# RECONNAISSANCE STUDY OF WATER AND BOTTOM MATERIAL QUALITY IN THE LOWER CALCASIEU RIVER, SOUTHWESTERN LOUISIANA, MAY 29-30, 1985

By C.R. Demas, Editor

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# CONTENTS

ILLUSTRATIONS

# TABLES

# CONVERSION FACTORS AND ABBREVIATIONS

For the convenience of readers who prefer to use inch-pound units rather than the metric (International System) units used in this report, values may be converted by using the following factors:

| Multiply metric unit | By | To obtain inch-pound unit |
|---|---|---|
| micrometer (µm) | 0.00003937 | inch (in.) |
| millimeter (mm) | 0.03937 | inch (in.) |
| centimeter per second (cm/s) | 0.0328 | foot per second (ft/s) |
| meter (m) | 3.281 | foot (ft) |
| cubic meter per second ($m^3/s$) | 35.31 | cubic foot per second ($ft^3/s$) |
| kilometer (km) | 0.6214 | mile (mi) |
| square kilometer ($km^2$) | 0.3861 | square mile ($mi^2$) |
| milliliter (mL) | 0.0338 | ounce, fluid (oz) |
| liter (L) | 33.82 | ounce, fluid (oz) |

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) as follows: °F = 1.8 X °C + 32.

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called "Sea Level Datum of 1929."

Disclaimer: The use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

# PREFACE

The presence and effects of toxic substances in the aquatic environment have been documented nationwide in recent years. Growing concern over the presence of toxic substances in water resulted in passage of the CLEAN WATER ACT of 1977. In that same year the U.S. Environmental Protection Agency established under the CLEAN WATER ACT of 1977 a list of 129 organic compounds and minor elements considered to be potential pollutants of our Nation's waterways. This list included 13 minor elements, asbestos, cyanide, and 114 organic compounds. In addition to the 129 substances, the National Academy of Science estimated that 66,000 chemicals are used commercially in the United States for a wide variety of purposes, all of which have potential to affect our Nation's waterways.

Unfortunately, information on toxic substances in the Nation's surface waters is lacking in the following areas: (1) the occurrence, magnitude, and distribution of toxic substances in surface waters, sediments, and biota; (2) limited understanding of the chemical, physical, and biochemical processes that govern the movement and fate of different types of toxic substances (organics and minor elements) in surface waters under changing hydrologic conditions; (3) suitability of sampling and analytical techniques for obtaining information about these different toxic substances in different hydrologic situations. The U.S. Geological Survey designed a program to enhance our knowledge in these areas to safeguard human health and to protect economically important fish and wildlife resources.

In 1985, the U.S. Geological Survey began the Toxic Substances Hydrology, Surface-Water Contamination Program to gather information and promote research to learn more about toxic substances in the environment. One area selected for study under this program is the lower Calcasieu River near Lake Charles, Louisiana. This river is representative of areas that are potentially threatened by the activities of industry. There are approximately 32 petrochemical and agrochemical plants along a 23-kilometer reach of the lower Calcasieu River from just south of Lake Charles to the Intracoastal Waterway. Products produced by these plants include ammonia, urea, chlorine, caustic soda, cracking material, gasoline, kerosene, coke, and polyolefins. Effluent discharges from these plants contain minor elements, sulfates, nutrients, phenols, and various organic compounds. Rivers such as the lower Calcasieu River have traditionally been used to assimilate industrial wastes; therefore, processes that act on these waste materials are important to the overall health of these ecosystems.

This study represents the combined efforts of the National Research Program, National Water Quality Laboratory in Arvada, Colorado, and the Louisiana District Office of the U.S. Geological Survey. It is designed to determine the biological and chemical fates of selected organic compounds, nutrients, and minor elements in the industrial reach and in transition zones between brackish and freshwater areas, and the processes involved in the degradation of these products in the water, suspended sediment, and bottom material of the lower Calcasieu River.

The purpose of this report is to describe the lower Calcasieu River surface-water toxics study area and methods of collection and analysis of samples, and to present preliminary results of the first sampling reconnaissance during May 29-30, 1985, on the river. The report is divided into four chapters: Chapter A describes the lower Calcasieu River study area and the occurrence of nutrients, minor elements, and organic compounds in water and bottom material collected during the Louisiana District reconnaissance study; Chapter B describes methods of collection and analysis, and results of a microbiological study of water and bottom material collected from the river; Chapter C describes the closed-loop-stripping method for extraction and concentration of semivolatile organic compounds from water, presents results, and discusses environmental fates of the organic compounds identified; Chapter D describes methods of analysis for organic compounds in water and bottom material, presents results, and discusses environmental fates of several organic compounds.

C.R. Demas
Editor

# CHAPTER A

# OCCURRENCE OF NUTRIENTS, MINOR ELEMENTS, AND ORGANIC COMPOUNDS IN WATER AND BOTTOM MATERIAL IN THE LOWER CALCASIEU RIVER, LOUISIANA

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## ABSTRACT

In 1985, the U.S. Geological Survey began a field study on the lower Calcasieu River to determine the biological and chemical fates of selected nutrients, minor elements, and organic compounds in an industrial reach and in the transition zones between brackish and freshwater areas of the lower Calcasieu River in southwestern Louisiana.

Analyses of samples collected during May 29-30, 1985, indicated that total ammonia as nitrogen in water occurred in concentrations exceeding 0.2 milligram per liter at two sites. Concentrations of ammonia exceeding 0.2 milligram per liter (containing un-ionized ammonia concentrations exceeding 0.02 milligram per liter) are considered toxic to freshwater aquatic life, however, it should be noted that toxicity of ammonia decreases as salinity increases. Chromium, mercury, iron, and manganese were the only minor elements that occurred in concentrations exceeding detection limits in water and bottom material. No acid-base/neutral organic compounds were detected in water, and only four volatile organic compounds (bromoform, chloroform, 1,2 dichloroethane, and chlorodibromomethane) were detected at any of the sites sampled. Volatilization caused by wind-driven turbulence and precipitation in the presence of saltwater appear to be the major determinants that affect the presence of minor elements and organic compounds in the lower Calcasieu River.

## INTRODUCTION

Previous data studies have documented the sources and occurrence of toxic substances in the lower Calcasieu River including: Demas (1976); Steinheimer and others (1981); Lurry (1983); Michael Schurtz (Louisiana Department of Environmental Quality, written commun., 1986); Michael Bastian (U.S. Environmental Protection Agency, written commun., 1986); and Dr. Edward Murray (McNeese State University, written commun., 1986). However, the processes that determine the movement and fate of these potentially hazardous substances in relation to the hydraulics of this tidal stream are not understood.

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In 1985, the U.S. Geological Survey, began a study on the lower Calcasieu River to determine the biological and chemical fates of selected minor elements, nutrients, and organic compounds, in the industrial reach and in the transition zones between brackish and freshwater areas. Selection of compounds and delineation of the river reach to be studied were determined by results of a reconnaissance survey conducted during May 29-30, 1985.

### Purpose and Scope

The purpose of this report is to describe the lower Calcasieu River study area, methods of sample collection, and present field and analytical results of the reconnaissance survey. Physical properties such as temperature, pH, dissolved oxygen, and specific conductance were recorded at time of collection of water samples to describe the water quality of the study sites and to indicate the presence of saltwater within the study area. Nutrients, minor elements, organic compounds, and bacteria were sampled in water and bottom material from the lower Calcasieu River upstream from Bayou Serpent (fig. A-1) to Cameron, where the river discharges to the Gulf of Mexico. Samples were collected to determine what compounds were present in the river, where they occurred, and which compounds should be selected for further study during the intensive phase of the project.

### Study Reach

The study reach (fig. A-1) includes the lower Calcasieu River from just south of Kinder, Louisiana, to Cameron, Louisiana, a distance of 64 km (kilometers). The study reach to be emphasized extends from the saltwater barrier upstream from Lake Charles to Burton Landing just north of the Intracoastal Waterway. The lower Calcasieu River has a drainage area of about 4,400 $km^2$ (square kilometers) and is characterized by low hydraulic gradient and slow velocity. Discharges at the Calcasieu River at Kinder range from 5.7 to 5,150 $m^3/s$ (cubic meters per second). Average discharge is 71 $m^3/s$ at this site (Carlson, and others, 1985).

The Calcasieu River basin lies within the Coastal Plain. The upper basin is characterized by hardwood forests, cypress, and related vegetation. Rice and soybeans are the principal crops harvested in the upper and middle parts of the basin, including the upper part of the study reach. The middle and lower part of the study reach is flat swamp and marshland. The Lake Charles urban and industrial areas dominate land use in this part of the study reach. Petrochemical and agrochemical plants use the river for effluent discharge (table A-1), water supply, and navigation. Downstream from Lake Charles, the river-estuarine system is dominated by offshore oil production activities and commercial fishing.

## METHODS OF STUDY

Nutrients, minor elements, and organic compounds were analyzed in water and bottom-material samples collected from 11 sites (table A-2) along the lower Calcasieu River (fig. A-1) on May 29 and 30, 1985. Physical properties

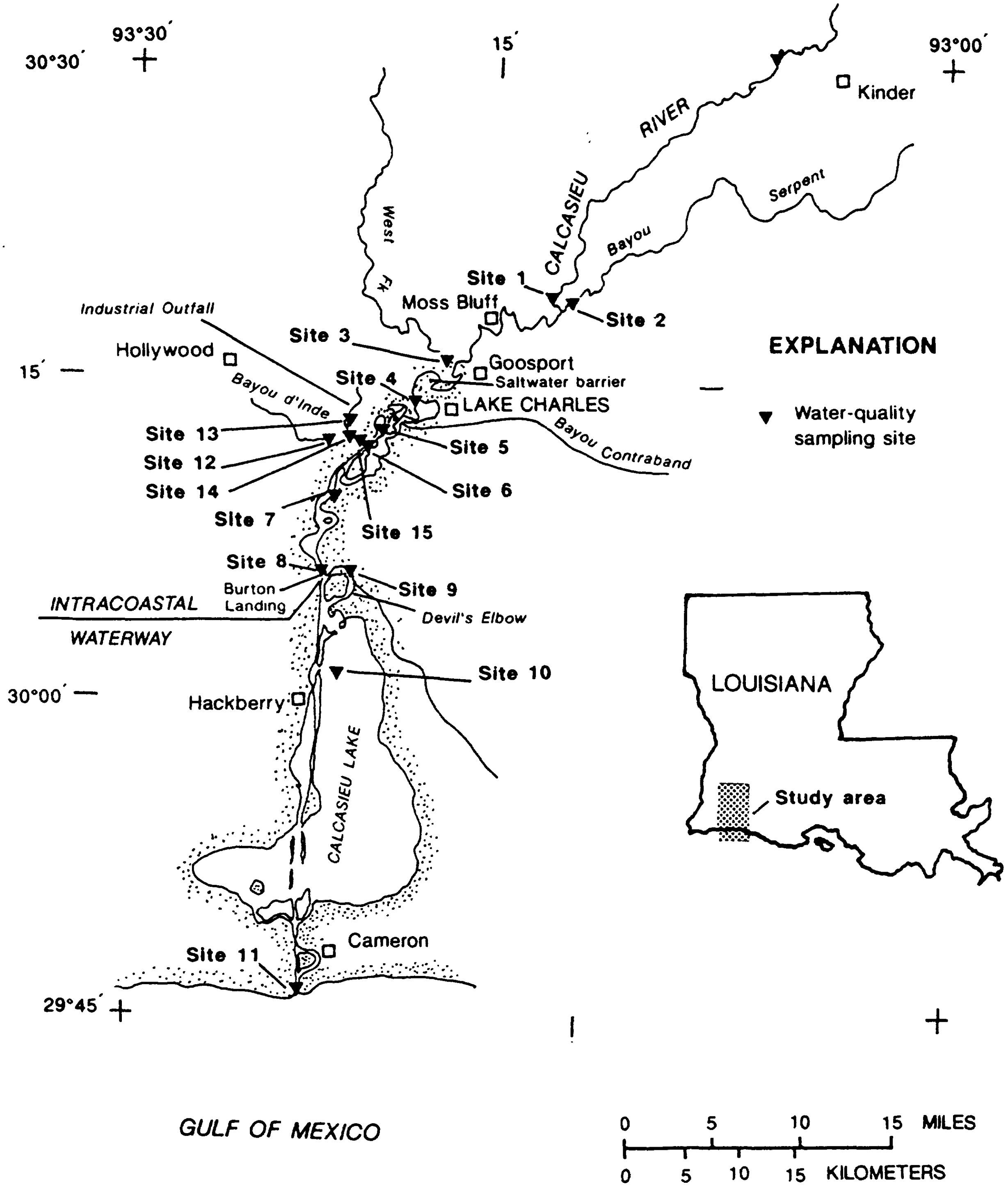

Figure A-1.--Calcasieu River surface-water toxics study area and water-quality sampling sites.

Table A-1.--Major industrial categories of the greater Lake Charles area, Louisiana, and their wastewater characteristics

[T, temperature; TSS, total suspended solids; O&G, oil and grease; BOD, biochemical oxygen demand; TOX, total organic halides; TOC, total organic carbon; $NH_3$, ammonia; $NO_3$, nitrate; COD, chemical oxygen demand; Cr, chromium; hex. Cr, hexavalent chromium; N, nitrogen; FC, fecal coliform; Cl, chloride; P, phosphorus; Zn, zinc; Cu, copper; Ni, nickel; Hg, mercury; Pb, lead; $H_2S$, hydrogen sulfide]

| Industrial category | Number of plants present | By-products | Wastewater characteristics monitored |
|---|---|---|---|
| Chemical manufacturing plants | 5 | Chemicals | pH, T, TSS, O&G, BOD, TOX, total P, TOC, $NH_3$, total Kjeldahl N, $NO_3$, total Cr |
| | | Polypropylene, high density polyethylene, and polyolefins | T, BOD, pH, COD, TSS, O&G, $NH_3$, TOC |
| | | Chemicals | T, pH, TSS, BOD, COD, $NH_3$, chlorinated hydrocarbons |
| | | Chemicals | Hg, Pb, Cr, TSS, BOD, total chlorinated hydrocarbons |
| | | Polymers and polyvinyl chloride | BOD, TSS, FC |
| Speciality chemical manufacturing plants | 1 | Speciality chemicals-olefins | TSS, Cu, Ni, lime, dichlorobromomethane, bromoform, chloroform, TOC, chlorodibromomethane, sodium aluminate |
| Synthetic rubber plant | 1 | Synthetic rubber and latex | T, BOD, COD, Cr, pH, TSS, O&G, $NH_3$ |
| Paint plant | 1 | Paint | TOC, O&G, pH |
| Oil refineries and related industries | | Oil refinery; produces naphtha, distillate and residual oil, and liquified propane gas | $NH_3$, $H_2S$, Cl, O&G, phenols, P |
| | | Products of petroleum cracking catalysts | T, BOD, pH, TSS, $NH_3$ |
| | | Oil products | BOD, COD, TSS, O&G, phenols, $NH_3$, $H_2S$, total Cr, hex. Cr, pH, flow |
| | | Petrochemicals | BOD, TSS, TOC, phenols, $H_2S$, O&G, $NH_3$, Zn |
| | | Regasification of liquified natural gas | T, TSS, BOD, O&G |
| | | Ammonia | $NH_3$, O&G, Cr |
| Fertilizer | 1 | Municipal sewage | $NH_3$, BOD, FC, pH, TSS |
| Domestic sewage treatment plants | 1 | Grinding and distribution of barite | Treated sanitary wastewater |
| Oil and gas drilling | 1 | Cryogenic air separation | O&G, Cr, pH |
| Others | 3 | Cement<br>Calcium chloride | T, pH<br>Rainwater runoff |

Table A-2.--Location of sampling sites for the lower Calcasieu River surface-water toxics study

| Site | Location |
|---|---|
| 1 | Calcasieu River east of Moss Bluff, La. |
| 2 | Bayou Serpent east of Moss Bluff, La. |
| 3 | West Fork Calcasieu River west-northwest of Goosport, La. |
| 4 | Calcasieu River at Buoy 130 at Lake Charles, La. |
| 5 | Calcasieu River at Buoy 114 at Lake Charles, La. |
| 6 | Calcasieu River at Bayou d'Inde. |
| 7 | Calcasieu River 6.2 kilometers south of Hollywood, La. |
| 8 | Calcasieu River at Burton Landing. |
| 9 | Calcasieu River at Devils Elbow. |
| 10 | Calcasieu Lake northeast of Hackberry, La. |
| 11 | Calcasieu River at Buoy 47, Cameron, La. |

such as temperature, pH, dissolved oxygen, and specific conductance were recorded vertically through the water column at each sampling site by using a Hydrolab Surveyor II monitoring system. Depth-integrated whole-water samples for analysis of nutrients, minor elements, volatile organic compounds (VOC), and acid-base/neutral extractable organic compounds were collected at each site. Water samples for nutrients, minor elements, and semivolatile organic compounds were collected in clean, baked, narrow-mouthed 1-L (liter) glass bottles by using an epoxy-coated wire basket sampler. VOC samples were collected by using a stainless steel sewage sampler and clean, baked 40 mL (milliliters) septum vials. The VOC samples were spiked in the field by using stable surrogate compounds provided by the National Water Quality Laboratory (NWQL). Surrogates were injected into the VOC samples through the Teflon septum cap by using a methanol-rinsed syringe provided by the laboratory. Bottom material analyzed for minor elements and nutrients was collected by using a Teflon-coated stainless-steel petite ponar and stored in clean, plastic freezer containers. Bottom material analyzed for acid-base/neutral extractable compounds was collected using a stainless-steel petite ponar and stored in clean, baked 1-L glass bottles.

