U. S. Fish and Wildlife Service
Region 2

THE IMPACT OF PETROLEUM HYDROCARBON AND BRINE CONTAMINANTS TO MACROINVERTEBRATE COMMUNITIES INHABITING LOTIC SYSTEMS AT HAGERMAN NATIONAL WILDLIFE REFUGE, GRAYSON COUNTY, TEXAS 1999

Prepared by
Craig M. Giggleman and Omar R. Bocanegra

Arlington Field Office
711 Stadium Drive, Suite #252
Arlington, Texas 76011

July 2000

Project ID No. 2N33/9920003

THE IMPACT OF PETROLEUM HYDROCARBON AND BRINE CONTAMINANTS TO MACROINVERTEBRATE COMMUNITIES INHABITING LOTIC SYSTEMS AT HAGERMAN NATIONAL WILDLIFE REFUGE, GRAYSON COUNTY, TEXAS 1999

PROJECT ID NO. 2N33/9920003

ABSTRACT

In May 1995, an initial contaminants survey of Hagerman National Wildlife Refuge was completed by the U.S. Fish and Wildlife Service. The results of that study combined with ongoing crude oil production activities at the Refuge, indicated that further investigations into the environmental impact of these petroleum production activities on natural resources at the Refuge were warranted. In April 1999, another contaminants investigation was initiated at the Refuge by the Service's Arlington, Texas, Ecological Services Field Office to determine the impact of possible residual petroleum hydrocarbon and brine contamination on macroinvertebrate communities inhabiting three lotic systems within the Refuge. The three streams selected for this study were Big Mineral Creek, Beaver Creek, and Sandy Creek. Surface water, sediment, and macroinvertebrate samples were collected from each of these streams and from Caney Creek, an un-impacted stream located off the Refuge serving as the control. Surface water samples were analyzed for bromide, chloride, lithium and sodium content to determine possible residual brine contamination, while sediment samples were analyzed for total petroleum hydrocarbons, benzene, ethylbenzene, toluene, and xylene content to determine possible residual crude oil contamination. Macroinvertebrate samples were collected from each stream and identified to the lowest taxonomic level possible. The resulting data were compared with surface water quality standards, water quality/sediment criteria protective of aquatic wildlife, and data from Caney Creek to evaluate the potential impact to macroinvertebrate communities inhabiting the streams within the Refuge.

The water chemistry analyses from this study indicated that residual brine did not appear to be present in any of the streams sampled on the Refuge. Residual total petroleum hydrocarbons, benzene, ethylbenzene, toluene, and xylene concentrations in sediments within Big Mineral Creek, Beaver Creek, and Sandy Creek from previous crude oil spills do not appear to be at levels that represent an ecological concern at this time. Considering that the streams sampled within the Refuge contained as diverse macroinvertebrate communities as Caney Creek, it appears that the impact of residual crude oil and brine contamination on the macroinvertebrate communities within these streams is negligible. Furthermore, based on the macroinvertebrate organisms inhabiting the streams, overall water quality within these streams appears to range from fair to good.

Acknowledgments: The authors are grateful to Mr. Jim Williams, Mr. Jim Fox, Ms. Karen Howard, and the remaining staff at Hagerman National Wildlife Refuge for providing physical and technical assistance essential in conducting this study. The authors wish to acknowledge Mr. Mike Armstrong, Mr. Jacob Lewis, and Ms. Tracy Ogle for providing valuable assistance in collecting and processing the macroinvertebrate samples. The authors are also grateful to Mr. Tom Cloud, Mr. Steve Robertson, Ms. Clare Lee, and Dr. Brian Cain for reviewing the document and providing insightful technical expertise in completing the study.

THE IMPACT OF PETROLEUM HYDROCARBON AND BRINE CONTAMINANTS TO MACROINVERTEBRATE COMMUNITIES INHABITING LOTIC SYSTEMS AT HAGERMAN NATIONAL WILDLIFE REFUGE, GRAYSON COUNTY, TEXAS 1999

PROJECT ID NO. 2N33/9920003

TABLE OF CONTENTS

INTRODUCTION 1
STUDY AREA 1
MATERIALS & METHODS 4
RESULTS & DISCUSSION 8
    WATER QUALITY 8
    SEDIMENTS 10
    MACROINVERTEBRATES 12
CONCLUSIONS & RECOMMENDATIONS 20
REFERENCES 21
ANALYTICAL METHODS . . . . . APPENDIX A
1999 CRUDE OIL RELEASE INTO HARRIS CREEK . . . . . APPENDIX B

