles to the Gulf of Mexico, draining over 40 percent of the United States and part of Canada. The Lower Mississippi River Basin begins at the mouth of the Ohio River (Cairo, Illinois) and encompasses parts of the states of Missouri, Kentucky, Arkansas, Tennessee, Mississippi, and Louisiana. The alluvial valley of the Lower Mississippi River is a broad, gently sloping lowland which begins below Cape Girardeau, Missouri, and extends to the Gulf of Mexico. This lowland extends more than 600 miles, varies in width from 30 to 125 miles and is bordered by abrupt escarpments. Tributary flows join the main river at various locations. The lowland extends up these tributaries many miles beyond the broad flat basins in the vicinity of the junctions.

The flow of the Mississippi River in the lower basin is large, ranging from a record high at Vicksburg, Mississippi, of 2,280,000 cubic feet per second (cfs) on May 4, 1927, to a low of 100,000 cfs on October 17, 1939. However, both extremes preceded control structures and probably never again will be approached.

Flows in the lower Mississippi River are affected by diversions into the Atchafalaya River through the Old River diversion channel near Coochie, Louisiana (approximately R.M. 315). The U. S. Geological Survey reports that "the average flow of the Mississippi River below the diversion channel is probably meaningless." A more realistic appraisal of flow conditions to be expected can be made using data from the Vicksburg gaging station. Continuous record has been collected at this site since 1931. The average flow of the river during that period was 551,100 cfs. Annual averages varied from a high of 843,900 cfs for the 1950 water year to a low of 272,000 cfs for the 1931 water year (69).

The main stem of the lower Mississippi River is leveed to near its mouth. Outside the levees the area comprises woodlands and large farms. The more important tributaries to the Mississippi River in the Lower Mississippi River Basin are the St. Francis, White, and Arkansas flowing from the west and the Hatchie, Wolf, Yazoo, and Big Black Rivers draining from the east. All of these discharge into the Mississippi above the Louisiana-Mississippi state line and their points of confluence are above the study area covered in this report.

The Atchafalaya River is the major distributary of the Mississippi River. Water diverted from the Mississippi River joins the Red River to form the Atchafalaya River. In addition to the Atchafalaya distributary, water from the Mississippi River is pumped over the levee at Donaldsonville, (R.M. 175) into Bayou Lafourche to provide raw water for four water plants located on this bayou. The Mississippi and Atchafalaya Rivers discharging into the Gulf, form an extensive and exceedingly valuable estuary which is the nursery ground for a large part of the Gulf of Mexico's commercial and sports marine fisheries. The Mississippi River, its tributaries and its distributary are valuable sources of fresh water commercial and game fish. As will be discussed later, fish caught in the main stem of the Mississippi River are no longer saleable because of tainted flesh.

The general area of interest in this study is the stretch of the Mississippi River main stem from the Louisiana-Mississippi state line, River Mile (R.M.) 305, to the Head of Passes at River Mile 0. The Head of Passes is the point at which the Mississippi divides into three channels and the delta begins. The initial area studied covered that portion of the river from St. Francisville, Louisiana, (R.M. 260) to New Orleans, Louisiana, (R.M. 105). It was later extended to Venice, Louisiana, (R.M. 2) to include industries located below New Orleans. Sixty industrial plants are located on, or adjacent to, the banks of the Mississippi River and discharge into it in this two hundred and fifty-eight mile water way. Among these are

the largest petroleum refinery in the United States, several smaller refineries and numerous and diverse petrochemical and chemical manufacturers. Most of these industries utilize the Mississippi River water as a process or cooling water source, or both, and all of them discharge their partially treated or, in some cases, untreated wastes under a State permit system to the river. All industries have submitted implementation plans to the State to treat their wastes. The State is requiring the equivalent of secondary treatment by December 31, 1972. Decreases and/or elimination of some of the problems described in this report can be expected after this date. Heavy metals such as mercury, arsenic, lead, zinc, copper, chromium, cadmium, and zinc have been found in waste discharges in addition to phenols, cyanides, and a wide array of organic compounds. These wastes are believed to be the major cause of offensive tastes and odors in the drinking water of the approximately 40 communities providing water to about 1.5 million people. In addition, there is reason to believe that tastes are being imparted to fish in this stretch of the river to such an extent that wholesale and retail fish dealers will not handle fish caught in these waters because of repeated complaints by customers of "off" flavors often described as "oily" or "chemical."

CHAPTER II

EVALUATION OF THE POLLUTION POTENTIAL OF INDUSTRIAL WASTE DISCHARGES

Wastes that are discharged to the Mississippi River from sixty industrial plants between St. Francisville, Louisiana (R.M. 260), and Venice, Louisiana (R.M. 2) have been collected and analyzed. These analyses have disclosed that these discharges contain excessive quantities of heavy metals and organics. Since the Mississippi River serves as the drinking water supply for over 1.5 million people below Baton Rouge, the addition of these manmade materials - many of them toxic and odorous - is undesirable.

DETERMINATION OF WATER AND WASTE CHARACTERISTICS

A two-part investigation was undertaken in the determination of characteristics of water and wastes. The first part was designed to remove and concentrate the trace organics from the raw and treated river water. In order to obtain sufficiently large samples of the organics to allow identification, a largescale, activated carbon filter - called a Mega Sampler - was used (see Appendix, Exhibit D - Analytical Techniques for description of the mega sampling). Eleven mega samples were collected during the course of the investigation (see Table 1). The chloroform extract of the mega samples provided the raw material for the identification of most of the higher boiling organics; the saturated carbon was also used in one procedure for direct elution of the lower-boiling organics.

The second phase of the study involved the sampling and analyses of the industrial waste discharges to the Mississippi River. Twenty gallon composite samples of the waste outfalls were collected. One portion of the composite was extracted with solvents for trace organic analysis, and portions of the balance were analyzed for up to twenty-seven physical and chemical parameters. (Analytical Techniques are described in Appendix, Exhibit D.) A list of all companies sampled, locations, sampling dates, and analytical results will be found in Exhibit F of the Appendix.

TABLE I
RAW AND FINISHED WATER MEGA SAMPLES COLLECTED

Date	Water Supply System	Sample Size (1000 gal)	Average River Flow (1000 cfs)	Type
Apr 1969	Crown Zellerbach	181	670	Raw
Jan 1970	Crown Zellerbach	121	570	Raw
Sept 1969	USPHS Hospital	96	205	Raw
Sept 1969	USPHS Hospital	228	205	Finished
Jan 1970	Carrollton	300	580	Finished
Mar 1969	Jeff. Parish #2	87	690	Raw
Mar 1969	Jeff. Parish #2	106	470	Raw
May 1969	Jeff. Parish #2	100	720	Raw
Jun 1969	Jeff. Parish #2	99	360	Raw
Aug-Sept 1969	Jeff. Parish #2	108	260	Raw
Aug-Sept 1969	Jeff. Parish #2	177	260	Finished

TOXIC SUBSTANCES

Everything in our environment is composed of chemical substances, and most of these pose minimal danger to man or the environment. However, some pose a serious danger, particularly those involved in redistribution and chemical alteration resulting from man's activities when he engages in economic exploitation and disposal.

Selected metals, their compounds, and certain synthetic organic chemicals are perhaps the best examples of toxic substances which can adversely affect man and his environment.

This investigation did not include analyses of toxic heavy metals in the finished municipal water supplies. However, because these metals all have soluble forms, and many are known to enter the food chain, e.g. mercury, a delineation of the major discharges of these substances is considered a critical part of this study.

HEAVY METALS, CYANIDES AND PHENOL

Metals are recovered from ore deposits either directly or as byproducts in the course of refining other metals. Metallic salts formed during these recovery and refining processes can escape as waste products into surface and ground water.

After substances enter the environment, they may be diluted or concentrated by physical forces, and they may undergo chemical changes, including combination with other chemicals that affect their toxicity. The substances may be picked up by living organisms which may further change and either store or eliminate them.

The results of the interaction between living organisms and chemical substances are often unpredictable, but such interaction may produce materials that are more dangerous than the initial pollutants. One example is the conversion of inorganic mercury into methyl mercury.

Synergism is another complicating interaction. Two or more compounds acting together may have an effect on organisms greater than the sum of their separate effects. For example, the toxic effects of mercuric salts are accentuated by the presence of trace amounts of copper (62). Cadmium acts as a synergist with zinc and cyanide in the aquatic environment to increase toxicity (53, 54, 55).

The presence of heavy metals in industrial waste depicted in Table 2 shows that the frequency of occurrence in quantities of five pounds or more per day in the forty-two waste samples listed was greatest for chromium and zinc at 29, next for lead at 22, and for other metals less frequently. Toxicity, or properties otherwise hazardous to humans or aquatic biota, vary widely and are discussed in brief detail below.

Lead gives greatest cause for concern of the three metals found most often because of the relatively large quantities discharged and the fact that, as reported in the Public Health Service Drinking Water Standards, 1962, (63) "when taken into the body, it can be seriously injurious to health, even lethal, if taken in by either brief or prolonged exposure. Prolonged exposure to relatively small quantities may result in serious illness or death." (63) The Public Health Service Drinking Water Standards place the following limits on lead as they relate to human health.

"Limits and Ranges of Lead Affecting Health

Physiologically safe in water:

Lifetime	- 0.05 mg/l
Short period, a few weeks-	2-4 mg/l

Harmful range in water:

Borderline	- 2-4 mg/l for 3 months
Toxic	- 8-10 mg/l, several weeks
Lethal	- unknown, but probably more than 15 mg/l, several weeks"

TABLE 2

INDUSTRIES HAVING HEAVY METALS DISCHARGES
FIVE POUNDS PER DAY OR GREATER¹

<u>Company</u> <u>Plant or Division</u>	<u>Location</u>	<u>Date</u> <u>Sampled</u>	<u>Heavy Metals² - #/Day</u>						
			<u>As</u>	<u>Pb</u>	<u>Cd</u>	<u>Cu</u>	<u>Cr</u>	<u>Hg</u>	<u>Zn</u>
Allied Chemical Corp. Ind. Chem. Div.	Baton Rouge	4-14-70			20	20	200		232
		7-25-70	15	570					
		*12-2/3-70		56					
		*7-19-71		78		7			
Spec. Chem. Div. Plastics Div. Geismar Complex	Baton Rouge	6-22-70		7					13
	Scotlandville	4-28-70					42		16
	Geismar	6-29-70	20	7	20	10	75		59
American Cyanamid Co.	Avondale	2-2-70		5			17		
		*7-26-71					68		6
BASF Wyandotte Corp.	Geismar	4-7-70		20			69		
		*2-10/11-71		172			52		
Borden, Inc. Borden Chem. Div.	Geismar	*6-28-71					28		15
The Celotex Corp.	Marrero	*9-21-70	43	10					44
C. F. Industries	Donaldsonville	11-16-70					28		
		*8-2-71							8
Chevron Chemical Co. Oronite Add. Div.	Belle Chasse	*1-25-71							8
		*8-10-71							22

TABLE 2 (Continued)

Company <u>Plant or Division</u>	<u>Location</u>	<u>Date Sampled</u>	<u>Heavy Metals² - #/Day</u>						
			<u>As</u>	<u>Pb</u>	<u>Cd</u>	<u>Cu</u>	<u>Cr</u>	<u>Hg</u>	<u>Zn</u>
Ciba-Geigy Chemical Corp.	St. Gabriel	8-25-70					6		
Copolymer Rubber & Chem. Corp.	Baton Rouge	1-14-70				38	26		
		5-3-71				6	16		14
Cos-Mar Plant, Borg Warner Corp., Marbon Div.	Carville	7-6-70					8		
		*5-19-71					9		
Crown Zellerbach Corp.	St. Francisville	11-2-70		56	6		34		
The Dow Chemical Co.	Plaquemine	*6-21/22-71			10	82			
E. I. DuPont de Nemours & Co., Inc.	LaPlace	3-2-70		36					
		*5-4-71		48					
		6-14-71		7					
Enjay Chemical Co.	Baton Rouge	6-9-71		5		47	13		46
Ethyl Corp.	Baton Rouge	1-14-70					8		22
		7-25-70		3700					
		4-27/28-71		529		36	12		20
		6-24-71		301					630
Freeport Mineral Co. Freeport Chem. Co. Div.	Uncle Sam	*10-5-70				36			216
		*11-3-70		250	38	**	188		

TABLE 2 (Continued)

Company Plant or Division	Location	Date Sampled	Heavy Metals ² - #/Day						
			<u>As</u>	<u>Pb</u>	<u>Cd</u>	<u>Cu</u>	<u>Cr</u>	<u>Hg</u>	<u>Zn</u>
Georgia Pacific Corp. Crossett Div.	Port Hudson	5-4-70				15	15		105
Gulf Oil Co., U.S.	Venice	*6-15-71							65
Gulf Oil Chemical Co.	Welcome	8-31-70					120		74
Hercules, Inc. Allemania Plant	Plaquemine	*11-23-70					42		
NO Hooker Chemical Co.	Hahnville	2-24-70		140			74		
		*5-25/26-71		485		8	55		72
		*6-7-71		889					
		*6-7/8-71		218					
Humble Oil & Ref. Co.	Baton Rouge	*6-8-71			7		35		140
Kaiser Alum. & Chem. Corp. Chemicals Div.	Baton Rouge	7-21-70		400					
		8-30/31-71		354	71		67		1080
		8-31/9-1-71		352	52		145		1317
	Chalmette	*11-30-70		40		396	36		
	Gramercy	3-31-70					14		61
		7-21-70	31	500					
		9-28/29-71		90					405
	Gramercy	9-29/30-71		61			5		187
		9-7/8-71		323	55		139		919
Metals Div.		9-8/9-71		148	32		112		423

TABLE 2 (Continued)

<u>Company</u> <u>Plant or Division</u>	<u>Location</u>	<u>Date</u> <u>Sampled</u>	<u>Heavy Metals² - #/Day</u>					
			<u>As</u>	<u>Pb</u>	<u>Cd</u>	<u>Cu</u>	<u>Cr</u>	<u>Hg</u> <u>Zn</u>
Monochem, Inc.	Geismar	*6-22/23-71						23
Monsanto Co.	Luling	2-9-70				104	52	10
Murphy Oil Corp.	Meraux	1-18-71					5	15
Rollins Purle, Inc.	Baton Rouge	*4-12-71		7				
Rubicon Chemicals, Inc.	Geismar	1-21-70					7	
Schuykill Metals Corp.	Baton Rouge	5-11-70		5				12
21 Shell Chemical Co.	Geismar	7-13-70				25		91
	Norco	2-16-70		36			7	
Stauffer Chemical Co. Ind. Chem. Div.	Baton Rouge	6-1-70		27				20
	St. Gabriel	*2-8-71		9				
Tenneco Oil Co.	Chalmette	1-11-71		48		11	11	25
Triad Chemicals	Donaldsonville	9-8-70					27	19
Union Tank Car Co.	Baton Rouge	*8-3-71	9					

¹The five pounds per day has been selected arbitrarily for screening purposes and does not imply that lesser quantities of heavy metals are acceptable.

²See Appendix, Exhibit F for additional data.

*Net loads (see explanation page 132)

**Interfering substances made determination invalid and/or questionable.

According to Boyland (8) in another study by him and co-workers, it was shown that lead salts induce cancer of the kidney in rats but do not appear to do so in men. On the other hand, Boyland (8) described studies by Dingwell and Lane which associated heavy exposure to lead with increased incidence of cerebrovascular catastrophies.

As stated above, lead was the third most prevalent metal in waste discharges containing five pounds or more per day. The Ethyl Corporation, manufacturers of tetra-ethyl lead, discharged the greatest amount, 3700 pounds in one day, on July 25, 1970. Since that time and in part as a result of this investigation, the company has undertaken an extensive program to reduce the lead in their wastes. The most recent sample, June 24, 1971, shows a considerable decrease to 301 pounds per day. A desirable goal is to reduce the lead in their effluent to concentrations not exceeding that found in Mississippi River water (mean of 0.05 ppm).

The Hooker Chemical Corporation at Hahnville shows relatively high lead in its discharge. Three samples collected in less than a month had concentrations representing the following loads.

<u>Date Sampled</u>	<u>Conc. Lead</u> <u>mg/l</u>	<u>Flow MGD</u>	<u>Lbs/Day</u>
May 26, 1971 (Comp.)	2.8	20.74	485
June 8, 1971 (Comp.)	1.2	22.18	218
June 7, 1971 (Grab)	4.8	22.18	890

The problem of high lead was discussed with the plant management when it was learned that a lead recycling facility which had been installed was a failure. A lead precipitation pond had been used successfully for several months but had recently been giving trouble. In order to eliminate the lead problem permanently, the company has begun a program of replacing all the lead seals on the caustic-chlorine cells with a new type of equipment that

will eliminate the lead completely. The first third of the cells are scheduled to be changed by September, 1971, the next third by the middle of 1972 and the last third by the end of 1972.

The Allied Chemical Corporation, Industrial Chemicals Division, (North Works), when informed that their lead discharges were in excess of 100 pounds per day, traced the source of the lead to their caustic-chlorine, Hooker diaphragm cells and initiated measures to impound and treat these wastes. Since then they have been discharging less than 80 pounds per day and plan to reduce this further.

The presence of lead in discharges from chlorine-caustic production units is due to the use of lead as a conductor in the anodes of diaphragm cells. The lead is sealed from the anolyte by a mastic. Because of various operation problems, the mastic cracks and allows the acidic anolyte to attack the lead. Most of the lead chloride thus formed leaks from the cells due to their type of construction. This lead chloride either drips to the sewers or is washed off the cells during washdown operations. There are five plants using diaphragm cells along the Mississippi River and their discharge of lead daily ranges from 15 - 200 pounds per day. There are two ways to cure this problem. The present graphite anodes can be replaced with dimensionally stable anodes (titanium metal) which require no lead in the anode of the cells. This eliminates the problem completely. The effluent from these plants can also be treated with carbonate at a pH of about 9. The resulting basic lead carbonate is then precipitated and can either be settled or filtered. This type of treatment system when properly operated will reduce the lead content to the 6 - 10 pound per day range.

Copper is not considered to be a cumulative systemic poison. It is an essential element in low concentrations in man's diet with a daily requirement estimated at 2.0 mg (63). However, even small doses, as low as 0.015 mg, (63)

are known to be lethal to algae, snails, mussels, barnacles, etc. (48) The Public Health Service Drinking Water Standards (63) for copper state, "Inasmuch as copper does not constitute a health hazard but imparts an undesirable taste to drinking water, it is reasonable to establish the concentration of 1.0 mg/l as the recommended limit."

Copper was found in wastes from thirteen industrial plants in amounts of five pounds or more per day. The largest load, 396 pounds, occurred in wastes from the Kaiser Aluminum & Chemical Corporation at Chalmette, Louisiana, on November 30, 1970.

Zinc has no known physiological effects on man except in high concentrations. However, zinc is toxic to fish, a characteristic that is intensified by synergism with copper. The Drinking Water Standards (63) state that, "Inasmuch as zinc in water does not cause serious effects on health but produces undesirable esthetic effects, it is recommended that concentrations of zinc be kept below 5.0 mg/l."

Zinc was one of the metals most frequently found in amounts of five pounds or more per day, in forty-two waste discharges. The greatest amount, 1,317 pounds, was found in the waste samples of the Kaiser Aluminum & Chemical Corporation, Baton Rouge, on August 31-September 1, 1971.

