

The State of Texas Clean Rivers Program

**Targeted Monitoring in the Cypress Basin:
Study of Contaminants at Caddo Lake Associated with
the Longhorn Army Ammunition Plant**

FINAL REPORT

prepared for
**Northeast Texas Municipal Water District
Hughes Springs, Texas**

for submission to

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1.0 Introduction

Caddo Lake, State of Texas Segment 0401, is currently on the Clean Water Act 303(d) list for not meeting designated use due to contamination exceedences from dissolved mercury and zinc in water, and for exceedances of pH and temperature criteria (Texas Natural Resource Conservation Commission, 1998). In November, 1995, the Texas Department of Health issued a health advisory due to elevated levels of mercury in fish tissue.

Longhorn Army Ammunition Plant (LHAAP) is located on the southwestern shore of Caddo Lake near Uncertain, Texas (Figure 1). The plant is owned by the federal government and has been in operation since 1942 as a munitions factory. The plant was placed on the National Priorities List as a superfund site in 1990 due to significant contamination by a number of organic contaminants (TDH, 1999) and monitoring of these contaminants and various clean-up activities at the plant has been on-going for the past 4 years. Monitoring reports show that significant levels of these contaminants have been found in LHAAP soils, as well as the sediment and water of the four natural drainages that run through the plant and empty into Caddo Lake (USACE, 1999). Because of stakeholder concern that these contaminants could be entering the lake via the drainages and through surface run-off following storm events, the Cypress Basin Clean Rivers Program Steering Committee authorized a targeted sampling plan to conduct preliminary surface water and sediment sampling to look for these contaminants. The primary objective of this study is to provide a preliminary assessment of the presence and extent of specific chemical contamination of Caddo Lake waters and sediment adjacent to the Longhorn Army Ammunition Plant. This study does not address the mercury, zinc, pH, or temperature issues.

The Caddo Lake Organic Contaminant Study took place through a cooperative program directed by Northeast Texas Municipal Water District (NETMWD) as a part of the Targeted Monitoring tasks in the Cypress Basin Clean Rivers Program. Program participants assisting NETMWD in planning, data collection, analysis, and reporting include Paul Price Associates, Inc. (PPA), Texas Natural Resource Conservation Commission (TNRCC), the Caddo Lake Institute (CLI) and its affiliates, and Steering Committee members.

1.1 Project Description

The Cypress Basin, located in northeast Texas, is a sub-basin of the Red River Basin and is drained by Big Cypress Bayou, which flows into Caddo Lake (Figure 1). Below the Lake O' the Pines, Big Cypress Bayou joins with Black Cypress Bayou and Little Cypress Bayou before flowing into Caddo Lake.

Figure 1

The climate of east Texas is generally subtropical with hot, humid summers and relatively mild winters. Temperatures typically average about 81°F in the summer. Winter freezes can be expected each year, but temperatures as low as zero Fahrenheit are rare (Golden et al., 1993). Annual rainfall averages about 50 inches with about 50 percent falling between April and September.

Caddo Lake is located within the Pineywoods ecoregion of Texas with a topography of irregular, rolling hills dissected by broad, flat floodplains and terraces (Cloud, 1995). At LHAAP, the elevation varies from Caddo Lake at 168.5 feet to 335 feet mean sea level. (USGS, 1978). Soils in east Texas are mostly light-colored to dark gray sands or sandy loams with clays common in the floodplains (Golden et al., 1993). The pine-oak forest characteristic of this region is an ecotone between the eastern pine forests and the oak-hickory forest of the post oak woodlands to the west. Although post oak and blackjack oak constitute the dominant climax overstory vegetation, loblolly and shortleaf pine are generally common. The bottomland forest is the most mesic habitat in eastern Texas, where the dense vegetation is generally comprised of water oak, willow oak, sweet gum, black gum, and river birch. A vegetational analysis using LANDSAT images of LHAAP showed that 66 percent of the 8,500 acres is mixed hardwood-pine, hardwood, and pine forests, while 23 percent is swamp dominated by extensive baldcypress stands (Shellman and Darville, 1995). Of special interest at LHAAP is about 1100 acres of bottomland hardwood forest along Harrison Bayou, which represents one of the few old-growth bottomland hardwood forests left in Texas (Burkett, 1994).

Geologically, Eocene rocks are found at the surface, but the lake is underlain by southeasterly dipping sand, clay, glauconite, and lignite of the Wilcox and Claiborne Groups of Tertiary age (Golden et al., 1993). Ground water resources include the Carrizo-Wilcox Aquifer and Queen City Aquifer (Golden et al., 1993). The Carrizo-Wilcox Aquifer occurs over the entire basin and consists of the Wilcox Group and the overlying Carrizo Formation of the Claiborne Group. The aquifer is made up of fine- to medium-grained sand and sandstone interbedded with clay and silt, and minor amounts of lignite in the Wilcox Group. Yields of high capacity wells average 200 gpm, but locally, wells produce up to 900 gpm.

