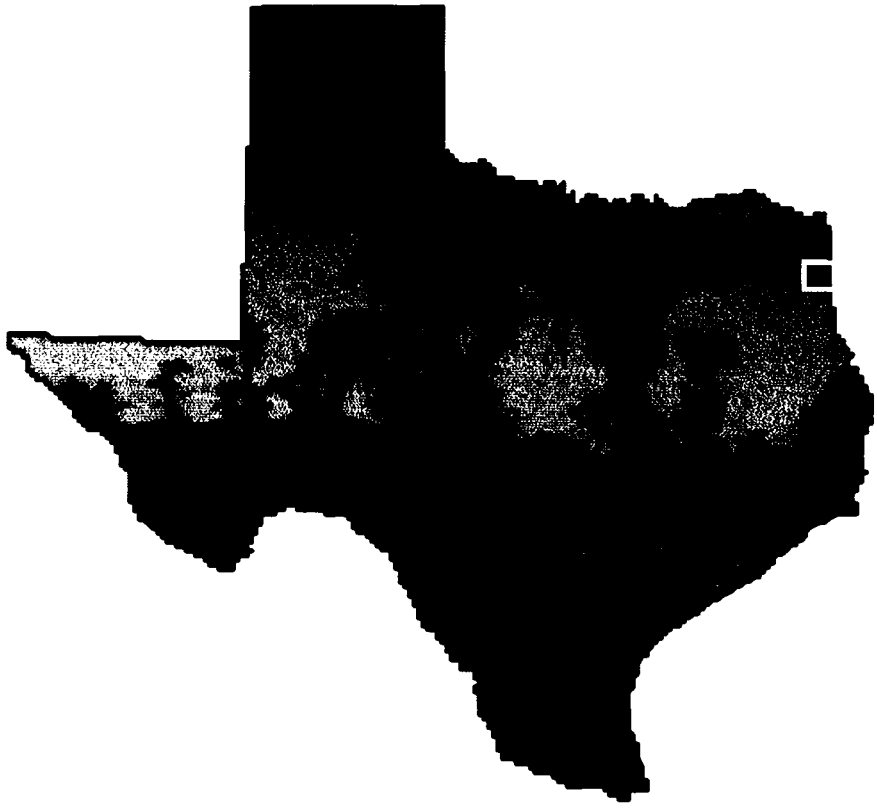
Investigation of Contaminants in Fish Tissue

Caddo Lake Biological Sampling and Risk Assessment for Longhorn Army Ammunition Depot



Texas Commission on Environmental Quality
Region 5

In cooperation with the U.S. Environmental Protection Agency
Region 6, Superfund Division

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The Texas Commission on Environmental Quality, Region 5, would like to thank the following for their help on this project:

- **US Environmental Protection Agency, Region 6, Superfund Division**
- **US Fish and Wildlife Service, Arlington and Karnack, TX**
- **Texas Parks and Wildlife Department, Marshall and Tyler, TX**
- **TALEM, Inc., Fort Worth, TX**

Abstract

Fish tissue (edible fillets and whole fish) from three areas of Caddo Lake, TX were collected from 23 February 2004 through 04 March 2004. A total of 213 fish were analyzed for metals, pesticides, polychlorinated biphenyls (PCBs), dioxins/furans, perchlorate, and semivolatile and volatile organic compounds to describe contaminant levels in edible tissue and whole fish.. Two sites, Goose Prairie Bayou and Harrison Bayou, receive drainage from a closed US Army munitions facility, Longhorn Army Ammunition Plant. The third site, Clinton Lake, is upstream of the facility and was used as a control.

Metals results indicated that mercury was present in edible tissue fillets from all sites and at elevated levels. Elevated results for mercury were expected given the current health advisory for mercury issued for Caddo Lake. Other metals (zinc, magnesium, iron, and manganese) were present in fillets and whole fish but at normal and expected levels.

Dioxins were present in all whole fish samples. Dioxin species detected included octachlorodibenzo-p-dioxin and 1,2,3,4,6,7,8-heptochlorodibenzo-p-dioxin. Total concentrations for hexachlorodibenzo-p-dioxins and tetrachlorodibenzofurans were also above detection limits and found solely in fish from Goose Prairie Bayou. Edible tissue fillets were free of dioxins with the exception of two fillets from the control site, Clinton Lake, in which octachlorodibenzo-p-dioxin was detected at 5.4 and 7.9 pg/g.

Pesticides, PCBs, and perchlorate were not detected in either edible tissue fillets or whole fish samples.

Semivolatiles were rarely detected and included cresols and phthalates. Cresol levels, found in whole fish only, were detected in low levels (0.45-1.8 mg/kg) and more commonly detected in samples from Clinton Lake. Phthalates were present in three fillets, two from Goose Priairie Bayou and one from Harrison Bayou.

One volatile compound, methyl ethyl ketone (2-butanone), was detected in whole fish samples from Clinton Lake.

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1.0 Introduction

This report, prepared by the Region 5 Office of the Texas Commission on Environmental Quality (TCEQ) for the U.S. Environmental Protection Agency (USEPA), Region 6, describes the procedures and results used to characterize contaminants in the tissues of fish found in Caddo Lake adjacent to the Longhorn Army Ammunition Plant (LHAAP) near Karnack, Texas.

213 fish were collected from 23 February to 04 March, 2004 at three sites within the lake. Two sites were adjacent to LHAAP with the third site located upstream of the facility and used as a control. Collected fish from each site were weighed, measured, filleted with skin on, and analyzed for a suite of chemicals and properties that included metals, semi-volatile organic compounds (SVOCs), volatile organic compounds (VOCs), pesticides, polychlorinated biphenyls (PCBs), dioxins/furans, perchlorate, and percent lipids. Analytes of concern were identified from an evaluation of sediment samples collected in Caddo Lake near LHAAP which indicated that there may be unacceptable risks from ingestion of fish from the area (Jacobs 2002) The modeling study, based on the sediment contamination levels, indicated that these constituents may be present in fish tissues at elevated levels and may pose a threat to humans consuming the fish. This sampling event focused on the constituents that were determined to pose the most significant threat to human health and the environment.

Additionally, the above mentioned analyses were conducted on whole fish from the control site and one site adjacent to LHAAP for the purposes of evaluating ecosystem health.

The analytical data were validated to verify sufficient precision, accuracy, completeness, and comparability. Validation of all analytical data was performed by an independent laboratory, the US EPA Houston Laboratory.

1.1 Site Location and History

Longhorn Army Ammunition Plant (LHAAP) is located in central east Texas in the northwest corner of Harrison County, approximately 14 miles northeast of Marshall, Texas, and approximately 40 miles west of Shreveport, Louisiana. The installation occupies 8,493 acres between State Highway 43 and the western shore of Caddo Lake, and is accessed by State Highways 43 and 134 (Figures 1-1 and 1-2).

LHAAP is a government-owned, contractor operated facility under the jurisdiction of the U.S. Army Armament, Munitions, and Chemical Command. Its former mission was to load, assemble, and pack pyrotechnic and illuminating/signal ammunition and solid propellant rocket motors.