LIST OF FIGURES & TABLES

Figure 1. Study Area 2
Figure 2. Hagerman National Wildlife Refuge 3
Figure 3A. Surface Water and Sediment Sampling Points at Hagerman National Wildlife Refuge . . . 5
Figure 3B. Surface Water and Sediment Sampling Points at Caney Creek 6
Figure 4A. Macroinvertebrate Sampling Points at Hagerman National Wildlife Refuge 7
Figure 4B. Macroinvertebrate Sampling Points at Caney Creek 8
Figure 5. Number of Individuals, Taxa and Diversity Indices for the Four Streams 18
Figure 6. Macroinvertebrate Trophic Group Composition of the Four Streams 19
Table 1. Surface Water and Sediment Sampling Sites on the Four Streams 5
Table 2. Macroinvertebrate Sampling Sites on the Four Streams 7
Table 3. Measured Water Quality Data from the Four Streams 9
Table 4. Analytical Results for Surface Water Samples from the Four Streams 9
Table 5. Analytical Results for Sediment Samples from the Four Streams 11
Table 6A. Groups of Macroinvertebrates and Number of Individuals from the Four Streams 13
Table 6B. Macroinvertebrates Collected from Caney Creek 14
Table 6C. Macroinvertebrates Collected from Beaver Creek 15
Table 6D. Macroinvertebrates Collected from Big Mineral Creek 16
Table 6E. Macroinvertebrates Collected from Sandy Creek 17

THE IMPACT OF PETROLEUM HYDROCARBON AND BRINE CONTAMINANTS TO MACROINVERTEBRATE COMMUNITIES INHABITING LOTIC SYSTEMS AT HAGERMAN NATIONAL WILDLIFE REFUGE, GRAYSON COUNTY, TEXAS 1999

PROJECT ID NO. 2N33/9920003

INTRODUCTION

In May 1995, an initial contaminants survey of Hagerman National Wildlife Refuge was completed by the U.S. Fish and Wildlife Service (Baker *et al.*, 1995). The results of that study, combined with ongoing crude oil production activities at the Refuge, indicated that further investigation into the environmental impact of these petroleum production activities on natural resources at the Refuge were warranted. In April 1999, another contaminants investigation was initiated at the Refuge by the Service's Arlington, Texas, Ecological Services Field Office to determine the impact of possible residual petroleum hydrocarbon and brine contamination on macroinvertebrate communities inhabiting three streams within the Refuge. Surface water, sediment, and macroinvertebrate samples were collected from each of these streams and from one un-impacted stream located off the Refuge. The resulting data were compared with surface water quality standards, water quality/sediment criteria protective of aquatic wildlife, and data from the un-impacted stream to evaluate the potential impact to macroinvertebrate communities inhabiting the streams within the Refuge.