Cadmium is recognized by the Public Health Service "to be an element of high toxic potential." (63) McKee and Wolf state (48), "Consumption of cadmium salts causes cramps, nausea, vomiting and diarrhea. Oral ingestion has been the cause of a number of human deaths." The 1962 Drinking Water Standards include the following, "...because suspicion has been cast on the presence of minute amounts of cadmium in the kidney as responsible for adverse renal arterial changes in man, concentrations of cadmium in excess of 0.01 mg/l in drinking water are grounds for rejection of the supply."

Studies by Schroeder (53, 54) linked hypertension to increased retention of cadmium in the kidneys when he noted that most human subjects dying from hypertensive complications showed in their kidneys either increased amounts of

cadmium or increased ratios of cadmium to zinc compared to subjects dying of a variety of other diseases. These findings in man have been substantiated experimentally in animals.

In additional studies, laboratory breeding mice exposed to concentrations of cadmium, lead, or selenium produced abnormal offspring (55).

A toxicology investigation of patients suffering from the "itai-itai" disease revealed the presence of a high content of cadmium in the bones and internal organs of the patients, in rice, other plants, and soil in a restricted district along the Jintsu River in Toyama Prefecture, Japan, upstream from point of waste discharge from a mine (39).

As a consequence of these findings, Kobayashu (39) conducted animal studies in which rats were fed cadmium. He observed that the experimental rats excreted more calcium than that assimilated from their food while the control group showed the opposite phenomena. This hypercalcium excretion is one of the characteristics of the itai-itai disease in humans. From these results, it was concluded that the itai-itai disease was induced by cadmium in waste from the mine.

In another Japanese study by Yamagato and Shigematsu (72) it was estimated that man consumes normally 60 micrograms of cadmium per day, but in the area of occurrence of itai-itai disease the consumption was more than 600 micrograms per day. The main source of the cadmium was foodstuffs, of which about half was contributed by rice.

Boyland (8) cited epidemiological evidence from an article by Kipling and Waterhouse which indicated that cadmium compounds were a cause of prostatic cancer in man. However, in a study by Roe and others, as stated by Boyland (8), cadmium compounds administered to rats were shown to induce testicular tumours of the interstitial cells.

This is an example of a frequently observed phenomenon of a carcinogen inducing tumours of different organs in different species. Cadmium resembles zinc in its chemistry but biologically it is a zinc antagonist. The prostate gland has a high content of zinc and it is perhaps for this reason, as attested by Boyland (8), that the chronic toxic effect of cadmium is exerted on this organ in man.

Cadmium in quantities of more than five pounds per day was present in eight waste discharges, the greatest load of 71 pounds per day occurring in a sample of wastes from Kaiser Aluminum & Chemical Corp., Baton Rouge, Louisiana, on August 31, 1971. Kaiser's waste discharge from the Metals Division at Gramercy had loads of 55 pounds per day on September 8, 1971 and 32 pounds per day on September 9, 1971. Concentrations corresponding to twenty pounds per day was present in samples from the discharges of the Allied Chemical Corporation at the Industrial Chemical Division, Baton Rouge, Louisiana, on April 14, 1970, and at the Geismar Complex, Geismar, Louisiana, on June 26, 1970. Reference to Exhibit F will disclose discharges of lesser amounts. As with other toxic heavy metals, the goal should be no cadmium discharged.

Chromium is not known to be either an essential or beneficial element in the body. Its toxic properties for man have not been clearly established. When inhaled, according to the 1962 Drinking Water Standards, chromium is a known carcinogenic agent for man. It is not known whether cancer will result from ingestion of chromium in any of its valence forms. The Public Health Service (63) concludes "that a concentration of 0.05 mg/l is sufficiently low to cause no effect on health."

In investigating pulmonary and gastric forms of chronic poisoning with chromium compounds, cardiovascular function was studied in 230 workers of a potassium bichloride industry. Kleiner and coworker (38) concluded that the disorders revealed in the bioelectric and mechanical activity of the myocardium could come both from the overcharging of the right heart in patients with pulmonary pathology and be also due to the general toxic effect of chrome on the vessels and the myocardium.

Chromium was one of the metals most frequently present in the forty-two waste discharges with a peak amount of 200 pounds per day being found in wastes from the Allied Chemical Corporation, Industrial Chemicals Division at Baton Rouge, Louisiana, on April 14, 1970. Chromium is widely used as a corrosion inhibitor in industrial cooling water systems particularly when such systems are closed. Since there are other corrosion inhibitors available to industry and ion-exchange techniques available for removing and recycling chromium, industry's goal should be essentially zero or no greater than background discharge.

Arsenic has toxic properties that are well known. There is evidence that it may be carcinogenic and the intake of as little as 100 mg usually results in severe poisoning. Even at low level intakes a considerable portion is retained with a single dose requiring as long as ten days for complete disappearance. This slow excretion is in part the basis for its cumulative effects (63). 1962 Drinking Water Standards of the Public Health Service states, "...the concentrations in excess of 0.05 mg/l are grounds for rejection of the supply."

Studies have shown that long periods of arsenic and molybdenum exposure changed the sex ratios of mice and rat offspring (53).

Four companies other than Kaiser (see following paragraphs for discussion of the Kaiser problem) were found to have arsenic in their waste discharges. These were the Allied Chemical Corporation plant at Geismar with 19.6 pounds per day, the Industrial Chemicals Division of Allied Chemical Corporation at Baton Rouge with 15.4 pounds per day, the Schuylkill Metals Corporation at Baton Rouge with 2.6 pounds per day, Union Tank Car Co. at Baton Rouge with 9.3 pounds per day, and the Celotex plant at Marrero. The latter plant was discharging over 43 pounds per day of arsenic at the time of sampling, September 21, 1970. They have a permit from the Louisiana Stream Control Commission to discharge 160 pounds per day. The arsenic in the wastes comes from arsenic trioxide which is used on exterior wood products to inhibit the growth of fungi and for termite control. At a meeting of the Louisiana Stream Control Commission on January 12, 1971, the Celotex Corporation advised that treatment to eliminate arsenic from the waste

discharge was under study. The Commission approved the report after stating that the industry will be expected to eliminate all arsenic after completion of the study and implementation of its findings.

The Kaiser Aluminum and Chemical Corporation is the fourth discharger of arsenic. A sample of waste from the Baton Rouge plant showed in excess of 0.061 pounds per day on July 21, 1970, and 31 pounds per day from the Gramercy plant on the same date. Later data, however, showed less than detectable quantities of arsenic in the Kaiser "red mud". Arsenic determinations on a high solids material such as spent bauxite are difficult to perform because of the interferences from high concentrations of iron, aluminum and other metals. In a report prepared by Kaiser on April 16, 1971, arsenic was reported to range from 6 to 300 pounds per day in the Baton Rouge plant's spent bauxite discharge and from 4 to 208 pounds per day in the Gramercy plant's discharge.

The other heavy metals contained in the spent bauxite include lead, manganese, zinc and traces of mercury. These are inherent in the raw material, bauxite, from which alumina is extracted. Since it is virtually impossible to remove these heavy metals from this waste material before discharging to the river, the only practical way to prevent these metals from reaching the river is through total solids impoundment. Kaiser attempted for many years to find a practical and ecologically sound method of total impoundment. Only recently, however, have they successfully demonstrated a technique for dewatering the "red mud". This method, still in the developmental stage, should allow Kaiser to retain on land the "red mud" solids and allow some recirculation of the spent caustic liquor. A market for these dried solids which contain high concentrations of iron hopefully will be developed by Kaiser. At the time of this writing, Kaiser plans to have the "red mud" out of the river by July, 1974 at the Gramercy plant and by July, 1975 at the Baton Rouge plant.

The other bauxite consumer located on the Mississippi River, in addition to the two Kaiser plants discussed above, is Ormet at Burnside. At the present time Ormet

retains and settles all of their muds and recycles the resulting clear liquor into the plant. Their discharge does not contain in any measurable amount the metals outlined above.

Mercury and mercuric salts are highly toxic to humans, although mercury was long thought environmentally inert. When discharged into a river, for example, it was believed to settle to the bottom and remain there. Then in 1960, it was reported that 111 persons had died or suffered serious neurological damage near Minamata, Japan as a result of eating fish and shellfish which had been contaminated by mercury discharged into Minamata Bay by a plastic manufacturing plant (35). Since then it has been shown that metallic mercury can be changed by bacteria under anaerobic conditions into methylmercury, a compound far more toxic than metallic mercury, and that it can enter the food cycle through uptake by aquatic plants, algae, lower forms of animal life and fish (56). Equally significant, studies have shown that the concentration factor in the fish could be 3000 or more to one (34). Thus, harmless levels of mercury in water can be concentrated to hazardous levels in fish.

Clegg (15) reported that the embryotoxic or teratogenic effects of alkyl mercurial compounds on laboratory animals result from direct toxic action of the compound on the fetus or embryo, and possibly also by damaging the gametes prior to fertilization.

The finding of mercury in finfish and shellfish in many parts of the United States in 1970 and the removal of large quantities of canned and frozen seafood from the market because of its high mercury content emphasize the undesirability of the release of mercury in any form or quantity to the waters of the Lower Mississippi River Basin or elsewhere in this nation.

The concern over mercury is well founded. Some organic mercury compounds are accumulated in humans, concentrate in the brain, cause tremors and mouth ulcers, and produce birth defects because of chromosome breakage. (9).

At the time of this study there were three plants along the lower Mississippi River operating mercury cell chlorine-caustic plants. BASF Wyandotte has committed to close down the operation of their mercury cells by December 31, 1973, and Stauffer Chemical will continue their operation, with the addition of removal systems. Dow Chemical at Plaquemine shut down permanently and dismantled the mercury cell caustic-chlorine cells, on December 23, 1970.

Analysis for mercury in waste discharges from the Dow Chemical Company of Plaquemine in January 1970 disclosed concentrations in the order of 2.4 ppm. This computed to a loss of several thousand pounds per day of mercury. Realizing that losses of this magnitude of a costly metal such as mercury could not realistically be sustained by an industry, it was presumed that the 25 minute composite collected contained a "slug" of mercury. Subsequent discussion with Dow personnel revealed that during the sampling period the company was in process of diverting their caustic-chlorine mercury cell wastes to provide a mercury treatment facility. Part of this construction involved the dredging of effluent canals containing high levels of mercury, apparently resulting in the release of slugs of mercury laden material in their outfall canal. Samples taken since that time disclosed only traces of mercury, generally below the minimum detectable concentration.

Mercury discharge from these plants occurs by routine losses from the cells, by carry over from the caustic system, and by air losses in the hydrogen system which falls to the ground and is either washed down to the effluent or carried into the effluent by rain. Normal removal systems consist of pH control, addition of sulfide for precipitation, settling, filtration, and activated carbon treatment of the effluent. With this type of treatment the mercury content of the effluent is reduced to less than 0.5 pounds of mercury per day. An examination of Exhibit F in the Appendix will show that mercury discharges of 0.5 pounds or more have been found in waste discharges from eleven plants.

Cyanides are toxic to man when ingested. The 1962 Public Health Service Drinking Water Standards (63), recommends that concentrations of cyanide in water be kept below 0.01 mg CN/l. The Public Health Service adds, "For the protection of the health of human populations, concentrations above 0.02 mg CN/l constitutes grounds for rejection of the supply."

McKee and Wolf (48) state that "...when toxicities are expressed in terms of the cyanide ion it must be realized that most of the cyanide in water is in the form of HCN. It is apparent that HCN rather than the cyanide ion is the major toxic principle. It must be recognized that toxicities may vary markedly with pH and a given concentration that is innocuous at pH 8 may become detrimental if the pH is lowered to 6 or less. On the other hand, Southgate reported that within the range of 6.0 to 8.5, pH had no effect on the toxicity of cyanides. In natural streams, cyanides deteriorate or are decomposed by bacterial action, so that excessive concentrations may be expected to diminish with time."

It appears that the toxic properties of this class of compounds may, under favorable conditions of pH and time, be expected to disappear. However, in view of the uncertainties of having a favorable pH and enough time for decomposition to be completed, it is the goal of the Environmental Protection Agency that no cyanides be discharged into the waters of the Lower Mississippi River or elsewhere in this nation.

Five industrial plants (see Appendix, Exhibit F) were found to have detectable quantities of cyanide in their wastes. These were Rubicon Chemicals, Ind. in Geismar which was discharging approximately 2.0 pounds per day; Monsanto Company, near Luling, Louisiana, discharging 30 pounds per day; American Cyanamid Company at Avondale, Louisiana, discharging 150 pounds per day on Feb. 2, 1970, but having reduced this to 1.44 pounds per day on June 26, 1971; Enjay Chemical Company at Baton Rouge discharging 4.4 pounds per day; and Allied Chemical Corp., Specialty Chemicals Division at Baton Rouge discharging 2.9 pounds per day.

Phenols, while toxic in concentrated solutions, are more objectionable for their taste and odor causing properties. The 1962 Public Health Service Drinking Water Standards limit the concentration of phenols to 0.001 mg/l because of tastes resulting from chlorination of water with higher concentrations.

Table 3 lists 17 plants discharging 10 pounds or more of phenols to the river each day. Since phenolic compounds are particularly objectionable in potable water supplies because of their taste and odor causing properties, no phenol should be discharged to the waters of the Lower Mississippi River.

Total Solids are being discharged by 32 industrial plants in quantities of 50,000 pounds per day or more and 25,000 pounds or more per day volatile solids are being discharged from 26 plants as indicated in Table 4. Within this range total solids loads discharged range from a maximum of 11.5 million pounds per day from the Dow Chemical Company plant to 52 thousand pounds per day by the Copolymer Rubber and Chemical Corporation at Baton Rouge. Kaiser Aluminum and Chemical Company at Baton Rouge discharged the highest volatile solids load - 1.5 million pounds per day. These industries are considered to be discharging excessive quantities of solids. All have been requested by the State to provide secondary treatment or its equivalent by December 31, 1972.

TABLE 3

INDUSTRIES DISCHARGING PHENOLICS IN QUANTITIES
OF TEN POUNDS PER DAY OR MORE

<u>Company</u>	<u>Division</u>	<u>Location</u>	<u>Date Sampled</u>	<u>Phenolics¹ #/Day</u>
Chevron Chemical Co.	Oronite Additives	Belle Chasse	*1-25-71	2970
			*3-1,2-71	97
			*3-18-71	125
			*8-10-71	288
Copolymer Rubber & Chem. Corp.		Baton Rouge	1-14-70	108
			5-3-71	35
Crown Zellerbach Corp.		St. Francisville	11-2-70	260
The Dow Chemical Co.		Plaquemine	1-20-70	34
Enjay Chemical Co.		Baton Rouge	1-15-70	266
			*4-6-71	168
			6-9-71	491
Freeport Minerals Co.	Freeport Chem. Co.	Uncle Sam	11-3-70	55
Georgia Pacific Corp.	Crossett Div.	Port Hudson	5-4-70	156
Hercules, Inc.	Allemania Plant	Plaquemine	11-23-70	16
Humble Oil & Refining Co.		Baton Rouge	1-15-70	1530
			*6-8-71	322

TABLE 3 (Continued)

<u>Company</u>	<u>Division</u>	<u>Location</u>	<u>Date Sampled</u>	<u>Phenolics¹ #/Day</u>
Kaiser Aluminum & Chem. Corp.	Metals Div.	Baton Rouge	1-19-70	106
			8-30/31-71	181
			8-31, 9-1-71	244
		Chalmette	*11-30-70	81
		Gramercy	9-7, 8-71	93
			9-8, 9-71	81
Monsanto Co.		Luling	5-26-70	94
Rubicon Chemicals, Inc.		Geismar	1-21-70	220
			4-14-71	134
³⁴ Stauffer Chemical Co.		St. Gabriel	*2-8-71	28
Union Carbide Corp.		Hahnville	1-22-70	74
UniRoyal, Inc.		Baker	7-6-71	185

¹ The method of analysis for phenol measures not phenol alone but a whole series of organic compounds that are called "phenolics."

* Net loads (see explanation page 132).

TABLE 4

INDUSTRIES WITH HIGH SOLIDS LOADS¹
TOTAL SOLIDS 50,000 POUNDS PER DAY OR MORE
VOLATILE SOLIDS 25,000 POUNDS PER DAY OR MORE

<u>Company</u>	<u>Division</u>	<u>Location</u>	<u>Date Sampled</u>	<u>Total Solids² #/day</u>	<u>Volatile Solids² #/day</u>
Allied Chem. Corp.	Ind. Chem. Div.	Baton Rouge	*7-19-71	6,307,100	849,100
	Specialty Chem.	Baton Rouge	6-22-70	322,000	
	Geismar Complex	Geismar	6-29-70	405,000	145,000
American Cyanamid Co.		Avondale	2-2-70	111,000	
BASF Wyandotte Corp.		Geismar	4-7-70		597,000
The Celotex Corp.		Marrero	9-21-70	270,000	230,000
Copolymer Rub. & Chem. Corp.		Baton Rouge	5-3-71	52,600	
			1-14-70	280,000	30,900
Crown Zellerbach Corp.		St. Francisville	11-2-70	620,000	320,000
The Dow Chemical Co.		Plaquemine	1-20-70	11,500,000	410,000
			*6-21/22-71	6,280,000	96,250
E. I. duPont de Nemours & Co. Inc.		LaPlace	3-2-70	98,000	32,000
Enjay Chemical Co.	Chemical Plant	Baton Rouge	1-15-70	394,000	134,000
			*4-6-71	199,600	
			6-9-71	170,100	37,000

TABLE 4 (Continued)

<u>Company</u>	<u>Division</u>	<u>Location</u>	<u>Date Sampled</u>	<u>Total Solids² #/day</u>	<u>Volatile Solids² #/day</u>
Ethyl Corporation		Baton Rouge	1-14-70 4-27/28-71	651,500 739,900	51,500
Freeport Minerals Co.	Freeport Chem.Div.	Uncle Sam	10-5-70	938,000	144,000
Georgia Pacific Corp.	Crossett Div.	Port Hudson	5-4-70	281,300	110,000
Getty Oil Co.		Venice	6-1-71	120,200	32,000
Gulf Oil Co., U.S.		Venice	*6-15-71	141,000	
ω Gulf Oil Company		Welcome	8-31-70	120,000	32,500
Hooker Chem. Corp.		Hahnville	2-24-70 *5-25/26-71	706,500 341,200	78,500
Humble Oil & Ref. Co.		Baton Rouge	1-5-70 *6-8-71	722,000 663,800	182,000 195,600
Kaiser Alum. & Chem. Corp.		Baton Rouge	1-19-70 *8-30/31-71 *8-31/9-1-71	9,070,000 5,084,500 4,435,000	1,530,000 4,802,900 ³ 4,144,200 ³
		Chalmette	*11-30-70	416,100	116,100
	Chemicals	Gramercy	3-31-70 9-28/29-71 9-29/30-71	496,400 206,600 208,800	69,000 8,200 ³ 11,700 ³

TABLE 4 (Continued)

<u>Company</u>	<u>Division</u>	<u>Location</u>	<u>Date Sampled</u>	<u>Total Solids² #/day</u>	<u>Volatile Solids² #/day</u>
Kaiser Alum. & Chem. Corp. (Continued)	Metals Div.	Gramercy	9-7/8-71 9-8/9-71	5,049,500 4,097,400	4,990,000 ³ 4,041,400 ³
Monochem, Inc.		Geismar	*6-22/23-71	74,300	
Monsanto Company		Luling	2-9-70	106,000	82,500
Occidental Chemical Co.		Hahnville	2-24-70	712,000	134,000
Rubicon Chemicals, Inc.		Geismar	1-21-70	58,000	
Shell Chemical Co.		Norco	2-16-70	482,500	103,000
Stauffer Chemical Co.	Ind. Chemical	St. Gabriel	*2-8-71	147,500	
Tenneco Oil Co.		Chalmette	1-11-71	147,400	26,300
Texaco, Inc.		Convent	8-17-70	67,600	
Union Carbide Corp.		Hahnville	1-22-70	1,850,000	299,000
UniRoyal, Inc.	UniRoyal Chem.	Geismar	*6-29/30-71	107,100	52,400

¹ The industries listed have total solids loads of 50,000 pounds per day or more and volatile solids loads of 25,000 pounds per day or more. These lower limits were arbitrarily selected for screening purposes and do not imply that lesser quantities of solids are acceptable.