LHAAP was established in October 1942 with the primary mission of producing trinitrotoluene (TNT) flake in the Plant 1 Area. Production of TNT continued through World War II until August 1945 when the plant went on standby status until February 1952. Pyrotechnic ammunition including photoflash bombs, simulators, hand signals, and tracers for 40-mm ammunition were manufactured from 1952 until 1956. The Plant 3 Area rocket motor facility began operation in November 1955. Production of rocket motors continued to be the primary

mission of LHAAP until 1965, when production of pyrotechnic and illuminating ammunition was re-established. Subsequent operations consisted of compounding pyrotechnic and propellant mixtures, loading, assembling and packing activities, and the maintenance and/or storage of standby facilities and equipment.

LHAAP was placed on the National Priorities List (NPL) on August 9, 1990, as a result of contamination released to the environment at the installation. After being listed on the NPL, the LHAAP, EPA, and TCEQ entered into a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Section 120 Agreement for remedial activities and LHAAP. The CERCLA Section 120 Agreement, referred to as a Federal Facility Agreement (FFA), became effective on December 30, 1991. The FFA specifies that remedial activities be conducted at 13 areas on LHAAP, and any others that are identified during the investigations.

1.2 Goals

This was a risk assessment study. The primary goal of this work was to determine contaminant residues in edible fish tissues in fish from Caddo Lake adjacent to the LHAAP site. The second, and lesser goal of the study, was to determine ecosystem health of Caddo Lake adjacent to the LHAAP site.

Figure 1-1. Location of LHAAP and proximity to Caddo Lake, TX

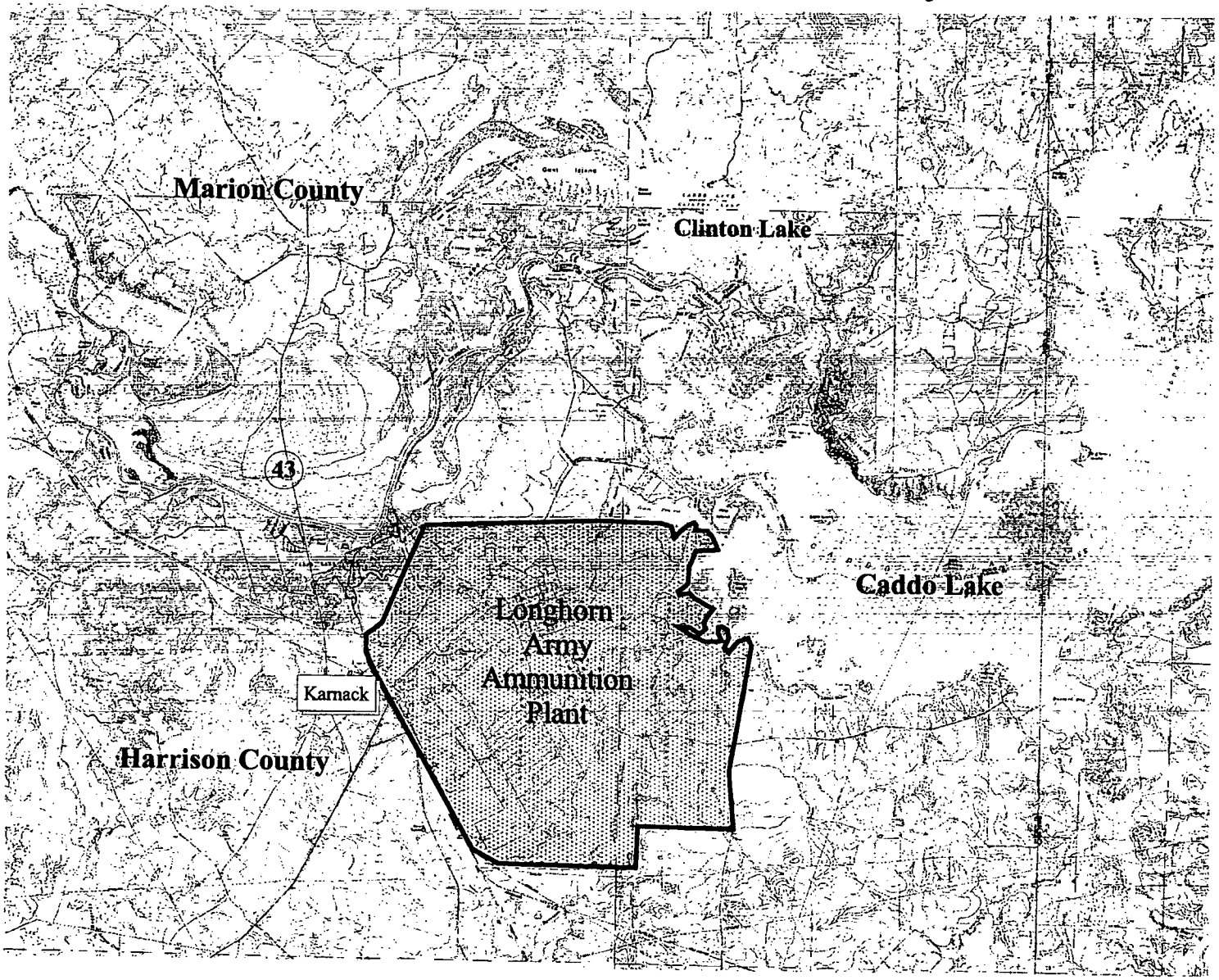

Image Data:
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2.0 Fish Tissue Collection, Processing, and Analysis

This section describes the sampling locations, fish species targeted, collection techniques, fish processing, and laboratory analytical methods for sampling conducted from 23 February to 04 March, 2004.

2.1 Sampling Locations

All surface water and associated runoff from LHAAP drains into Caddo Lake via four drainage systems that cross portions of the installation. These systems are known as Goose Prairie Bayou, Central Creek, Harrison Bayou, and Saunder's Branch.

Sampling locations included those waters of Caddo Lake adjacent to the drainage systems flowing through or from LHAAP. Specifically, those waters in the Goose Prairie and Harrison Bayou region of the lake were fished. Fish from an additional area, Clinton Lake, which is upstream of LHAAP, were used as controls. Sampling locations are found in Figures 2-1 and 2-2.

The three locations are typically shallow (<1-2m) and suitable for sampling only during late fall, winter, and early spring. In warmer months, aquatic vegetation is extremely dense and becomes unpassable, particularly when lake levels are pool depth and below. Consequently, dissolved oxygen levels exhibit large diurnal swings. Low oxygen levels present an obstacle to larger species of fish and study areas are probably most populated during the cooler months of the year. Currently, all three sites are noted for dissolved oxygen concerns in the State's 2002 303d listings.

Every effort was made to first collect fish at or near the points at which sediment was sampled in previous studies (Shaw 2004). A Global Positioning System (GPS) was used to locate the exact areas of sediment sampling. Waters were then fished from that point outward while making every effort to stay in the general area of the Goose Prairie Bayou and Harrison Bayou drainages, as well as Clinton Lake.