All samples were stored on ice after collection. Samples were prepared and treated in the field, according to methods listed in Brown and others (1970). Minor element and nutrient analyses were performed at the NWQL of the U.S. Geological Survey, according to methods listed in Fishman and Friedman (1985). Samples were analyzed at the NWQL for acid-base/neutral extractable organic compounds, according to methods listed in Wershaw and others (1983).

## Physical Properties

Water-temperature, pH, dissolved-oxygen, and specific-conductance data (table A-3) were recorded concurrently with the collection of water and bottom-material samples. These measurements indicate that the two upstream

Table A-3.--Temperature, pH, dissolved-oxygen, and specific-conductance values in water observed during the first Calcasieu River reconnaissance sampling survey, May 29-30, 1985

| Site | Date | Time | Depth (meters) | Temperature °C | pH (units) | Dissolved oxygen (milligrams per liter) | Specific conductance (microsiemens per centimeter at 25 °C) |
|---|---|---|---|---|---|---|---|
| 1 | 5-29 | 1630 | 0.2 | 27.9 | 6.8 | 9.1 | 63 |
| | | | 5.5 | 26.0 | 6.2 | 6.4 | 62 |
| 2 | 5-29 | 1735 | .2 | 27.4 | 6.6 | 8.6 | 59 |
| | | | 4.9 | 24.5 | 6.0 | .6 | 117 |
| 3 | 5-29 | 1855 | .2 | 27.2 | 6.6 | 6.2 | 363 |
| | | | 5 | 23.3 | 6.2 | .3 | 502 |
| | | | 8 | 24.9 | --- | .3 | 4,160 |
| | | | 11 | 25.3 | 6.5 | .4 | 8,250 |
| 4 | 5-30 | 1950 | .2 | 27.9 | 7.6 | 8.1 | 5,730 |
| | | | 4 | 27.5 | 7.2 | 5.5 | 7,680 |
| | | | 8 | 26.5 | 7.2 | 1.1 | 20,000 |
| | | | 13 | 24.6 | 7.2 | .4 | 25,700 |
| 5 | 5-30 | 1615 | .2 | 29.3 | 8.5 | 9.2 | 13,100 |
| | | | 6.1 | 28.7 | 8.4 | 8.1 | 13,500 |
| 6 | 5-30 | 1530 | .2 | 29.0 | 8.6 | 10.0 | 14,400 |
| | | | 2.7 | 28.4 | 8.2 | 7.2 | 15,500 |
| 7 | 5-30 | 1435 | .2 | 27.9 | 8.2 | 7.4 | 17,100 |
| | | | 8.5 | 26.3 | 7.5 | .8 | 23,600 |
| 8 | 5-30 | 1340 | .2 | 27.5 | 8.2 | 7.4 | 17,400 |
| | | | 3 | 27.4 | 8.2 | 7.2 | 17,400 |
| 9 | 5-30 | 1315 | .2 | 27.5 | 8.2 | 7.7 | 16,100 |
| | | | 7 | 27.0 | 8.0 | 6.1 | 17,900 |
| 10 | 5-30 | 1215 | .2 | 26.8 | 8.2 | 7.2 | 20,000 |
| 11 | 5-30 | 1100 | .2 | 27.1 | 8.0 | 4.8 | 34,500 |
| | | | 3 | 27.1 | 8.0 | 4.7 | 34,500 |
| | | | 6 | 27.0 | 8.1 | 5.0 | 34,600 |

sites (sites 1 and 2) located above the confluence of the main stem and the West Fork were low in specific conductance--less than 120 µS/cm (microsiemens per centimeter at 25 °C); slightly acidic--pH ranged from 6.0 to 6.8 units; and well oxygenated at the surface--dissolved oxygen ranged from 8.6 to 9.1 mg/L (milligrams per liter). Water containing high dissolved-solids concentrations (indicated by specific-conductance values greater than 5,000 µS/cm) was first detected at site 3 at a depth below 8 m (meters). This site is approximately 1 km upstream from the saltwater barrier. Specific conductance at this site ranged from 363 µS/cm at the surface to 8,250 µS/cm at a depth of 11 m. Dissolved-oxygen concentrations were relatively high (6.2 mg/L) at the surface at this site but decreased rapidly with depth (0.3 mg/L at 5 and 8 m). Water at this site was slightly acidic (pH ranged from 6.2 to 6.6).

Water near the surface was well oxygenated at sites 4 through 11 downstream from the saltwater barrier. The pH at these sites ranged from 7.2 to 8.6. Specific conductance was high and ranged from 5,730 µS/cm at the surface at site 4 to 34,500 µS/cm at the surface at site 11. The Calcasieu River at site 4 was the only site below the saltwater barrier that had substantial stratification in the water column. Specific conductance at site 4 ranged from 5,730 µS/cm at the surface to 25,700 µS/cm at the bottom. Dissolved oxygen also was stratified at site 4 and ranged from 8.1 mg/L at the surface to 0.4 mg/L at a depth of 13 m. All other sites, except site 7, had little or no variation in specific conductance or dissolved oxygen with depth. This indicates that the lower part of the study reach is a relatively well mixed river-estuary system.

## Chemical Constituents

### Nutrients

Concentrations of nutrients varied widely for different constituents in the lower Calcasieu River (table A-4). Nitrite plus nitrate concentrations in whole water (total), whole water filtered through a 0.00045 mm (millimeter) filter (dissolved), and bottom material were low at all sites and ranged from below the levels of detection of 0.1 mg/L as nitrogen for water and 2 mg/kg (milligrams per kilogram) as nitrogen for bottom material to 0.2 mg/L as nitrogen in whole water and 2 mg/kg as nitrogen in bottom material. In contrast, ammonia as nitrogen and organic nitrogen as nitrogen were present in high concentrations. For example, total ammonia as nitrogen in water ranged from 0.07 to 1.3 mg/L as nitrogen. Inorganic nitrogen at concentrations greater than 0.3 mg/L are considered indicative of eutrophic waters (Taylor, 1980). Highest concentrations of total ammonia in water were observed at sites 6, 7, and 11. Sites 6 and 7 receive industrial effluent that contains ammonia, whereas site 11 is downstream from two fish processing plants in the town of Cameron. The maximum concentrations of total ammonia in water occurred at site 7. Eight kilometers downstream at site 8 the total ammonia concentration in water decreased to near background levels (0.17 mg/L). This decrease in concentration was probably caused by two factors: (1) high biological activity as indicated by a pH of 8.2 and dissolved-oxygen concentrations near saturation of 94 percent and (2) volatilization due to turbulence caused by 24 to 40 km/h (kilometers per hour) wind. Ammonia in its un-ionized form ($NH_3$) is considered toxic to freshwater aquatic life at

Table A-4.--Concentrations of nutrients in bottom material and water samples collected from the lower Calcasieu River, Louisiana, May 29-30, 1985

[mg/L, milligrams per liter; g/kg, grams per kilogram; mg/kg, milligrams per kilogram; <, actual value is known to be less than the value shown; dashes indicate no data available]

| Site | Carbon, organic dissolved as C (mg/L) | Carbon, organic suspended as C (mg/L) | Carbon, organic bottom material as C (g/kg) | Carbon, inorganic bottom material as C (g/kg) | Nitrite plus nitrate, total as N (mg/L) | Nitrite plus nitrate dissolved as N (mg/L) | Nitrite plus nitrate bottom material as N (mg/kg) | Nitrogen ammonia, total as N (mg/L) | Nitrogen ammonia, dissolved as N (mg/L) | Nitrogen ammonia, bottom material as N (mg/kg) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 9.2 | 1.1 | 0.2 | 0.1 | <0.1 | <0.10 | <2 | 0.08 | 0.07 | 1.9 |
| 2 | 7.2 | 1.2 | 16 | .1 | <.1 | <.10 | <2 | .11 | .10 | 58 |
| 3 | 8.9 | .5 | 11 | .1 | .2 | .14 | <2 | .16 | .16 | 12 |
| 4 | 6.8 | .5 | 18 | .1 | .2 | .17 | <2 | .17 | .20 | 23 |
| 5 | 6.7 | 1.3 | 6.1 | .1 | .1 | .1 | <2 | .07 | .10 | 3.8 |
| 6 | 7.4 | 1.1 | 73 | .2 | <.1 | ----- | 2 | .29 | ---- | 4.7 |
| 7 | 7.9 | .9 | 28 | .8 | .2 | .18 | <2 | 1.3 | 1.2 | 2.4 |
| 8 | 6.5 | .9 | 11 | .2 | <.1 | <.10 | <2 | .17 | .17 | 4.9 |
| 9 | 7.8 | .9 | 56 | .1 | <.1 | <.10 | 2 | .13 | .11 | 4.0 |
| 10 | 7.8 | 1.7 | 7.4 | .8 | <.1 | <.10 | <2 | .16 | .15 | 7.6 |
| 11 | 6.5 | .6 | 3.0 | 2.2 | <.1 | <.10 | <2 | .43 | .34 | 7.4 |

| Site | Nitrogen, organic total as N (mg/L) | Nitrogen, organic dissolved as N (mg/L) | Nitrogen, ammonia plus organic total as N (mg/L) | Nitrogen, ammonia plus organic dissolved as N (mg/L) | Nitrogen, ammonia plus organic bottom material as N (mg/kg) | Phosphorous total as P (mg/L) | Phosphorous dissolved as P (mg/L) | Phosphorous bottom material as P (mg/kg) | Moisture content by weight (percent) | Solids, volatile bottom material (mg/kg) | Humic and fulvic acid (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.72 | 0.43 | 0.8 | 0.5 | <20 | 0.06 | 0.03 | 38 | 22.8 | 2,380 | 0.7 |
| 2 | .69 | .50 | .8 | .6 | 1,600 | .07 | .04 | 360 | 53.3 | 60,300 | 1.6 |
| 3 | ---- | .54 | .6 | .7 | 770 | .06 | .02 | 260 | 52.2 | 35,300 | 2.6 |
| 4 | .53 | .40 | .7 | .6 | <20 | .05 | .02 | 560 | 54.9 | 57,200 | 1.8 |
| 5 | ---- | 1.1 | 1.0 | 1.2 | <20 | .09 | .04 | 180 | 36.7 | 47,600 | 1.6 |
| 6 | .71 | ---- | 1.0 | --- | 3,200 | .08 | ---- | 520 | 72.5 | 152,000 | 1.8 |
| 7 | .70 | .70 | 2.0 | 1.9 | 2,000 | .07 | .05 | 780 | 72.7 | 105,000 | 1.7 |
| 8 | .83 | .43 | 1.0 | .6 | 1,100 | .06 | .02 | 360 | 49.3 | 41,600 | 1.9 |
| 9 | 1.3 | .39 | 1.4 | .35 | 1,700 | .05 | .01 | 330 | 73.2 | 123,000 | 1.3 |
| 10 | 1.0 | .55 | 1.2 | .7 | <20 | .09 | .05 | 440 | 49.3 | 35,900 | 2.1 |
| 11 | .37 | .16 | .8 | .5 | <20 | .06 | .03 | 330 | 34.0 | 30,900 | 1.8 |

concentrations exceeding 0.02 mg/L (U.S. Environmental Protection Agency, 1978). Concentrations of un-ionized ammonia can be calculated from total ammonia by using a conversion factor based on water temperature and pH (U.S. Environmental Protection Agency, 1978). Based on the above conversion factor, values of total ammonia at site 6 (0.29 mg/L as N) and site 7 (1.3 mg/L as N) exceeded concentrations established by the U.S. Environmental Protection Agency for total ammonia which contain an un-ionized ammonia concentration greater than 0.020 mg/L. It should be noted, however, that un-ionized ammonia concentrations decrease with increasing salinity, and information is lacking on the acute and chronic toxicity of ammonia in saltwater (U.S. Environmental Protection Agency, 1978).

Total phosphorus concentrations as phosphorus in water was distributed relatively evenly throughout the study reach and ranged in concentration from 0.05 to 0.09 mg/L. Dissolved phosphorus concentrations as phosphorus in water had a similar distribution pattern and ranged from 0.01 to 0.05 mg/L. Phosphorus concentrations in bottom material, except for site 1 (38 mg/kg), ranged in concentration from 180 to 780 mg/kg. Highest concentrations of phosphorus in bottom material were present at sites 4 (560 mg/kg), 6 (520 mg/kg), and 7 (780 mg/kg). Phosphorus was analyzed in water samples to determine availability for phytoplankton growth. The presence of total phosphorus at high concentrations (greater than 0.03 mg/L, Taylor and others, 1980) indicates that phytoplankton is not limited in growth by phosphorus and this partially explains changes in nitrogen concentrations observed throughout the study area.

Dissolved organic carbon (DOC) in water was present in highest concentrations at sites 1 (9.2 mg/L) and 3 (8.9 mg/L), upstream from the saltwater barrier. The high concentrations of DOC observed at sites 1 and 3 occur naturally as a result of drainage from bordering forests and swamps upstream. DOC concentration at site 2, a small tributary entering the Calcasieu River downstream from site 1, was 7.2 mg/L. It appears that water from this tributary had significantly less DOC than the main branch and, as shown by the DOC at site 3, did not significantly affect the DOC of the main branch. DOC concentrations decreased at sites 4 and 5, 6.8 and 6.7 mg/L, respectively. This decrease in DOC was caused by precipitation of the hydrophobic fraction of the DOC in water as it comes in contact with saltwater (Thurman, 1985).

Concentrations of nitrogen, phosphorus, and carbon varied in bottom material collected from the lower Calcasieu River study reach. For example ammonia as nitrogen was present in concentrations ranging from 1.9 mg/kg at site 1 to 58 mg/kg downstream at site 2, a distance of less than 0.5 km (table A-4). Highest concentrations of ammonia in bottom material were present in the study reach at site 2 and site 4 (23 mg/kg). Why ammonia was detected in such high concentrations in this reach is unclear at this time. High concentrations of organic nitrogen, total organic carbon, volatile solids, and phosphorus in bottom material were detected at these sites. High concentrations of organic nitrogen, total organic carbon, volatile solids, and phosphorus in bottom material also were detected at sites where ammonia in bottom material was not present in large concentrations. This indicates several different sources of nitrogen to the river bed.

The high concentrations of organic carbon, phosphorus, ammonia, and organic nitrogen, in water collected from the lower Calcasieu River, especially the reach between sites 4 and 8, are comparable with those documented for eutrophic systems (Taylor and others, 1980). Possible sources of these nutrients to the lower Calcasieu River include industrial and municipal discharges, and wildlife (especially waterfowl).

## Minor Elements

Whole- and filtered-water, and bottom-material samples were analyzed for minor elements. Results of these analyses are shown in table A-5. Arsenic, cadmium, cobalt, lead, selenium, and zinc occurred in concentrations at or below levels of detection in water and bottom-material samples. Barium, chromium, copper, iron, manganese, and mercury, in contrast, occurred at relatively higher concentrations in either or both water and bottom-material samples.

Barium and chromium were detected in high concentrations compared to other minor elements present in the study area only in bottom material. Barium was present in concentrations ranging from 30 to 360 µg/g (micrograms per gram). Highest concentrations of barium in bottom material were detected at sites 4 through 11, downstream from the saltwater barrier. The distribution of barium in bottom material, a component of drilling mud, corresponded well with the oil and gas drilling activity observed along the entire study reach. Chromium, in contrast, was present in concentrations of 200 and 330 µg/g at sites 6 and 7, respectively. Chromium concentrations in bottom material at the other sites ranged from 20 to 90 µg/g, indicating that the high values observed at sites 6 and 7 are probably related to industrial discharges. Unfortunately, no criteria are presently available for determining toxic concentrations of minor elements in bottom material.