The Queen City Aquifer occurs in a wide band across the central part of the Cypress Basin and consists of interbedded fine- to medium-grained sand, clay, glauconite, and lignite. Total thickness ranges up to about 500 feet. Well yields are generally low, but locally, wells produce as much as 200 gpm.

1.2 Station Descriptions and Sampling Dates

Four natural drainages are located on the LHAAP, two of which have been identified by the USACE as being significantly contaminated and are studied in this project. Harrison Bayou, the largest of the four drainages, runs in a northerly direction across the eastern edge of LHAAP and empties into Harrison Bayou Bay of Caddo Lake. Goose Prairie Creek runs in a northeasterly direction along the western portion of LHAAP and empties

into the southwestern corner of Goose Prairie Bay of Caddo Lake. This creek drains through much of what is referred to as the production area of the LHAAP.

Contamination monitoring has been conducted by the USACE at various locations on LHAAP and has included soil, groundwater, surface water, and stream sediment sampling. Samples have been taken between and following storm events, which have been defined by Bud Jones (formerly of TNRCC), as storms where precipitation exceeded 0.1 inches at LHAAP and which had observable runoff. Documentation provided to the Technical Review Committee of LHAAP reveals that organic contaminants have been detected and quantified in either stream water and/or stream sediments.

During the summer and fall of 1998, eight surface water and four sediment samples were taken at four stations in Caddo Lake (Figure 2). Two stations were located at Harrison Bayou, one at the mouth of the bayou and one located approximately 100m in a northerly direction into the lake. The other two stations were located at the mouth of Goose Prairie Creek and approximately 100m in an easterly direction into Goose Prairie Bay. Following discussion with Corps personnel and a walk down Goose Prairie Creek to the lake, it was discovered that there are at least two major sites where creek water enters the lake. Therefore, during the second sampling event, the Goose Prairie samples were taken at locations approximately 100m to the east of the original site.

Surface water samples were taken on July 15, 1998 and on November 6, 1998 less than 24 hours following a light rain (<0.1inch) at LHAAP. Sediment samples were taken at all four sites on November 6, 1998.

2.0 Materials and Methods

Sampling methods used in collecting the study data were consistent with the procedures outlined in the Surface Water Quality Monitoring Procedures Manual (TNRCC, 1997) and the Cypress Basin Quality Assurance Project Plan for Fiscal Year 1998-1999.

Parameters measured or sampled for are listed in Table 1. Field parameters were taken at 0.3m with a pre-calibrated YSI multiparameter instrument. Surface water samples were taken by grab sampling at a 0.3m depth. Water sample containers used for the analysis of volatile organic chemicals were VOA glass vials with Teflon-lined lids. The containers were filled to overflowing and then capped without trapping air bubbles. Sediment samples were taken using a pre-cleaned Ekman dredge. A minimum of three dredge samples were taken at each site and composited in a pre-cleaned plastic container. Samples were placed in quart, glass containers with Teflon-lined lids. The jars were filled to the top attempting to eliminate all air from the jars. All samples were immediately placed on a ice and transported to Ana-Lab Corporation of Kilgore, Texas, for analysis. TNRCC-approved methods for all organic contaminant parameters were performed by the laboratory. A listing of the EPA methods used is shown in Table 2. A trip blank provided by Ana-Lab was used each sampling day.

Figure 2

Table 1.

Caddo Lake/LHAAP Organic Contaminant Study
Field and Laboratory Parameters.

Field Parameters	Storet Code
Water Temperature (°C)	00010
Dissolved Oxygen (mg/L)	00300
pH (s.u.)	00400
Specific Conductance (<i>umhos/cm</i>)	00094
Secchi Depth (m)	00078
Organic Contaminants in Water	
Acetone	81552
Carbon Disulfide	77041
trans-1,2 Dichloroethene	34546
1,1-Dichloroethene (1,1 Dichloroethylene)	34501
Methyl Ethyl Ketone 2-Butanone	81595
Methylene Chloride	34423
Trichloroethene (Trichloroethylene)	39180
Vinyl Chloride	39175
Ammonium Perchlorate	61209
Organic Contaminants in Sediments	
Acetone	75059
Carbon Disulfide	78544
trans-1,2 Dichloroethene	34549
1,1-Dichloroethene (1,1 Dichloroethylene)	34504
Methyl Ethyl Ketone 2-Butanone	75078
Methylene Chloride	34426
Trichloroethene (Trichloroethylene)	34487
Vinyl Chloride	34495
Ammonium Perchlorate	61737

Table 2.