Figure 2-1. Fish Tissue Sampling Locations and Major Drainages from LHAAP

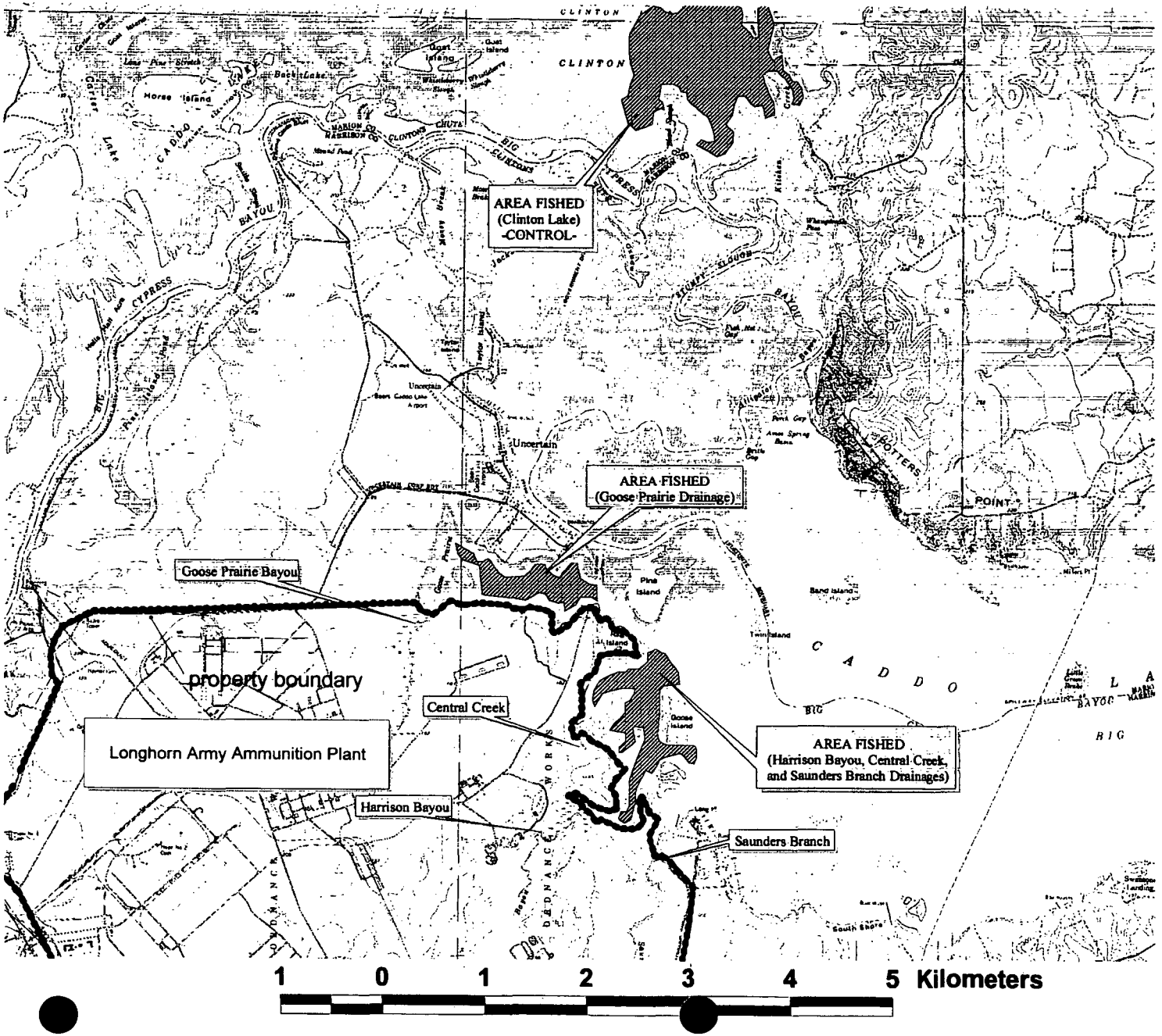

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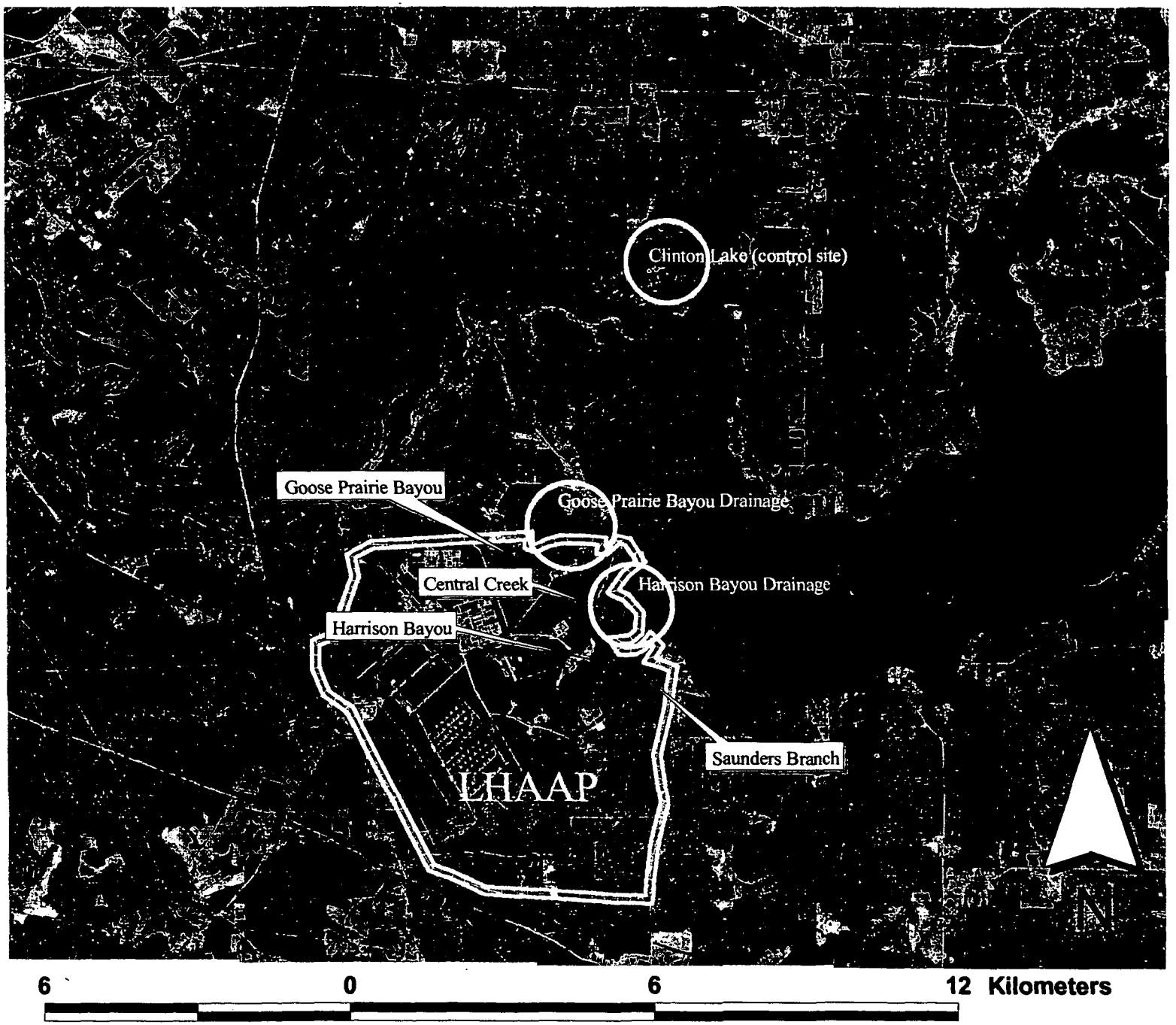
Figure 2-2. Aerial Photographs, Sampling Locations and Major Drainages from LHAAP