² See Appendix, Exhibit E for additional data.

³ Total suspended solids

* Net loads (see explanation page 132)

TRACE HEAVY METALS IN PHOSPHATE ROCK WASTES

There are three companies along the lower Mississippi River producing phosphoric acid by digesting phosphate rock with sulfuric acid. These companies are Allied Chemical at Geismar, Freeport Chemical at Uncle Sam and Occidental at Taft. The Freeport plant is the largest plant of this type in the United States. The rock as mined is a combination calcium phosphate-calcium fluoride compound. As with most minerals there is a large number of impurities including heavy metals associated with the rocks in small concentrations. The basic process converts the calcium ion to calcium sulfate which is filtered from the phosphoric acid. The resulting calcium sulfate containing many of the impurities is slurried and discharged into the river. These discharges contain substantial amounts of fluorides as well as arsenic, cadmium, chromium, copper, nickel and lead. Generally all of the metal impurities can be removed by settling of the gypsum.

At present under state permits Occidental and Allied must impound the gypsum when the river flow is below 200,000 cfs. Freeport must impound when the sulfate content of their intake water is above 75 ppm.

The Refuse Act Permit Program will require total impoundment of the suspended solid gypsum by mid 1974 and a reduction of the total sulfates to the river by 90% by the end of 1975.

ORGANIC CHEMICALS

The presence of organic chemicals in the water of the Lower Mississippi River are objectionable for two reasons; they are believed to be the primary cause of the taste and odors in the finished water supplies and contribute to the tainting of the fish flesh. Further, these compounds are objectionable from a public health standpoint because of their toxic nature. (See discussion on toxicities later in the report.)

It should be emphasized that quantification of the organics were not attempted in this investigation. In the concentrations in the river they are usually referred to as "trace" organics and are estimated to be in the "parts per billion" to "parts per million" range.

Forty-eight organic chemicals have been found in raw or finished water from three water plants - The U. S. Public Health Service Hospital at Carville, Louisiana, the Jefferson Parish #2 Water Plant at Marrero, Louisiana, and the Carrollton Water Plant at New Orleans. Of these, thirteen have been found in wastes from seven industrial plants. An additional forty organic chemicals have been found in wastes from eleven industrial plants, including the seven mentioned above, which have not yet been found in the raw or finished waters of the three municipal plants. A complete list of 88 organic chemicals ranging from acetone to xylene which have been isolated and identified by June 30, 1971, and the streams in which they were found, appears in Table 16.

For the convenience of the reader, Tables 5 through 10 which follow present data on each of the three water plants and industries whose wastes contain organics found in the respective water plant's raw or finished waters. The total number of compounds found in the different water supplies varies from plant to plant. No significance should be attached to these numbers. Different laboratories and differing amounts of time were spent in isolating these compounds from the extracts. Many additional compounds were indicated on the GLC chromatograms, but time limitations prevented their identification.

Three organic compounds have been found in the finished water supply of the U. S. Public Health Service Hospital at Carville and in effluents from three industries as shown in Table 5. A total of eleven organic compounds have been found at Carville as shown in Table 6.

TABLE 5
ORGANIC COMPOUNDS IN THE FINISHED WATER AT THE
PUBLIC HEALTH SERVICE HOSPITAL AT CARVILLE, LA.
AND IDENTIFIED IN WASTES OF SPECIFIED INDUSTRIES

<u>COMPANY</u>	<u>ORGANIC COMPOUND</u>
Enjay Chemical Co. (Baton Rouge)	ethyl benzene
	vinyl benzene
	toluene
Foster Grant Co., Inc.	vinyl benzene
UniRoyal, Inc.	vinyl benzene

TABLE 6
LIST OF ALL ORGANIC COMPOUNDS
FOUND IN THE U. S. PUBLIC HEALTH
SERVICE HOSPITAL FINISHED WATER

acetylene dichloride
benzene
carbon tetrachloride
chloroform
1,2-dichloroethane
dimethyl sulfoxide
ethyl benzene
methyl chloride
propyl benzene
toluene
vinyl benzene

Twelve organic compounds have been found in the finished water supply of the Carrollton Water Plant of the City of New Orleans and in effluents from seven industries as shown in Table 7. A total of thirty-six organic compounds have been found at New Orleans as shown in Table 8.

TABLE 7
ORGANIC COMPOUNDS FOUND IN THE CARROLLTON
WATER PLANT (NEW ORLEANS) FINISHED WATER AND
IDENTIFIED IN WASTES OF SPECIFIED INDUSTRIES

<u>COMPANY</u>	<u>ORGANIC COMPOUND</u>
Copolymer Rubber & Chem. Corp. (Baton Rouge)	acetophenone vinyl benzene
Crown Zellerbach Corp.	a-camphanone dimethoxy benzene endo-2-camphanol exo-2-camphanol o-methoxy phenol p-menth-en-1-8-ol
Georgia Pacific Corp.	a-camphanone dimethoxy benzene endo-2-camphanol exo-2-camphanol o-methoxy phenol p-menth-en-1-8-ol
Enjay Chemical Co. (Baton Rouge)	ethylbenzene toluene vinyl benzene
UniRoyal, Inc.	isopropyl benzene vinyl benzene
Foster Grant Co., Inc.	vinyl benzene
Rubicon Chemicals, Inc.	nitrobenzene

TABLE 8
LIST OF ALL ORGANIC COMPOUNDS
FOUND IN THE CARROLLTON WATER
PLANT (NEW ORLEANS) FINISHED WATER

acetone	dichloroethyl ether
acetophenone	dimethoxy benzene
benzene	2,6-dinitro toluene
bromobenzene	endo-2-camphanol
bromochlorobenzene	ethyl benzene
bromoform	exo-2-camphanol
bromophenyl phenyl ether (positional isomer?)	hexachlorobenzene
butyl benzene	1-isobrobenyl-4-isopropyl benzene (1,2 isomer)
a-camphanone	isocyanic acid
chlorobenzene	methyl biphenyl
chloroethyl ether	methyl chloride
chloromethyl ether	nitrobenzene
chloroform	o-methoxy phenol
chloronitrobenzene	p-menth-en-1-8-ol
chloropyridine	tetrachloroethylene
dibromobenzene	toluene
dichlorobenzene (positional isomer)	1,1,2-trichloroethane
1,2-dichloro-ethane	vinyl benzene

Four organic compounds have been found in the raw water supply of the Jefferson Parish #2 Water Plant at Marrero and in the effluents of four industries as shown in Table 9. A total of fifteen organic compounds have been found in the Jefferson Parish raw water supply as shown in Table 10.

TABLE 9

ORGANIC COMPOUNDS IN THE RAW WATER AT THE
JEFFERSON PARISH #2 WATER PLANT AND
IDENTIFIED IN WASTES OF SPECIFIED INDUSTRIES

<u>COMPANY</u>	<u>ORGANIC COMPOUND</u>
Copolymer Rubber & Chem. Corp. (Baton Rouge)	acetophenone
Crown Zellerbach Corp.	a-camphanone
	p-menth-en-1-8-ol
Georgia Pacific Corp.	a-camphanone
	p-menth-en-1-8-ol
Rubicon Chemicals, Inc.	nitrobenzene

TABLE 10

LIST OF ALL ORGANIC COMPOUNDS FOUND IN THE
JEFFERSON PARISH #2 WATER PLANT - RAW WATER

a-camphanone	methyl-b-tolyl ketone
biphenyl	nitroanisol
bis-chloroisopropyl ether	nitrobenzene
bromophenyl phenyl ether	O-phenyl anisole
bis-chloroethyl ether	p-menth-en-1-8-ol
bis-chloroisopropyl ether	1-propyl-2-methylnaphthalene
dichlorobutene	triethylene glycol dimethyl ether
2-methyl biphenyl	

Table 11 is a listing of those industries which were found to have high organic waste discharges as measured by their COD (chemical oxygen demand) and TOC (total organic carbon) loads. Both the TOC and COD are a measure of some inorganic compounds. Thirteen industries listed are discharging 40,000 pounds per day or more of COD and ten are discharging 20,000 pounds per day or more to TOC. These industries are considered to be discharging excessive organic loads. All have been requested by the State to provide secondary treatment or its equivalent by December 31, 1972.

TABLE 11

INDUSTRIES WITH HIGH ORGANIC WASTE LOADS¹
 CHEMICAL OXYGEN DEMAND 40,000 POUNDS PER DAY OR MORE
 TOTAL ORGANIC CARBON 20,000 POUNDS PER DAY OR MORE

<u>Company Plant or Division</u>	<u>Location</u>	<u>Date of Sample</u>	<u>Chemical Oxygen Demand² (#/day)</u>	<u>Total Organic Carbon² (#/day)</u>
Borden, Inc. Borden Chem. Div.	Geismar	*6-28-71	74,900	
The Celotex Corp.	Marrero	9-21-70	88,000	
Chevron Chemical Co. Ornite Additives Div.	Belle Chasse	*8-10-71	45,300	
Copolymer Rub. & Chem. Co.	Baton Rouge	1-4-70	76,400	28,700
Crown Zellerbach Corp.	St. Francisville	11-2-70	170,000	84,000
Dow Chemical Co.	Plaquemine	1-20-70 *6-21/22-71	380,000 57,750	120,000
Enjay Chemical Co. Chemical Plant	Baton Rouge	1-15-70 *4-6-71 6-9-71	553,600 206,800 111,700	233,000 47,400
Ethyl Corp.	Baton Rouge	1-14-70	42,400	
Freeport Minerals Co. Freeport Chem. Co. Div.	Uncle Sam	11-3-70	60,000	

TABLE 11 (Continued)

<u>Company</u> <u>Plant or Division</u>	<u>Location</u>	<u>Date</u> <u>of</u> <u>Sample</u>	<u>Chemical</u> <u>Oxygen Demand</u> ² <u>(#/day)</u>	<u>Total Organic</u> <u>Carbon</u> ² <u>(#/day)</u>
Georgia Pacific Corp. Crossett Div.	Port Hudson	5-4-70	101,000	25,200
Humble Oil & Ref. Co.	Baton Rouge	1-15-70	213,000	**
		*6-8-71	61,300	7,700
Kaiser Alum. & Chem. Corp.	Baton Rouge	1-19-70	173,000	27,000
		8-30/31-71	80,400	67,600
		8-31/9-1-71	87,500	76,400
Metals Div.	Gramercy	9-7/8-71	80,100	48,200
		9-8/9-71	70,600	27,000
47 Shell Chemical Co.	Norco	2-16-70	82,200	24,000
Union Carbide Corp.	Hahnville	1-22-70	342,000	120,000
		*4-21-71	149,900	46,100

¹The industries listed have COD loads equal to or greater than 40,000 pounds per day and/or TOC loads equal to or greater than 20,000 pounds per day. These lower limits were arbitrarily selected for screening purposes and do not imply that lesser quantities of organics are acceptable.

²See Appendix, Exhibit F for additional data.

*Net loads (see explanation page 132)

**Interfering substances made determination invalid and/or questionable.

TASTE AND ODOR*

Early in the study it became evident that, although objectionable tastes and odors were occurring in treated water from plants using the Mississippi River as their source of raw water, the compounds believed to cause tastes and odors were present in amounts too small to be identified directly in the water. Since experience elsewhere had demonstrated the feasibility of adsorbing trace organics on activated carbon to be later removed by extraction with suitable solvents and concentrated until measurable quantities were available for analysis, it was decided that this approach would be used.

A program of threshold odor testing was initiated at six plants, listed in Table 12; in January, 1969 and continued through March, 1971 at the Crown Zellerbach and Carrollton Water Plants, and for one year at the remaining four plants. Samples were collected once each week from each plant and the threshold odor number (T.O.) was determined by the Environmental Protection Agency odor panel. Operators at each of these plants were trained in the odor test and panels were established. Daily odor testing was performed and results were returned to the Baton Rouge office. These results, though not as conclusive as those of the larger Environmental Protection Agency panel, also, indicated that odor problems were more severe below the industrial complexes.

* The determination of threshold odor involves the comparison of varying concentrations of odor bearing water with a sample of odor free water until a concentration is reached that is of the least definitely perceptible odor. The resulting ratio by which the sample has been diluted is called the "Threshold Odor Number" (T.O.). The presence, or absence, of odors is determined by smelling, or "sniffing," a sample that has been allowed to stabilize at room temperature. A "panel" or group of five or more testers is preferred. For most purposes the threshold of a group can be expressed as the geometric mean (GM) of the individual threshold.

The "average" threshold numbers in Table 12 are not as significant as the maximum numbers. From January, 1969 through November, 1970 the T.O. was equal to or greater than 13 in the raw water at the Carrollton Water Plant. Six times during that period the T.O. was 20 or larger and in January, 1969 a maximum of 45 was reached.

TABLE 12
RAW RIVER WATER
1969 THRESHOLD ODORS

Station	River Mile	Average Threshold Odor Numbers
Crown Zellerbach, St. Francisville	260	7.3
USPS Hospital, Carville	191	12.8
Colonial Sugar Co., Gramercy	146	10.0
St. Charles Plant No. 1, New Sarpy	125	11.3
Carrollton Plant, New Orleans	105	11.3
Jefferson Parish Water Works #2, Marrero	99	12.0

Although not apparent in the tabular T.O. results, there was a distinct qualitative difference in the odor of the water at St. Francisville and that collected at the downstream sites. The description of the odor at the former was predominantly "earthy" or "musty", while at the latter sampling points it was usually described as "chemical" or "petrochemical."

In addition to the determination of tastes and odors as just described, wastes from sixty industrial plants were examined. All were found to have discernible tastes and odors. In order to evaluate the odor potential of each plant's waste discharge, the threshold odor number of the fresh raw waste was multiplied by the daily average discharge (in gallons). This value called "Odor Contribution" gives an estimate of the rate (in gallons per day) of river water to which a "threshold" or detectable odor would be imparted.

Detailed results will be found in the Appendix, Exhibit H which lists plants in order of decreasing odor contribution. It will be seen that plant discharges having the same characteristics as the samples analyzed will contribute detectable odors at a rate ranging from 758 billion gallons per day (the Crown Zellerbach Corporation at St. Francisville) to as low as fifty thousand gallons (Argus Chemical Company at Hahnville). Since 323 billion gallons per day is considered the average flow at New Orleans, it can readily be seen that if the wastes from the Crown Zellerbach Corporation at St. Francisville were the only ones discharged to the Mississippi River, more than double the average river flow would be required to dilute them to a point of no detectable odor. And this assumes that no part of water treatment, such as chlorination, would increase the taste and odor producing characteristics as in the case of phenolics. Wastes from Enjay Chemical Company at Baton Rouge, with an odor contribution ranging from 345 to 744 billion gallons per day, or those from the Hooker Chemical Corporation at Hahnville, with an odor contribution ranging from 38 to 449 billion gallons per day, or those from Humble Oil and Refining Company at Baton Rouge, with an odor contribution of 135 to 331 billion gallons per day, are capable of producing detectable tastes and odors in the Mississippi River under average flow conditions. Under minimum stream flow conditions of 129 billion gallons per day the odor intensity will be increased about two and a half times. The interpretation of these results must be qualified, however, because the threshold odor test as performed does not evaluate the "persistency" of the odors with time and in contact with the aquatic environment.

It is apparent that the strength of many of the odors in the waste streams are partially dissipated in the river - either thru biological degradation and/or physical dispersion or evaporation. Many of the compounds, however, do persist and find their way into the finished water supplies and contribute to the higher threshold odor numbers at the downstream location. Normal water treatment processes do not remove the low-level, soluble organics. Continuous use of activated carbon would probably be required to remove the trace organics in the water supplies.

TAINTING OF FISH FLESH

In addition to trouble with tastes and odors in potable water supplies, it had been reported that objectionable odors are present in the flesh of fish caught in the lower Mississippi River in Louisiana to such an extent that they cannot be sold. In November, 1969 commercial fishermen and wholesale and retail fish dealers in the Simmesport (near R.M. 302) and New Orleans areas reported that no fish taken from the Mississippi River could be sold because of bad tastes. The dealers would not buy, hence the fishermen fished elsewhere.

In June, 1971 the same dealers and fishermen in the Simmesport and New Orleans areas were interviewed and had the same answers - a kerosene, oily taste so strong that the fish could not be sold. This condition was reported to exist the year 'round. Most retailers refuse to attempt to market fish taken from the Mississippi River because of oily tastes of their flesh.

These two surveys indicated that water quality criteria established by the State of Louisiana were being violated, i.e. taste and odors must be "below levels of detection following normal water treatment and below levels that will produce objectionable odor in food fish and seafood." (Emphasis added)

In order to obtain more direct, scientific evidence of this fish tainting problem, on October 18, 1971, a fish flesh tainting study was undertaken on the lower Mississippi River to determine if taste and odor criteria were being violated and which areas were out of compliance. Seven stations were established between St. Francisville, Louisiana, and Belle Chasse, Louisiana (Tables 13 and 14). At each station, a fish trap consisting of a hoop net with the throat laced shut was placed near each bank in approximately five feet of water. In each net were placed from four to six channel catfish, Ictalurus punctatus, weighing between three quarters and one and one half pounds. The fish were obtained from a local market which in turn was supplied by Mississippi delta fish farmers. This insured that the fish were of high taste quality and not tainted with industrial

or municipal waste. The test fish were placed in a one thousand gallon tank at the laboratory for several days before introduction into the river so that weak or diseased individuals could be detected and eliminated. This screening process was later discontinued when market fish in good condition became available. With the purchase of each group of fish, five were dressed, wrapped in aluminum foil, and frozen as a control to be later shipped with the test fish for analysis.

The test fish were transported to the stations in a live box with aeration. After a seventy-two hour exposure in the river, they were removed from the nets and dressed immediately. Each fish was individually wrapped in aluminum foil and placed in a plastic bag on wet ice. The samples were then returned to the laboratory on the same day and frozen.

All samples were shipped frozen on dry ice to Oregon State University, Department of Food Science and Technology for a flavor evaluation. The frozen samples were received at the Flavorium and stored in a freezer at -10°F until tested. For testing, each frozen sample was enclosed in aluminum foil, placed on a broiler type pan and cooked in a large commercial style gas oven at 400°F for approximately ninety minutes until the flesh flaked from the bone.

The cooked fish in each sample were boned, lightly mixed to insure uniform serving samples, then placed in the top of a double boiler over hot water to keep warm for serving.

The samples were served in paper cups coded with three digit random numbers except for one cup which was labeled "ref" and contained the control sample. A duplicate control sample was included with the coded samples for scoring. The judges scored the intensity of off-flavor on the following scale: 7 (no off-flavor), 6 (slight off-flavor), 5 (moderate off-flavor), 4 (strong off-flavor), 3 (very strong off-flavor), 2 (extremely strong off-flavor), 1 (totally unacceptable). Scores of 6 and below were interpreted as in violation of Louisiana stream water quality standards on taste and odor for foodfish.