EPA Laboratory Methods Used for Contaminant Analysis and Minimum Analytical Limits Reported by Ana-Lab.

Contaminant	EPA Method	Water Sample MAL¹ (µg/L)	Sediment Sample MAL¹ (µg/L)
Acetone	8260B	50.0	2500
Carbon Disulfide	8260B	5.00	2500
trans-1,2-Dichloroethene	8260B	5.00	250
1,1-Dichloroethylene	8260B	5.00	250
Methyl Ethyl Ketone (2-Butanone)	8260B	50.0	2500
Methylene Chloride	8260B	5.00	10
Trichloroethylene	8260B	5.00	250
Vinyl Chloride	8260B	10.0	500
Ammonium Perchlorate	Ion chromatography	40/10	100

1. MAL = Minimum Analytical Level, which according to Ana-Lab Corporation takes into account the instrument detection limit, method detection limit, and practical quantification limit, and any dilutions and/or concentrations performed during sample preparation.

3.0 Results

On the first monitoring day, Caddo Lake was experiencing typical summer-like conditions with very low water levels. The two creeks had no visible flow. The depth of Harrison Bayou at its mouth was measured as 0.23m, while at the mouth of Goose Prairie Creek was only large, isolated pools with a depths of about 0.20m. The Caddo Lake level on that day was 167.86 feet msl which is about one foot below spillway level. During the November monitoring event, the lake was at 168.83 feet msl, which is approximately spillway level. On that day, a small current was detected at the mouth of Harrison Bayou, but no current was found at the mouth of Goose Prairie Creek.

Field parameter results from both monitoring days is shown in Table 3. Temperature and dissolved oxygen values are typical for Caddo Lake during the summer and fall months. Some of the pH values are lower than is normal for Caddo Lake, which typically has pH values 5.8 – 7.0. Specific conductance during the July sampling date was three to four times higher than is normal for Caddo Lake. This is probably due to the extremely low water levels that existed during that sampling period.

The results for the laboratory analysis of water and sediment samples are shown in Tables 4 and 5. All water and sediment contaminant results for both monitoring events were below detection limits. Trip blanks were used during each sampling period, and laboratory analysis resulted in no detection of any of the contaminants tested. The MAL for ammonium perchlorate in water was 40 µg/L for the July samples and 10 µg/L for the November samples.

4.0 Discussion

Previous sampling data from the USACE of surface water and stream sediment on the LHAAP site has shown the presence of ammonium perchlorate and various volatile organic contaminants (USACE, 1999). The USACE continues to find some of these chemicals in the soil, groundwater and surface water on LHAAP as recent as 28 April 1999 (USACE, 1999). Currently, contaminated groundwater is being pumped from approximately 25 feet below surface, treated to remove volatile solvents, and then the effluent is released into Harrison Bayou to attempt to reduce the levels of these compounds from entering into Caddo Lake. Data obtained during our study, however, show that these contaminants were not evident in concentrations above detection limits in the water column or sediments at the four selected stations adjacent to LHAAP during the summer and fall of 1998.

As a part of recent USACE studies of the LHAAP contamination, surface water samples were sent to two different labs for analysis. Results from the two laboratories showed ammonium perchlorate concentrations of 1,410 and 1,500 µg/L, respectively, in Harrison Bayou at the treated groundwater discharge outfall, and concentrations of 38 and 75 µg/L, respectively, at a site within one hundred meters of Caddo Lake but still within the LHAAP boundaries (USACE, 1999). In addition to ammonium perchlorate, concentrations of about 2 µg/L of trichloroethylene and cis-1,2-dichloroethene were

Table 3.

Field Parameters at the Four Monitoring Stations in Caddo Lake
Adjacent to LHAAP.

Sampling Site	Sampling Date	Temperature (°C)	Dissolved Oxygen (mg/l)	pH (S.U.)	Specific Conductance (μ mhos/cm)	Secchi Depth (m)
Goose Prairie Bay	7/15/98	34.5	0.2	5.9	289	> 0.18
Goose Prairie Creek	7/15/98	33.0	0.0	5.8	380	> 0.10
Harrison Bayou	7/15/98	28.5	0.0	6.5	402	> 0.23
Harrison Bayou Bay	7/15/98	31.4	4.7	6.7	184	> 0.36
Goose Prairie Bay	11/6/98	11.9	3.4	5.4	90	0.35
Goose Prairie Creek	11/6/98	10.5	1.9	4.9	80	0.36
Harrison Bayou	11/6/98	12.9	4.5	6.0	125	0.60
Harrison Bayou Bay	11/6/98	13.0	5.8	5.9	115	0.61

Table 4.