2.2 Target Species

The fish species were selected based on the "Caddo Lake Angler Opinion Survey, 12/96 - 08/97", Texas Parks and Wildlife Department, which identified the fish species commonly consumed from the lake. In addition, the species were selected to represent a range of possible fish exposures to any contamination. The samples were of legal length and were filleted to best represent the portion of the fish that is most likely consumed.

At each of the three (3) sampling locations, collections included a minimum of seven (7) individual fish samples, plus quality control samples, of each species identified below. All fish retained for human health analysis were of legal size as set by the Texas Parks and Wildlife Department. Target fish species included:

- Largemouth bass (*Micropterus salmoides*): minimum length 14";
- Channel catfish (*Ictalurus punctatus*): minimum length 12";
- Either black or white crappie (*Pomoxis nigromaculatus or annularis*): minimum length 10"; and
- Sunfish (*Lepomis* species - not mixed): no length limit. Composited.

Additionally, for assessing ecosystem health, eight (8) whole brown bullhead (*Ameiurus nebulosus*) were submitted from both the Goose Prairie and Clinton Lake sites. *A. nebulosus* represents a different ecological group (i.e. bottom feeder and omnivore) than those of the above. In this regard, the bullhead serves as a barometer of ecosystem health since bottom-feeding species may accumulate high contaminant concentrations from direct physical contact with contaminated sediment and/or by consuming benthic invertebrates and epibenthic organisms that live in contaminated sediment (USEPA 2000). Results from whole fish samples will also support a detailed ecological risk assessment that is currently being planned by the US Army Corps of Engineers.

Note: The proposed fish species to be used for ecosystem health analysis (whole fish samples) was originally the common carp (*Cyprinus carpio*). However, none were collected during the course of sampling. After a discussion with US Fish and Wildlife Service (USFWS) and USEPA personnel, it was decided to use the bullhead as a surrogate for the carp.

2.3 Fish Collection

Fish collection was conducted in accordance with procedures put forth in the study Quality Assurance Project Plan (QAPP)/Field Sampling Plan (FSP) (Cook, Erny 2004) which is found in Attachment 1. Personnel included members of the TCEQ, USEPA, and USFWS. Initially, attempts were made to collect fish using three methods; boat electrofisher, gill net, hoop and/or frame traps. Gill netting and trapping yielded only non-target fish or under-sized target fish. Ultimately, netting and trapping were abandoned in favor of electrofishing. All fish sampled for this project were obtained by electrofishing barring one largemouth bass (*M. salmoides*) captured in a trap in the mouth of Harrison Bayou.

The boat-mounted electrofisher equipment is manufactured by Smith-Root, Inc. It consists of a double boom-umbrella array system powered by an onboard generator (Photograph 1).

Photograph 1. Electrofishing boat and personnel.

Controlled by one of the personnel in the front of the boat, a current is produced which stuns the fish and draws them to the surface. Once stunned, fish were netted and placed into a pre-cleaned/rinsed live well containing native water.

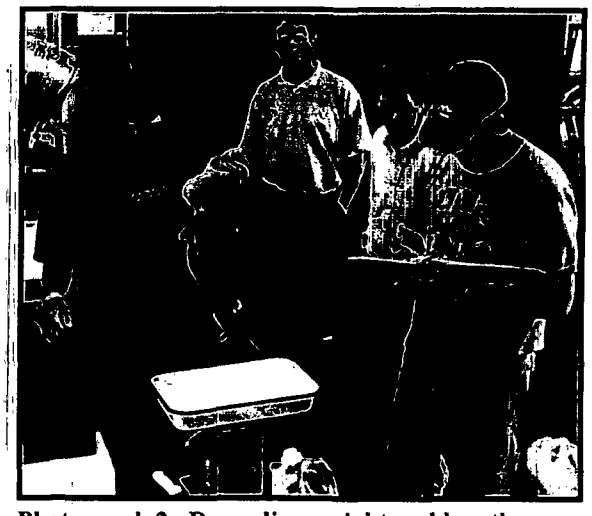
The boat was drifted or slowly powered over probable fish habitat. In some cases, vegetation or shallow water prevented electrofishing efforts. A second boat, "follow boat", was utilized for capturing fish that were stunned but slow to rise to the surface. The follow boat was also equipped with live well which was cleaned, rinsed, and filled with native water.

All fish were captured at one site before proceeding to the next site with the exception of the brown bullhead which were used for whole fish samples. Sampling order was as follows: Harrison Bayou drainage; Goose Prairie Bayou drainage; Clinton Lake (control site). As per the QAPP/FSP, common carp were to be used as the whole fish samples. Once sampling was underway, it was determined that due to the absence of carp, another species was needed for the whole fish samples. Brown bullhead were used as surrogates and were collected from the Goose Prairie Bayou area after the sampling of Clinton Lake. No bullhead (and therefore no whole samples) were collected from Harrison Bayou.

When electrofishing was terminated, and before fish were processed, the daily catch was culled. The largest Fish of each species were retained in the live well and smaller individuals were returned to the lake. Fish were kept in the live well and transported to the processing area.

2.4 Fish Processing in Field

All fish were processed on LHAAP grounds inside the fire house at designated tables/stations. All fish were processed on the day they were captured. Processing was in accordance with the QAPP/FSP. Processing consisted of the following: Identification of species; length measurement; weight measurement; fish identification number assignment, packaging of fish; chain of custody generation. Fish were submitted intact from the field and fillets were harvested by the contract laboratory, TALEM, Inc.



Photograph 2. Recording weight and length measurements of a Largemouth Bass.

Once gloved, personnel removed individual fish

from the live well and determined species. The fish was then measured (total length) and weighed. Species, length, and weight was recorded in a log book as well as date, record keeper, whether or not the sample was a composite of several fish, and any abnormalities (i.e. ulcers, fin rot) associated with the fish. After weighing, spines were removed from the fish to prevent punctures during packaging.