During each exposure period, water samples were collected for odor analyses. The samples were taken at a depth of one foot near each fish trap and placed on wet ice for transport to the Baton Rouge laboratory for taste and odor analysis.

DISCUSSION

Flavor scores were highest at St. Francisville, the uppermost station (MR-01). Only small industrial and municipal waste discharges into the River are located on this stretch of the river. There was no appreciable difference in flavor scores between the right (west) and left (east) bank (Figure 1). The slight decrease in flavor scores from the control was probably the result of the natural background conditions in the River. The taste panel judged the test fish at this station as having a slight off-flavor.

Threshold odors in the water were also the lowest (inverse scale from flavor scores) at St. Francisville (Figure 2). Odors on the left bank were slightly higher than the right bank.

Immediately below station MR-01 and fifteen to twenty miles above the next downstream station MR-02, are two large paper mills discharging into the river. It was anticipated that these discharges would degrade flavors at station MR-02. However, no decrease in flavor scores occurred (Table III). The taste panel judged the test fish as having a slight off-flavor. As paper mill waste is well known for its ability to taint fish flesh, the station was apparently far enough downstream to allow sufficient dilution to eliminate any problem. Nevertheless, threshold odors in the water were higher, especially along the right bank.

At station MR-03, located immediately below the Baton Rouge industrial complex, were found the lowest off-flavor scores of the study. This station was also unique in that the greatest variation between left and right bank scores was found. Practically all the Baton Rouge industry is located on the left bank. The river along this area is

straight for five miles followed by a gradual bend to the right. Fish in the trap along the left bank exhibited the worst flavor of any during the survey whereas those along the right bank had scores only slightly lower than station MR-02 above the Baton Rouge industry. The panel judged test fish on the left bank as having an extremely strong off-flavor and those on the right only slightly off-flavor.

Threshold odors in the water followed the same pattern, with the left bank station having the strongest odors of any station sampled. The only exception was the right bank with less of an odor than its counterpart at the adjacent upstream station.

Station MR-04 was located thirty-five miles below MR-03 and immediately above the Geismar industrial area. At this point, off-flavor scores along the left bank had increased dramatically over the previous station. Scores along the opposite bank, however, decreased by an almost equal amount making left and right bank scores nearly identical. The taste panel judged the test fish on both sides of the river as containing a strong off-flavor.

Threshold odors in the water on the left bank had decreased to near the pre-Baton Rouge levels. Right bank levels were slightly lower than at the previous station with the overall result being that both banks recorded similar threshold odors. The upstream waste load had apparently, by this time, become uniformly mixed.

As in the Baton Rouge area, the Geismar industry is located on the left bank of the river. This fact was evident by the data obtained at station MR-05 located just below Geismar. Left bank flavor scores decreased, the result of off-flavor producing waste in the Geismar area being discharged along that shore. This waste was, however, quite restricted to the left bank as right bank scores were slightly higher than the previous upstream station. The panel judged the test fish on the left bank as containing a very strong off-flavor with the right bank having a strong off-flavor.

Threshold odor levels for the wastes generally followed the same pattern as the fish with higher threshold levels along the left bank. However, levels also increased, to a lesser extent, along the right bank.

Between Geismar and the next downstream station MR-06, is a moderately industrialized sixty mile stretch of river. Off-flavor scores increased significantly at this station. For the first time, left bank scores were noticeably higher than the right bank. Right bank scores were apparently suppressed by a four-industry complex on that shore five miles upstream. The panel judged the test fish on both banks as containing a moderate off-flavor.

This increase in water quality was not evident in the threshold odor scores. Except for a slight decrease in the left bank and slight increase in the right bank, levels varied little from the adjacent upstream station.

The last station, MR-07, was located approximately thirty miles below New Orleans, and downstream of all major industry in that area. Contrary to expectations, the New Orleans area had little effect on the flavor of the test fish. Scores on both banks were similar to those found above New Orleans. A municipal treatment plant discharge was discovered immediately above the right bank fish trap on the day the nets were picked up. This, in addition to an oil refinery two miles above the station, probably prevented the right bank scores from approaching the level of those on the left bank. The panel judged the test fish on both banks as moderately off-flavor.

Threshold odors decreased on the left bank while the right bank showed a slight increase. This resulted in stronger water odors on the right bank than the left which had occurred only once before at MR-02.

All stations below Baton Rouge were found out of compliance with Louisiana stream standards in regard to objectionable taste and odor in food fish.

CONCLUSIONS

Industrial discharges into the Mississippi River significantly taint the flesh of test fish placed down-river of these discharges. These discharges are undoubtedly the primary cause of the off-flavor in native fish in this reach of the river.

TABLE 13

STATION LOCATIONS
LOWER MISSISSIPPI RIVER FISH TAINTING STUDY
OCTOBER - NOVEMBER 1971

<u>Station</u>	<u>Location</u>
MR-01	Four miles below St. Francisville, Louisiana.
MR-02	Four miles above Baton Rouge, Louisiana.
MR-03	Six miles below Baton Rouge, Louisiana.
MR-04	Six miles above Geismar, Louisiana.
MR-05	Three miles below Geismar, Louisiana.
MR-06	Two miles above Luling, Louisiana.
MR-07	Twenty four miles below Greater New Orleans bridge.

TABLE 14

STATION DATA
LOWER MISSISSIPPI RIVER FISH TAINTING STUDY

<u>Station</u>	<u>Date</u>	<u>R.M.</u>	<u>Stage</u>	<u>Air Temp.</u>	<u>Station Depth*</u>	<u>Sample Depth</u>	<u>Water Temp.</u>	<u>D.O.</u>	<u>pH</u>
MR-01R	10-19-71	261	6.4	22.0	9'	1'	21.5	8.5	7.8
						8'	22.0	8.4	7.8
MR-01L	10-19-71	261.5	6.4	22.0	10'	1'	21.5	8.0	7.8
						9'	22.0	7.8	7.7
MR-02R	10-27-71	236.5	6.0	24.0	4'	1'	21.5	8.1	7.5
						3'	22.0	7.7	7.6
MR-02L	10-27-71	236.5	6.0	24.0	5'	1'	21.5	8.2	7.4
						4'	22.0	8.8	7.3
MR-03R	10-27-71	225.3	6.0	27.0	4'	1'	22.5	8.5	7.6
						3'	23.5	8.5	7.7
MR-03L	10-27-71	225.8	6.0	27.5	4'	1'	21.5	7.4	7.6
						3'	23.5	7.4	7.6
MR-04R	11-1-71	191.3	5.3	23.5	7'	1'	21.5	7.3	7.6
						6'	22.5	7.3	7.6

* Fish Cage Depth

TABLE 14 (Continued)

<u>Station</u>	<u>Date</u>	<u>R.M.</u>	<u>Stage</u>	<u>Air Temp.</u>	<u>Station Depth*</u>	<u>Sample Depth</u>	<u>Water Temp.</u>	<u>D.O.</u>	<u>pH</u>
MR-04L	11-1-71	191.3	5.3	23.5	14'	1'	21.5	7.5	7.6
						13'	23.0	7.2	7.6
MR-05R	11-1-71	182.2	5.3	26.0	10'	1'	22.0	7.3	7.5
						9'	22.0	7.2	7.6
MR-05L	11-1-71	182.2	5.3	22.5	8'	1'	22.0	7.1	7.7
						7'	22.0	7.2	7.8
MR-06R	11-5-71	123.0	3.8	17.5	2'	1'	22.0	6.8	7.7
MR-06L	11-5-71	122.5	3.8	19.0	8'	1'	21.0	7.4	7.6
						7'	22.0	7.4	7.4
MR-07R	11-15-71	71.8	2.4	---	11'	1'	18.0	7.8	7.9
						10'	18.0	7.5	7.9
MR-07L	11-15-71	71.8	2.4	---	6'	1'	18.0	7.6	7.8
						5'	18.0	7.8	7.9

* Fish Cage Depth

TABLE 15

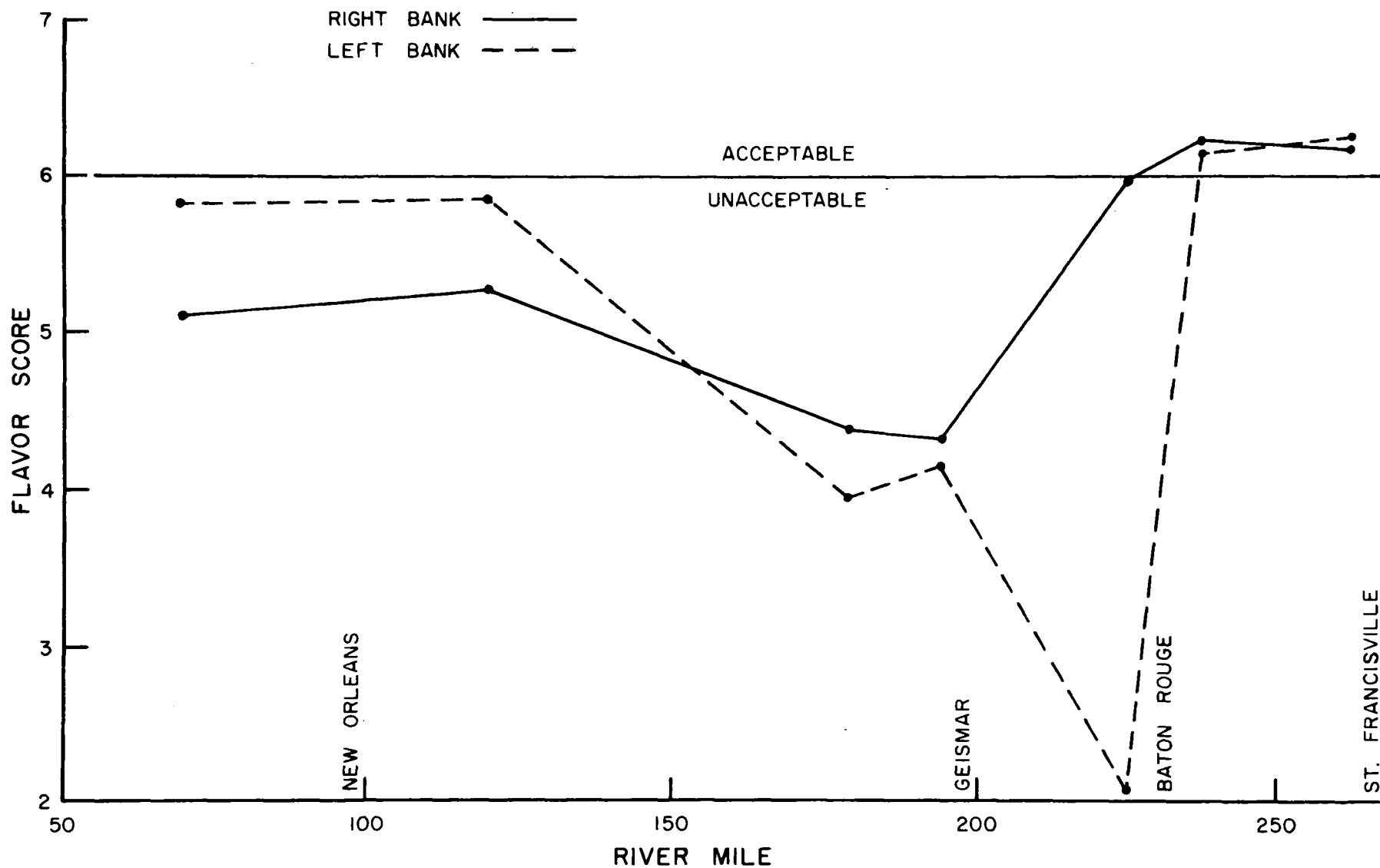
FLAVOR (FISH) AND THRESHOLD ODOR (WATER) DATA
 LOWER MISSISSIPPI RIVER FISH TAINING STUDY
 OCTOBER - NOVEMBER 1971

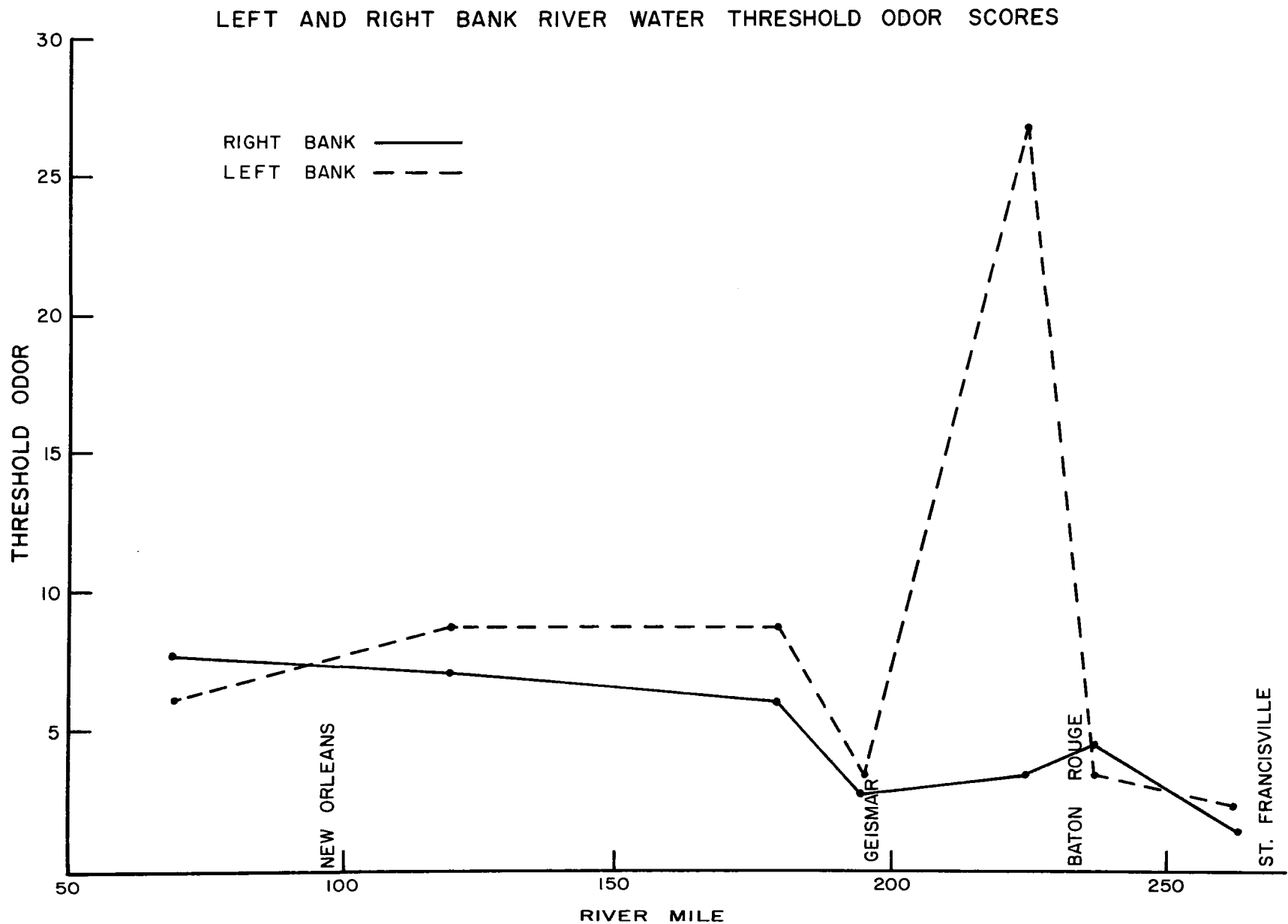
Station	Water	Off-flavor (Raw Data)	Off-flavor* (Corrected Data)	Panel's Evaluation Off-flavor
	Threshold Odor			
Control		6.1	7.0	
MR-01L	2.4	5.5	6.2	Slight
MR-01R	1.7	5.4	6.1	Slight
**LSD (05)		0.4		
Control		6.5	7.0	
MR-02R	4.8	5.8	6.2	Slight
MR-03L	26.9	1.9	2.0	Extremely Strong
MR-03R	3.7	5.7	6.1	Slight
**LSD (05)		0.6		
Control		5.6	7.0	
MR-04L	3.6	3.4	4.1	Strong
MR-04R	3.0	3.6	4.3	Strong
MR-05L	9.0	3.2	3.9	Very Strong
MR-05R	6.3	3.6	4.4	Strong
MR-06L	8.7	4.9	5.9	Moderate
MR-06R	7.3	4.4	5.3	Moderate
**LSD (05)		0.8		
Control		6.0	7.0	
MR-02L	3.7	5.4	6.1	Slight
MR-07L	6.3	5.1	5.9	Moderate
MR-07R	8.0	4.5	5.1	Moderate
**LSD (05)		0.5		

* Data Normalized to a Perfect Control Score of 7.0.

** Least Significant Difference at the Five Percent Level.

FISH FLAVOR SCORES, NORMALIZED WITH A MAXIMUM CONTROL SCORE OF 7





TOXICITY OF SELECTED ORGANIC CHEMICALS

The effects of low-level organics, such as were found in the drinking water supplies along the Mississippi River in Louisiana, on the health of people consuming the water is not easily determined. These chemicals may be harmless or toxic in a very short period, or their effects may not be evidenced for several years.

Because some of the compounds found in the water supplies are suspected toxicants under special experimental conditions, and because of the dearth of knowledge regarding their low-level effects, it is important that all identified sources of these compounds be controlled as rapidly as the technology for their control becomes available.

A general discussion of some known toxic and/or carcinogenic effects of the chemical found either in the finished water supplies or in industrial discharges follows. Details of toxicity studies are presented in Tables 17 thru 19, with references included for each study. Table 16 lists the identified organics and identifies water supplies in which they were found as well as the individual effluent discharges which were their sources to the river.

Table 17 contains available chronic toxicological information on chemicals found in the finished water supplies. Large gaps of information exist for chronic toxicity and the greatest proportion of chronic toxicological data available on organic chemicals is contained in the Russian literature. The doses presented for chronic toxicity are those which elicited an effect and where this was not available, the doses used are presented. (45) All doses are oral unless otherwise indicated.

Table 18 contains acute toxicological information on chemicals found in water. LD50 in mammals form the highest proportion of acute toxicity information available. Data on non-mammalian species were included when available. All

doses are oral unless otherwise indicated. LD₅₀ is the dose at which 50% of the animals die. TLM designates the median tolerance limit which is the concentration which kills 50% of fish for the indicated time in hours. LC is the concentration in the gaseous form which will kill the test animals in a given time period. The acute toxicity data is useful for determining relative toxicity and for chronic toxicity.

Table 19 contains information regarding the carcinogenic (cancer causing) properties of some of the organic chemicals found in the water supplies.

The references following this chapter are selected to represent literature in this field.

DISCUSSION

There is growing evidence that a significant proportion of malignancies may be initiated or promoted by environmental factors (6, 8, 9, 13, 17, 21, 52, 64,). Unlike the great epidemic diseases of the past, present diseases associated with development and aging of the human organism are of complex etiology; multiple factors are involved.

In view of these observations, The Food and Drug Administration has become very cognizant of the importance of carcinogenic (cancer causing), teratogenic (malformation causing), and mutagenic (capable of causing inheritable mutations) of pharmaceutical agents and chemicals used as food additives. As a result, food additives with carcinogenic properties are barred from use regardless of how carcinogenicity was demonstrated on animals. In contrast, these types of data have not been used as limiting indices in water quality criteria. Yet, because of physiological requirements, danger from the presence of these agents in water is greatly increased.