Mercury was present in concentrations above levels of detection in both whole-water and bottom-material samples collected downstream from the saltwater barrier. The highest level of mercury in whole-water samples was 0.2 µg/L (micrograms per liter) at sites 4, 9, and 11. This concentration exceeds the criteria of 0.14 µg/L set for marine aquatic life by the U.S. Environmental Protection Agency (1978). Mercury in bottom material ranged in concentration from 0.01 µg/g at site 1 to 0.80 µg/g at site 6. Highest concentrations of mercury in bottom material occurred at site 6 (0.80 µg/g) and site 7 (0.50 µg/g). The presence of mercury in bottom material at these sites is probably a result of industrial discharges released in the area during the mid 1970's (Michael Schurtz, Louisiana Department of Environmental Quality, oral commun., 1986).

Iron and manganese were present in both water and bottom-material samples collected throughout the study reach. Both elements are important because of their ability to form complexes and transport other minor elements and organic compounds in the form of oxide coatings on particulate matter. Total recoverable manganese in water was unevenly distributed within the study reach. Concentrations of total recoverable manganese ranged from 80 µg/L at sites 7 and 11 to 380 µg/L at site 3 with most concentrations occurring in the 100 to 200

Table A-5.--Concentrations of minor elements in bottom material and water samples collected from the lower Calcasieu River, Louisiana, May 29-30, 1985

[µg/L, micrograms per liter; µg/g, micrograms per gram; <, acutal value is known to be less than the value shown; dashes indicate no data available]

| Site | Arsenic, total recoverable as As (µg/L) | Arsenic, dissolved as As (µg/L) | Arsenic recoverable bottom material as As (µg/g) | Barium, total recoverable as Ba (µg/L) | Barium, dissolved as Ba (µg/L) | Barium, recoverable bottom material as Ba (µg/g) | Cadmium total recoverable as Cd (µg/L) | Cadmium, dissolved as Cd (µg/L) | Cadmium, recoverable bottom material as Cd (µg/g) | Chromium, total recoverable as Cr (µg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | <1 | <1 | 1 | <100 | <100 | 200 | 1 | <1 | <1 | <10 |
| 2 | <1 | <1 | 6 | <100 | <100 | 30 | 1 | <1 | <1 | <10 |
| 3 | <1 | <1 | 4 | <100 | <100 | 40 | 1 | <1 | <1 | <10 |
| 4 | <1 | <1 | 2 | <100 | <100 | 240 | 1 | <1 | <1 | 10 |
| 5 | <1 | <1 | 4 | <100 | <100 | 350 | 1 | <1 | <1 | 10 |
| 6 | <1 | <1 | 8 | <100 | <100 | 160 | 1 | 1 | <1 | 10 |
| 7 | <1 | <1 | 11 | <100 | <100 | 190 | 1 | 1 | <1 | 10 |
| 8 | <1 | <1 | 5 | <100 | <100 | 180 | 1 | <1 | <1 | 20 |
| 9 | <1 | <1 | 12 | <100 | <100 | 70 | 1 | <1 | <1 | 10 |
| 10 | <1 | <1 | 6 | <100 | <100 | 360 | 1 | 1 | <1 | 20 |
| 11 | <1 | <1 | 6 | <100 | <100 | 70 | 1 | 2 | <1 | 30 |

| Site | Chromium, dissolved as Cr (µg/L) | Chromium, recoverable bottom material as Cr (µg/g) | Cobalt, total recoverable as Co (µg/L) | Cobalt, dissolved as Co (µg/L) | Copper, total recoverable as Cu (µg/L) | Copper, dissolved as Cu (µg/L) | Copper, recoverable bottom material as Cu (µg/g) | Iron, total recoverable as Fe (µg/g) | Iron, dissolved as Fe (µg/L) | Iron, recoverable bottom material as Fe (µg/g) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | <10 | 70 | 2 | <1 | 3 | 2 | 5 | 1,000 | 200 | 5,400 |
| 2 | <10 | 20 | 1 | <1 | 2 | 3 | <1 | 1,500 | 500 | 1,900 |
| 3 | <10 | 30 | 3 | 1 | 5 | 2 | 3 | 1,100 | 250 | 2,200 |
| 4 | <10 | 80 | 2 | 1 | 3 | 3 | 8 | 330 | 40 | 6,400 |
| 5 | 10 | 30 | 2 | <1 | 6 | 5 | 4 | 200 | 40 | 1,400 |
| 6 | <10 | 200 | 1 | 2 | 6 | 3 | 110 | 150 | 40 | 4,900 |
| 7 | 10 | 330 | 1 | <1 | 4 | 4 | 61 | 180 | 60 | 14,000 |
| 8 | 10 | 70 | 1 | <1 | 4 | 2 | 9 | 270 | 40 | 5,300 |
| 9 | 10 | 90 | 1 | <1 | 6 | 1 | 8 | 510 | 50 | 13,000 |
| 10 | 10 | 70 | 2 | <1 | 6 | 3 | 8 | 1,700 | 90 | 6,700 |
| 11 | 20 | 40 | 2 | <1 | 5 | 2 | 3 | 1,300 | 90 | 3,300 |

Table A-5.--Concentrations of minor elements in bottom material and water samples collected from the lower Calcasieu River, Louisiana, May 29-30, 1985--Continued

| Site | Lead, total recoverable as Pb (µg/L) | Lead, dissolved as Pb (µg/L) | Lead, recoverable bottom material as Pb (µg/g) | Manganese, total recoverable as Mn (µg/L) | Manganese, dissolved as Mn (µg/L) | Manganese, recoverable bottom material as Mn (µg/g) | Mercury, total recoverable as Hg (µg/L) | Mercury, recoverable bottom material as Hg (µg/g) | Selenium, total recoverable as Se (µg/L) | Selenium, dissolved as Se (µg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 30 | 100 | <10 | 310 | <0.1 | 0.01 | <1 | <1 |
| 2 | 9 | 2 | 10 | 150 | 30 | 300 | <.1 | .06 | <1 | <1 |
| 3 | 8 | 9 | 10 | 380 | 310 | 340 | <.1 | .03 | <1 | <1 |
| 4 | 13 | 5 | 30 | 160 | 90 | 170 | .2 | .09 | <1 | 2 |
| 5 | 8 | 8 | 10 | 110 | <10 | 260 | <.1 | .06 | <1 | <1 |
| 6 | 11 | <1 | 30 | 110 | <10 | 160 | .1 | .80 | <1 | <1 |
| 7 | 10 | <1 | 70 | 80 | 10 | 590 | .1 | .50 | <1 | <1 |
| 8 | 7 | 6 | 20 | 90 | 10 | 140 | .1 | .09 | <1 | <1 |
| 9 | 10 | 3 | 20 | 100 | 10 | 160 | .2 | .03 | <1 | <1 |
| 10 | 8 | <1 | 10 | 180 | 20 | 180 | .1 | .05 | <1 | <1 |
| 11 | 6 | 1 | 10 | 80 | 30 | 170 | .2 | .05 | <1 | <1 |

| Site | Silver, total recoverable as Ag (µg/L) | Silver, dissolved as Ag (µg/L) | Zinc, total recoverable as Zn (µg/L) | Zinc, dissolved as Zn (µg/L) | Zinc, recoverable bottom material as Zn (µg/g) |
|---|---|---|---|---|---|
| 1 | <1 | <1 | 10 | 10 | 22 |
| 2 | <1 | <1 | 20 | 10 | 1 |
| 3 | <1 | <1 | 10 | 20 | 9 |
| 4 | <1 | <1 | 20 | 20 | 32 |
| 5 | <1 | <1 | 10 | 10 | 14 |
| 6 | 1 | <1 | 20 | 10 | 69 |
| 7 | <1 | <1 | -- | 40 | 90 |
| 8 | <1 | <1 | 10 | 20 | 27 |
| 9 | <1 | <1 | 20 | 20 | 24 |
| 10 | <1 | <1 | 20 | 20 | 30 |
| 11 | -- | 3 | -- | 40 | 17 |

µg/L range. Total recoverable manganese in bottom material generally was lower in the saltwater reaches sampled and higher in the freshwater reaches sampled. Values of total recoverable manganese in bottom material ranged from 310 to 340 µg/g at freshwater sites 1 through 3 and from 140 to 260 µg/g at saltwater sites 4 through 11. Site 7 was an exception to this observation and had the highest manganese value (590 µg/g) detected in bottom material.

Total recoverable iron and dissolved iron in water showed a definite decrease in concentration moving from freshwater to saltwater. Total recoverable iron in water ranged from 1,500 to 1,000 µg/L at freshwater sites 1 through 3 and from 330 to 150 µg/L at saltwater sites 4 through 8. Sites 9 through 11 (located south of the Intracoastal Waterway) showed an increase in total recoverable iron in water from 510 to 1,700 µg/L. This increase in total recoverable iron in water can be explained by the increase in turbulence and subsequent resuspension of bottom material that occurs in the study reach south of the Intracoastal Waterway. This increase in turbulence south of the Intracoastal Waterway is caused by the strong southerly winds prevalent in the study reach during the late spring and summer months, and dissipation of tidal forces. M.J. Forbes (U.S. Geological Survey, written commun., 1986) reported that 80 percent of the energy of the incoming tide in the lower Calcasieu River is dissipated south of the Intracoastal Waterway. Further supporting this observation is the lack of a comparable increase of dissolved iron in samples collected south of the Intracoastal Waterway. Dissolved-iron concentrations ranged from 500 to 200 µg/L at sites 1 through 3 (freshwater), 60 to 40 µg/L at sites 4 through 8 (saltwater, north of Intracoastal Waterway), and 50 to 90 µg/L at sites 9 through 11 (saltwater, south of Intracoastal Waterway). This minor increase in dissolved-iron concentrations in water samples collected at sites 9 through 11 indicates that the major increase in total recoverable iron in water is caused by an increase in the suspended phase. Future studies will investigate whether particulate iron is simply precipitating on exposure to saltwater or if it complexes with naturally occurring organic compounds and subsequently flocculates with these organic compounds in the presence of saltwater.

Iron in bottom material ranged from 1,900 to 5,400 µg/g at sites 1 through 3 (freshwater) and from 1,400 to 14,000 µg/g at sites 4 through 11 (saltwater). It would be expected that iron concentrations would be highest in the saltwater areas because of precipitation of particulate and dissolved iron carried by the freshwater as it came in contact with saltwater. This appears to be the condition in the lower Calcasieu River at site 3, immediately above the saltwater barrier (2,200 µg/g), and site 4, immediately below the saltwater barrier (6,400 µg/g); however, results are inconclusive due to the varying concentrations at the other downstream sites.

### Organic Compounds

Detection limits for acid-base/neutral extractable organic compounds and VOC's in water are listed in table A-6. None of the acid-base/neutral extractable organic compounds (table A-6) were detected in water samples from any of the sites sampled. Also, with the exception of sites 5 and 6, none of the VOC's listed were detected in water samples from any of the sites sampled.

## Table A-6.--Acid-base/neutral extractable and volatile organic compounds analyzed from the lower Calcasieu River samples, May 29-30, 1985

[All values are in micrograms per liter and represent lowest levels of detection]

Volatile organic compounds

| Compound | Concentration | Compound | Concentration | Compound | Concentration |
|---|---|---|---|---|---|
| Benzene | 3.0 | Methylene chloride | 3.0 | 1,2-Dichloroethane | 3.0 |
| Bromoform | 3.0 | Styrene | 3.0 | 1,2-Dichloropropane | 3.0 |
| Carbon tetrachloride | 3.0 | Tetrachloroethylene | 3.0 | 1,3-Dichloropropene | 3.0 |
| Chlorobenzene | 3.0 | Toluene | 3.0 | 1,2-Transdiolethylene | 3.0 |
| Chloroethane | 3.0 | Trichloroethylene | 3.0 | 2-Chloroethyl vinyl ether | 3.0 |
| Chloromethane | 3.0 | Trichlorofluoromethane | 3.0 | 1,2-Dichlorobenzene | 3.0 |
| Chloroform | 3.0 | Vinyl chloride | 3.0 | 1,3-Dichlorobenzene | 3.0 |
| Dibromochloromethane | 3.0 | 1,1-Dichloroethylene | 3.0 | 1,4-Dichlorobenzene | 3.0 |
| Dichlorobromomethane | 3.0 | 1,1-Dichloroethane | 3.0 | 1,2-Dibromoethylene | 3.0 |
| Dichlorodifluoromethane | 3.0 | 1,1,1-Trichloroethane | 3.0 | 1,2-Trans-Dichloroehtylene | 3.0 |
| Ethylbenzene | 3.0 | 1,1,2-Trichloroethane | 3.0 | Cis-1,3-Dichloropropene | 3.0 |
| Methyl bromide | 3.0 | 1,1,2,2,-Tetrachloroethane | 3.0 | Trans-1,3-Dichloropropene | 3.0 |

Acid-base/neutral extractable organic compounds

| Compound | Concentration | Compound | Concentration | Compound | Concentration |
|---|---|---|---|---|---|
| Acenaphthene | 5.0 | Fluoranthene | 5.0 | 1,4-Dichlorobenzene | 5.0 |
| Acenaphthylene | 5.0 | Fluorene | 5.0 | 1,3-Dichlorobenzene | 5.0 |
| Anthracene | 5.0 | Hexachlorobenzene | 5.0 | Bis (2-chloroethoxy) methane | 5.0 |
| Benzo [a] anthracene |  | Hexachlorobutadiene | 5.0 | Bis (2-Chloroethyl) ether | 5.0 |
| 1,2-benzanthracene | 5.0 | Hexachlorocyclopentadiene | 5.0 | Bis (2-chloroisopropyl) ether | 5.0 |
| Benzo [a] pyrene | 10.0 | Hexachloroethane | 5.0 | 2-Chloronaphthalene | 5.0 |
| Benzo [b] fluoranthene | 10.0 | Indeno (1,2,3-CD) pyrene | 10.0 | 2-Chlorophenol | 5.0 |
| Benzo [g,h,i] perylene | 10.0 | Isophorone | 5.0 | Bis (2-ethylhexyl) phthalate | 5.0 |
| Benzo [k] fluoranthene | 10.0 | N-nitrosodi-N-propylamine | 5.0 | 2-nitrophenol | 5.0 |
| Butyl benzyl phthalate | 5.0 | N-nitrosodiphenylamine | 5.0 | 2,4-Dichlorophenol | 5.0 |
| 4-Chloro-3-methyl- |  | Naphthalene | 5.0 | 2,4-Dimethylphenol | 5.0 |
| phenol | 30.0 | Nitrobenzene | 5.0 | 2,4-Dinitrophenol | 20.0 |
| Chrysene | 10.0 | N-nitrosodimethylamine | 5.0 | 2,4-Dinitrotoluene | 5.0 |
| Di-n-Butyl phthalate | 5.0 | Pentachlorophenol | 5.0 | 2,4,6-Trichlorophenol | 20.0 |
| Di-n-Octylphthalate | 10.0 | Phenanthrene | 5.0 | 2,6-Dinitrotoluene | 5.0 |
| Diethyl phthalate | 5.0 | Phenol | 5.0 | 4-Bromophenyl phenyl ether | 5.0 |
| Dimethyl phthalate | 5.0 | Pyrene | 5.0 | 4-Chlorophenyl phenyl ether | 5.0 |
| 4,6-Dinitro-2-methyl- |  | 1,2-Dichlorobenzene | 5.0 | 4-Nitrophenol | 30.0 |
| phenol | 30.0 | 1,2,4-Trichlorobenzene | 5.0 |  |  |

Table A-7 lists the VOC's detected at sites 5 and 6. Bromoform was detected in the highest concentrations (21 and 19 µg/L, respectively) while other compounds such as chlorodibromomethane, chloroform, and 1,2-dichloroethane were detected in concentrations at or near detection limits (3.0 µg/L). All four of the VOC's detected were present at site 6 while only bromoform and chloroform were present at site 5. Presence of VOC's at site 6 is probably attributed to material being discharged into an outfall canal which is a tributary to Bayou d'Inde. Possible sources of VOC's at site 5 are tidally-caused upstream movement of these compounds from Bayou d'Inde, industrial outfall inputs into Bayou Contraband, or spillage from barges or freighters that pass through the area.

Table A-7.--Volatile organic compounds detected in water samples from the lower Calcasieu River, Louisiana, May 29-30, 1985

[All values are listed in micrograms per liter; dashes indicate value below level of detection]

| Site | Bromoform | Chlorodibromomethane | Chloroform | 1,2-dichloroethane |
|---|---|---|---|---|
| 5 | 21 | --- | 3.3 | --- |
| 6 | 19 | 3.1 | 3.2 | 4.0 |

The low concentration of organic compounds, especially volatiles, detected in the samples was surprising because of a strong odor of petroleum by-products present at many of the sampling sites in the industrial area of the study reach. Possible explanations for the lack of detection of these organic compounds (table A-6) are: (1) low solubility of many of the organic compounds in saltwater, (2) volatilization to the atmosphere of volatile compounds through turbulence caused by wind, and (3) dilution effect on VOC concentrations caused by sampling techniques. Collection of depth-integrated samples rather than point samples at sites where saltwater stratification exists and denser VOC's might be associated with the denser saltwater at the bottom of the water column may result in dilution of VOC's.