Following contact with the scale and after removal of fins, the fish were then rinsed with metals grade DI water prior to packaging in ZipLock® or equivalent bags. Fish not destined for metals analysis were wrapped in aluminum foil, dull side to the fish, before placement in bags. Each bag contained a unique identification number on the inside of the bag as well as a duplicate ID tag taped to the outside of the bag. This ID number was also recorded next to the species, weight, and length information in the logbook. In addition to the identification number, the tags also contained information as to the required analysis. If there was doubt about the integrity of the bag, the sample was double-bagged. In certain cases (sunfish species), composite samples were necessary to ensure enough tissue for analysis. Sunfish were grouped by species and submitted as one species - species were not mixed. Composite samples consisted of 3-10 individuals. Each composite was assigned one identification number as if it was a single fish. Once packaged, fish were wrapped in bubble wrap and placed into a cooler and taken to another table where chain of custody documentation was generated. FORMS II LITE was utilized for chain of custody (COC) generation and request for analysis. Chain of custodies were placed in plastic bags and taped to the top of the cooler. Ice was then bagged and placed into cooler prior to shipment. Coolers were then sealed with tape and signed custody seals. Samples were either shipped overnight or driven to the laboratory the following day.

2.5 Fish Processing in Laboratory

To minimize field contamination of fish tissues, all fillets were harvested under controlled laboratory settings by TALEM, Inc. Filleting procedures were in accordance with the QAPP/FSP. Once received, coolers containing fish were examined to ensure an intact custody seal. When opened, temperature inside the cooler was obtained and a visual inspection of the contents was performed. COCs were examined and initialized. The laboratory ensured that work areas were free of metals and organic contaminants. All personnel handling samples were gloved in powder less examination gloves. Prior to filleting the fish were rinsed with de-ionized water to minimize effects of possible contamination during shipment. Samples were filleted on a polypropylene cutting board that was covered in aluminum foil with the dull side of the foil toward the fish. Aluminum foil was not placed on the cutting board for fillets undergoing metals analysis. The plastic cutting board, glass jars, stainless steel knives with plastic handles, scales, etc. were

Photograph 3. Rinsing of fish prior to fillet harvest.

cleaned with pesticide-grade methylene chloride and allowed to air-dry. Electric knives were not used. Aluminum foil covering the cutting board, when used, was replaced between each sample. The knife and cutting board was rinsed with distilled water between samples. With the exception of catfish, fish were scaled and filleted with skin on. All fish, with the exception of bullhead used for whole body analysis, were filleted. Bullhead were used for whole body analysis and not filleted.

After obtaining fillets, tissue was homogenized and divided for designated analyses. For composite samples, each fish was filleted and the composite was homogenized. For some composite samples, only the left fillet of each fish was harvested due to an overabundance of tissue.

2.6 Chemical Analysis

Fillets were analyzed for metals, VOCs, SVOCs, dioxins/furans, pesticides, PCBs, perchlorate, and % lipids. For fillets, analysis for each chemical occurred at the following frequencies:

Fillet from Bass or Catfish or Crappie or Sunfish*	Metals Analysis	Dioxins Furans	Pesticides PCBs	VOCs	SVOCs	Perchlorate	% Lipids
Fish 1	X	X					X
Fish 2	X	X					X
Fish 3	X	X					X
Fish 4	X	X					X
Fish 5	X						X
Fish 6	X						X
Fish 7	X						X
Fish 8			X	X	X	X	X

* Sunfish samples were composites of fillets

Whole fish samples (bullhead) were analyzed for the same chemicals but at different frequencies:

Whole fish samples (brown bullhead)	Metals Analysis	Dioxins Furans	Pesticides PCBs	VOCs	SVOCs	Perchlorate	% Lipids
Fish 1	X	X					X
Fish 2	X	X					X
Fish 3	X	X					X
Fish 4	X	X					X
Fish 5			X	X	X	X	X
Fish 6			X	X	X	X	X
Fish 7			X	X	X	X	X
Fish 8			X	X	X	X	X

Filleting and laboratory processing as well as analysis for VOCs, SVOCs, Pesticides, and PCBs was coordinated by TALEM, Inc. of Forth Worth, TX. Analysis of other chemicals was outsourced to the following:

Laboratory	Analysis	Contact Information
Severn-Trent, Sacramento, CA	Dioxins/Furans	John Gildersleeve, 916/374-4381
Texas Tech University, Lubbock, TX	Perchlorate	Todd Anderson, 806/885-4567
Texas A&M University, College Station, TX	%Lipids	Delbert Gatlin, 979/847-9333

Quality control checks such as replicates, equipment blanks, and matrix spikes were done on an approximately 10% basis.

Analytical methods used include the following:

Parameter	Analytical Method Number
Pesticides/PCBs	SW-846 Method 8081 B/8082A
TAL Metals	SW-846 Method 6010 B/7471
Dioxin/Furans	SW-846 Method 8280 A
Volatiles	SW-846 Method 8260 B
Semivolatiles	SW-846 Method 8270 C
Perchlorate	EPS 314 (modified)
Lipids	chloroform/methanol extraction (Folch *et. al*)

The usability of the analytical data was evaluated in accordance with USEPA requirements. Usability of analytical data was evaluated by the USEPA Region 6 laboratory located in Houston, TX. The analytical results are described in **Section 3.0**.

3.0 Summary of Analytical Results

Data concerning the total number of fish collected, species collected, lengths, weights, date of collection, and analyses received are found in Appendix A.

The results of analysis of fish tissue collected from Goose Prairie Bayou, Harrison Bayou, and Clinton Lake indicate that metals, dioxins/furans, one VOC, and limited SVOCs were the detected compounds. Perchlorate, PCBs (see section 3.6), pesticides, herbicides, and expolsives were not detected in fish tissue. Full analaytical results are given in Appendix B and USEPA verified results in Appendix C. The following sections, and tables 3-1 through 3-5, summarize the results of the detected compounds. Request for analysis/COC documentation can be found in Appendix D.

Quality control/quality assurance results (spikes, calibrations, equipment rinsates, duplicates) can be found in Appendices B and C.

3.1 Mercury

Mercury was detected in fillets of higher level predators (fish eating species) from all sites and one channel catfish (*I. punctatus*) from Harrison Bayou. Concentrations and species are listed in Tables 3-1 through 3-3 and graphically in Figures 3-1 and 3-2.

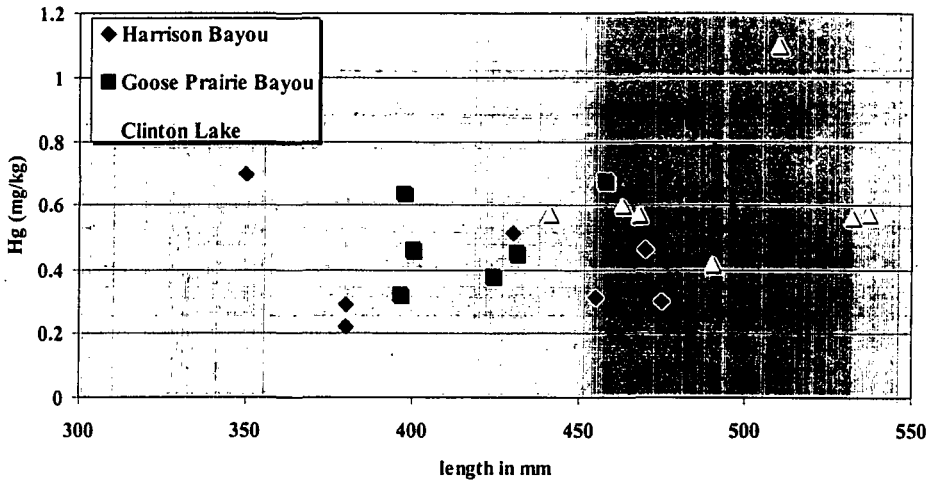


Figure 3-1. Mercury concentrations in Largemouth Bass (*M. salmoides*).