In terms of human health, total exposure of a human being to a given substance from all parts of his environment - air, water, and food - must be considered, and the interaction of these substances both within and outside the body must be evaluated.

A tremendous number of synthetic organic chemicals have been introduced into our water supplies (45, 52, 58). As previously stated, 88 have been isolated and identified either in industrial waste discharges or in water supplies in the Lower Mississippi River in Louisiana (see Table 20). Some of these compounds have been shown to be carcinogenic in experimental animals. A smaller number have been singled out as capable of causing cancer in humans. Infrequently, others have been identified as teratogenic or mutagenic.

Six chemicals found in either the finished water supplies of the New Orleans Carrollton Plant or U. S. Public Health Service Hospital, or both, induce histopathological changes in chronic animal studies (see Table 17).

Only three of the chemicals, benzene, carbon tetrachloride and chloroform, found in the finished waters have been indicated as being carcinogenic and may be considered chronic toxicants (see Table 19).

Equally significant, chronic toxicological data was not available for most of the organic chemicals found so far in these water supplies. Furthermore, there may be a myriad of organic chemicals, not yet isolated and identified, such as the pesticides, that could be present in these water supplies which are carcinogenic, teratogenic, or mutagenic.

It is clear that society must weigh carefully the expenditures for corrective action, both industrial and municipal against the costs it may have to pay in terms of present or future health impairment of its people stemming from man-made hazards.

In examining this dilemma, thought must be given to questions like the following which were posed to the Gross Committee (44):

How are the long-term effects of chronic exposure to low concentrations of toxic agents acting singly or in concert with other chemical or physical agents assessed?

How are susceptible subgroups within the population which may be at special risk because of age, sex, genetic background, or pre-existing physical impairments identified?

To what extent are diseases of unknown etiology, such as chronic degenerative diseases affecting the cardiovascular and respiratory systems aggravated by exposure to environmental agents?

There are no quick and easy solutions. The effects of toxic substances on man vary according to the nature of the substance, the quantity of the substance to which a person is exposed, the duration of exposure, the constitution of the person, including age, sex, health, and genetic makeup.

Because of the number of variables involved, chronic animal toxicity studies used in establishing limiting indices for Water Quality Criteria can only be used as a starting point.

All of the toxicity studies referenced in this report were initiated with healthy animals. The various tolerances set by governmental agencies based on these animal studies and extrapolated for humans are for healthy individuals; as health conditions deteriorate, the environmental stresses from the toxic chemicals are magnified.

The water consumers at the U. S. Public Health Service Hospital at Carville and at private and local governmental hospitals in New Orleans are not healthy people, but are patients with debilitating impairment of vital organs, i.e., the liver, kidneys, urinary bladder, lungs, heart and blood vessels. These organs compose the body's detoxication system. This system has evolved to protect the individual from the toxic effects of naturally-occurring foreign compounds of the diet by rapid metabolic transformation and excretion.

Since the hospital patients are suffering from various vital organ impairments, their protection is diminished, and the insult of the various heavy metals and toxic chemicals on their health is therefore much greater than it is on the general population.

Another grave situation involves the potential chronic effect of these contaminants on the health of the young children of the New Orleans area, not because of any organ disorder, but resulting from underdevelopment of certain enzyme systems needed for metabolizing foreign compounds.

These two groups of people, plus the senior citizens, are the most susceptible to the detrimental effects of these drinking water contaminants, because of their inherent biochemical conditions.

It is mandatory to single out potentially harmful substances and prevent them from entering those bodies of waters that will be used for drinking or food sources until it is clearly demonstrated that they pose no threat to human health or aquatic life. Determination of additional substances that might be harmful in long-term, low level exposures will require improved knowledge of the specific compounds that are entering receiving waters. It will also require considerable more research in epidemiology, in addition to laboratory animal studies. Priorities will have to set, attacking first those chemicals having an oral LD50 value of less than 100 mg/kg or TLm value of less than 20 mg/l (LD50 - lethal dose that will kill 50 percent of test animals over a given time period. TLm - median tolerance limit - concentration that will kill 50 percent of test animals over a given time period.)

ORGANIC CHEMICALS ISOLATED FROM RAW & FINISHED WATERS AND INDUSTRIAL WASTES

[illegible]

TABLE 16 (Continued)

[illegible]

TABLE 16 (Continued)

ORGANIC COMPOUND	CARROLLTON FINISHED WATER	JEFF. PAR. #2 RAW WATER	P.H.S. HOSPITAL FINISHED WATER	CHEVRON CHEM.	COPOLYMER	CROWN ZELLERBACH	ENJAY CHEM.	FOSTER GRANT	GEORGIA PACIFIC	HUMBLE OIL & REF.	SHELL CHEM.	RUBICON CHEM.	UNIROYAL, INC.	BASF WYANDOTTE
2,6-dinitrotoluene	X													
m-divinylbenzene													X	
n-dodecane										X				
n-eicosane										X				
4-ethenyl-1-cyclohexane													X	
ethyl benzene	X		X				X							
ethyl heptane (positional isomer?)										X				
ethyl hexyl phthalate														X
4-ethyl pyridine													X	
4-ethyl styrene													X	
endo-2-camphanol						X			X					
exo-2-camphanol	X					X			X					
n-heptadecane					X									
hexachlorobenzene	X													
n-hexadecane					X									
isocyanic acid	X													
1-isopropenyl-4-isopropyl- benzene (or 1,2 isomer)	X												X	
1-isopropenyl-3-isopropyl- benzene													X	
o-methoxyphenol	X					X			X					

TABLE 16 (Continued)

[illegible]

TABLE 16 (Continued)

ORGANIC COMPOUND	CARROLLTON FINISHED WATER	JEFF. PAR. #2 RAW WATER	P.H.S. HOSPITAL FINISHED WATER	CHEVRON CHEM.	COPOLYMER	CROWN ZELLERBACH	ENJAY CHEM.	FOSTER GRANT	GEORGIA PACIFIC	HUMBLE OIL & REF.	SHELL CHEM.	RUBICON CHEM.	UNIROYAL, INC.	BASF WYANDOTTE
1-propyl-2-methylnaphthalene		X												
p-menth-1-en-8-ol	X	X				X			X					
tetrachloroethylene	X													
tetradecane					X						X			
n-tetradecane											X			
74 toluene	X		X				X							
1,1,2-trichloro ethane	X													
n-tridecane											X			
1,3,5-trichlorophenol													X	
triethylene glycol dimethyl ether		X												
vinyl benzene	X		X		X		X	X					X	
o-xylene							X			X				
p-xylene							X			X				

TABLE 17

MAMMALIAN CHRONIC TOXICITY OF ORGANIC POLLUTANTS FOUND IN FINISHED
WATER FROM CARROLLTON AND U. S. PUBLIC HEALTH SERVICE HOSPITAL

<u>Ref</u>	<u>Organic Compound</u>	<u>Chronic Toxicity</u>		
		<u>Species</u>	<u>Dose</u>	<u>Effect</u>
45	Chloroform	Guinea Pig	0.4 mg/Kg	Increase in Vitamin C in adrenals.
			35 mg/Kg	Decrease in blood catalase; decrease in phagocytic capacity of leucocytes; structural lesions in liver, heart muscle and stomach wall; fatty infiltration, necrobiosis, and cirrhosis of liver parenchyma, lipoid degeneration and proliferation of interstitial cells in myocardium, and acute edema of the submucous and muscular layers of the stomach.
		Albino Rat	0.4 mg/Kg	No effect.
			125 mg/Kg	Decrease in conditioned reflex; decrease in cholinergic activity; histological changes.
			12.5 mg/Kg	Affects conditioned reflexes by fourth month.

TABLE 17 (Continued)

<u>Ref</u>	<u>Organic Compound</u>	<u>Chronic Toxicity</u>		
		<u>Species</u>	<u>Dose</u>	<u>Effect</u>
45	Dichlorobenzene	Rat	0.003 mg/Kg daily for 5 months	No significant effect.
45	Methylethyl Ketone	Warm Blooded Animals		No significant effects.
45	Hexachlorobenzene	Rats	0.005 mg/Kg daily for 4 months	Changes in conditioned reflexes.
45	Xylene	Rat	4 and 48 mg/Kg daily for 5 1/2 months	Occasional variation in hemoglobin, erythrocytes, and leucocytes; marked eosinophilia; change in reticulocyte number.
			48 mg/Kg daily for 5 1/2 months	Lymphopenia
45	Ethyl Benzene	Rabbit	5 mg/Kg in drink- ing water	Effect on: CNS, growth, morpholog- ical composition of blood, pathological and histological changes in organs.

TABLE 17 (Continued)

<u>Ref</u>	<u>Organic Compound</u>	<u>Chronic Toxicity</u>		
		<u>Species</u>	<u>Dose</u>	<u>Effect</u>
45	Toluene	Rabbit	0.25, 1.0, and 10 mg/Kg for 9 1/2 and 5 months	No significant effects.
45	Dimethylsulfoxide	Fish	High conc. or over long period of time	Change in number of various blood components; histopathological changes in liver, kidney, brain, gills, and spleen.

TABLE 18

ACUTE TOXICITY OF ORGANIC POLLUTANTS

<u>Ref</u>	<u>Organic Chemical</u>	<u>Species</u>	<u>Oral LD₅₀</u> <u>mg/Kg</u>	<u>96 hr</u> <u>TLm mg/l</u>	<u>LC₅₀</u> <u>ppm</u>	<u>Toxic Effect</u>
78	Acetone	rabbits	5300			
	Acetophenone	rats	3000			
	Acetylene dichloride	mice			15,000	
	Benzaldehyde	rats	S.C. ¹ 5000			
	Benzene	rats	5700			Chronic: bone marrow depression & aplasia, rarely leukemia. CNS depression, paralysis, convulsions have been observed in experimental animals.
45		sunfish		35-37		
	Biphenyl	rats	2200			
	Borneol	rabbits	2000			
	Bromoform	rabbits	S.C. 1000			
	Camphor	rats	S.C. 2200*			

1. Subcutaneously injected.

TABLE 18 (Continued)

<u>Ref</u>	<u>Organic Chemical</u>	<u>Species</u>	<u>Oral LD₅₀</u> <u>mg/Kg</u>	<u>96 hr</u> <u>TLm mg/l</u>	<u>LC₅₀</u> <u>ppm</u>	<u>Toxic Effect</u>
	Carbon Tetrachloride	mice rat rabbit guinea pig	5700 5700 5700		10,000	Liver and kidney damage
45	Chloroform	rat	1900			
	Cresol	man				Chronic poisoning from oral or percutaneous absorption may produce nervous disorders, mental changes, skin eruptions, jaundice, oliguria, & uremia.
		mosquito fish		10-24		
	p-Dichlorobenzene	rats	I.P. ¹ 2560			
	B,B'-Dichloroethyl- ether	rats	105,000			Continuous exposure, may cause portal cirrhosis, subacute yellow atrophy of liver. May cause liver & kidney damage.

1. Injected inter-peritoneally.

TABLE 18 (Continued)

<u>Ref</u>	<u>Organic Chemical</u>	<u>Species</u>	<u>Oral LD₅₀</u> <u>mg/Kg</u>	<u>96 hr</u> <u>TLm mg/l</u>	<u>LC₅₀</u> <u>ppm</u>	<u>Toxic Effect</u>
	Dimethyl Sulfoxide	rats	20000			
	Ethylbenzene	mice			10,400	
	Ethylene Dichloride	rats	770,000			Liver and kidney injury
	Guaiacol	rats	S.C. 900,000			
		rabbits	I.V. ² 3700			
45		perch		70-80 (48 hrs)		
80	Isocyanic Acid					Chronic exposure may cause fatigue and weakness.
	Isopropenyl	rats	3000			
	Methyl Chloride	mice			3150	Injury to liver & kidneys.
45	Naphthalene	rat	2000			
		sunfish		4-5		
	Nitrobenzene	rats	700,000**			
	Phenol	rats	530,000			

2. Injected intravenously.

TABLE 18 (Continued)

<u>Ref</u>	<u>Organic Chemical</u>	<u>Species</u>	<u>Oral LD₅₀</u> <u>mg/Kg</u>	<u>96 hr</u> <u>TLm mg/l</u>	<u>LC₅₀</u> <u>ppm</u>	<u>Toxic Effect</u>
45		catfish		16.7		
	Styrene	rats			2000	
	Tetrachloro- ethylene	mice	8850		6000	
	Toluene	rats	S.C. 5000		6000	
		sunfish		61-65 (lethal in 1 hour)		
81	2,4,5-Trichlorophenol	rats	2960			
	2,4,6-Trichlorophenol	rats	820,000			
	Xylene	rats	4000**		6000	
45		sunfish		47-48 (lethal in 1 hour)		

54 All data were obtained from the Eighth Edition of Merck Index, except where indicated.

* M.L.D.

** LD which is essentially the LD 100.

TABLE 19

CARCINOGENICITY IN MAMMALS OF ORGANIC POLLUTANTS IN WATER SUPPLIES

This Table presents available information on Carcinogenicity of Chemicals which are pollutants of New Orleans water supplies.

<u>Ref</u>	<u>Organic Compound</u>	<u>Routes</u>	<u>Dose</u>	<u>Species</u>	<u>Tumor Results</u>
31	P-Cresol	Skin	3% in alcohol 3 times weekly	Mouse	Negative
		Skin	3% in alcohol 3 times weekly	Rat	Negative
31	Carbon Tetrachloride	Oral	0.125-0.5 ml/Kg 3x wk in 1:1 soln & corn oil	Dog	0/8 Out of eight animals no tumors.
		Oral	0.2 ml of 2% olive oil soln 2x wk interval 3% soln given weekly for 17 wks	Mouse	+ / 37 Tumors showed - number not own

TABLE 19 (Continued)

<u>Ref</u>	<u>Organic Compound</u>	<u>Routes</u>	<u>Dose</u>	<u>Species</u>	<u>Tumor Results</u>
31	Carbon Tetrachloride (Cont'd)	Oral	0.1 ml of 40% soln in olive oil, 3x wk for 45-66 doses/ 13 1/2 wks	Mouse	Positive
31	Chloroform	Oral	8 x 10 ⁻⁴ and 4 x 10 ⁻⁴ ml dose in olive oil every 4 days, 30 times	Mouse	7/20
			2% in diet/ 13 months		0/40
56	Tetrachloroethylene	Oral	0.33 mg/Kg, 8 doses at 4d. intervals	Rat	0/18

TABLE 19 (Continued)

<u>Ref</u>	<u>Organic Compound</u>	<u>Routes</u>	<u>Dose</u>	<u>Species</u>	<u>Tumor Results</u>
57	Naphthalene	Oral	In oil (in syn- thetic diet) 6 times a wk, 10-20 mg until dose of 10g/ rat in food	Rat	Negative Cataracts induced
57	p-Dichlorobenzene	Oral	500 mg/Kg fed 5d/wk for total of 263 doses	Rabbit	0/7
57	Toluene	Oral	118,354, or 590 mg/Kg/d. in 2-3 ml olive oil soln emulsified & 5-10% aqueous soln of acacia for 138 feed- ings.	Rat	Negative

TABLE 19 (Continued)

<u>Ref</u>	<u>Organic Compound</u>	<u>Routes</u>	<u>Dose</u>	<u>Species</u>	<u>Tumor Results</u>
57	Acetone	Skin	0.2 ml of 100% 2x wk for 1 yr	Mouse	Negative
31	Acetophenone	S.C. or I.V.	Daily/ 40 day	Rabbit	Negative
57	Benzene	Skin	Twice weekly	Mouse	+ / 21
56	Guaiacol	S.C.	1-4% in olive oil, 26 inj (S.C.)	Rat	Negative
31	Xylene	Skin	Weekly applica- tion	Mouse	Negative

CHAPTER III

WATER QUALITY STANDARDS VIOLATIONS

The water quality standards of the State of Louisiana and the Federal government relating to taste and odor producing substances are being violated by industrial waste discharges to the Lower Mississippi River in Louisiana. On February 12, 1968, The Honorable Stewart Udall, then Secretary of the Interior, advised Governor John McKeithen of Louisiana by letter that the water quality standards of Louisiana had been approved. SPECIFIC CRITERIA (b) Taste and Odor - of these standards reads as follows:

Taste and odor producing substances shall be limited to concentrations in the waters of the state that will not interfere with production of potable water by reasonable water treatment methods, or impart unpalatable flavor to food fish, including shellfish, or result in offensive odors arising from the stream or other wise interfere with reasonable use of the water.

Municipal water plants using the Lower Mississippi River as their source of raw water include those of New Orleans, Jefferson Parish, the U. S. Public Health Service Hospital at Carville, Louisiana, and others. As shown earlier in Tables 5 through 10, thirty-six organic compounds have been isolated from the treated water from the Carrollton Water Plant serving New Orleans, fifteen in the raw water of the Jefferson Parish Marrero Plant and twelve in the finished water at the U. S. Public Health Service Hospital. Allowing for duplication, or finding the same compound in more than one water supply, a total of forty-eight compounds have been identified in the water supplies of these three plants.

Twelve of the compounds listed above have been identified in waste discharges from seven industries. These compounds, and industrial plants in whose wastes they have been found, are listed in Tables 5 through 10 pages 40 through 45 of this report.

These compounds and many others not identified are believed to be the primary cause of the taste and odors of these water supplies and in the fish caught in this reach of the river.

CHAPTER IV

INDUSTRIAL WASTE TREATMENT

The following information in Table 20 was compiled to reflect the current status of industrial waste treatment on the lower Mississippi River in Louisiana as well as the proposed treatment as presented to the Louisiana Stream Control Commission in a series of permit review meetings as authorized by P.L. 89-234 during the latter part of 1970 through early 1971. Many of these facilities are presently under construction and a few have been completed. In addition, some industries have had later meetings with the Louisiana Stream Control Commission and modifications and improvements to the proposed treatment facilities shown in Table 20 were accepted by the Commission. Current status of the state's approved waste abatement plans can be obtained from the Executive Secretary of the Louisiana Stream Control Commission, P. O. Drawer FC, Louisiana State University, Baton Rouge, Louisiana, 70803.

Further, the Environmental Protection Agency in conjunction with the U. S. Army Corps of Engineers has initiated the Refuse Act Permit Program under Section 13 of the River and Harbor Act of 1899 and Executive Order No. 11574. This has resulted in the development of waste abatement programs by industry which in some instances go beyond what was required by the State of Louisiana. Information regarding the current status of these permit applications and implementation plans for waste abatement can be obtained from the U. S. Army Corps of Engineers' District Office in New Orleans whose address is P. O. Box 60267, New Orleans, Louisiana, 70160 or the Environmental Protection Agency, Region VI office in Dallas Texas, whose address is Enforcement Division, Permits Branch, 1600 Patterson Street, Suite 1100, Dallas, Texas 75201.