## SUMMARY

Water-temperature, pH, specific-conductance, and dissolved-oxygen data indicate that the lower Calcasieu River study reach includes areas of low specific conductance--less than 120 µS/cm with little stratification upstream from the confluence of the main stem and the West Fork and high specific conductance (34,500 µS/cm) downstream from the saltwater barrier. Data indicate that the lower Calcasieu River estuarine system is generally well mixed downstream from site 4.

Ammonia as nitrogen and organic nitrogen occurred in concentrations exceeding 0.2 mg/L in whole-water samples at sites 6 and 7. Concentrations of ammonia in whole-water samples decreased to background levels of 0.17 mg/L

8 km downstream, probably as a result of high biological activity and volatilization.

At sites 6 and 7 total recoverable chromium and mercury in bottom material were detected at concentrations exceeding 100 and 0.4 µg/g, respectively. Presence at these sites is probably a result of past industrial practices. Total recoverable mercury in water was detected in concentrations exceeding 0.1 µg/L at sites 4, 9, and 11. Total recoverable manganese in water was detected in concentrations ranging from 80 to 380 µg/L and was unevenly distributed throughout the study reach. Total recoverable iron in water occurred in concentrations ranging from 180 to 1,500 µg/L and showed a definite decrease in concentrations from freshwater to saltwater.

Acid-base/neutral extractable organic compounds were not detected in any of the water samples collected. Volatile organic compounds including bromoform, chlorodibromomethane, chloroform, and 1,2-dichloroethane were detected only at sites 5 and 6. Bromoform was detected at concentrations of 21 and 19 µg/L at sites 5 and 6, respectively, and was the only organic compound detected at concentrations significantly greater than detection limits (3.0 µg/L). Absence of VOC's in samples collected at sites 4, 7, and 8 was probably caused by volatilization to the atmosphere through wind-induced turbulence.

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(p. 19 follows)

# CHAPTER B

# MICROBIAL CONTENT OF WATER AND BOTTOM MATERIAL IN THE LOWER CALCASIEU RIVER, LOUISIANA

By D.M. Updegraff[1]

## ABSTRACT

Water and bottom material were sampled from the lower Calcasieu River during May 29 and 30, 1985, and analyzed for total bacteria. Viable and direct microscopic counts were performed on water and bottom-material samples. Viable counts were performed using both marine and freshwater agar depending on the salinity at the site at time of collection.

Microbial counts were characteristic of eutrophic systems. Bacteria showed distinct preferences for saltwater or freshwater agar depending on ambient salinity at time of collection. Bacteria counts in water increased in a downstream direction from brackish water to saltwater.

## INTRODUCTION

Bacterial samples were collected from the lower Calcasieu River during May 29 and 30, 1985. Bacterial samples were collected in conjunction with chemical samples to determine if bacterial population densities could be used as an indication of environmental stress.

The purpose of the report is to document methods of analyses used in the microbial assessment of water and bottom material collected from the lower Calcasieu River, and present the results of this work. Samples were collected from a limited number of sites (table B-1) that were considered representative of the different habitats present in the lower Calcasieu River study reach and analyzed using viable and direct microscopic counts.

## METHODS OF STUDY

Seven samples of water and eight samples of underlying bottom material were collected from the lower Calcasieu River study reach (table B-1). (See figure A-1 and table A-2 for site locations.) The seven water and eight bottom-material samples were placed in heat sterilized glass containers, and refrigerated at 4 °C until analyzed during the week of June 10-14, 1985.

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Table B-1.--List of bacteria sampling sites and description of bottom material collected from the lower Calcasieu River, Louisiana, May 29-30, 1985

| Site | Description of bottom material |
|---|---|
| 1 | Clean, fine sand. |
| 4 | Silt and sand, gray. |
| 5 | Do. |
| 6 | Black mud, fibrous debris. |
| 7 | Black mud. |
| 8 | Do. |
| 9 | Do. |
| 11 | Do. |

Viable counts were carried out on the water and bottom-material samples. Viable counts were performed using both marine agar (ZoBell's no. 2216 agar, Difco) and freshwater agar (ZoBell's no. 2216 agar prepared with deionized water), depending on the salinity at the site at the time of collection. Viable counts were carried out on 1/10, 1/100, 1/1,000, and 1/10,000 dilutions prepared in sterile 50 percent seawater (50 percent aged seawater and 50 percent deionized water). Sterilization of water blanks and culture media was carried out by autoclaving at 121 °C for 15 minutes. Plate counts were performed using both the pour plate and the spread plate method using 0.1 mL (milliliter) of each dilution as the inoculum (Stanier and others, 1976). The highest dilution factor ($10^5$) was obtained by plating 0.1 mL of the 1/10,000 dilution. Bottom material sample platings of this dilution were done by the spread plate method and carried out in duplicate. Plates were incubated at 23 to 25 °C for 5 and 7 days and then counted using a Quebec colony counter.

Direct microscopic counts were performed on 1.0 mL water samples and 1.0 g (gram) bottom-material samples diluted in 50 percent seawater filtered through a 0.00045 mm (millimeter) membrane filter (Millipore). A 1.0 mL sample of water added to a 9.0 mL blank gave a suitable concentration of microorganisms. The counts in the sediments were much higher than those in the water, and it was necessary to dilute the sediments 1/100 and 1/1,000 in 50 percent sterile seawater to obtain satisfactory counts. The microbes were stained with 1.1 mL of 0.1 percent (w/v) acridine orange in 2 percent formaldehyde, added to the 10 mL of diluted sample for 3 to 5 minutes, and either 1/10 of the sample (1.11 mL) or the entire sample (11.1 mL) was filtered through a specially prepared 25 mm diameter 0.0002 mm Nucleopore filter. The methods used in this study are those of Hobbie and others (1977).

## MICROBIAL CONTENT OF WATER AND BOTTOM MATERIAL

Direct counts and means of combined spread and pour-plate counts are presented in table B-2. Duplicates were run on each dilution and spread plate counts agreed within 20 percent of the mean value in most instances. At a few

## Table B-2.--Microbial counts in water and bottom-material samples from the lower Calcasieu River, Louisiana, May 29-30, 1985

[CFU, colony forming unit; mL, milliliter; g, gram; all values represent mean of counts]

| | Water samples | | | Bottom material samples | | |
|---|---|---|---|---|---|---|
| | Plate count | | | Plate count | | |
| Site | CFU/mL X $10^4$ fresh-water agar | CFU/mL X $10^4$ sea-water agar | Direct microscopic count bacterial cells/mL X $10^4$ | CFU/g X $10^6$ fresh-water agar | CFU/g X $10^6$ sea-water agar | Direct microscopic count bacterial cells/g X $10^6$ |
| 1 | 6.7 | 2.2 | 65 | 1.0 | 0.4 | 5.4 |
| 4 | 2.4 | 3.4 | 17 | 5.1 | 3.8 | 13.5 |
| 5 | 1.1 | 6.7 | 24 | 2.7 | 3.8 | 5.4 |
| 6 | .47 | 8.0 | 37 | .6 | .7 | 8.1 |
| 7 | .78 | 8.0 | 37 | 2.9 | 6.3 | 8.1 |
| 8 | 3.5 | 10.0 | 37 | 2.2 | 4.8 | 8.1 |
| [a]9 | ---- | ---- | -- | 2.1 | 3.2 | 16 |
| 11 | .73 | 20.0 | 51 | .5 | 4.4 | 4.0 |

[a] No water sample was collected at site 9.

sites, large spreading colonies obscured other colonies in a few plates, leading to low counts. Counts at these sites were calculated from the dilution with the highest count to minimize the effects of overgrowth. The agreement between pour plate and spread plate counts was satisfactory. Again, most counts were within plus or minus 20 percent of the mean value of pour plate and spread plate counts.

Direct microscopic counts also are presented in table B-2. In most instances the 1.11 mL samples gave sufficient bacteria to count, and resulted in higher total counts than the 11.1 mL sample. The direct microscopic-counts data are calculated from the 1.11 mL sample counts.

The bottom material samples proved much more difficult to count accurately than water samples for two reasons. First, the bottom material contained a great deal of particulate inorganic and organic matter, which obscured many of the bacterial cells. Second, it is possible that organic matter in the sample may have absorbed most of the dye, resulting in inadequate staining of the bacteria and low counts. The bottom-material data reported in table B-2 were from the more dilute samples. These counts were used because the two dilutions did not agree well, and the less diluted samples were considered less accurate because of the reasons stated above.

The data show bacterial counts in all samples in concentrations characteristic of eutrophic systems. As expected, the sample from freshwater, site 1, gave a higher count in freshwater agar than in seawater agar, and those samples collected from seawater, sites 7, 8, and 11, gave much higher counts in the seawater agar. Similar counts in both the freshwater and seawater agar were observed in bottom-material samples collected at the brackish-water sites 4 and 5 indicating the presence of a euryhaline bacterial community. Bacteria in water samples at site 4 showed similar euryhaline abilities to the bacteria in the bottom-material samples at sites 4 and 5. Bacteria in water samples at site 5, which had a higher salinity than site 4, did not exhibit euryhaline characteristics and grew much better in the saltwater agar than in the freshwater agar.

Bacteria counts were much higher in the bottom-material samples compared to those in the overlying water samples which is typical for rivers, lakes, and estuaries. Highest bacteria concentrations in the brackish and saltwater areas were for samples from site 11, the site closest to the Gulf of Mexico. Bacteria counts in bottom material showed no trends in a downstream direction. Plate counts and direct microscopic counts were high in both brackish and seawater samples.

## SUMMARY

Bacterial populations in water and bottom material collected from the lower Calcasieu River study reach were determined using both viable and direct microscopic counts. Viable counts were performed on both freshwater and seawater agar. Bacteria grew best on the agar similar to the salinity that was present at the site during times of collection. An exception to this were samples collected at brackish-water sites. Bacteria at these sites grew equally well in fresh and seawater agar indicating the presence of a euryhaline bacteria population. Direct microscopic counts of bottom-material samples had to be diluted to obtain satisfactory counts. Bacterial counts were typical of eutrophic systems. Bacterial counts in water increased in a downstream direction from brackish water to saltwater. Bacterial counts were higher in bottom-material samples than in overlying water samples.

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## CHAPTER C

# THE OCCURRENCE AND DISTRIBUTION OF SEMIVOLATILE ORGANIC COMPOUNDS IN THE LOWER CALCASIEU RIVER, LOUISIANA, BY USE OF THE CLOSED-LOOP-STRIPPING ISOLATION PROCEDURE

By L.B. Barber, II[1]

## ABSTRACT

Semivolatile organic compounds were sampled in water from seven sites along the lower Calcasieu River during May 29 and 30, 1985. Semivolatile organic compounds were isolated and concentrated from river water by using the closed-loop-stripping method. This method allows for quantification of organic compounds in the 0.01 to 50.0 micrograms per liter range. The semivolatile organic matrix detected in the water column of the lower Calcasieu River was relatively simple and concentrations of specific organic compounds were very low with respect to the overall pollutant load for the system. The organic water chemistry reflected the possible influence of a complex set of physicochemical variables, including volatilization, sorption, biotransformation, photolysis, dilution, and precipitation caused by strong ionic strength gradients in the study reach, all acting to attenuate pollutant levels in the water column.

Relatively high levels of volatile halogenated compounds were detected throughout the study reach indicating that parts of the system have an organic contaminant load that exceeds assimilation capacity, at least with respect to elimination by volatilization. Hydrophobic organic compounds such as the chlorinated benzenes were detected in low concentrations in water in the lower Calcasieu River. These low concentrations are probably caused by sorption of these compounds to bottom sediments.

## INTRODUCTION

During May 1985, a sampling trip by the U.S. Geological Survey was conducted to provide preliminary data on the occurrence and distribution of volatile and semivolatile organic solutes in the water column of the Calcasieu River, southern Louisiana. This work was carried out in conjunction with efforts to characterize the bulk organic water chemistry, sediment organic chemistry, and microbiota that are reported on elsewhere in this report.

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During the sampling period May 29-30, 1985, wind activity was considerable, and small craft warnings had been issued. This resulted in a high degree of turbulence, particularly at the air-water interface. Velocity measurements generally indicated turbulence with depth, and in almost all instances horizontal flow could be measured across the entire water column (P.B. Curwick, U.S. Geological Survey, oral commun., 1985). The river is primarily a tidal, wind driven system with an active dredged shipping channel. Although the sampling was conducted in early spring, the average water temperature ranged from 28 °C at the surface at site 1 to 29 °C at the surface at site 6 (table A-3).

The purpose of this report is to describe the closed-loop-stripping (CLS) method of isolation and concentration of volatile and semivolatile organic compounds in water, present analytical results, and discuss the environmental fates of some of the organic compounds identified from samples collected from the lower Calcasieu River. Sampling was conducted at 7 of the 11 study sites and restricted to the organic compounds present in unfiltered water. (See figure A-1 and table A-2 for site locations.)

## DESCRIPTION OF PROCEDURE

### Sample Collection

Sites 1, 4 through 8, and 11 (fig. A-1 and described in Chapter A) were sampled for semivolatile organic compounds in water from the lower Calcasieu River, Louisiana. These samples included an upstream control from the relatively nonimpacted freshwater region. The salinity of the river increased in the downstream direction to nearly that of seawater at the Cameron site (site 11). Inorganic and bulk-organic data on the water samples are presented in tables A-4, A-5, A-6, and A-7.

Samples were collected in 1-liter glass pesticide bottles with Teflon-lined caps that had been thoroughly cleaned and baked at 350 °C for 12 hours. Samples were collected by using an epoxy-coated steel basket sampler and were depth integrated through the entire water column. Immediately upon collection, the samples were placed on ice and subsequently stored at 4 °C until time of analysis.

### Extraction Procedures

Three extraction methods were used to isolate and concentrate the volatile and semivolatile organic compounds from the water samples prior to gas chromatograph-mass spectroscopy (GC-MS) analysis for specific compound identification and quantification. Two of these methods, liquid-liquid extraction (LLE) and purge and trap (PT) are routinely used by the National Water Quality Laboratory (NWQL) for extracting organic contaminants from natural water samples. Acid-base/neutral extractables were isolated using method 0-3117-83 (Wershaw and others, 1983), which is a pH adjusted LLE using methylene chloride. Purgeable compounds were extracted using PT method 0-3115-83 (Wershaw and others, 1983), which sparges a sample with helium and traps the organic compounds onto tenax adsorbent, followed by thermal desorption. The third method, CLS is not currently being used by the laboratory system so the methodology will be discussed in some detail here.

The CLS method of Grob (1973) and Grob and Zurcher (1976) was used with some modification (Barber and others, 1984; Coleman and others, 1983). In this study, 1-liter water samples were heated to 40 °C and continuously purged for 2 hours with charcoal-filtered laboratory air in an air-tight glass Teflon-nickel system. Compounds were stripped from the water and trapped onto a 5.0 mg (milligrams) activated-carbon filter, which was then serially eluted with 50 µL (microliters) of distilled-in-glass methylene chloride. The methylene chloride extract was collected in a calibrated glass vial, sealed, and stored at -20 °C until GC-MS analysis for organic compound identification and quantification. The concentration factor of approximately 20,000 for the CLS method used in this study allowed the quantification of compounds in the 0.01 to 50.0 µg/L (micrograms per liter) range. The CLS samples were shipped to the NWQL where they were stripped within 7 days of collection.

Charcoal traps were cleaned by serial extractions by using methanol, acetone, and methylene chloride, and then placed in an oven at 100 °C for 20 minutes immediately prior to being used to prevent carryover between samples. The CLS apparatus pump and lines were flushed between samples with methanol followed by methylene chloride, then heated to 80 °C, and allowed to pump laboratory air with a charcoal trap in place for 30 minutes. Regular analysis of trap blanks and prestripped distilled water blanks indicated no evidence of compound carryover between samples. Similarly, evaluation of the sample and blank processing sequence indicated no carryover between analysis of samples and blanks.