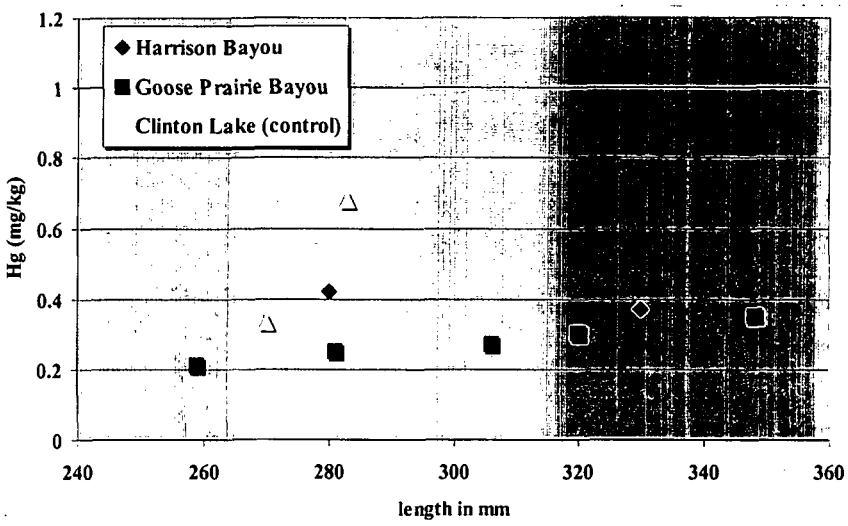


Figure 3-2. Mercury concentrations in Black Crappie (*P. nigromaculatus*)

3.2 Metals, excluding Mercury

Zinc, magnesium, iron, and manganese (whole fish only) were commonly detected in all fish tissue. Levels of these metals above detection limit were expected and are presented in Appendices B and/or C, not Table 3-1 through 3-5. No other metals were detected.

3.3 Dioxins/Furans

Dioxins were detected primarily in whole fish samples but also in fillets from two fish from Clinton Lake (Tables 3-3 through 3-5). Fillets contained Octachorodibenzo-p-dioxin at 5.4 and 7.9 pg/g.

Dioxins were present in all whole fish submitted from Goose Prairie Bayou and Clinton Lake. (no whole fish were submitted from Harrison Bayou). Two target dioxin species were detected, Octachlorodibenzo-p-dioxin, and 1,2,3,4,6,7,8,-Heptochlorodibenzo-p-dioxin. The highest concentrations of both dioxin species were found in a single fish harvested from Goose Prairie Bayou. The dioxin species Octachlorodibenzo-p-dioxin was detected in the greatest concentration from all fish. The dioxin homologues Total HxCDD and Total HpCDD were also detected in fish from both regions. One homologue, Total TCDF was detected in a single fish from Goose Prairie Bayou.

3.4 VOC

One Volatile Organic Compound was detected in whole fish, Methyl Ethyl Ketone (2-butanone). Values ranged from 0.08-0.20 mg/kg. All four detections were from fish collected in Clinton Lake (control site).

3.5 SVOC

The Semivolatile Organic Compounds detected were cresols and phthalates. Meta + para cresols

were detected in whole fish samples from a single fish from Goose Prairie Bayou and three fish from Clinton Lake. Values from Clinton lake ranged from 0.66-1.8 mg/kg. The value from Goose Prairie Bayou was 0.45 mg/kg. One species of phthalate, Bis (2-Ethylhexyl) Phthalate, was detected in two fillets from Goose Prairie Bayou and one fillet from Harrison Bayou. Levels were 0.38, 0.61, and 0.46 mg/kg, respectively.

3.6 PCBs

A single detection for Polychlorinated BiPhenyl 1232 was reported in a whole fish from Goose Prairie Bayou. However, upon review by the EPA laboratory (Appendix C), the result (0.31 mg/kg) was qualified with the following:

"PCB 1232 was reported at a concentration above the laboratory QL in sample 2890 (tag 241). However, the identification was qualified as tentative ("N") because of poor match of elution patterns for the sample and the standard. The reviewer also qualified this PCB concentration as estimated ("J") because the quantitation peaks chosen by the analyst were not representative of PCB 1232."

Consequently, the value is treated as a non-detect. No other PCBs were detected.

Table 3-1. Summary of Detected Analytes in Edible Tissue Fillets. Harrison Bayou.

Fillets					
Fish Species	Trophic Status	Tag ID	Element or Compound	Concentration	Notes
M. salmoides	P	101	Mercury, Total	0.46 mg/kg	
M. salmoides	P	102	Mercury, Total	0.31 mg/kg	
M. salmoides	P	103	Mercury, Total	0.30 mg/kg	
M. salmoides	P	104	Mercury, Total	0.51 mg/kg	
P. nigromaculatus	P	107	Mercury, Total	0.42 mg/kg	
P. nigromaculatus	P	109	Mercury, Total	0.37 mg/kg	
L. gulosus (c)	P	112	Mercury, Total	0.28 mg/kg	
L. gulosus (c)	P	116	Mercury, Total	0.22 mg/kg	
M. salmoides	P	122	Mercury, Total	0.22 mg/kg	
M. salmoides	P	123	Mercury, Total	0.29 mg/kg	
M. salmoides	P	124	Mercury, Total	0.70 mg/kg	
I. punctatus	IF	126	Mercury, Total	0.30 mg/kg	
*M. salmoides**	P	1134	Bis (2 Ethylhexyl) Phthalate	0.46 mg/kg	

P = piscivorous
IF = invertebrate feeder
(c) Denotes composite sample
*** Denotes duplicate to Tag 134**

Table 3-2. Summary of Detected Analytes in Edible Tissue Fillets. Goose Prairie Bayou.