TABLE 20
PROPOSED OR EXISTING INDUSTRIAL WASTE TREATMENT

<u>COMPANY</u>	<u>TYPE OF WASTE</u>	<u>EXISTING</u>	<u>TREATMENT</u> <u>PROPOSED TO STATE OF LA.</u>
Allied Chem. Corp. Ind. Chem. Div. (Baton Rouge)	Chemical and Petrochemical	In-process recovery systems, lime neutralization pond, organic recovery system, impounding basin to treat lead and chrome.	Meet best practical treat- ment for organics by January 1, 1973.
Allied Chem. Corp. Spec. Chem. Div. (Baton Rouge)	Chemical (Chlo- rides, Sulfates, Fluorides, Chro- mates)	HCl discharged to Mississippi River, all other wastes dis- charged to batture for settling.	Separation and treatment of sanitary wastes, construct compounding basin for calcium sulfate residue.
Allied Chem. Corp. Plastics Div. (Scotlandville)	Petrochemical	Suspended solids removed in settling chamber with mechanical skimmer.	Reduce chromates by 40% and eliminate excessive uses of recirculated cooling water.
Allied Chem. Corp. Geismar Complex (Geismar)	Agri-chemical and Petrochemical	Impound Gypsum- bioxidation pond.	Conversion of oxidation and settling ponds for ethylene and nitrogen plants to biological systems. Maximum recycling of water from HF and phos- phoric acid plant. (Comple- tion Dec. 1972)

TABLE 20 (Continued)

<u>COMPANY</u>	<u>TYPE OF WASTE</u>	<u>EXISTING</u>	<u>TREATMENT</u> <u>PROPOSED TO STATE OF LA.</u>
Allied Chem. Corp. Ind. Chem. Div. (Marrero)	Inorganic Chemical	None	None
American Cyanamid Co. (Avondale)	Chemical	Three deep well disposal systems - Organic recovery system (Completion 6-1-71); Sanitary waste treatment (Completion 5-1-71); Chromate reduction (Completion 6-1-71).	Surface water collection system (Completion 10-1-71).
Argus Chem. Corp. 8 (Hahnville)	Petrochemical	Separators and skimmers.	None-Considered equivalent of secondary.
Avondale Shipyards, Barge cleanings Inc. (Avondale)		Dilution, Rated aeration sewage treatment plant - Capacity 11,000 gpd, oil-water separator, steam stripping of water solubles.	Neutralization, activated carbon filtration, controlled release of non-volatile, non-toxic chemicals.
BASF Wyandotte Corp. (Geismar)	Petrochemical	Organic wastes separated, neutralized, or incinerated.	Incineration of organics; recycling for recovery of chlorides; stabilization pond; oil skimmer.

TABLE 20 (Continued)

<u>COMPANY</u>	<u>TYPE OF WASTE</u>	<u>EXISTING</u>	<u>TREATMENT</u> <u>PROPOSED TO STATE OF LA.</u>
Borden, Inc. Borden Chem. Div. (Geismar)	Petrochemical	Waste handling system (central collection system), stabilization lagoon.	Separation of process and uncontaminated surface run- off, secondary treatment (Completion 1972); deep well disposal - chromates (Completion 1971-72)
The Celotex Corp. (Marrero)	Bagasse	Diversion of sewage to Jefferson Parish-Marrero waste treatment process.	Recirculation and rinse of cellulose fiber through alterations in piping and storage of used process water (Completion 1972)
¹⁶ C.F. Industries (Donaldsonville)	Chemical	Neutralization pond, aeration pond.	Add baffles to aeration pond to correct short- circuiting.
Chevron Chem. Co. Oronite Add. Div. Oak Point Plant (Belle Chasse)	Organic Chem.	API oil-water separator, mechanical belt oil skimmer.	Holding tanks, air flotation, coalescing units (1&2), final settling, segregation of process and storm water drainage, deep well dis- posal (Completion 1st quarter 1972).

TABLE 20 (Continued)

<u>COMPANY</u>	<u>TYPE OF WASTE</u>	<u>EXISTING</u>	<u>TREATMENT</u> <u>PROPOSED TO STATE OF LA.</u>
Ciba-Geigy Chem. Corp. (St. Gabriel)	Agri-chemical	Deep well disposal, "Oxigest" system for sanitary waste.	Chromate removal, impounding basin (Completion 1971), in-plant improvements to reduce effluent 50%.
Copolymer Rubber & Chem. Corp. (Baton Rouge)	Petrochemical	Oil and grease trap, steam stripping of styrene, removal of rubber particles by screens and hydrocyclones, surge system to handle plant upsets, segregation of storm and process water.	Dissolved air flotation (Completion 1971), coalescing system, activated sludge bio-oxidation system.
8 Copolymer Rubber & Chem. Corp. (Addis)	Petrochemical	Precipitation basin, oxidation	None-Treatment incorporated into plant design and considered equivalent of secondary.
Cos-Mar Plant, Marbon Div. of Borg Warner (Carville)	Petrochemical	Aerated packaged plant for sanitary wastes, chlorination of intake water.	Contracted consultants to determine concentrations and substance in effluent streams, possibility of process modifications, surface water run-off.

TABLE 20 (Continued)

<u>COMPANY</u>	<u>TYPE OF WASTE</u>	<u>EXISTING</u>	<u>TREATMENT</u> <u>PROPOSED TO STATE OF LA.</u>
Crown-Zellerbach Corp. (St. Francisville)	Paper Mill	Extended aeration, activated sludge for sanitary waste, fiber recovery equipment.	Primary treatment consisting of primary clarifier, sludge storage lagoon (Completion Dec. 1972). Secondary treatment - aerated stabilization basin (Completion last quarter 1973).
The Dow Chem. Co. (Plaquemine)	Petrochemical	API separator, coalescers, in-plant changes.	Deep well disposal and incineration of chlorinated hydrocarbons.
W E. I. duPont de Nemours & Co., Inc. (LaPlace)	Petrochemical	Deep well disposal, clarifier, oxidation pond for sanitary wastes.	None
Enjay Chem. Co. Chem. Plant (Baton Rouge)	Petrochemical	API separators, in-plant changes.	River water replacement project, stabilization tank, trickling filters (Completion mid 1973).
Enjay Chem. Co. Plastics Plant (Scotlandville)	Petrochemical	API separator, pellet removal	None-Considered equivalent of secondary.

TABLE 20 (Continued)

<u>COMPANY</u>	<u>TYPE OF WASTE</u>	<u>EXISTING</u>	<u>TREATMENT</u>	<u>PROPOSED TO STATE OF LA.</u>
Ethyl Corp. (Baton Rouge)	Petrochemical	Filtration from T.E.L. process for lead reduction, settling basins, lead impounding basin, oil and solids traps.		None
Foster Grant Co., Inc. (Baton Rouge)	Petrochemical	Skimmer ponds, API separator		Collection lines and sumps to collect tank car heels and wash waters, retention basin for non-process surface waters.
Freeport Chem. Co. Div. of Freeport Minerals Co. (Uncle Sam)	Chemical	Impound CaSO_4 when sulfate in Mississippi River is over 75 ppm.		Study to reduce flouride discharges to the Mississippi River.
Freeport Sulphur Co. (Port Sulphur)	Carbon-sulphur compound (carsul)	None		None
Georgis Pacific Corp., Port Hudson Pulp Plant (Port Hudson)	Paper Mill	None		Primary treatment (Completion end 1972). Secondary treatment (Completion Oct. 1973).

TABLE 20 (Continued)

<u>COMPANY</u>	<u>TYPE OF WASTE</u>	<u>EXISTING</u>	<u>TREATMENT</u> <u>PROPOSED TO STATE OF LA.</u>
Getty Oil Co. (Venice)	Ship Ballast	Oil skimmers	None
Goodyear Tire & Rubber Co. (Plaquemine)	Petrochemical	Collection pit with skimmer.	Waste is handled by Dow Chemical Company.
Gulf Oil Co., U.S. (Venice)	Oil refinery	Packaged disposal plant for sanitary wastes, API separator, retention pond and skimming.	Air flotation.
Gulf Oil Chem. Co. (Welcome)	Agri-chemical, Petrochemical	In-plant controls resulting in secondary treatment (Agri-chemical plant).	Primary settling tanks and secondary air flotation (Styrene Monomer plant 1970-71).
Hercules, Inc. Allemania Plant (Plaquemine)	Organic Chemical	Secondary treatment.	None
Hooker Chem. Corp. (Hahnville)	Chemical	Process design to avoid con- tamination of effluent, neutralization, chromate reduction, recovery and recycling of organic materials.	Recycling and equipment changes to eliminate lead, further organics removal, absorption of HCl.

TABLE 20 (Continued)

<u>COMPANY</u>	<u>TYPE OF WASTE</u>	<u>EXISTING</u>	<u>TREATMENT</u> <u>PROPOSED TO STATE OF LA.</u>
Humble Oil & Refining Co. (Baton Rouge)	Oil refinery	In-plant controls, oil-water separators.	90% reduction of intake water use, expand aerated lagoon, in-plant control (Completion 1972). Based on pilot studies, determine secondary treatment (activated carbon or biological oxidation (Completion 1974-75)).
Jackson Brewing Co. Brewery (New Orleans)		None (Only discharge is once through cooling water from Mississippi River and wells.) Brewery and washing waste discharged to city sanitary system.	None
Kaiser Alum. & Chem. Corp. (Baton Rouge)	Spent Bauxite	None (for spent bauxite).	Impoundment or steel production (Completion 1975-76) for spent bauxite. Other waste streams - removal of settleable solids.
Kaiser Alum. & Chem. Corp. (Chalmette)	Primary Metal	Condenser water-none. Surface runoff-oil booms. Scrubber water-none.	Condenser water-none. Surface runoff-none Scrubber water-eliminate or treat.

TABLE 20 (Continued)

<u>COMPANY</u>	<u>TYPE OF WASTE</u>	<u>EXISTING</u>	<u>TREATMENT</u> <u>PROPOSED TO STATE OF LA.</u>
Kaiser Alum. & Chem. Corp. (Gramercy)	Spent Bauxite and chemical	None (for spent bauxite). Settling pond, impoundment of gypsum.	Activated sludge, impoundment or steel production (Completion 1975-76).
Melamine Chem. Inc. (Donaldsonville)	Ammonia	None	Settling ponds, aerators.
Monochem, Inc. (Geismar)	Petrochemical	Phenols-Activated carbon, decantation, filtration, oxidation, aeration. Carbon-Filtration.	None
56 Monsanto Co. (Luling)	Chemical	Segregation and Concentration of organics.	Secondary by 1972.
Murphy Oil Co. (Meraux)	Oil refinery	Segregation of non-contaminated storm water.	Reduce BOD 70%, reduce phenols 90% (Completion Dec. 1972).
Occidental Chem. Co. (Hahnville)	Inorganic chemical	Retention pond.	None
Rollins-Purle, Inc. (Baton Rouge)	Pollution abatement plant	Thermal, biological, chemical	None

TABLE 20 (Continued)

<u>COMPANY</u>	<u>TYPE OF WASTE</u>	<u>EXISTING</u>	<u>TREATMENT</u> <u>PROPOSED TO STATE OF LA.</u>
Rubicon Chem., Inc. (Geismar)	Petrochemical	Deep well disposal.	Additional pretreatment prior to deep well disposal
Schuykill Metals Corp. (Baton Rouge)	Secondary lead smelter	Settling ponds.	None
Shell Chem. Co. (Geismar)	Petrochemical	Incineration, deep well disposal, recycling	Secondary HCl disposal well.
Shell Chem. Co. (Norco)	Petrochemical	Incineration, deep well disposal, process unit recovery facilities, segre- gation, neutralization.	None
Stauffer Chem. Co. (Baton Rouge)	Petrochemical	Control by process design- stripping towers.	None
Stauffer Chem. Co. (St. Gabriel)	Chemical	Two sludge settling ponds, two sulfide treatment ponds, pH control, two sand filters.	None
Tenneco Oil Co. (Chalmette)	Oil refinery	Deep well disposal, API sep- arators, biological oxidation.	None

TABLE 20 (Continued)

<u>COMPANY</u>	<u>TYPE OF WASTE</u>	<u>EXISTING</u>	<u>TREATMENT</u> <u>PROPOSED TO STATE OF LA.</u>
Texaco, Inc. (Convent)	Oil refinery	Deep well disposal, API separators, oxidation ponds, settling ponds.	None
Triad Chemicals (Donaldsonville)	Ammonia, urea	Aeration pond, neutralization pond.	In-plant process modifications.
Union Carbide Corp. (Hahnville)	Petrochemical	Neutralization, clarifiers, retention pond, skimmers, storm water collection lagoon.	In-process modifications, deep well disposal, secondary biological treatment (Completion Dec. 1973).
UniRoyal, Inc. ☞ (Scotlandville)	Plastic resins	Lime-alum clarification	Bio-oxidation (Completion mid 1972).
UniRoyal, Inc. (Baton Rouge)	Petrochemical	API separator	None-Effluent is incorporated into Enjay's waste lines and will be treated by their treatment facilities.
UniRoyal, Inc. UniRoyal Chem. Div. (Geismar)	Synthetic rubber	Settling pond, neutralization	Deep well disposal (Completion 1972).

TABLE 20 (Continued)

<u>COMPANY</u>	<u>TYPE OF WASTE</u>	<u>EXISTING</u>	<u>TREATMENT</u> <u>PROPOSED TO STATE OF LA.</u>
Universal Foods Corp., Red Star (Belle Chasse)	Yeast	Pilot plant studies	Present abatement schedule following completion of pilot plant studies.
Vulcan Materials Co., Chem. Div. (Geismar)	Petrochemical	Segregation of storm water run-off, in-process modification.	Elimination of source of waste stream.
Witco Chem. Corp. Sonneborn Div. (Gretna)	Oil additives	API separator, skimmer	Secondary or equivalent by Dec. 1972.

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APPENDIX

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EXHIBIT A

STATE OF LOUISIANA
STREAM CONTROL COMMISSION
P. O. DRAWER FC
UNIVERSITY STATION
BATON ROUGE, LOUISIANA 70803

March 23, 1967

Mr. James M. Quigley, Commissioner
Federal Water Pollution Control Administration
U.S. Department of Interior
633 Indiana Avenue, N.W.
Washington, D.C. 20242

Dear Mr. Commissioner:

For a number of years, Louisiana has been among the Nation's leaders in the production and refining of petroleum. During the past ten years, Louisiana has taken its place among the Nation's leaders in the manufacture of basic petro-chemical and other chemical products. These manufacturing plants have located and are locating in Louisiana because of the availability of vast mineral resources, an apparent, inexhaustible supply of good quality water for process use, and because of the benefits associated with water transportation, and because of availability of plant sites.

Virtually all of these plants return cooling and other types of process water to the streams. Many of these returned waters contain small fractions of the complex chemicals being manufactured. These fractions find their way to Louisiana's very rich estuaries. The Mississippi River is the only available source of raw water for potable supplies for more than 1,500,000 people.


Louisiana's Water Pollution Control Authority, the Louisiana Stream Control Commission, inaugurated a permit system for industrial waste discharge to public waters in 1940. Known toxins and other chemicals that by calculated concentration in the receiving stream may be toxic or otherwise harmful to humans and other forms of life are denied in the permit to discharge. Despite the afore-mentioned, we have become concerned about the degradation properties or lack thereof of some of these materials in the aquatic environment. There is also concern about

the possible combination of these materials in the ecosystem and the effects produced by their synergism and/or antagonism. Possible accumulation of these materials and their effects on the biota, stream bed, and other sites are unknown. A good case in point is the recent fish kills in the Mississippi River. Such incidents have raised questions about other organic and inorganic chemicals entering Louisiana via the Mississippi River which drains approximately 40% of the continental United States.

If there is to be continuing positive assurances given our water using public that their waters will remain safe, potable supplies in light of the ever increasing discharge of complex chemicals to our water resources, there is need for more information than is presently available or, at the present time, we are staffed and geared to obtain.

For the reasons and concerns cited, it is requested that technical assistance as provided in Section 5 (b) of Public Law 84-660, as amended, be made available to the State of Louisiana. Specifically this assistance is requested in the fresh and estuarine waters of the Mississippi River in Louisiana and the Calcasieu River, a watershed located entirely within this state, but discharging to our coastal region. Specific information is desirable and needed on the effects on water quality and aquatic life that may be exhibited by the presence of organic chemicals in the above cited aquatic environments. We feel the need to be advised of processes that could be used in treating or removing specific chemicals from waste streams and costs associated with their treatment and/or removal.

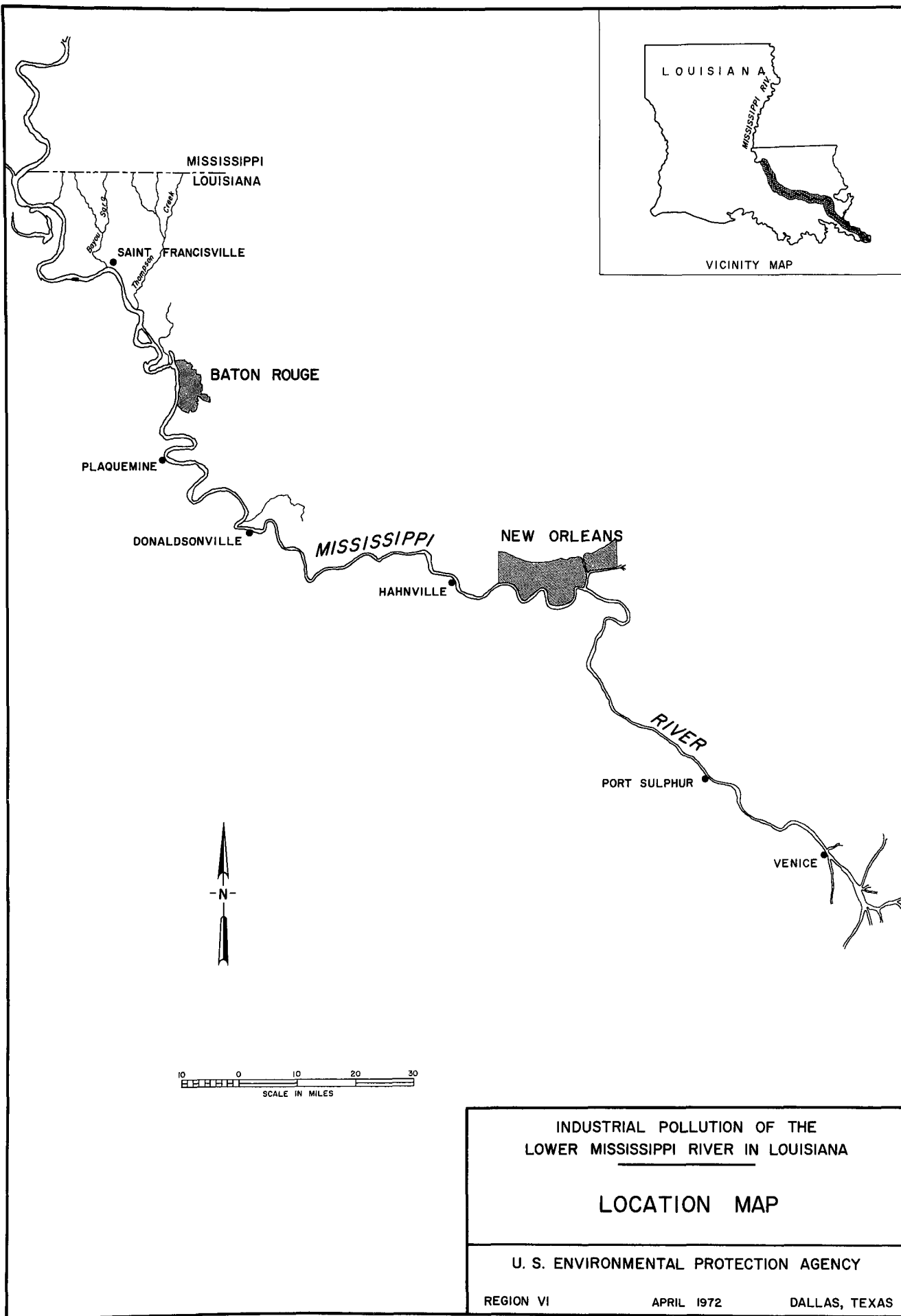
Very truly yours,



Leslie L. Glasgow
Chairman

Louisiana Stream Control Commission

FMM



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AVAILABLE
DIGITALLY**

EXHIBIT D

ANALYTICAL TECHNIQUES

1. RAW AND FINISHED WATER

Mega Sampling

The "Mega" sampler is used to extract trace organics from large volumes of water. It is a portable unit comprising filters to remove suspended solids followed by beds of granular activated carbon. These units are connected in series, water entering the filters for removal of suspended solids and then flowing through the activated carbon units where organic compounds are adsorbed on the carbon surface and thus removed from solution.