## Instrumentation

The GC-MS analysis of the CLS extracts was performed using a Hewlett Packard 5985 GC-MS system equipped with a 0.21 mm (millimeter) inside diameter, 25 m (meters) fused silica capillary column with 0.20 µm (micrometer) SE-54 crosslinked 5 percent phenyl-methyl silicon stationary phase (Hewlett Packard Ultra II). One to two microliters of methylene chloride extract were injected into the column using a splitless technique with injector temperature maintained at 250 °C and the port vent opened after 30 seconds. Helium carrier gas with a linear velocity through the GC column of 28 cm/s (centimeters per second) was used. Samples were injected with the column temperature at 30 °C, and after 10 minutes the temperature was increased to 300 °C at a rate of 6 °C per minute. Temperature was held at 300 °C for 5 minutes, after which the sample run was terminated. Mass spectra were acquired from 40 to 450 amu (atomic mass units) at a rate of 2 scans per second. The electron energy was 70 electron volts, and the source temperature was maintained at 200 °C. Source pressure at 25 °C was approximately 3 X $10^{-6}$ torr.

Tentative compound identification was based on matching of sample mass spectra with those in the National Bureau of Standards (1978) mass spectra library using a Hewlett Packard 1000 data system. All computerized matches were manually evaluated to assure the quality of identification. Identification of selected targeted compounds was confirmed by matching mass spectra and retention times of the sample compound with authentic standards analyzed under identical conditions.

## Surrogate Standards

To provide a means of quantification for compounds identified in the CLS extracts and to monitor sample behavior from the time of collection until analysis, a homologous series surrogate-internal standard spiking scheme was used. In addition to the CLS surrogate standards, surrogate compounds incorporated into the LLE and PT laboratory protocol were also added to the field spiking mixture so that each sample for a particular type of analysis was also spiked with the surrogate compounds for the other two methods. In this way the surrogate-internal standard allowed method evaluation in addition to providing quantification capability. The compounds listed in table C-1 were dissolved in methanol at concentrations of approximately 200 ng/µL (nanograms per microliter). An aliquot of this mixture was injected into the water samples at a concentration of 1.0 µg/L for the CLS samples and 20.0 µg/L for the LLE and PT samples at the time of collection. These spikes undergo all phases of sample storage, processing, and analysis.

Table C-1.--Surrogate and internal standards for the three isolation procedures used for method evaluation and compound quantification

| Surrogate standards | Internal standards |
|---|---|
| Purge and trap (PT) | |
| Bromochloromethane | Fluorobenzene |
| 1-Bromo-2-chloroethane | |
| 1,4-Dichlorobutane | |
| Closed-loop stripping (CLS) | |
| 1-Chlorohexane | 1-Chlorooctane |
| 1-Chlorododecane | |
| 1-Chlorooctadecane | |
| Liquid-liquid extraction (LLE) | |
| $d_5$ Phenol | Perdeuteronaphthalene |
| 1,4-Dibromobenzene | Perdeuterophenanthrene |
| 2,4-Dibromophenol | Perdeuterocrysene |
| 2,2'-Difluorobiphenyl | |
| 2,4,6-Tribromophenol | |
| 4,4'-Dibromobiphenyl | |

A series of internal standards (table C-1) were added to the methylene chloride extract (water sample for PT) immediately prior to GC-MS analysis at a concentration equal to the surrogate standards, assuming 100 percent recovery efficiency. Concentrations of compounds identified in the CLS extracts were calculated against 1-chlorododecane using baseline corrected total ion current peak areas, assuming a mass spectrometer response factor of 1. Assuming that compounds of interest behave in a similar manner as the surrogate standards, losses or changes occurring during sample processing will be compensated by the calculation. This method corrects for recovery efficiency and is independent of the final extract volume and concentration factor. When considering the recovery of compounds in replicate analysis, concentrations were calculated against the internal standard.

These three methods isolate different types of compounds at different concentration levels. The relation between compound selectivity and sensitivity is shown in figure C-1. The LLE method isolates the broadest range of compounds and is able to determine classes from low molecular weight halocarbons up to moderately low volatility compounds, such as PNA's (polynuclear aromatics). However, LLE of 1-liter samples has a detection limit of approximately 10 µg/L. The PT method most effectively isolates highly volatile compounds such as tetrachloroethene, and has a detection limit of approximately 3 µg/L. The CLS isolated a broad range of compounds from the high to intermediate volatility range, and overlaps well with the PT and LLE, but most importantly has a detection limit almost two-orders of magnitude lower than the PT and three-orders lower than the LLE using the same sample size.

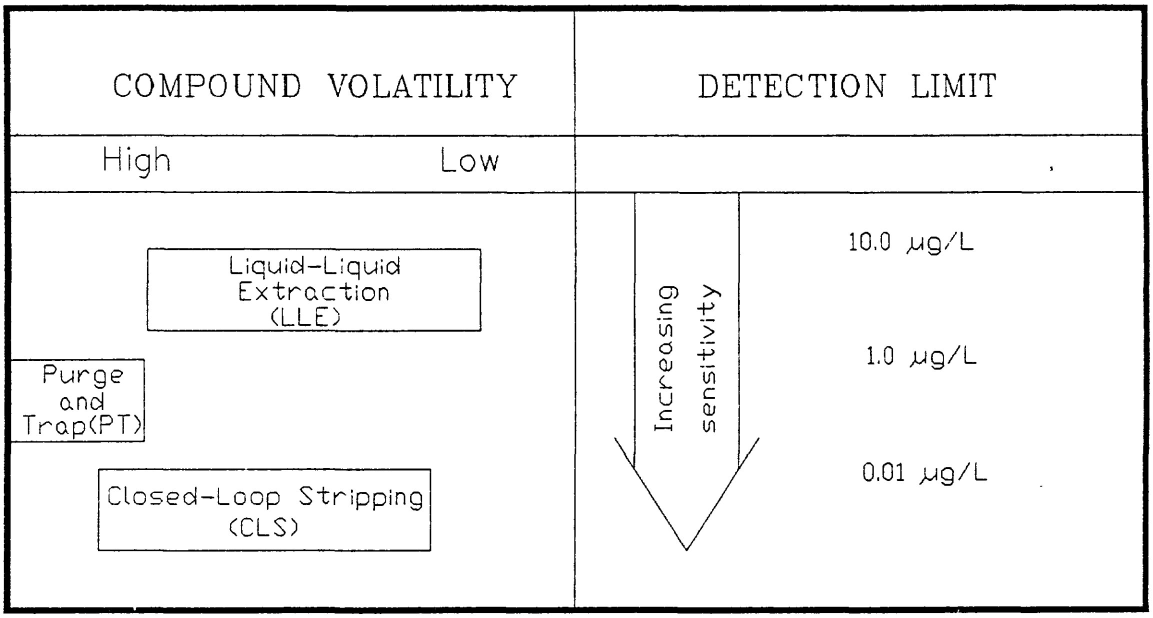

Figure C-1.--Relation between sensitivity and compound selectivity for volatile organic compound isolation procedures.

## OCCURRENCE AND DISTRIBUTION OF SEMIVOLATIVE ORGANIC COMPOUNDS

Concentrations of specific volatile to semivolatile organic compounds in river and coastal seawaters are generally reported to be on the order of micrograms per liter levels (Schwarzenbach and others, 1978; Gschwend and others, 1982; Wakeham and others, 1983; Zoeteman and others, 1980) unless heavily affected by industrial effluents. Zoeteman and others (1980) present data on highly affected waters and indicate that once the chemicals disperse from the vicinity of the outfall, concentrations can be rapidly diminished to submicrograms per liter concentrations. Concentrations near heavy sources of contamination may be several orders of magnitude greater than concentrations at a short distance away.

Because of the low concentrations of specific organic contaminants occurring in the lower Calcasieu River at the time and places at which the samples were collected, the LLE data were of limited value because no contaminants were detected. This does not mean no contaminants were present, but rather the contaminants were present at concentrations below the detection limit of the LLE method. The PT method was of only slightly greater value, and only one compound, bromoform, was commonly identified (table A-7). However, the detection of bromoform indicates the selectivity of the PT method, which is most efficient in isolating volatile organic compounds, such as the halocarbons, a class of organic compounds frequently encountered in the environment. The CLS method proved to be of most value and identified the greatest number of compounds in the river water, most at submicrogram per liter concentrations.

Results from the CLS analysis are summarized in table C-2. Only a limited number of organic compounds were recovered from the river water. Duplicate analyses for sites 1 and 7 were consistent in the compounds identified, and concentrations were within 15 percent. Recovery of surrogate standards by CLS provided information on recovery efficiency for a wide range of organic compounds and confirms the integrity of the sample and analytical results. Most of the surrogates from the LLE and PT methods were recovered by CLS, with the exception of highly volatile bromochloromethane, the soluble bromophenols, and high boiling point dibromobiphenyl. Recovery of the other compounds in table C-1 in the river samples ranged from 20 percent to over 80 percent. Recovery of surrogate standards is affected not only by analytical methodology but also by biodegradation of the organic compounds in the water samples, volatilization during sample transfer, the influence of a complex natural sample matrix, and loss of hydrophobic compounds caused by sorption onto either the sample container walls or suspended sediments. As a result, recoveries were about 25 percent greater in distilled water blanks than for the water samples. Analysis of surrogate and internal standard data indicates a detection limit of approximately 5 ng/L (nanograms per liter) for compounds in the intermediate volatility range.

The concentrations of specific semivolatile organic compounds determined by CLS in the river water samples were generally quite low and the number of organic compounds restricted. The only organic compound identified at site 1 was heptadecane ($C_{17}$ hydrocarbon) which was also a major component of the sediments (Pereira, Chapter D of this report). However, other specific compounds

Table C-2.--Results of closed-loop-stripping analysis of samples from the lower Calcasieu River, Louisiana, May 29-30, 1985

[Concentrations in micrograms per liter; <, actual value is known to be less than the value shown; (SS) surrogate standard; (IS) internal standard]

| Compound | Blank | Site<br>1 | 4 | 5 | 6 | 7 | 8 | 11 |
|---|---|---|---|---|---|---|---|---|
| 1. Trichloroethene | <0.01 | <0.01 | 0.04 | 0.39 | 0.64 | <0.01 | 0.07 | <0.01 |
| 2. Dibromomethane | <.01 | <.01 | .11 | .13 | .24 | .21 | <.01 | <.01 |
| 3. Bromodichloromethane | <.01 | <.01 | <.01 | .23 | .26 | <.01 | <.01 | <.01 |
| 4. 1-Bromo-2-chloroethane (SS) | .15 | .20 | .09 | .17 | .17 | .14 | .14 | .26 |
| 5. 1,1,2-Trichloroethane | <.01 | <.01 | <.01 | .29 | .37 | <.01 | <.01 | <.01 |
| 6. Dibromochloromethane | <.01 | <.01 | .34 | 2.00 | 2.22 | .35 | .06 | <.01 |
| 7. Tetrachloroethene | <.01 | <.01 | .68 | 2.95 | 3.20 | .78 | .26 | <.01 |
| 8. 1,1,1,2-Tetrachloroethane | <.01 | <.01 | <.01 | .06 | .08 | <.01 | <.01 | <.01 |
| 9. 1-Chlorohexane (SS) | .64 | .32 | .44 | .60 | .47 | .37 | .50 | .28 |
| 10. Tribromomethane | <.01 | <.01 | 3.43 | 23.68 | 22.57 | 2.98 | .54 | <.01 |
| 11. 1,4-Dichlorobutane (SS) | .65 | .39 | .52 | .64 | .54 | .45 | .56 | .75 |
| 12. 1,1,2,2-Tetrachloroethane | <.01 | <.01 | <.01 | .08 | .06 | <.01 | <.01 | <.01 |
| 13. 1-Chlorooctane (IS) | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 14. Pentachloro-1,3-butadiene | <.01 | <.01 | <.01 | .23 | .20 | <.01 | <.01 | <.01 |
| 15. 1,3-Dibromobenzene (SS) | .67 | .42 | .63 | 1.06 | .84 | .62 | .63 | .66 |
| 16. Hexachloro-1,3-butadiene | <.01 | <.01 | .15 | .58 | .61 | .07 | <.01 | <.01 |
| 17. 2,2-Difluoro-biphenyl (SS) | .83 | .22 | .84 | 1.51 | 1.31 | .79 | .78 | .85 |
| 18. 1-Chlorododecane (SS) | .91 | .12 | .14 | .37 | .33 | .17 | .41 | .21 |
| 19. Pentadecane | <.01 | <.01 | .05 | .49 | .28 | .14 | .25 | .09 |
| 20. $C_{20}$ | <.01 | <.01 | <.01 | .17 | .04 | <.01 | <.01 | <.01 |
| 21. 1-Tetradecanol | <.01 | <.01 | <.01 | <.01 | .12 | <.01 | <.01 | <.01 |
| 22. Heptadecane | <.01 | .20 | <.01 | .08 | .10 | .0 | .04 | <.01 |
| 23. 1-Chlorooctadecane (SS) | .54 | <.01 | .05 | .21 | .10 | <.01 | <.01 | <.01 |

identified in the bottom material were not identified in the water column. Algae are the most likely source of heptadecane (W.E. Pereira, U.S. Geological Survey, oral commun., 1985).

Organic compounds were detected at a number of sites downstream of the saltwater barrier including sites 4 through 8 and 11. The largest number of different organic compounds and the highest concentrations were detected at site 6. Figure C-2 shows a reconstructed total ion chromatogram for site 6. The peak numbers correspond to compounds listed in table C-2. The concentrations of most contaminants were relatively low with respect to the surrogate and internal standards that were added at 1.0 µg/L. The dominant semivolatile organic compound found in the water samples was tribromomethane (TBM) which occurred at over 20 µg/L at sites 5 and 6. Associated with TBM, but detected at much lower concentrations, were dibromomethane, bromodichloromethane, and

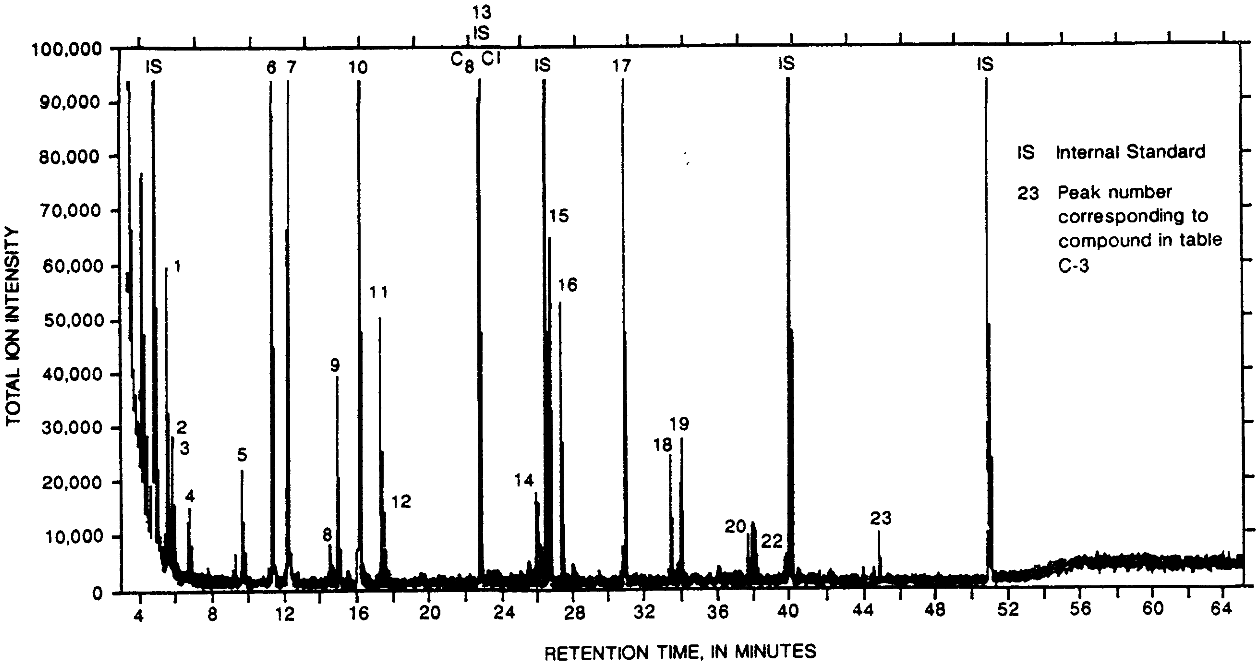

Figure C-2.--Reconstructed total ion chromatogram of closed-loop-stripping extract for Bayou d'Inde, site 6, lower Calcasieu River, Louisiana.

dibromochloromethane. Although bromoform has been reported as a constituent in some of the waste effluents discharging into the river (C.R. Demas, U.S. Geological Survey, oral commun., 1985), it is postulated here to be the result of halogenation of naturally occurring organic compounds. Significant amounts of chlorine are discharged into Bayou d'Inde (U.S. Environmental Protection Agency, 1975) which can convert bromide into the bromine radical and in turn initiates the haloform reaction. At moderate bromide concentrations in solution, bromoform and the other brominated analogs dominate over chlorinated compounds (Jolley and others, 1980). The presence of the whole suite of bromination reaction products suggests an in-situ source rather than discharge of bromoform in the outfalls. The high concentrations of bromoform in the water column also suggest that it may be formed in situ because volatilization would result in a relatively short half-life for bromoform under the environmental conditions present during the sampling trip, and bromoform should maintain concentrations at low micrograms per liter levels. Otherwise, bromoform would have to be a dominant constituent in the outfall effluents relative to other volatile organic compounds identified which occurred at the lower concentrations as discussed below.