Fillets					
Fish Species	Trophic Status	Tag ID	Element or Compound	Concentration	Notes
M. salmoides	P	201	Mercury, Total	0.46 mg/kg	
M. salmoides	P	202	Mercury, Total	0.38 mg/kg	
M. salmoides	P	204	Mercury, Total	0.45 mg/kg	
M. salmoides	P	205	Mercury, Total	0.68 mg/kg	
M. salmoides	P	222	Mercury, Total	0.32 mg/kg	
M. salmoides	P	232	Mercury, Total	0.64 mg/kg	
P. nigromaculatus	P	206	Mercury, Total	0.27 mg/kg	
P. nigromaculatus	P	207	Mercury, Total	0.35 mg/kg	
P. nigromaculatus	P	208	Mercury, Total	0.30 mg/kg	
P. nigromaculatus	P	224	Mercury, Total	0.25 mg/kg	
P. nigromaculatus	P	225	Mercury, Total	0.21 mg/kg	
L. gulosus (c)	P	214	Mercury, Total	0.23 mg/kg	
M. salmoides	P	234	Bis (2-Ethylhexyl) Phthalate	0.38 mg/kg	
I. punctatus	IF	236	Bis (2-Ethylhexyl) Phthalate	0.61 mg/kg	J

P = piscivorous
IF = invertebrate feeder
(c) Denotes composite sample

Notes: J Estimated value.

Table 3-3. Summary of Detected Analytes in Edible Tissue Fillets. Clinton Lake (control site).

Fillets					
Fish Species	Trophic Status	Tag ID	Element or Compound	Concentration	Notes
M. salmoides	P	301	Mercury, Total	0.57 mg/kg	
M. salmoides	P	302	Mercury, Total	0.57 mg/kg	
M. salmoides	P	303	Mercury, Total	0.42 mg/kg	
M. salmoides	P	304	Mercury, Total	0.60 mg/kg	
P. nigromaculatus	P	306	Mercury, Total	0.68 mg/kg	
P. nigromaculatus	P	307	Mercury, Total	0.33 mg/kg	
L. gulosus (c)	P	311	Mercury, Total	0.21 mg/kg	J, ^
L. gulosus (c)*	P	1311	Mercury, Total	0.22 mg/kg	J, ^
M. salmoides	P	322	Mercury, Total	0.57 mg/kg	
M. salmoides	P	323	Mercury, Total	0.56 mg/kg	
M. salmoides	P	324	Mercury, Total	1.1 mg/kg	
*M. salmoides**	P	1324	Mercury, Total	1.2 mg/kg	
M. salmoides	P	303	Octachlorodibenzo-p-dioxin	7.9 pg/g	1
I. punctatus	IF	313	Octachlorodibenzo-p-dioxin	5.4 pg/g	1

P = piscivorous
IF = invertebrate feeder
(c) Denotes composite sample
*** Denotes duplicate to above listed Tag ID**

Notes: J Result is estimated because of outlying quality control parameters such as matrix spikes, serial dilution, etc., or the result is below the CRQL.

^ High bias. Actual concentration may be lower than the concentration reported.

1 The contract laboratory assigned a "J" flag (estimated value) to the result solely because it was below the laboratory reporting limit which was 2X the laboratory DL. In the opinion of the EPA Laboratory reviewer, the "J" flag was unnecessary because the result was within the demonstrated instrument calibration range.

Table 3-4. Summary of Detected Analytes in Whole Fish. Goose Prairie Bayou.

Whole Body					
Fish Species	Trophic Status	Tag ID	Element or Compound	Concentration	Notes
A. nebulosus	omni	240	Cresols, meta- & para-, total	0.45 mg/kg	J
A. nebulosus	omni	241	Polychlorinated Biphenyl 1232	0.31 mg/kg	N, J
A. nebulosus	omni	218	Octachlorodibenzo-p-dioxin	140 pg/g	
A. nebulosus	omni	218	1,2,3,4,6,7,8-Heptochlorodibenzo-p-dioxin	16 pg/g	
A. nebulosus	omni	218	Total HxCDD	6.8 pg/g	
A. nebulosus	omni	218	Total HpCDD	32 pg/g	
A. nebulosus	omni	219	Octachlorodibenzo-p-dioxin	14 pg/g	
A. nebulosus	omni	219	Total HpCDD	2.9 pg/g	
A. nebulosus	omni	220	Octachlorodibenzo-p-dioxin	20 pg/g	
A. nebulosus	omni	220	1,2,3,4,6,7,8-Heptochlorodibenzo-p-dioxin	4.1 pg/g	1
A. nebulosus	omni	220	Total HpCDD	4.1 pg/g	
A. nebulosus	omni	221	Octachlorodibenzo-p-dioxin	15 pg/g	
A. nebulosus	omni	221	Total TCDF	1.4 pg/g	
A. nebulosus *	omni	1221	Octachlorodibenzo-p-dioxin	14 pg/g	
A. nebulosus *	omni	1221	Total TCDF	0.91pg/g	

omni = omnivore

*** Denotes duplicate to above listed Tag ID**

Notes: J **Estimated value.**

N **Identification is tentative.**

1 **The contract laboratory assigned a "J" flag (estimated value) to the result solely because it was below the laboratory reporting limit which was 2X the laboratory DL. In the opinion of the EPA Laboratory reviewer, the "J" flag was unnecessary because the result was within the demonstrated instrument calibration range.**

Table 3-5. Summary of Detected Analytes in Whole Fish. Clinton Lake (control site).

Whole Body					
Fish Species	Trophic Status	Tag ID	Element or Compound	Concentration	Notes
A. nebulosus	omni	338	Methyl Ethyl Ketone (2-butanone)	0.14 mg/kg	1, J, v
A. nebulosus	omni	339	Methyl Ethyl Ketone (2-butanone)	0.20 mg/kg	1, J, v
A. nebulosus	omni	339	Cresols, meta- & para-, total	0.66 mg/kg	J
A. nebulosus	omni	340	Methyl Ethyl Ketone (2-butanone)	0.20 mg/kg	1, J, v
A. nebulosus	omni	340	Cresols, meta- & para-, total	0.84 mg/kg	J
A. nebulosus	omni	341	Methyl Ethyl Ketone (2-butanone)	0.08 mg/kg	1, J, v
A. nebulosus	omni	341	Cresols, meta- & para-, total	1.8 mg/kg	
A. nebulosus	omni	317	Octachlorodibenzo-p-dioxin	30 pg/g	
A. nebulosus	omni	317	1,2,3,4,6,7,8-Heptochlorodibenzo-p-	4.9 pg/g	2
A. nebulosus	omni	317	Total HpCDD	7.7 pg/g	
A. nebulosus *	omni	1317	Octachlorodibenzo-p-dioxin	33 pg/g	
A. nebulosus *	omni	1317	1,2,3,4,6,7,8-Heptochlorodibenzo-p-	4.7 pg/g	2
A. nebulosus *	omni	1317	Total HpCDD	7.4 pg/g	
A. nebulosus	omni	318	Octachlorodibenzo-p-dioxin	22 pg/g	
A. nebulosus	omni	318	1,2,3,4,6,7,8-Heptochlorodibenzo-p-	2.9 pg/g	2
A. nebulosus	omni	318	Total HpCDD	2.9 pg/g	
A. nebulosus	omni	319	Octachlorodibenzo-p-dioxin	15 pg/g	
A. nebulosus	omni	320	Octachlorodibenzo-p-dioxin	22 pg/g	
A. nebulosus	omni	320	1,2,3,4,6,7,8-Heptochlorodibenzo-p-	4.0 pg/g	2
A. nebulosus	omni	320	Total HpCDD	4.0 pg/g	

omni = omnivore

*** Denotes duplicate to above listed Tag ID**

Notes: 1 **All MS recoveries were below the QC limits.**

J **Result is estimated because of outlying quality control parameters such as matrix spikes, serial dilution, etc., or the result is below the CRQL.**

v **Low biased. Actual concentration may be higher than the concentration reported.**

2 **The contract laboratory assigned a "J" flag (estimated value) to the result solely because it was below the laboratory reporting limit which was 2X the laboratory DL. In the opinion of the EPA Laboratory reviewer, the "J" flag was unnecessary because the result was within the demonstrated instrument calibration range.**

4.0 Fish Condition/Health

Field notes were made on the general condition and appearance of harvested fish (Appendix A). The general condition of fish from all three sites was excellent with very few individuals noted for abnormalities. Most noted abnormalities concerned scarring and parasites. There were no noticeable differences in the health of fish between sites.