Two samplers were used during the study; one with three rapid sand filters followed by eight stainless steel containers for holding the carbon. The second, more compact unit, comprised two sand filters followed by four carbon units. Both units are capable of extracting organics from water in quantities up to 300,000 gallons per run.

Carbon Drying

A carbon drying oven is basically a forced-air, low temperature oven with a series of stainless steel trays for holding the carbon. The oven has the capacity of drying two mega cylinders of carbon in 4 days.

Mega Extraction

Organics adsorbed on the activated carbon from mega samples of raw and finished water were removed by extraction.

The extractor is basically a large soxhlet extractor made of stainless steel (Middleton, et. al.). Chloroform was used as the extracting solvent. Samples were reduced in volume by distillation to approximately 500 ml.

Fractionation and Identification of Organics in Carbon-Chloroform Extract

The carbon chloroform extract (CCE) was first fractionated by a combination of steam distillation and silica gel column chromatography. Further separation into compounds or groups of compounds was achieved by preparative gas chromatography (GLC). This procedure is shown schematically on the flow sheet in Figure D-1. Since the project was initially designed to identify odor-causing organics, each GLC fraction trapped in a cold trap-silica gel U-tube was subjected to a threshold odor evaluation (Exhibit E). The important odorous fractions were then further purified by GLC preparative techniques and identified by infrared (IR) spectrophotometry initially and, during the latter part of the study, by mass spectroscopy.

2. INDUSTRIAL WASTES

Sampling Procedures

Industrial wastes were collected by grab sampling techniques or, in some instances, were composited. Individual waste streams were sampled and composited in proportion to flow. All flow values were provided by the industry. A total of thirty gallons of composite (later twenty-five gallons when bioassays were discontinued) were collected.

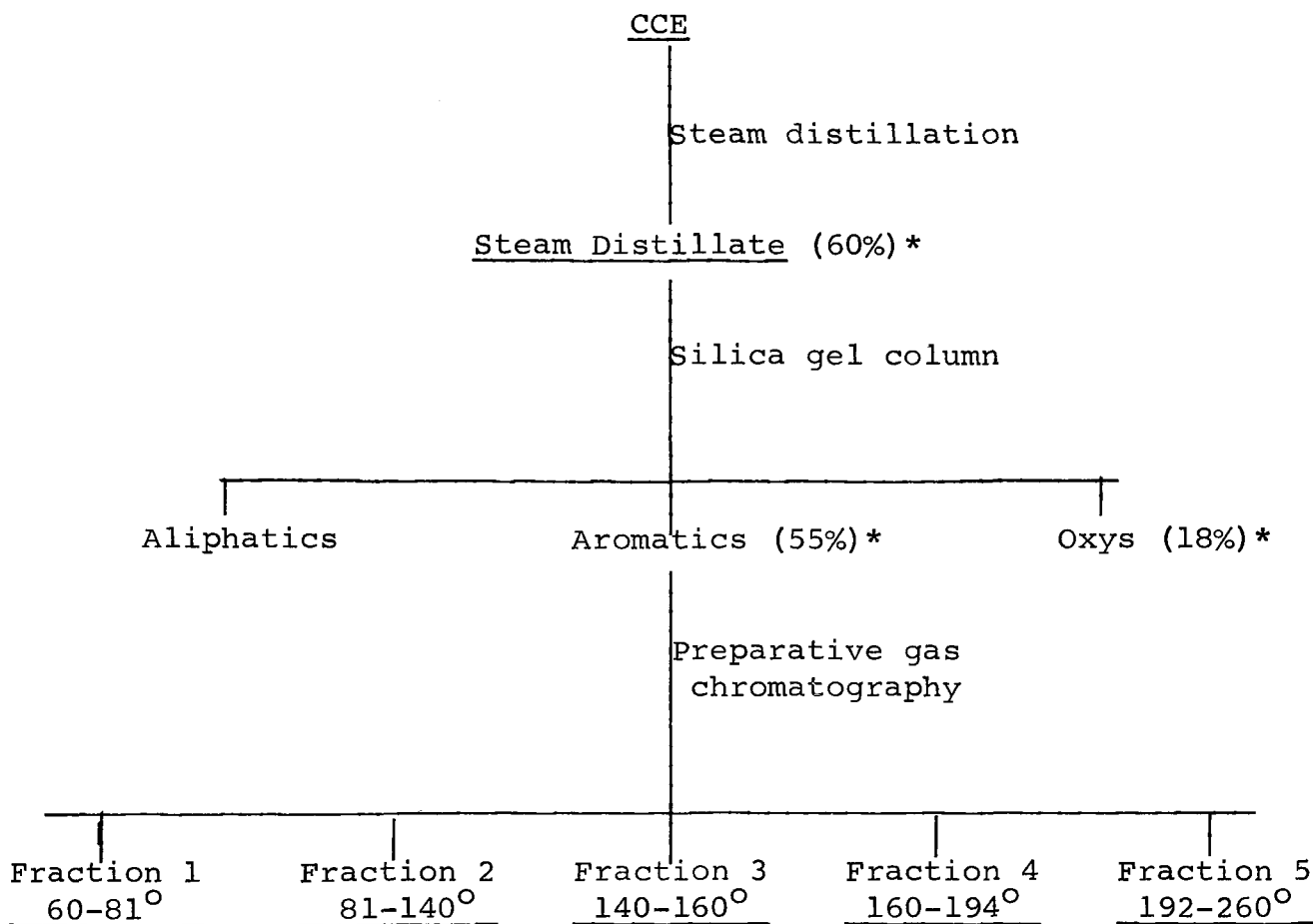
Organic Analyses

Twenty gallons of the composited waste was extracted with immiscible solvents in a liquid-liquid procedure showed schematically on the attached flow chart (Figure D-2).

The concentrated fraction of this extract was used for the identification of individual organic compounds. Identification procedures parallel the techniques used in the CCE extracts of the raw and finished water as previously described. Emphasis in the early part of the study was on the identification of the odorous fractions of the wastes.

Figure D-1

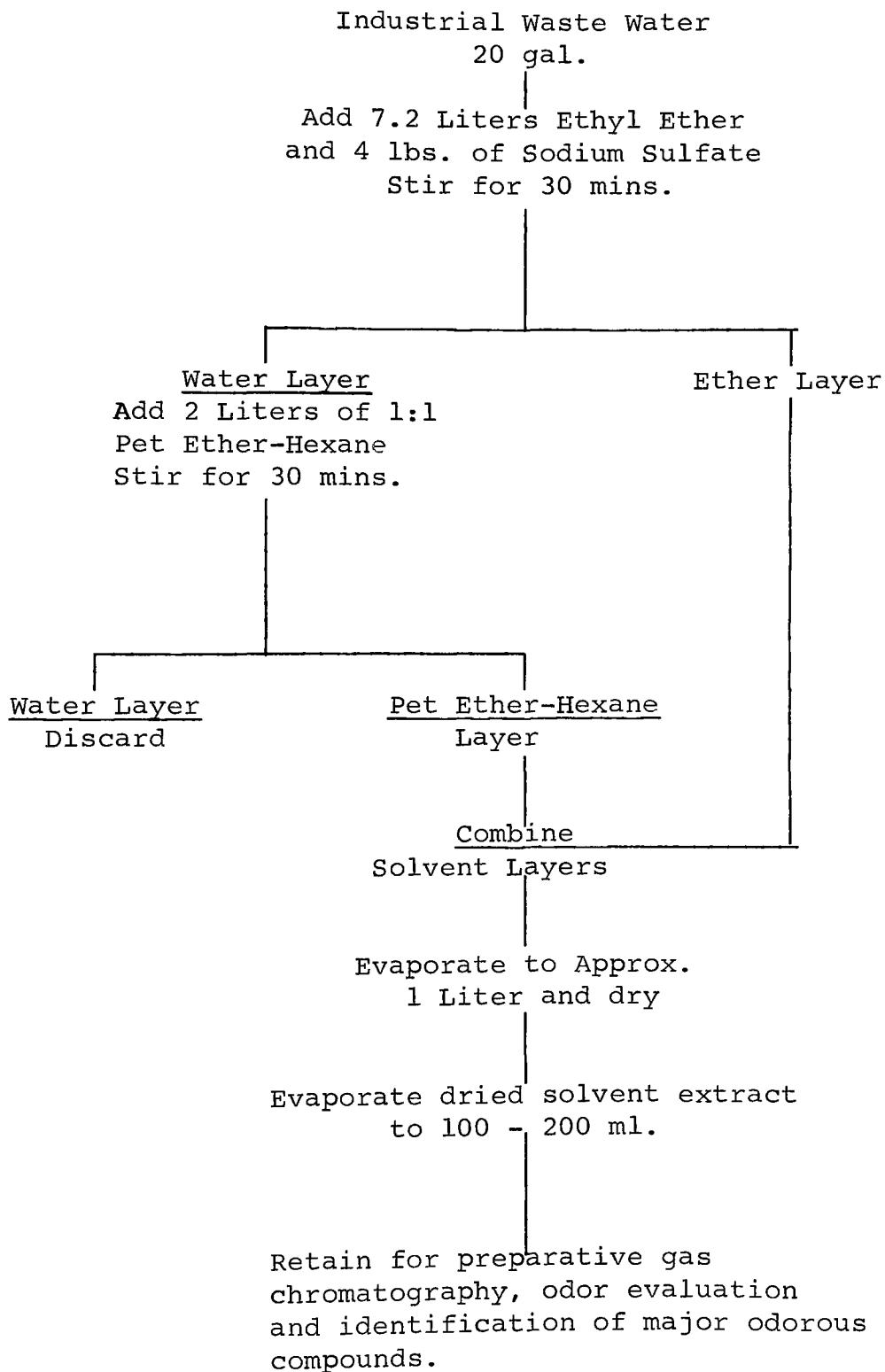
Flow Sheet
Fractionation of Lower Mississippi
Carbon Chloroform Extract



* Numbers in parentheses indicate percentage of total odor of parent fraction contained in daughter fraction. These percentages vary with different samples.

Figure D-2

Flow Chart of Industrial Waste Water Extraction



Other Parameters

The waste of each industry sampled was subjected to a detailed analysis. The following parameters were determined on most samples: flow, temperature, pH, conductivity, hardness, alkalinity and/or acidity, chlorides, sulfates, solids (total and volatile), chemical oxygen demand (COD), total organic carbon (TOC), phenols, oil and grease, phosphorous, cyanide, sodium, potassium, arsenic, lead, iron, cadmium, copper, chromium, mercury and zinc and threshold odor number.

All of these analyses were performed by procedures described in the FWQA methods manual.

Methodology Used in Organic Identification

The organic fractions separated from either the CCE's of the river water or the solvent extracts of the industrial wastes, were identified by several different procedures including separations by preparative GLC; trapping in the cold or in solvents, followed by identification by infrared spectroscopy. Other laboratories used the newer, GLC-Mass Spectroscopy approach. Certain low boiling compounds were identified by a combination of differential thermal analysis (DTA) followed by mass spectroscopy. Since each laboratory used a unique approach, standard procedures are unavailable; however, below is a list of the laboratories and senior chemists who participated in these investigations. It is suggested that these individuals be contacted directly for details on the methodology.

Robert S. Kerr Water Research Center
U. S. Environmental Protection Agency
P. O. Box 1198
Ada, Oklahoma 74820
Dr. William Dunlap

Southeast Water Laboratory
U. S. Environmental Protection Agency
College Station Road
Athens, Georgia 30601
Dr. Ron Webb

Robert A. Taft Engineering Center
4676 Columbia Parkway
Cincinnati, Ohio 45226
Mr. Charles Mashni

Baton Rouge Facility
U. S. Environmental Protection Agency
2695 N. Sherwood Forest Drive
Baton Rouge, Louisiana 70814
Mr. Mike Garza

Bureau of Sport Fisheries & Wildlife
Denver Federal Center, Building 16
Denver, Colorado 80225
Mr. R. E. White

The Dow Chemical Company
Waste Control
Midland, Michigan 48640
Mr. C. E. Hamilton

EXHIBIT E

THRESHOLD ODOR*

(Consistent Series Method)

STORET NO:

60°C 00086

ROOM TEMP: 00085

1. Scope and Application

- 1.1 This method is applicable to the determination of finished waters, surface waters, domestic and industrial wastes, and saline waters.
- 1.2 Highly odorous samples are reduced in concentration proportionately before being tested. Thus, the method is applicable to samples ranging from nearly odorless natural waters to industrial wastes with threshold odor numbers in the thousands.

2. Summary of Method⁽¹⁾

- 2.1 The sample of water is diluted with odor-free water until a dilution that is of the least definitely perceptible odor to each tester is found. The resulting ratio by which the sample has been diluted is called the "threshold odor number" (T.O.).
- 2.2 People vary widely as to odor sensitivity, and even the same person will not be consistent in the concentrations he can detect from day to day. Therefore, panels of not less than five persons, and preferably 10 or more, are recommended to overcome the variability of using one observer.⁽²⁾
 - 2.2.1 As an absolute minimum, two persons are necessary: One to make the sample dilutions and one to determine the threshold odor.

3. Sample Handling and Preservation

- 3.1 Water samples must be collected in glass bottles with glass or Teflon-lined closures.

* Methods of Chemical Analysis of Water and Wastes, "Threshold Odor (Consistent Series Method)" Environmental Protection Agency, Water Quality Office, Analytical Quality Control Laboratory, Cincinnati, Ohio, 1971.

3.1.1 Plastic containers are not reliable for odor samples and must not be used.

3.2 Odor tests should be completed as soon as possible after collection of the sample. If storage is necessary, collect at least 1000 ml of sample in a bottle filled to the top. Refrigerate, making sure no extraneous odors can be drawn into the sample as the water cools.

4. Interferences

4.1 Most tap waters and some waste waters are chlorinated. It is often desirable to determine the odor of the chlorinated sample as well as of the same sample after removal of chlorine. Dechlorination is achieved using sodium thiosulfate in exact stoichiometric quantity.

4.1.1 It is important to check a blank to which a similar amount of dechlorinating agent has been added to determine if any odor has been imparted. Such odor usually disappears upon standing if excess reagent has not been added.

5. Apparatus

5.1 Odor-free glassware: Glassware must be freshly cleaned shortly before use, with non-odorous soap and acid cleaning solution followed by rinsing with odor-free water. Glassware used in odor testing should be reserved for that purpose only. Rubber, cork, and plastic stoppers must not be used.

5.2 Constant temperature bath: A water bath or electric hotplate capable of maintaining a temperature control of $\pm 1^{\circ}\text{C}$ for performing the odor test at 60°C . The temperature bath must not contribute any odor to the odor flasks.

5.3 Odor Flasks: Glass stoppered 500 ml (ST 32) Erlenmeyer flasks, or wide-mouthed 500 ml Erlenmeyer flasks equipped with Petri dishes as cover plates.

NOTE: Narrow-mouth vessels are not suitable for running odor tests. Potential positive bias due to color and/or turbidity of water sample under observation can be eliminated by wrapping odor flasks in aluminum foil, painting flasks with non-odorous paint, or by using red actinic Erlenmeyer flasks.

- 5.4 Sample Bottles: Glass bottles with glass or Teflon-lined closures.
- 5.5 Pipets, measuring: 10.0 and 1.0 ml graduated in tenths.
- 5.6 Graduate cylinders: 250, 200, 100, 50, and 25 ml.
- 5.7 Thermometer: 0-110°C ($\pm 1^\circ\text{C}$), chemical or metal stem dial type.
- 5.8 Odor free water generator: See Figure 1.

6. Reagents

- 6.1 Odor-free water: Odor-free dilution water must be prepared as needed by filtration through a bed of activated carbon. Most tap waters are suitable for preparation of odor-free waters, except that it is necessary to check the filtered water for chlorine residual, unusual salt concentrations, or unusually high or low pH. All these may affect some odorous samples.

Where supplies are adequate, distilled water avoids these problems as a source of odor-free water. A convenient odor-free water generator may be made as shown in Figure 1. Pass tap or distilled water through the odor-free water generator at a rate of 0.1 liter/minute. When the generator is first started, it should be flushed to remove carbon fines before the odor-free water is used. The carbon cartridge,⁽³⁾ or a comparable assembly, is also suitable.

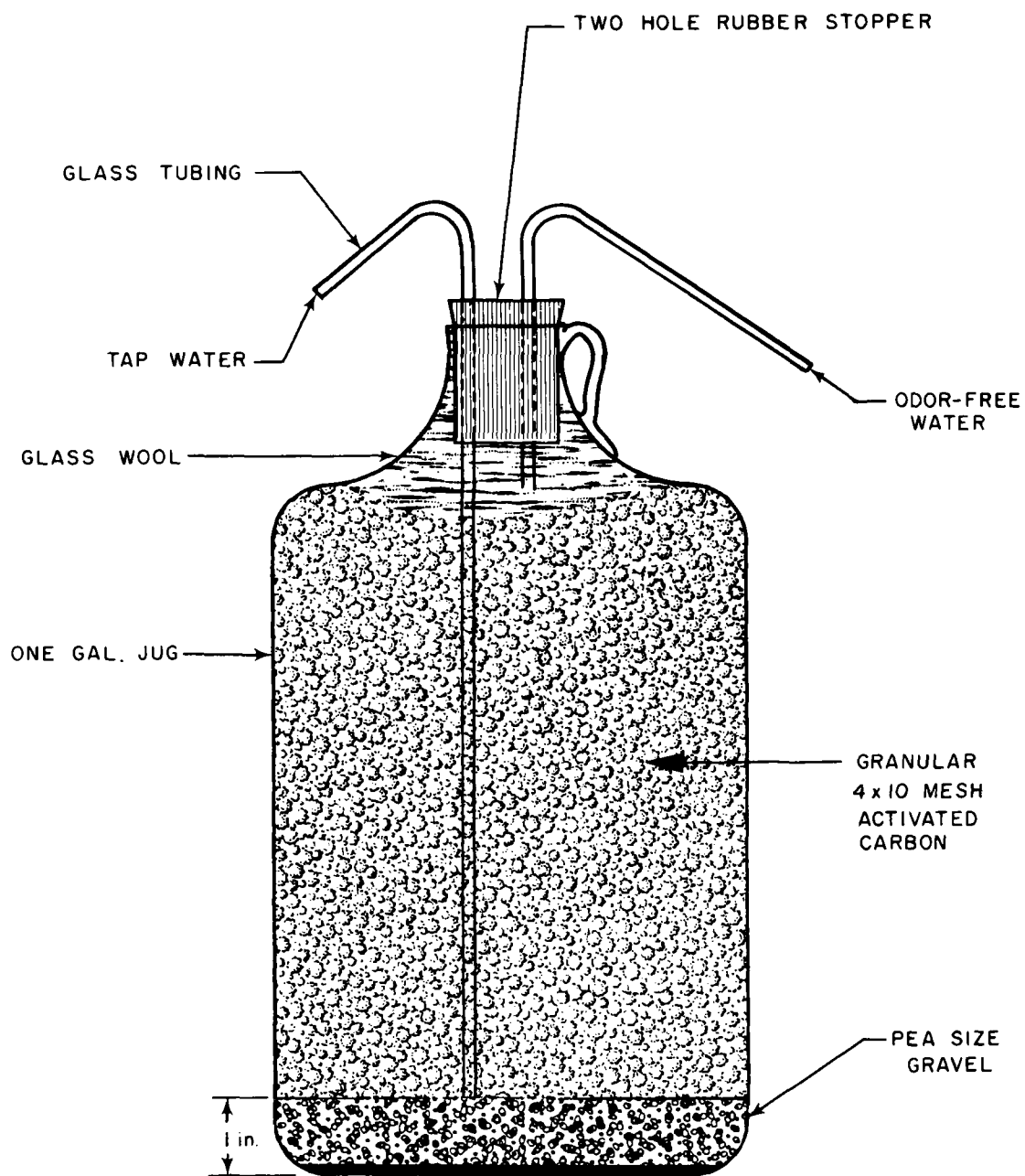


FIG. E-1 ODOR-FREE WATER GENERATOR

6.1.1 The quality of water obtained from the odor-free water generator should be checked daily at the temperature tests are to be conducted (room temperature and/or 60°C). The life of the carbon will vary with the condition and amount of water filtered. Subtle odors of biological origin are often found if moist carbon filters are permitted to stand idle between test periods. Detection of odor in the water coming through the carbon indicates a change of carbon is needed.