Other semivolatile halogenated organic compounds identified in the river include trichloroethane, tetrachloroethene, pentachlorobutadiene, and hexachlorobutadiene. Of these compounds, tetrachloroethene was the most concentrated and was present in concentrations greater than 3 µg/L at site 6 (table C-2). The other compounds occur at submicrogram levels, but also have maximum concentrations at site 6. The major industry discharging into Bayou d'Inde near site 6 manufactures tetrachloroethene by a process from which trichloroethene, trichloroethane, and tetrachloroethane, and hexachlorobutadiene are among the by-products (U.S. Environmental Protection Agency, 1975). Thus, the most likely source of these pollutants in the system is direct discharge from the industrial outfall. Heptadecane and several other long-chained hydrocarbons were also detected in these water samples but were probably of natural origin.

Concentrations of all pollutants were greatest at site 6 and decreased in concentration and number in the upstream and downstream directions. Although many of the other organic compounds in table C-2 were absent, significant levels of tetrachloroethene were detected as far upstream as site 4 and as far downstream as site 8, indicating considerable dispersion in both directions. The water at sites 5 and 6 was very similar in both composition and concentrations, indicating a relatively large region of uniform organic contamination. Whether this area originates from a single source or multiple sources cannot be evaluated from this preliminary data. However, the nature and distribution of the pollutants indicate that the industrial outfall into Bayou d'Inde is the primary source of the chlorinated hydrocarbons.

Although the concentrations of semivolatile organic compounds present in the water samples collected from the river are relatively low, they indicate a substantial input at the source. Initial concentrations of low molecular weight hydrocarbons in the effluent must have been considerable (hundreds of micrograms per liter) in order to maintain concentrations on the order of micrograms per liter at distances of thousands of meters. Reasons for this estimation are the rapid volatilization rates for low molecular weight halocarbons predicted for such a warm turbulent system (half-lifes on the order of minutes to hours) and the long residence time (days to weeks) of the midchannel water column relative to the outfall discharge. Low concentrations of volatile organic compounds also reflect dilution of the outfall by mixing with the river and the influence of other attenuating mechanisms such as sorption, biotransformation, hydrolysis, photolysis, and low solubility in saltwater.

## SUMMARY

Semivolatile organic compounds were sampled in water from seven sites along the lower Calcasieu River during May 29 and 30, 1985. These organic compounds were isolated and concentrated from river water by using the CLS method. This method allows for quantification of organic compounds in the 0.01 to 50.0 µg/L range. The semivolatile organic matrix of the Calcasieu River water column, identified by this isolation procedure, was relatively simple and concentrations of specific organic compounds were low with respect to the overall pollutant load for the system. The organic water chemistry reflected the possible influence of a complex set of physicochemical variables, including volatilization, sorption, biotransformation, photolysis, and dilution, all acting to attenuate pollutant levels in the water column. The influence of volatilization and sorption on concentrations of organic compounds are probably enhanced by the lowered solubility of these organic compounds that results from the strong ionic strength gradients in the study reach. These processes operate in such a manner as to maintain water-column concentrations (including both the aqueous phase and suspended sediment) of most specific compounds at concentrations lower than 0.001 to 0.01 µg/L, even though the river appears to have a large organic compound load.

The presence of relatively high levels of volatile halogenated compounds throughout the study reach indicate that parts of the system have an organic contaminant load that exceeds assimilation capacity, at least with respect to elimination by volatilization. Bromoform, the most commonly detected volatile organic compound, was probably the result of halogenation of naturally occurring organic compounds. Hydrophobic compounds, such as the chlorinated benzenes, were detected in low concentrations in the lower Calcasieu River.

These low concentrations are probably caused by sorption of these compounds to bottom material. Absence of major organic bottom material contaminants, such as the chlorinated benzenes in the water column, indicate that the assimilatory capacity of the sorptive solid phase has not been exceeded.

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(p. 35 follows)

# CHAPTER D

# DISTRIBUTION OF ORGANIC COMPOUNDS IN THE LOWER CALCASIEU RIVER, LOUISIANA, WITH SPECIAL EMPHASIS ON HALOARENES

By W.E. Pereira, C.E. Rostad, Robert Keck, and C.T. Chiou[1]

## ABSTRACT

Water and bottom-material samples were collected from the lower Calcasieu River in southwestern Louisiana during May 1985, to determine the distribution and concentrations of potentially toxic manmade organic compounds in this river-estuarine system.

One such group of compounds, the haloarenes, were detected in water and bottom-material samples from the lower Calcasieu River. These compounds are less soluble in saltwater than in freshwater and were found to precipitate in the river. Therefore, bottom material in the lower Calcasieu River serves as a major sink for these compounds.

Phenols, 1,3-dichlorobenzene, 1,2-dichlorobenzene, hexachlorobutadiene, hexachlorobenzene, and phenanthrene also were present in part per million range of concentrations in bottom material from the lower Calcasieu River and its tributary Bayou d'Inde. Results indicate that the lower molecular weight chlorinated benzenes have been transported to greater distances relative to hexachlorobenzene, indicating a chromatographic effect in lower Calcasieu River bottom material due to differential sorption to sediments caused by different log-K values of haloarene isomers.

## INTRODUCTION

The lower Calcasieu River, in Louisiana, is part of a river-estuarine ecosystem affected by petrochemical and agrochemical industries. There are approximately 32 such industries along a 22.4 km (kilometers) reach, many of which discharge organic waste materials into this riverine system (fig. D-1). Some of these materials contain manmade organic compounds, such as petroleum hydrocarbons, polycyclic aromatic hydrocarbons (Steinheimer and others, 1981), volatile halogenated hydrocarbons, and haloarenes.

The haloarenes are a class of chlorinated aromatic compounds that are toxic to aquatic organisms such as algae and fish (Moore and Ramamoorthy, 1984). Because these compounds have relatively high log-K (octanol/water)

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[1] U.S. Geological Survey, Denver, Colorado.

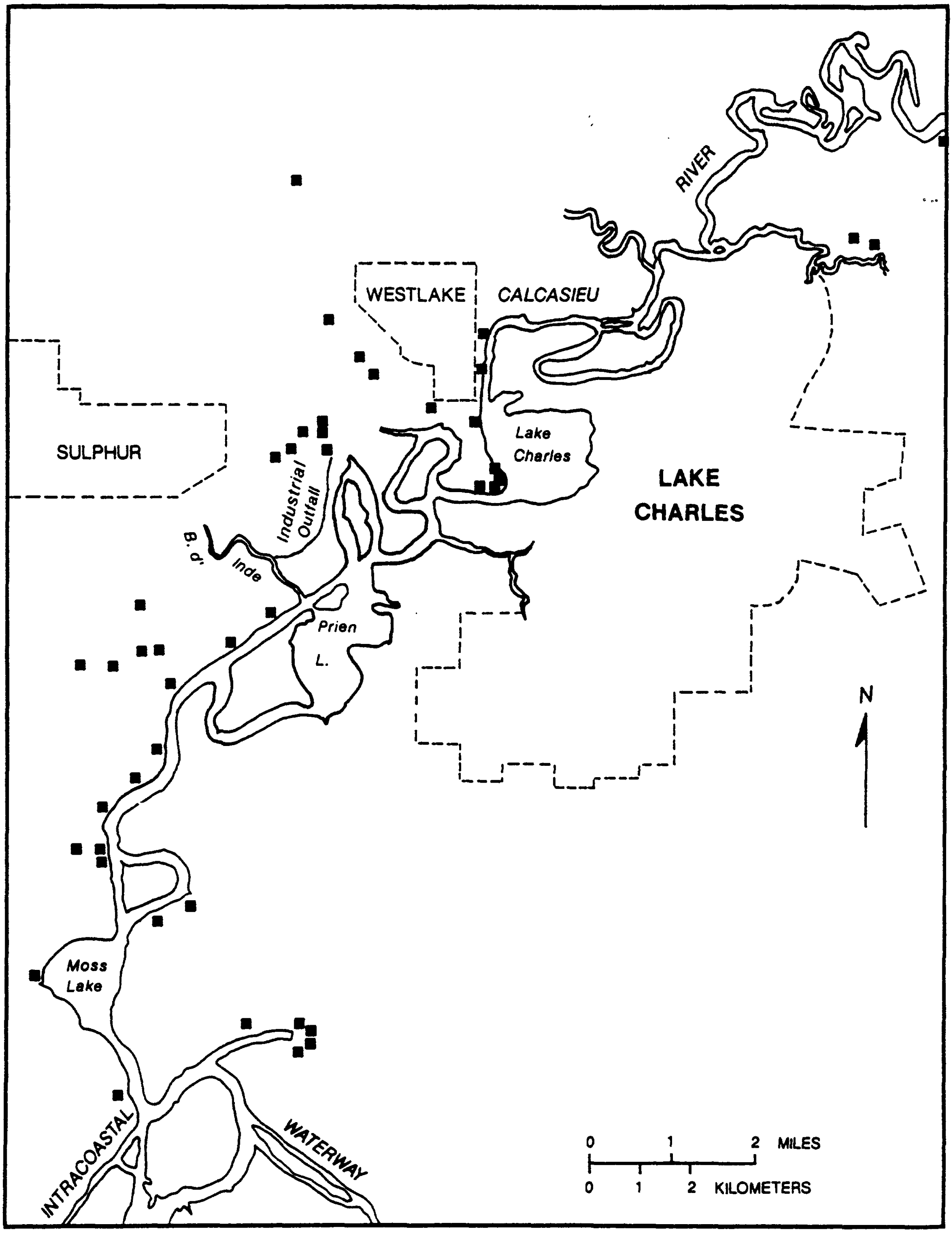


Figure D-1.--Industrial development along the lower Calcasieu River, Louisiana.

values, they are sorbed strongly by sedimentary organic material, and bioconcentrate in lipid tissues of aquatic organisms. In the lower Calcasieu River, where specific-conductance values range from approximately 6,000 to 32,000 µS/cm (microsiemens per centimeter at 25 °C), the haloarenes are precipitated out. Therefore, the sedimentary organic material is a major sink for these compounds. Little information is known concerning the fate and movement of haloarenes in suspended sediments and bottom materials in this river-estuarine environment.

In 1985, the U.S. Geological Survey began an interdisciplinary study to investigate the fate and movement of organic contaminants in the lower Calcasieu River. Samples were collected May 29-30, 1985, to determine the organic classes of organic compounds present in this river-estuarine system, and to investigate the potential environmental fates of these manmade organic compounds within the system.

The purpose of this report is to describe the methodology used in analysis of organic compounds present in bottom material and water, present the results, and discuss the fate and movement of selected classes of organic compounds in the lower Calcasieu River.

## SAMPLE COLLECTION AND ANALYSIS

### Bottom Material

#### Sample Collection

Samples of bottom material were collected at each site using a stainless-steel Ponar grab sampler. The grab sampler was manually operated from an anchored boat at each site. Bottom-material samples were transferred with a stainless-steel spatula to precleaned and baked wide-mouth glass jars, provided with Teflon-lined screw caps. Samples were chilled on ice and shipped to the National Water Quality Laboratory (NWQL) for analysis.

#### Sample Preparation

Approximately 150 g (grams) of each bottom-material sample was weighed into a lyophilization flask and lyophilized overnight. The flask and dry bottom material were then reweighed. Thus, the dry weight of the bottom material was obtained. Each sample was gently mixed in a glass mortar and pestle and transferred to an airtight glass container.

#### Sample Extraction

Twenty grams of the dried bottom material were transferred to the thimble of a Soxhlet extractor, and extracted with 200 mL (milliliters) of benzene-methanol mixture (3:1 ratio) for 24 hours. The extract was concentrated on a water bath in a Kuderna-Danish apparatus to a volume of approximately 9 mL, and made up to a volume of 10 mL with benzene. A procedural blank was simultaneously carried out with the benzene-methanol solvent (3:1 ratio).

Each sample was thoroughly mixed on a vortex mixer. One-hundred microliters of each extract was transferred to a 1-mL vial containing approximately 5 mg (milligrams) of copper powder and mixed on a vortex mixer. Internal standards for quantification ($d_8$-naphthalene, $d_{10}$-phenanthrene, and $d_{12}$-chrysene) were added to each vial, and the extracts analyzed by gas chromatograph-mass spectroscopy (GC-MS).

## Instrumental Analysis

Instrumental analysis was performed on a Hewlett Packard Model 5880 GC coupled to a Finnigan Model 3200 MS equipped with an Incos data system. The GC was equipped with a wall-coated open-tubular fused-silica capillary column, 30-m (meters) long by 0.25 mm (millimeter) internal diameter coated with SE-54. The linear velocity of helium through the column was 25 cm/s (centimeters per second); injections were made using the splitless-injection technique. The GC oven temperature was maintained at 50 °C for 4 minutes and then increased at 6 °C per minute to a maximum of 300 °C, with a hold time of 20 minutes. The MS was operated in the electron-impact mode using an ionizing voltage of 70 ev (electron volts) and an ionization current of 250 µA (microamperes). The instrument was repetitively scanned from 40 to 450 amu (atomic mass units) in 0.5 seconds.

## Recovery Studies of Organic Compounds from Bottom Material

During the initial extraction of bottom material, it became apparent that existing methodology in use by the NWQL was unsuitable for the isolation and analysis of organic contaminants in bottom material. Because of the high-moisture content (72 percent), the high organic carbon content (2.5 percent, dry weight), and the highly cohesive consistency of the bottom material, the standard wet-extraction procedure using methylene chloride-methanol solvent system resulted in poor recoveries of organic compounds. To overcome this problem, the alternative approach of freeze drying of bottom material prior to extraction was investigated. A sample of bottom material from site 6 was spiked with six surrogate organic compounds, freeze dried, ground with a pestle in a glass mortar, and thoroughly mixed. Two 20-g portions of dried bottom material were extracted separately in Soxhlet apparatus with a benzene-methanol mixture (3:1 ratio), and with methylene chloride. The solvents were evaporated in Kuderna-Danish devices to a volume of 10 mL. One hundred microliters of each extract were transferred to glass vials. To each vial, 2 to 5 mg of copper powder were added (to precipitate sulfur). Vial contents were then mixed on a vortex mixer. After the addition of internal standards for quantification ($d_8$-naphthalene, $d_{10}$-phenanthrene, and $d_{12}$-chrysene), the extracts were analyzed by GC-MS. A sample of wet bottom material was also extracted by the wet-extraction procedure using a mixture of methylene chloride and methanol (Wershaw and others, 1983). Concentrations of selected organic compounds in bottom material at site 6, as determined by the different methods are shown in table D-1. Table D-2 shows recovery data of the added surrogates.

The data in table D-2 show that the freeze-drying procedure results in relatively little loss of added surrogate compounds. Although these data are to be regarded as preliminary information collected on one selected bottom-

## Table D-1.--Concentrations of selected organic compounds in bottom material from site 6, Bayou d'Inde, Louisiana

[Values in micrograms per kilogram]

| Compound | Freeze-dried method |  | Wet-extraction method |
|---|---|---|---|
|  | Benzene/ methanol | Methylene chloride | Methylene chloride/ methanol |
| Phenol | 2,700 | 4,600 | 31 |
| 1,3-Dichlorobenzene | 2,110 | 2,300 | 330 |
| 1,2-Dichlorobenzene | 850 | 790 | 24 |
| 1,2,4-Trichlorobenzene | 290 | 250 | 71 |
| Naphthalene | 65 | 70 | 16 |
| Hexachlorobutadiene | 580 | 540 | 170 |
| Hexachlorobenzene | 9,700 | 18,000 | 1,100 |
| Phenanthrene | 650 | 810 | 68 |

## Table D-2.--Percent recovery data for surrogate organic compounds added to site 6, Bayou d'Inde bottom-material samples

| Compound | Freeze-dried method |  | Wet-extraction method |
|---|---|---|---|
|  | Benzene/ methanol | Methylene chloride | Methylene chloride/ methanol |
| $d_5$-Phenol | 83 | 54 | 75 |
| 1,4-Dibromobenzene | 61 | 71 | 49 |
| 2,4-Dibromophenol | 69 | 93 | 43 |
| 2,2'-Difluorobiphenyl | [a]22 | 91 | 98 |
| 2,4,6-Tribromophenol | 112 | 103 | 71 |
| 4,4'-Dibromobiphenyl | 111 | 76 | 93 |

[a] Interference (poor-peak integration).

material sample, the data from freeze-dried samples emphasize the inadequacies of the wet-extraction procedure. Furthermore, extraction of freeze-dried material with methylene chloride may be the method of choice, as a benzene-methanol mixture tends to extract natural organic compounds in addition to the pollutants. The natural organic compounds eventually may cause plugging of GC columns after repeated use.