Laboratory Results for Surface Water Samples Taken at all Four Stations on Caddo Lake
Adjacent to LHAAP on 2 July 1998 and 6 November 1998.

Parameter	Concentrations in Water (μ g/L)		MAL ¹ (μ g/L)
	6/2/98	11/6/98	
Acetone	ND	ND	50.0
Carbon Disulfide	ND	ND	50.0
trans-1,2-Dichloroethene	ND	ND	5.0
1,1-Dichloroethylene	ND	ND	5.0
Methyl Ethyl Ketone (Butanone)	ND	ND	50.0
Methylene Chloride	ND	ND	10.0
Trichloroethylene	ND	ND	5.0
Vinyl Chloride	ND	ND	10.0
Ammonium Perchlorate	ND	ND	40.0/10.0

1. MAL = Minimum Analytical Level, which according to Ana-Lab Corporation takes into account the instrument detection limit, method detection limit, and practical quantification limit, and any dilutions and/or concentrations performed during sample preparation.

2. ND = below detection limit

Table 5.

Laboratory Results for Sediment Samples Taken at all Four Stations on Caddo Lake
Adjacent to LHAAP on 6 November 1998.

Parameter	Result ($\mu\text{g}/\text{kg}$)	MAL ¹ ($\mu\text{g}/\text{kg}$)
Acetone	ND ²	2500
Carbon Disulfide	ND	2500
trans-1,2-Dichloroethene	ND	250
1,1-Dichloroethylene	ND	250
Methyl Ethyl Ketone (Butanone)	ND	2500
Methylene Chloride	ND	500
Trichloroethylene	ND	2500
Vinyl Chloride	ND	500
Ammonium Perchlorate	ND	100

1. MAL = Minimum analytical limit. According to Ana-Lab, the MAL takes into account the Instrument Detection Limit (IDL), Method Detection Limit (MDL), and Practical Quantitation Limit (PQL), and any dilutions and/or concentrations performed during sample preparation (EQL).

2. ND = below detection limit

found on 24 March 1999 in Harrison Bayou surface water near the treated groundwater outfall when sampled during the USACE monitoring (USACE, 1999). Non-detect concentrations of both chemicals were found at four other sites downstream from this site. Therefore, at this point in time it appears that little, if any, ammonium perchlorate or any of the other volatile organic chemicals tested for within this study are ending up in Caddo Lake. Perhaps another round of coordinated sampling with the USACE or other agency should be considered by the Clean Rivers Program during Fiscal Year 2000. TNRCC is currently considering the possibility of more intensive sampling for ammonium perchlorate within Caddo Lake to determine the existence of this compound within Caddo Lake near the LHAAP.

5.0 Literature Cited

- Burkett, V. 1994. Personal Communication. National Wetlands Research Center: Lafayette, Louisiana.
- Cloud, T.J. 1995. A Characterization of Habitats and Fish and Wildlife Management Opportunities at Cypress Bayou Basin, Texas and Louisiana. U.S. Fish and Wildlife Service: Arlington, Texas.
- Darville, R.G. and D.K. Shellman, Jr. 1995. Initial Species Inventory for Longhorn Army Ammunition Plant, Karnack, Texas. Completion Report for Contract DACA56-94-M-0985 for the Tulsa District, Corps of Engineers. Caddo Lake Institute.
- Golden, M.L., A.C. Peer and S.E. Brown, Jr. 1994. Soil Survey of Harrison County, Texas. U.S. Department of Agriculture, Soil Conservation Service.
- Texas Department of Health. 1999. Public Health Assessment: Longhorn Army Ammunition Plant, Harrison County, Texas. CERCLIS No. TX 6213820529. Texas Department of Health: Austin, Texas.
- Texas Natural Resource Conservation Commission. 1997. Surface Water Quality Monitoring Procedures Manual. TNRCC: Austin, Texas.
- Texas Natural Resource Conservation Commission. 1998. State of Texas 1998 Clean Water Act Section 303(d) List and Schedule for Development of Total Maximum Daily Loads. TNRCC, publication SFR-58. Texas Natural Resource Conservation Commission: Austin, Texas.
- United States Army Corps of Engineers. 1999. Report to the Technical Review Committee of the Longhorn Army Ammunition Plant, 2 June 1999. United States Army Corps of Engineers: Tulsa District
- United States Geological Survey. 1978. Karnack, Texas 7.5 Minute Series Topographic Map. USGS.