Dioxins were present in all whole fish submitted from Goose Prairie Bayou and Clinton Lake. The results are most likely due to the close association of the fish with the lake bottom/sediments, but primarily because the whole fish was analyzed, including internal organs and other fatty regions where dioxins concentrate. Two target dioxin species were detected, Octachlorodibenzo-p-dioxin, and 1,2,3,4,6,7,8,-Heptochlorodibenzo-p-dioxin. The highest concentrations of both dioxin species were found in a single fish harvested from Goose Prairie Bayou. With the exception of the above mentioned fish, results among the two sites were in the same order of magnitude. The dioxin species Octachlorodibenzo-p-dioxin was detected in the greatest concentration from all fish. These findings are consistent with those of Shaw in which dioxins in sediment had higher concentrations of Octachlorodibenzo-p-dioxin (Shaw 2004). The dioxin homologues Total HxCDD and Total HpCDD were also detected in fish from both regions. Species of dioxins detected are considered less toxic species. One furan homologue, Total TCDF was detected in a single fish from Goose Prairie Bayou.

Perchlorate, PCBs, herbicides, pesticides, and explosives were not detected in edible fillets or whole fish samples from any of the three sites.

6.0 Data Usability Summary

The purpose of this section is to evaluate the usability of the generated study data.

No circumstances occurred in the field to render data unusable. The QAPP/FSP was followed with the exception of two deviations. One: The primary target fish for whole fish analysis was the common carp (*C. carpio*). Due to the absence of carp in collections, a surrogate fish, the brown bullhead (*A. nebulosus*) was substituted. Similar to the carp in ties to the benthos, and readily available, the bullhead served as the barometer for ecosystem health; Two: Originally, as stated in the QAPP/FSP, all collections were to be completed at one sampling location before moving to the next. Collections in Goose Prairie Bayou for edible fillets were made and then sampling commenced for the final site, Clinton Lake. After Clinton Lake was sampled for all fish (fillets and whole fish), Goose Prairie Bayou sampling commenced for bullhead for whole fish samples. Live wells were thoroughly washed and rinsed between sites. Neither deviations from the QAPP/FSP invalidate the data.

All laboratory data was reviewed for usability by the US EPA Laboratory in Houston, TX. The complete review of all data can be found in Appendix C. A summary of invalidated/non-usable data can be found in Appendix E.

7.0 Literature Cited

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Attachment 1

Caddo Lake Biological Sampling and Risk Assessement
Longhorn Army Ammunition Depot

Combined Quality Assurance Project Plan and Field Sampling Plan for the Investigation of Contaminants in Fish Tissue

Caddo Lake Biological Sampling and Risk Assessment

Longhorn Army Ammunition Depot

COMBINED QUALITY ASSURANCE PROJECT PLAN AND FIELD SAMPLING PLAN FOR THE INVESTIGATION OF CONTAMINANTS IN FISH TISSUE

February 6, 2004

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5.0 Summary and Conclusions

Analytical results indicate that five metals (mercury, zinc, magnesium, manganese, and iron) were present above detection limits in fillets and/or whole fish samples. Metal levels in fillets were similar among sites. Of the five detected metals, only zinc and mercury are routinely considered in analysis of fillets for human consumption. The health-based assessment comparison (HAC) value for zinc currently used by the Department of State Health Services (DSHS) (formerly Texas Department of Health) is 700 mg/kg. This level is 1.5-2 orders of magnitude greater than zinc levels detected in edible fillets from Caddo Lake. Mercury in fish tissue (fillets) has been documented in Caddo Lake by the TCEQ (Crowe 1996) and by the DSHS (Currently, a Consumption Advisory for Fish Tissue (largemouth bass, freshwater drum) exists for Caddo Lake, TDH 1995). Therefore, mercury in fillets was expected in fish-eating species taken in all study areas. Largemouth bass, black crappie, and some warmouth (a fish-eating sunfish) had measurable mercury levels in fillets. Concentrations were generally similar among sites. Mercury was not detected in whole fish samples.

Methyl Ethyl Ketone (2-butanone), a VOC and Bis (2-Ethylhexyl) Phthalate, a SVOC were detected sporadically in whole fish and fillets, respectively. Both are considered lab contaminants. No other VOCs were detected.

One additional SVOC was detected, a cresol. Four detections for the meta + para variants of cresol occurred in whole fish. Three detections were from Clinton Lake (upstream control site) and one from Goose Prairie Bayou. Whole fish samples are most likely to produce detectable levels of cresols because the compound is distributed to all major organs (Papa 1995). It is unclear as to the source of the compound(s). All detected quantities are considered low (for rough comparison, the current TCEQ screening level for total cresol in an *edible fillet* is 887 mg/kg, TCEQ 2003). Due to the low levels detected, cresols are not considered a threat to the ecosystem health of Caddo Lake.

Dioxins in Caddo Lake sediments were sampled in 2000-2002 by Shaw Environmental, Inc. Results indicated widespread presence of dioxins in Harrison Bayou, Goose Prairie Bayou, and Clinton Lake sediments with generally higher concentrations in samples collected from Clinton Lake, upstream of the LHAAP facility (Shaw 2004). Dioxin species detected in fillets/whole fish samples were consistent with those detected in the lake sediments.

In edible tissue fillets harvested from fish collected at both Harrison Bayou and Goose Prairie Bayou sites, no dioxin compounds were detected. Two fillets from separate fish in Clinton Lake contained Octachlorodibenzo-p-dioxin. This species of dioxin is not documented for the high toxicity as that exhibited by the better known tetra-chlorinated dioxins. The fillets were harvested from a largemouth bass (*M. salmoides*) and a channel catfish (*I. punctatus*). Possible factors contributing to the dioxin levels in these fish are the generally higher levels of dioxins in Clinton Lake sediments, bottom-dwelling nature of catfish (contact with sediment), higher fatty content of catfish fillet, and the bass fillet submitted skin-on (higher fat content). The only detected dioxins in edible tissue were harvested in the control area upstream of the LHAAP facility, it is therefore suggested that LHAAP is not the likely source of dioxins in edible tissue fillets.