The experiment suggests as one possibility that organic solvents, including bridging polar solvents, are not able to effectively penetrate interstitial spaces and pores between and inside individual bottom-material grains because of strong dipole interactions between the mineral surface and water molecules. Therefore, the extracting solvent does not compete effectively with water for wetting the mineral surface and its associated organic matter, resulting in low recoveries of organic compounds.

## Water

### Acid-Base/Neutral Extractable Organic Compounds

The May 29-30, 1985, reconnaissance survey of the Calcasieu River involved eight sites where numerous samples were taken, including water samples for organic analysis. One liter of water was taken for acid-base/neutral organic analysis. These samples were spiked in the field with surrogate organic standards for field recovery studies. The surrogate standards would measure degradation, volatilization, and adsorption onto sample containers of the organic constituents while in transit to the laboratory for acid-base/neutral organic analysis by GC-MS. The surrogate standards were recovered within the acceptable range (30-130) by the acid-base/neutral analysis. However, the levels of organic compounds were lower than the detection limits of the current methodology and instrumentation (Chapter A). To overcome this limitation, in future studies, a much larger water sample (up to 16 L, liters) may be required. The low level of organic compound contaminants in the water column may be the result of precipitation in the presence of saltwater, with the organic compounds partitioning primarily on the bottom material.

### Bonded-Phase Extraction

Forty-milliliter samples were taken for field application of a new procedure, concentration of organic compounds on a small bonded-phase extraction column. After passing the sample, spiked with surrogate standards through the column onsite to trap the organic compounds, only the small, lightweight column was shipped back to the laboratory for elution and analysis. Shipping costs are minimized and additional sample preparation is minimal. The procedure worked well, and surrogate recovery was in the expected range (30 to 130 percent). However the level of the organic compounds were too low to be seen by this method, using the small 40-mL sample. The small size taken was due partly to complications from suspended sediment encountered onsite. The precipitation of organic compounds in the presence of saltwater, sometimes used in conjunction with the bonded-phase column to increase recoveries, had already occurred in the water column. This procedure is not as effective on surface water as originally thought, and is not being considered for further study.

# DISTRIBUTION OF ORGANIC COMPOUNDS

## Organic Carbon

Dissolved organic carbon (DOC), fractionation, pH, and specific conductance studies were performed on water samples collected at selected sites along the river. (See figure A-1 for site location.) These results are shown in table D-3. Site 1 is situated upstream of the saltwater barrier and serves as a control site. This reach of the river is freshwater as evidenced by the low specific conductance of 65 µS/cm. Site 11, near the Gulf of Mexico, is seawater (32,800 µS/cm). Results in table D-3 show that the DOC decreases downstream from sites 1 to 6 (7.7 to 4.1 mg/L, milligrams per liter, respectively). The DOC fractionation results indicate that although the hydrophobic neutrals, and the total carbon in the hydrophilic fraction remain relatively constant throughout the riverine system, the hydrophobic-acid fraction decreases dramatically in going through the transition zone from freshwater to saltwater. This decrease suggests that humic acids and other hydrophobic acids such as long-chain fatty acids are precipitated or flocculated out of the water column, probably by the salting-out effect.

Table D-4 shows the carbon and moisture analyses of bottom material collected at selected sites along the lower Calcasieu River. Bottom material from site 1 was generally coarse sand with a low organic-carbon content (0.01 percent dry weight). Bottom material at sites 6, 7, and 9 had relatively higher content of organic carbon. Marsh plant fibers in bottom material from sites 6 and 9 are responsible for the high organic content. The high organic-carbon content at site 7 was caused by an oil phase derived from petroleum products.

## Biogenic Organic Compounds in Bottom Material

Several organic compounds were identified in bottom-material samples collected at various sampling sites along the lower Calcasieu River (table D-5). These organic compounds were upstream of the saltwater barrier where no industries are present (control site), as well as downstream near industrialized areas. Therefore, these compounds are probably of biogenic origin. Phenol (a priority pollutant) is probably derived from degradation of aromatic compounds such as the amino acid tyrosine. The origin of these compounds requires further investigation.

Several alkanes also were identified in bottom material. Alkanes present in bottom material from site 1, upstream of the saltwater barrier, are shown in figure D-2. Alkanes from $C_{15}$ to $C_{25}$ were identified. These organic compounds are probably derived from freshwater algae. Alkanes in bottom material from site 4 are shown in figure D-3. For comparative purposes, figure D-4 shows alkanes in bottom material from the Cowlitz River, Washington. Chromatograms D-3 and D-4 both show a bimodal distribution, maximizing at $C_{17}$ in the first mode and $C_{29}$ in the second. Alkanes in the first mode are probably derived from algae, and those in the second mode are derived from surface waxes of higher plants (Pereira and others, 1982). The pronounced odd-even predominance between $C_{19}$ and $C_{33}$ indicates that these compounds are of biogenic origin.

## Table D-3.--Dissolved organic-carbon fractionation of water samples at selected sites on the lower Calcasieu River, Louisiana, May 29-30, 1985

[Number in parentheses is the percentage of the total dissolved organic carbon in that fraction; dashes indicate hydrophilic fractions could not be determined because of high specific conductance and low total dissolved organic carbon value; ND, not detected; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 °C; partial percentages may not equal total percentages due to rounding]

| Site | Dissolved organic carbon (mg/L) | pH (units) | Specific conductance (µS/cm) | Hydrophobic fraction | | | | Hydrophilic fraction | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Total | Acids | Bases | Neutrals | Total | Acids | Bases | Neutrals |
| | | | | (milligrams carbon per liter) | | | | | | | |
| 1 | 7.7 | 7.1 | 65 | 4.2(54) | 3.1(40) | ND(-) | 1.1(14) | 3.5(46) | 2.6(34) | 0.4(6) | 0.5(6) |
| 4 | 6.4 | 7.6 | 6,690 | 2.8(45) | 1.7(27) | ND(-) | 1.1(17) | 3.5(55) | ------- | ------ | ------ |
| 7 | 6.2 | 8.2 | 16,100 | 2.5(41) | 1.1(18) | ND(-) | 1.4(23) | 3.7(59) | ------- | ------ | ------ |
| 11 | 4.1 | 8.2 | 32,800 | 1.8(44) | .5(12) | ND(-) | 1.3(33) | 2.3(56) | ------- | ------ | ------ |

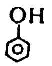
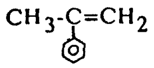
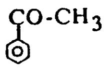
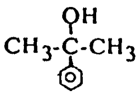
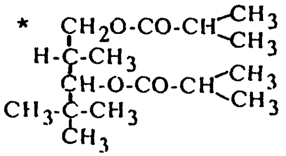
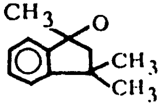
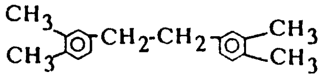
## Table D-4.--Carbon and moisture analyses of bottom material from the lower Calcasieu River, Louisiana

[<, actual value is known to be less than the value shown]

| Site | Physical appearance | Carbonate carbon | Total carbon | Organic carbon | Moisture |
|---|---|---|---|---|---|
| | | Percent | | | |
| 1 | Coarse sand.............. | 0.01 | 0.02 | 0.01 | 18.4 |
| 4 | Gray silt and sand....... | <.01 | .91 | .91 | 59.1 |
| 5 | Gray silt and sand....... | <.01 | .72 | .72 | 27.5 |
| 6 | Black clay and silt with much fibrous debris.... | <.01 | 2.43 | 2.43 | 74.1 |
| 7 | Black silt and clay oil.. | .04 | 1.78 | 1.74 | 72.7 |
| 8 | Gray silt and clay....... | .01 | .68 | .67 | 46.3 |
| 9 | Gray silt and clay and fibrous debris......... | .01 | 1.67 | 1.66 | 52.6 |
| 11 | Gray silt and clay with shells................. | .31 | .50 | .19 | 18.7 |

Table D-5.--Biogenic organic compounds in bottom material of the lower Calcasieu River, Louisiana

[All values are in micrograms per kilogram dry sediments; NQ, not quantitated, NA, not analyzed; dashes indicate not detected]

| Compound | Site numbers<br>1 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|
|  | 8,200 | 3,200 | 6,000 | 3,600 | NA | 2,500 | 4,100 | 3,000 | 2,100 |
|  | 300 | ----- | 1,200 | 2,200 | NA | 170 | NQ | 2,500 | ----- |
|  | 1,300 | 700 | 3,600 | 3,000 | NA | 490 | 800 | 5,700 | 5,100 |
|  | 390 | 1,500 | 1,600 | 330 | NA | ----- | 830 | 640 | ----- |
| *  | 12,000 | 2,600 | ----- | NQ | NA | 1,100 | ----- | 6,000 | ----- |
| *  | 14,000 | ----- | 1,700 | ----- | NA | ----- | ----- | 1,100 | ----- |
| *  | 5,800 | ----- | <25 | ----- | NA | ----- | ----- | ----- | ----- |

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* Tentative identification.

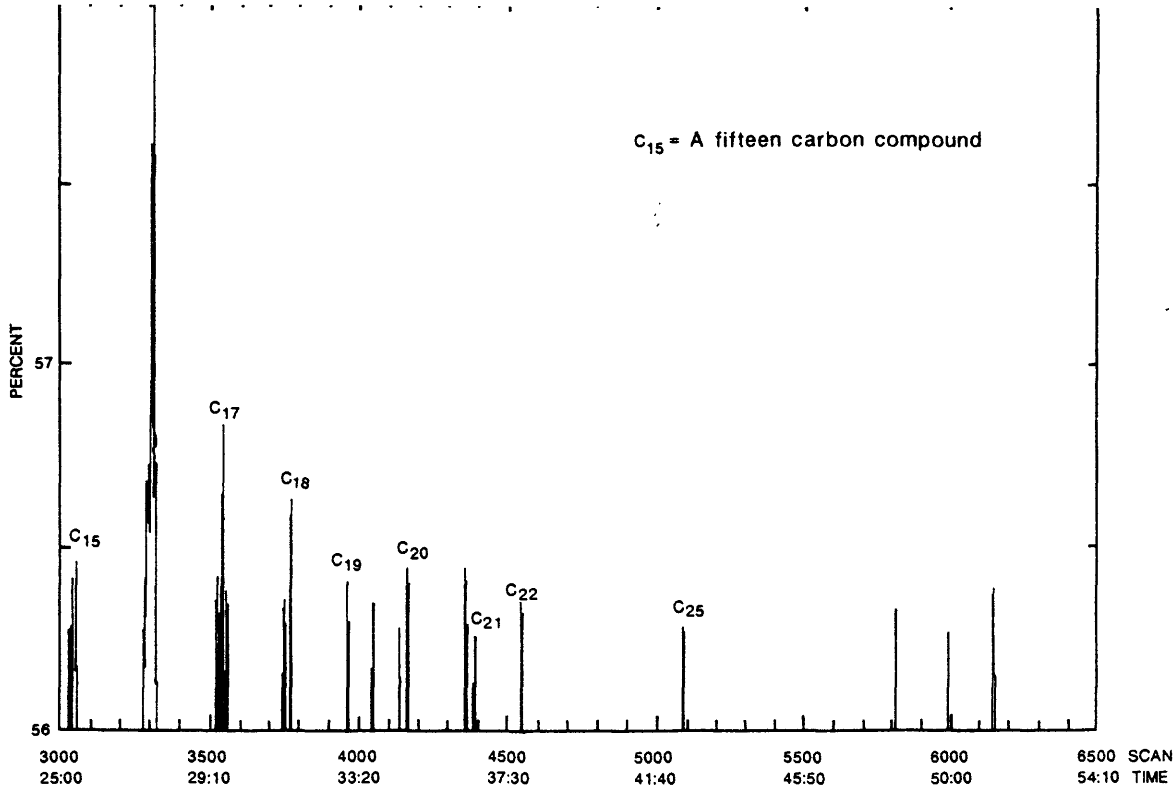

Figure D-2.--Mass chromatogram of alkanes in bottom material from the lower Calcasieu River at site 1, 6.2 kilometers east of Moss Bluff, Louisiana.

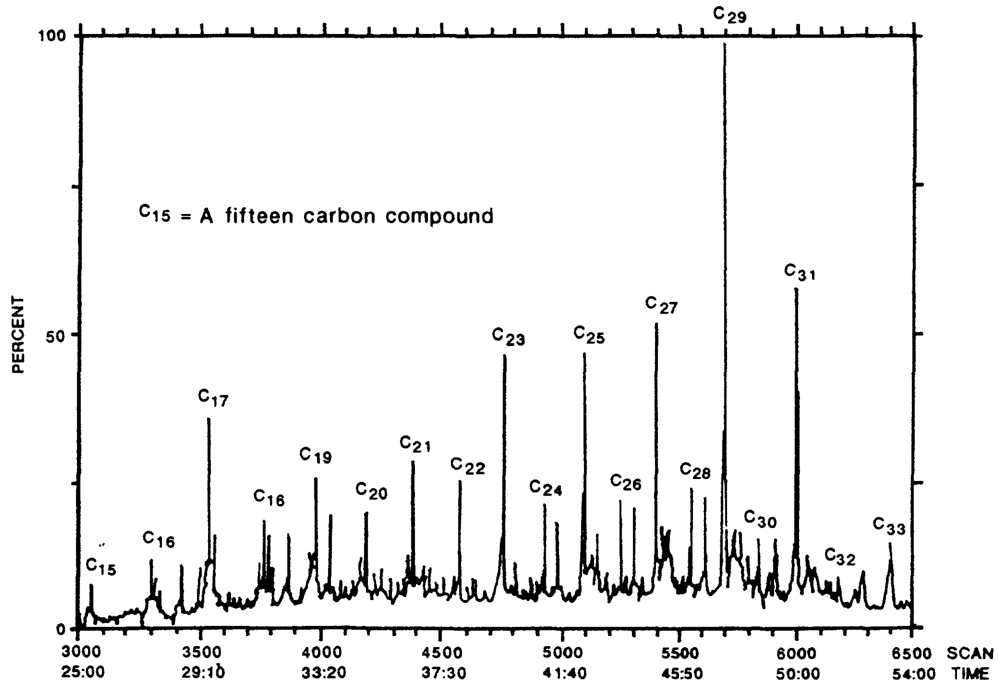

Figure D-3.--Reconstructed mass chromatogram characteristic of alkanes in bottom material from the lower Calcasieu River at site 4, Lake Charles, Louisiana.

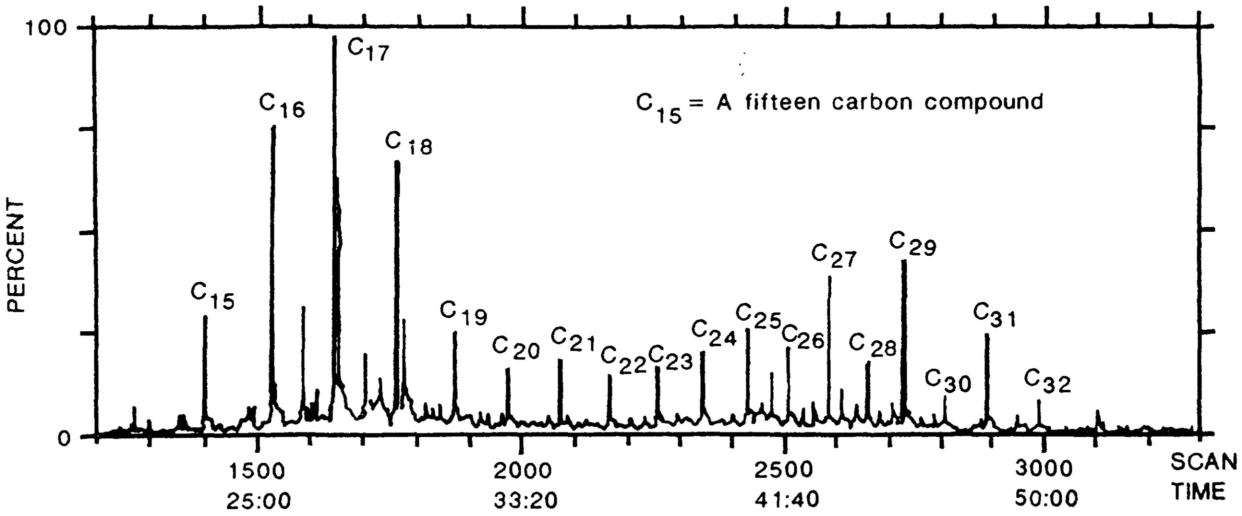

Figure D-4.--Reconstructed mass chromatogram characteristic of alkanes in bottom material from the Cowlitz River, Washington.