7. Procedure

7.1 Precautions: Selection of persons to make odor tests should be carefully made. Extreme sensitivity is not required, but insensitive persons should not be used. A good observer has a sincere interest in the test. Extraneous odor stimuli such as those caused by smoking and eating prior to the test or through the use of scented soaps, perfumes, and shaving lotions must be avoided. The tester should be free from colds or allergies that affect odor-response. Frequency of tests must not be so great as to induce fatigue. Frequent rests in an odor-free atmosphere are recommended.

The room in which the tests are to be conducted should be free from distractions, drafts, and other odor. In certain industrial atmospheres, a special odor-free room may be required, ventilated by air filtered through activated carbon and maintained at a constant comfortable temperature and humidity⁽⁴⁾.

For precise work a panel of five or more testers should be used. The persons making the odor measurements should not prepare the samples and should not know the dilution concentrations being evaluated. These persons should have been made familiar with the procedure before participating in a panel test. Always start with the most dilute sample to avoid tiring the senses with the concentrated sample. The temperature of the samples during testing should be kept within 1 degree of the specified temperature for the test.

7.2 Threshold Measurement: The ratio by which the odor-bearing sample has to be diluted with odor-free water for the odor to be just detectable by the odor test is the "threshold odor number" (T.O.). The total volume of sample and odor-free water used in each test is 200 ml. The proper volume of odor-free water is put into the flask first; the sample is then added to the water. Table 1 gives the dilutions and corresponding threshold numbers.

Table 1. Threshold Odor Number Corresponding to Various Dilutions

Sample Volume (ml) Diluted to 200 ml	Threshold Odor Number
200	1
100	2
50	4
25	8
12.5	16
6.3	32
3.1	64
1.6	128
0.8	256

7.3 Determine the approximate range of the threshold odor by:

7.3.1 Adding 200 ml, 50 ml, 12.5 ml, and 3.1 ml of the sample to separate 500 ml glass-stoppered Erlenmeyer flasks containing odor-free water to make a total volume of 200 ml. A separate flask containing only odor-free water serves as the reference for comparison. If run at 60°C, heat the dilutions and the reference in the constant temperature bath to 60°C ($\pm 1^\circ\text{C}$).

- 7.3.2 Shake the flask containing the odor-free water, remove the stopper, and sniff the vapors. Test the sample containing the least amount of odor-bearing water in the same way. If odor can be detected in this solution, more dilute samples must be prepared as described in 7.3.3. If odor cannot be detected in the first dilution, repeat the above procedure using the sample containing the next higher concentration of the odor-bearing water, and continue this process until odor is clearly detected.
- 7.3.3 If the sample being tested requires more extensive dilution than is provided by Table 1, an intermediate dilution is prepared from 20 ml of sample diluted to 200 ml with odor-free water. Use this dilution for the threshold determination. Multiply the T.O. obtained by ten to correct for the intermediate dilution. In rare cases more than one tenfold intermediate dilution step may be required.
- 7.4 Based on the results obtained in the preliminary test, prepare a set of dilutions using Table 2 as a guide. One or more blanks are inserted in the series, in the vicinity of the expected threshold, but avoiding any repeated pattern. The observer does not know which dilutions are odorous and which are blanks. He smells each flask in sequence, beginning with the least concentrated sample and comparing with a known flask of odor-free water, until odor is detected with utmost certainty.

Table 2. Dilutions for Various Odor Intensities

Sample Volume in Which Odor First Noted			
200 ml	50 ml	12.5 ml	3.1 ml
Volume (ml) of Sample to be Diluted to 200 ml			
200	100	52	(Intermediate Dilution, See 7.3.3)
100	50	25	
50	25	12.5	
25	12.5	6.3	
12.5	6.3	3.1	

- 7.5 Record the observations of each tester by indicating whether odor is noted (+ sign) in each test flask.

For example:

ml sample								
diluted to 200 ml	12.5	0	25	0	50	100	200	
Response	-	-	+	-	+	+	+	

8. Calculations

- 8.1 The threshold odor number is the dilution ratio at which odor is just detectable. In the example above (7.5), the first detectable odor occurred when 25 ml sample was diluted to 200 ml. Thus, the threshold is 200 divided by 25, equals 8. Table 1 lists the threshold numbers that correspond to common dilutions.
- 8.2 Anomalous responses sometimes occur; a low concentration may be called positive and a higher concentration in the series may be called negative. In such a case, the threshold is designated as that point of detection after which no further anomalies occur. For instance:

ml sample							
diluted to 200 ml	6.3	12.5	0	25	50	100	
Response	+	-	-	+	+	+	
				↓			
				threshold			

8.3 Calculations of panel results to find the most probable average threshold are best accomplished by appropriate statistical methods. For most purposes, the threshold of a group can be expressed as the geometric mean (G.M.) of the individual thresholds. The geometric mean is calculated in the following manner:

8.3.1 Obtain odor response as outlined in procedure and record results. For example:

Table 3. Sample Odor Series

ml of Odor-free water	ml of Sample	Observer Response*				
		1	2	3	4	5
188	12.5	-	-	-	-	-
175	25	-	⊕	-	+	⊕
200	0	-	-	-	-	-
150	50	⊕	+	-	-	+
200	0	-	-	-	-	-
100	100	+	+	⊕	⊕	+
0	200	+	+	+	+	+

*Circled plus equals threshold level.

8.3.2 Obtain individual threshold odor numbers from Table 1.

<u>Observer</u>	<u>T.O.</u>
1	4
2	8
3	2
4	2
5	8

8.3.3 The geometric mean is equal to the nth root of the product of n numbers. Therefore:

$$4 \times 8 \times 2 \times 2 \times 8 = 1024,$$

$$\text{and } \sqrt[5]{1024} = \frac{\log 1024}{5} = \frac{3.0103}{5} = 0.6021,$$

$$\text{and anti-log of } 0.6021 = 4 = \text{T.O.}$$

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

9.2 A threshold number is not a precise value. In the case of the single observer, it represents a judgment at the time of testing. Panel results are more meaningful because individual differences have less influence on the result. One or two observers can develop useful data if comparison with larger panels has been made to check their sensitivity. Comparisons of data from time to time or place to place should not be attempted unless all test conditions have been carefully standardized and some basis for comparison of observer intensities exists.

References

1. Standard Methods, 13th Edition, Amer. Public Health Asso., New York, N.Y., p. 248, Method 136 (1971).
2. ASTM, Comm E-18, STP 433, Basic Principles of Sensory Evaluation; STP 434, Manual on Sensory Testing Methods; STP 440, Correlation of Subjective-Objective Methods in the Study of Odors and Taste; Phil., Pennsylvania (1968).
3. Standard Methods, 12th Ed., Amer. Public Health Asso., New York, N.Y., 1965, p. 213.
4. Baker, R. A., "Critical Evaluation of Olfactory Measurement". Jour WPCF, 34, 582 (1962).

ANALYTICAL RESULTS

INDUSTRIAL WASTE DISCHARGES

* An asterisk (*) by the date sampled indicates net load contributions for all parameters on that date, while an asterisk (*) by an individual value means that only that parameter value is a net load calculation. These net load values were obtained by subtracting the concentration of the intake water parameter from the comparable effluent discharge parameter concentration and the net pounds per day discharged were calculated on this difference. All other load values were calculated by using only the concentrations found in the plant effluent and therefore represent gross contribution of these plants.

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DETECTION LIMITS

The analytical method chosen for each parameter has a minimum detection limit. Analytical results below these limits are indicated in "Analytical Results, Industrial Waste Discharges" with a + since they are considered unreliable.

Detection limits for parameters reported in this document are listed below:

<u>PARAMETER</u>	<u>DETECTION LIMIT</u>
Conductivity	10.0 Micromhos
Solids - Total	9.X mg/l
Solids - Volatile	9.X mg/l
Chemical Oxygen Demand	
Low (5-50 mg/l)	5.X mg/l
High (1000 mg/l+)	250.X mg/l
Total Organic Carbon	1.X mg/l
Phenol	0.001X mg/l
Oil & Grease	5.X mg/l
Cyanide	1.X mg/l (titration)
	0.005X mg/l (colorimetric)
Iron - Fe	0.004X mg/l
Sodium - Na	0.001X mg/l

Potassium -	K	0.005X mg/l
Arsenic -	As	0.25X mg/l
Lead -	Pb	0.01X mg/l
Cadmium -	Cd	0.001X mg/l
Copper -	Cu	0.005X mg/l
Chromium -	Cr	0.01X mg/l
Mercury -	Hg	0.0002X mg/l
Zinc -	Zn	0.005X mg/l

EXHIBIT G

INDUSTRIAL WASTE THRESHOLD ODOR NUMBERS AND ODOR CONTRIBUTIONS

<u>Company and Location</u>	<u>Plant or Division</u>	<u>Date Sampled</u>	<u>Discharge (mgd)</u>	<u>Threshold Odor Number</u>	<u>Odor Contribution (bgd)</u>
Crown Zellerbach Corp. St. Francisville		11-2-70	33.5	22,600	758
Enjay Chem. Co. Baton Rouge	Chem. Plant	4-6-71	29.25	25,436	744
		6-9-71	10.08	55,746	562
		1-15-70	25.63	13,460	345
Hooker Chem. Corp. Hahnville		2-24-70	21.60	20,800	449
		5-25/26-71	20.74	1,836	38
139 Humble Oil & Ref. Co. Baton Rouge		1-15-70	190.0	1,740	331
		6-8-71	83.63	1,616	135
Union Carbide Corp. Hahnville	Chem. & Plas- tics Div.	1-22-70	325.0	872	283
		4-21-71	345.1	16	6
Georgia Pacific Corp. Port Hudson	Crossett Div.	5-4-70	18.5	13,800	255
Dow Chemical Co. Plaquemine		1-20-70	540.0	215	116
		6-21/22-71	576.0	14	8
BASF Wyandotte Chem. Geismar		4-7-70	3.74	13,730	51

INDUSTRIAL WASTE THRESHOLD ODOR NUMBERS AND ODOR CONTRIBUTIONS (Continued)

<u>Company and Location</u>	<u>Plant or Division</u>	<u>Date Sampled</u>	<u>Discharge (mgd)</u>	<u>Threshold Odor Number</u>	<u>Odor Contribution (bgd)</u>
Copolymer Rubber & Chem. Co. Baton Rouge		5-3-71	4.32	9,555	41
		1-14-70	5.76	1,710	10
Shell Chemical Co. Geismar	Geismar Plant	7-13-70	30.2	742	22
Borden, Inc. Geismar	Borden Chem. Div.	6-28-71	21.6	928	20
The Celotex Corp. Marrero		9-21-70	12.0	1,250	15
Rubicon Chemicals, Inc. Geismar		1-21-70	0.4	33,600	13
		4-14-71	0.23	2,249	0.5
Chevron Chem. Co. Belle Chasse	Oronite Additives Div.	3-1/2-71	1.15	8,100	9.3
		1-25-71	0.72	9,224	6.6
		8-10-71	0.58	570	0.33
Ethyl Corp. Baton Rouge		1-14-70	14.4	556	8.0
		4-27/28-71	14.4	117	1.7
Shell Chem. Co. Norco		2-16-70	43.92	171	7.5

INDUSTRIAL WASTE THRESHOLD ODOR NUMBERS AND ODOR CONTRIBUTIONS (Continued)

<u>Company and Location</u>	<u>Plant or Division</u>	<u>Date Sampled</u>	<u>Discharge (mgd)</u>	<u>Threshold Odor Number</u>	<u>Odor Contribution (bgd)</u>
Kaiser Alum. & Chem. Chalmette		11-30-70	408.0	18	7.3
Tenneco Oil Co. Chalmette		1-11-71	27.36	249	6.8
Freeport Chem. Co. Uncle Sam	Div. of Free- port Minerals	10-5-70	144.0	35	5.04
Kaiser Alum. & Chem. Baton Rouge		1-19-70	7.2	476	3.42
Cos-Mar Plant of Borg Warner Corp. Carville		7-6-70 5-19-71	0.47 0.47	7,125 4,778	3.35 2.23
Occidental Chem. Co. Hahnville		2-24-70	5.04	454	2.28
American Cyanamid Co. Avondale		2-2-70 7-26-71	4.87 4.85	452 80	2.20 0.38
UniRoyal, Inc. Baker		7-6-71 1-19-70	3.17 3.17	631 354	2.00 1.12

INDUSTRIAL WASTE THRESHOLD ODOR NUMBERS AND ODOR CONTRIBUTIONS (Continued)

	<u>Company and Location</u>	<u>Plant or Division</u>	<u>Date Sampled</u>	<u>Discharge (mgd)</u>	<u>Threshold Odor Number</u>	<u>Odor Contribution</u>
						<u>(bgd)</u>
	UniRoyal, Inc. Baton Rouge		5-25-70	0.86	2,242	1.92
	E.I. duPont de Nemours & Co., Inc. LaPlace		3-2-70 5-4-71	36 28.8	49 6	1.76 0.17
	Allied Chem. Corp. Baton Rouge	Ind. Chem. Div.	4-14-70 7-19-71	43.0 46.51	39 29	1.68 1.34
142	Gulf Oil Co., U.S. Venice		6-15-71	129.6	8	1.03
	Texaco, Inc. Convent		8-17-70	2.62	306	0.80
	Hercules, Inc. Plaquemine		11-23-70	0.6	1,296	0.76
	Kaiser Alum. & Chem. Gramercy	Chem. Div.	3-31-70	27.07	26	0.70
	C.F. Industries Donaldsonville		11-16-70	2.02	289	0.58
	Allied Chem. Corp. Geismar	Geismar Complex	6-29-70	4.1	112	0.46

INDUSTRIAL WASTE THRESHOLD ODOR NUMBERS AND ODOR CONTRIBUTIONS (Continued)

<u>Company and Location</u>	<u>Plant or Division</u>	<u>Date Sampled</u>	<u>Discharge (mgd)</u>	<u>Threshold Odor Number</u>	<u>Odor Contribution (bgd)</u>
UniRoyal, Inc. Geismar	UniRoyal Chem.	6-29/30-71	1.1	387	0.42
Murphy Oil Corp. Meraux		1-18-71	10.8	32	0.35
Foster Grant Co., Inc. Baton Rouge		6-8-70	0.53	584	0.31
Universal Foods Corp. Belle Chasse	Red Star Yeast Operations	5-24/25-71	0.5	549	0.28
Ciba-Geigy Chem. Corp. St. Gabriel		8-25-70	1.5	176	0.26
Witco Chem. Corp. Gretna	Sonneborn Div.	3-30-71	0.115	215	0.24
Monsanto Company Luling		2-9-70	1.73	114	0.19
Getty Oil Co. Venice		6-1-71	0.84	215	0.18
Enjay Chemical Co. Baton Rouge	Plastics Plant	8-24-71 6-15-70	1.05 0.75	167 174	0.17 0.13

INDUSTRIAL WASTE THRESHOLD ODOR NUMBERS AND ODOR CONTRIBUTIONS (Continued)

<u>Company and Location</u>	<u>Plant or Division</u>	<u>Date Sampled</u>	<u>Discharge (mgd)</u>	<u>Threshold Odor Number</u>	<u>Odor Contribution (bgd)</u>
Triad Chemicals Donaldsonville		9-8-70	1.3	116	0.15
Melamine Chem., Inc. Donaldsonville		6-16-71	0.11	951	0.10
Allied Chem. Corp. Scotlandville	Plastics Div.	4-28-70 7-12-71	3.17 1.29	32 25	0.10 0.03
Vulcan Materials Co. Geismar	Chem. Div.	10-26-70	0.25	279	0.07
Monochem, Inc. Geismar		6-22/23-71	1.44	48	0.07
Allied Chem. Corp. Baton Rouge	Spec. Chem. Div.	6-22-70	1.65	40	0.07
Copolymer Rubber & Chem. Co. Addis	Addis Plant	10-12-70	1.32	38	0.05
Gulf Oil Co. Welcome	Chem. Dept.*	8-31-70	2.74	19	0.05
Stäuffer Chem. Co. Baton Rouge		6-1-70	2.45	15	0.04

* Bought out by WillChemCo, Inc. July 1, 1971

INDUSTRIAL WASTE THRESHOLD ODOR NUMBERS AND ODOR CONTRIBUTIONS (Continued)

<u>Company and Location</u>	<u>Plant or Division</u>	<u>Date Sampled</u>	<u>Discharge (mgd)</u>	<u>Threshold Odor Number</u>	<u>Odor Contribution (bgd)</u>
Schuylkill Metals Corp. Scotlandville		5-11-70	0.18	108	0.02
Union Tank Car Co. Baton Rouge		8-3-71	0.183	84	0.015
Jackson Brewing Co. New Orleans		3-8-71	2.16	5.6	0.01
Rollins-Purle, Inc. Baton Rouge		4-12-71	0.32	36	0.01
Goodyear Tire & Rubber Co. Plaquemine	Chem. Plant	4-19-71	6.48	1.7	0.01
Avondale Shipyards Avondale		9-22-70	0.04	258	0.01
Freeport Sulphur Co. Port Sulphur		3-22-71	0.144	4.4	0.006

INDUSTRIAL WASTE THRESHOLD ODOR NUMBERS AND ODOR CONTRIBUTIONS (Continued)

<u>Company and Location</u>	<u>Plant or Division</u>	<u>Date Sampled</u>	<u>Discharge (mgd)</u>	<u>Threshold Odor Number</u>	<u>Odor Contribution (bgd)</u>
Stauffer Chem. Co. St. Gabriel	Industrial	2-8-71	1.12	5.3	0.006
Allied Chem. Corp. Marrero	Ind. Chem. Div.	2-22-71	0.003	19	0.00006
Argus Chem. Corp. Hahnville		3-15-71	0.031	1.6	0.00005