## Manmade Organic Compounds

Because of the complexity of the Calcasieu River and the numerous associated petrochemical and agrochemical industries, it was decided to focus the reconnaissance study on the Bayou d'Inde area (fig. A-1). Results indicated the presence of numerous haloarenes, a class of hydrophobic chlorinated compounds, and polycyclic aromatic hydrocarbons associated with bottom material in the Bayou d'Inde area, at sites 12 through 15.

One of the major industries near Bayou d'Inde manufactures perchloroethylene and trichloroethylene by chlorination processes (U.S. Environmental Protection Agency, 1975). By-products of this manufacturing process include hexachlorobenzene and hexachlorobutadiene. These chlorinated organic compounds, and several other haloarenes were identified in bottom material from Bayou d'Inde (sites 13-15). These compounds are shown in tables D-6 through D-8. Data in these tables indicate that the major classes of organic compounds identified include chlorobenzene isomers, chlorinated butadiene isomers, chlorinated styrene isomers, and miscellaneous compounds such as octachloronaphthalene, dichlorodiphenylether, and heptachlorocyclohexadiene.

Compounds identified in bottom material 0.4 km upstream of an industrial outfall (site 12) that enters Bayou d'Inde are shown in table D-9. These compounds are mainly alkylated polycyclic aromatic hydrocarbons, indicating they are probably derived from petroleum products (Steinheimer and others, 1981).

Table D-6.--Concentrations of selected chlorinated benzene compounds in bottom material from Bayou d'Inde, Louisiana

[In milligrams per kilogram dry bottom material; ND, not detected]

| Compound | 0.4 Kilometers upstream from industrial outfall site 12 | Industrial outfall site 13 | 0.4 Kilometers downstream from industrial outfall site 14 | 0.8 Kilometers downstream from industrial outfall site 15 |
|---|---|---|---|---|
| Chlorobenzene | ND | ND | 1.7 | 0.04 |
| 1,3-Dichlorobenzene | 3.4 | 5.6 | 52.3 | 12.4 |
| 1,4-Dichlorobenzene | 1.7 | 3.9 | 38.6 | 4.5 |
| 1,2-Dichlorobenzene | ND | .3 | .2 | ND |
| 1,3,5-Trichlorobenzene | ND | 6.8 | 5.5 | 1.1 |
| 1,2,4-Trichlorobenzene | ND | 11.9 | 8.4 | 1.2 |
| 1,2,3-Trichlorobenzene | ND | .6 | ND | ND |
| 1,2,3,5-Tetrachlorobenzene | ND | 4.6 | 1.9 | .5 |
| 1,2,4,5-Tetrachlorobenzene | ND | 1.9 | .5 | ND |
| 1,2,3,4-Tetrachlorobenzene | ND | 1.6 | .4 | ND |
| Pentachlorobenzene | ND | 23.2 | 16.3 | 3.7 |
| Hexachlorobenzene | 2.5 | 279 | 103 | 58.8 |

Table D-7.--Concentrations of selected chlorinated butadiene compounds in bottom material from Bayou d'Inde, Louisiana

[In milligrams per kilogram dry bottom material; ND, not detected]

| Compound[1] | Industrial outfall site 13 | 0.4 kilometers downstream from industrial outfall site 14 | 0.8 kilometers downstream from industrial outfall site 15 |
|---|---|---|---|
| Dichlorobutadiene isomer | 0.09 | 0.7 | ND |
| Trichlorobutadiene isomer | .12 | .11 | ND |
| Trichlorobutadiene isomer | 1.0 | 2.1 | 0.11 |
| Trichlorobutadiene isomer | .35 | 1.2 | ND |
| Trichlorobutadiene isomer | 3.7 | 8.3 | .53 |
| Tetrachlorobutadiene isomer | .8 | .47 | ND |
| Tetrachlorobutadiene isomer | .26 | ND | ND |
| Tetrachlorobutadiene isomer | .12 | ND | ND |
| Tetrachlorobutadiene isomer | .24 | ND | ND |
| Pentachlorobutadiene | 4.8 | 1.2 | ND |
| Hexachlorobutadiene | 16.0 | 20.0 | 3.0 |

[1] The selected chlorinated organic compounds were not detected at 0.4 kilometers upstream from the industrial outfall.

### Table D-8.--Concentrations of selected chlorinated organic compounds in bottom material from Bayou d'Inde, Louisiana

[In milligrams per kilogram dry bottom material; ND, not detected]

| Compound[1] | Industrial outfall site 13 | 0.4 kilometers downstream from industrial outfall site 14 | 0.8 kilometers downstream from industrial outfall site 15 |
|---|---|---|---|
| Heptachlorocyclohexadiene | 2.3 | 13.0 | 4.0 |
| Dichlorodiphenylether | 1.9 | ND | ND |
| Heptachlorostyrene | .68 | 1.68 | ND |
| Octachlorostyrene | 1.5 | 2.6 | 3.7 |
| Octachloronaphthalene | 1.6 | 1.9 | .84 |

[1] The selected organic compounds were not detected at site 12, 0.4 kilometers upstream from the industrial outfall.

### Table D-9.--Concentrations of polycyclic-aromatic compounds in bottom material from Bayou d'Inde, Louisiana

[Site 12, 0.4 kilometers upstream from industrial outfall. Concentration, in micrograms per kilogram; ND, not detected]

| Compound | Concentration | Compound | Concentration |
|---|---|---|---|
| Naphthalene,2-methyl- | 360 | Phenanthrene,dimethyl- | 2,300 |
| Biphenyl | 1,100 | Fluoranthene | 640 |
| Biphenylether | 8,700 | Pyrene | 8,300 |
| Naphthalene,1,3-dimethyl- | 320 | Phenanthrene,trimethyl- | 1,000 |
| Naphthalene,2,3-dimethyl- | 560 | Do | 1,100 |
| Naphthalene,trimethyl isomer | 3,500 | Do | 1,900 |
| Do | 180 | Pyrene,methyl- | 1,700 |
| Do | 690 | 11H-Benzo [a] fluorene | 2,900 |
| Do | 700 | Benzo [b] fluorene | 4,300 |
| Naphthalene,2,3,5-trimethyl- | 600 | Pyrene,methyl- | 1,600 |
| Naphthalene,2-methyl-1-propyl- | 400 | Do. | 740 |
| Naphthalene,1-(1,1-dimethylethyl)- | 1,000 | Pyrene,dimethyl- | 1,200 |
| 9H-Xanthene | 1,300 | Terphenyl | 190 |
| Naphthalene,1-methyl-7(1-methylethyl). | 580 | Benzo [b] naphthol [2,1-D] thiophene | 900 |
| 9H-Fluorene,3-methyl- | 660 | Triphenylene | 6,700 |
| 1,1'-Biphenyl,2,3'-dimethyl | 460 | Chrysene | ND |
| Phenanthrene | 4,200 | Benzonaphthothiophene,methyl- | 690 |
| Dibenzothiophene,4-methyl- | 560 | Benz [a] anthracene,methyl- | 1,500 |
| Phenanthrene,4-methyl- | 4,600 | Benzo [b] fluoranthene | ND |
| Phenanthrene,methyl- | 5,600 | Benzo [k] fluoranthene | 1,700 |
| Naphthothiophene,dimethyl | 1,600 | Benzo [e] pyrene | 5,100 |
| Naphthalene, 2-phenyl | 2,300 | Benzo [a] pyrene | 1,000 |
| Phenanthrene,dimethyl- | 2,100 | Perylene | 1,300 |
| Do | 5,000 | Benzo [g,h,i] perylene | 600 |

## Distribution of Haloarene Isomers in Bottom Material

Haloarenes identified in bottom material in the Bayou d'Inde area, are organic compounds that have relatively high log-K (octanol/water) values. Log-K values are experimentally determined by partitioning the compound of interest between octanol and distilled water. Octanol is used as a model to study the partitioning of organic compounds between water and an organic phase, such as lipid tissue of stream biota or organic matter associated with suspended sediment and bottom material. However, because of the high salinity and conductivity of water in the study area, the water solubility of the haloarenes is decreased, and their partition coefficients are significantly increased. Therefore, the bottom material in the Bayou d'Inde area serves as a major sink for the haloarenes. Partition coefficients of selected haloarenes were experimentally determined in octanol/distilled water and in octanol/Bayou d'Inde water. These results are shown in table D-10. The data in table D-10 indicate that partition coefficients in the octanol/Bayou d'Inde water system are generally 20 percent higher than in the octanol/water system. The data suggest that the salting-out effect may play a significant role in the fate and transport of haloarenes in the Calcasieu River.

Differences in log-K values of haloarene isomers suggested that these compounds may be differentially sorbed to suspended sediments and bottom material. Differential sorption to sediments during transport in the lower Calcasieu River would affect the distribution of haloarene isomers, resulting in a chromatographic effect. To investigate the chromatographic effect, samples of bottom material were collected in Bayou d'Inde near an industrial outfall (site 13) and at two other sites, 0.4 km (site 14) and 0.8 km (site 15) downstream from the outfall. Hexachlorobenzene is generally considered to be a relatively stable and refractory compound in aquatic systems (Moore and Ramamoorthy, 1984). Because of its high log-K value, hexachlorobenzene is

Table D-10.--Partition coefficients of selected haloarene isomers

[$K_{ow}'$ = octanol/Bayou d'Inde water partition coefficient; $K_{ow}$ = octanol/distilled water partition coefficient]

| Compound | Log $K_{ow}'$ | Log $K_{ow}$ | $\frac{K_{ow}'}{K_{ow}}$ |
|---|---|---|---|
| Chlorobenzene | 2.92 | 2.84 | 1.20 |
| 1,3-Dichlorobenzene | 3.58 | 3.50 | 1.20 |
| 1,4-Dichlorobenzene | 3.56 | 3.47 | 1.23 |
| 1,2-Dichlorobenzene | 3.56 | 3.49 | 1.17 |
| 1,3,5-Trichlorobenzene | 4.40 | 4.31 | 1.23 |
| 1,2,4-Trichlorobenzene | 4.09 | 4.02 | 1.18 |
| 1,2,3-Trichlorobenzene | 4.20 | 4.14 | 1.15 |
| 1,2,3,5-Tetrachlorobenzene | 4.67 | 4.59 | 1.20 |
| 1,2,4,5-Tetrachlorobenzene | 4.71 | 4.70 | 1.02 |
| 1,2,3,4-Tetrachlorobenzene | 4.67 | 4.60 | 1.18 |
| Pentachlorobenzene | 5.27 | 5.20 | 1.18 |
| Hexachlorobenzene | 5.59 | 5.50 | 1.23 |
| Hexachloro-1,3-butadiene | 5.17 | 4.90 | 1.86 |

found mainly associated with the sediment phase. Therefore, it serves as a useful manmade marker compound in suspended sediments and bottom material. The ratio of chlorinated benzene isomers to hexachlorobenzene, as a function of distance from the outfall, is shown in figure D-5. These preliminary results, with one exception, show that the lesser chlorinated benzenes have been transported greater distances relative to hexachlorobenzene and indicate a chromatographic effect. Further work, in progress, will enhance our understanding of the mechanism of sorption and transport of haloarenes in sediments.

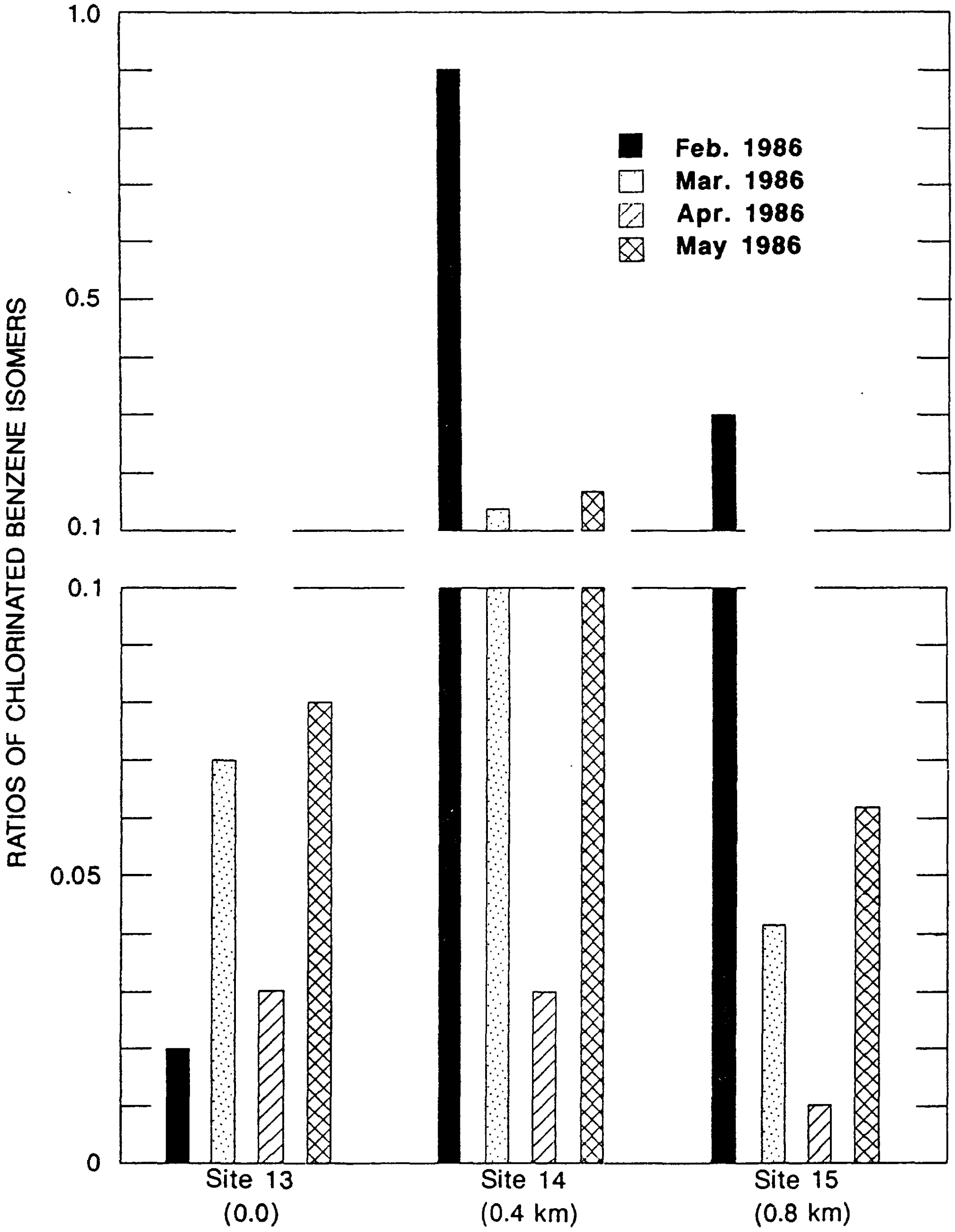

Figure D-5.--Ratios of haloarene isomers to hexachlorobenzene as a function of distance from an industrial outfall leading into Bayou d'Inde, Louisiana.

## SUMMARY

One class of organic compounds identified at high levels in bottom material was the haloarenes, a class of chlorinated aromatic compounds that are toxic to aquatic organisms. In the lower Calcasieu River the haloarenes are precipitated. Therefore, the bottom material in the lower Calcasieu River probably serves as a major sink for these compounds.

Water and bottom-material samples collected from the lower Calcasieu River were analyzed to determine the presence of different classes of organic compounds present in the system. Results from bottom-material analyses indicated that freeze drying bottom material prior to extraction with methylene chloride resulted in more efficient extraction of organic compounds than conventional wet-extraction techniques.

Phenols, 1,3-dichlorobenzene, 1,2-dichlorobenzene, hexachlorobutadiene, hexachlorobenzene, and phenanthrene were found in part per million range of concentrations in bottom-material samples collected from the lower Calcasieu River and its tributary Bayou d'Inde.

Partition coefficients of selected haloarenes were experimentally determined between octanol/Bayou d'Inde water and octanol/distilled water. Results showed partition coefficients in octanol/Bayou d'Inde water were generally 20 percent higher than in octanol/distilled water, indicating that the presence of saltwater affects the fate and transport of haloarenes in the lower Calcasieu River.

Results also showed that the lesser chlorinated benzenes have been transported to greater distances relative to hexachlorobenzene, indicating a chromatographic effect in lower Calcasieu River bottom material due to differential sorption to sediments caused by different log-K values of haloarene isomers.

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