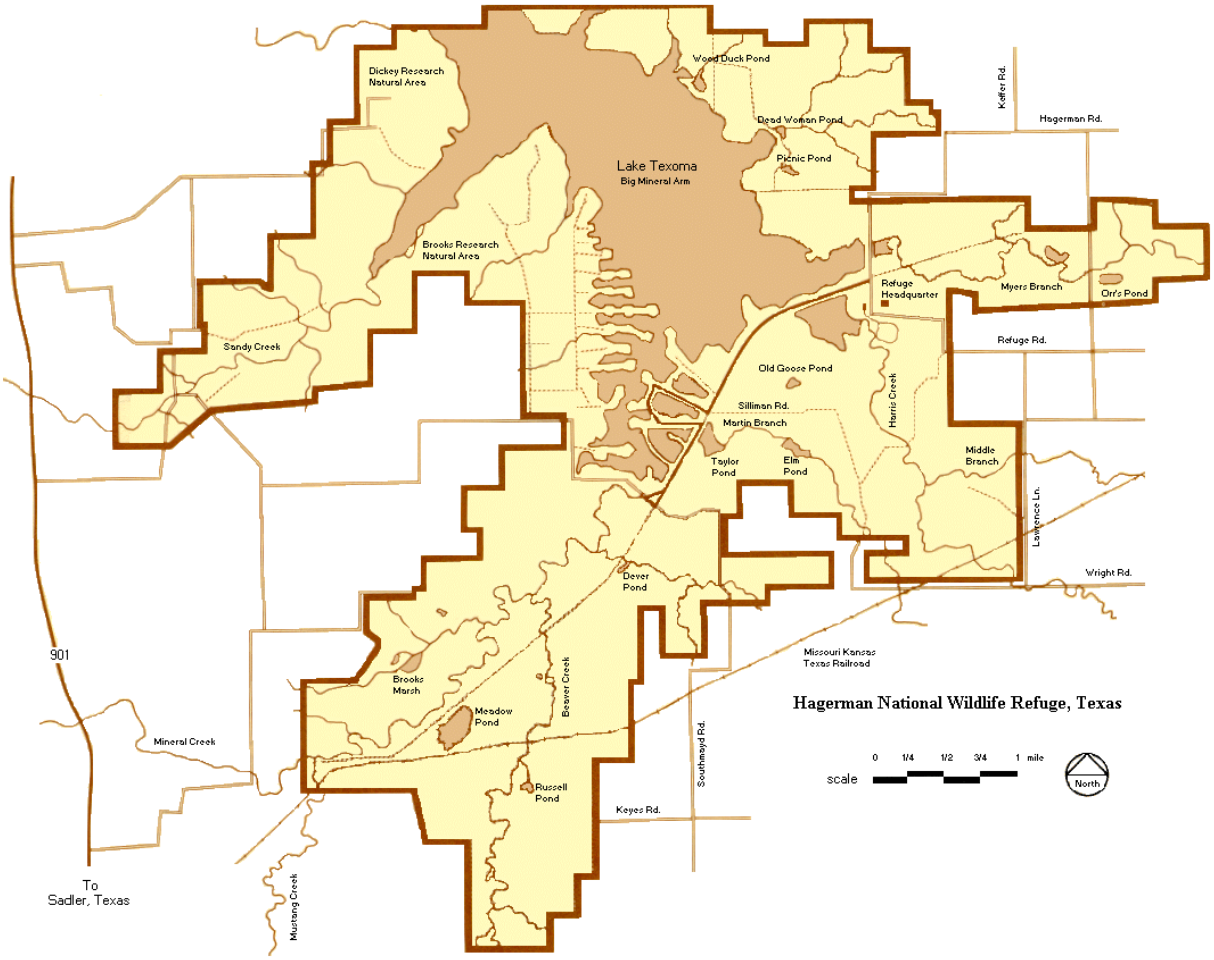
STUDY AREA

Hagerman National Wildlife Refuge is located within the cross timbers/blackland prairie ecoregions of the Red River Valley (Baker *et al.*, 1995) on the southern end of the Big Mineral Arm of Texoma Reservoir in Grayson County, Texas (Figure 1). The entire Refuge lies within the drainage of Texas Red River Segment No. 0203 (TNRCC, 1996b). The Refuge consists of 11,320.0 acres (4,581.2 hectares), of which approximately 3,000.0 acres (1,241.1 hectares) forms marshland and aquatic habitat (Baker *et al.*, 1995). The Refuge provides suitable habitat for 62 fish species, 13 amphibian species, 40 reptilian species, 36 mammalian species, and 273 avian species (USFWS, 1997). In addition to the Big Mineral Arm of Texoma Reservoir, the Refuge receives surface water inflow from Sandy Creek, Big Mineral Creek, Beaver Creek, Elba Creek, Harris Creek, Martin's Branch, Mustang Creek, and Meyers' Branch. Geologically, the Refuge overlays the Woodbine and Trinity Aquifers (TWC, 1989). The Refuge also overlays the Big Mineral Oil Field. Consequentially, there are approximately 147 active crude oil production wells and 15 crude oil and/or brine storage batteries located within the confines of the Refuge. Since 1973, an estimated 400,000 gallons (1,514,000 liters) of crude oil and/or brine have been released into the environment in and around the Refuge from these and surrounding petroleum production facilities (TNRCC, 1997; TPWD, 1997).

Mineral Creek (Figure 2), also known as Big Mineral Creek, flows northward through the south-central portion of the Refuge into the Big Mineral Arm of Texoma Reservoir. This lotic system's watershed encompasses approximately 55.3 square mile (143.2 square kilometers). It is an intermittent system characterized by steep banks, long runs and negligible riffle habitat; however, it contains perennial pools due to the influx of treated waste water from the City of Whitesboro. Substrate within the stream ranges from silt to medium sized sand. On May 17, 1994, an estimated 200.0 barrels (8,400 gallons or 31,794.0

Figure 1. Study Area (Maptech, 1998).

Figure 2. Hagerman National Wildlife Refuge, Grayson County, Texas (USFWS, 1989).



liters) of brine and 10 barrels (420.0 gallons or 1,589.7 liters) of crude oil were released into this stream (TPWD, 1997). On June 16, 1996, another 100.0 barrels (4,200.0 gallons or 15,897.0 liters) of mixed crude oil and brine were released into the stream, and on September 8, 1996, an estimated 8,600.0 barrels (361,200.0 gallons or 1,367,142.0 liters) of crude oil from a ruptured pipeline were released into pasture land adjacent to the stream (TPWD, 1997).

Beaver Creek (Figure 2) is an intermittent tributary of Big Mineral Creek that drains approximately 24.5 square miles (63.5 square kilometers). Like Big Mineral Creek, this stream is characterized by steep banks, long runs and very little riffle habitat. Substrate within the stream ranges from medium sized sand to silt. No reported oil or brine spills have occurred in this creek; however, crude oil collection pipelines are located within this stream's watershed.

Sandy Creek is an intermittent lotic system, containing perennial pools that flows eastward through the western portion of the Refuge into the Big Mineral Arm of Texoma Reservoir (Figure 2). This stream contains long runs with some riffles and its watershed encompasses approximately 23.4 square miles (60.6 square kilometers). Substrate within this stream ranges from fine to coarse sized sand. On January 3,

1989, an unknown quantity of mixed brine and crude oil was spilled adjacent to this creek, and on August 1, 1992, an estimated 50.0 barrels (2,100.0 gallons or 7,948.5 liters) of crude oil were released into the creek (TPWD, 1997).

Mustang Creek and Martin's Branch are intermittent tributaries of Big Mineral Creek which have no documented oil and/or brine contamination (Figure 2). Elba Creek is an intermittent tributary of Beaver Creek that has no documented oil and/or brine contamination. Meyer's Branch (Figure 2) is an intermittent stream that flows through the northeastern portion of the Refuge. Harris Creek (Figure 2) is an intermittent stream that contains perennial pools and flows through the southeastern portion of the Refuge. On October 26, 1991, approximately 185.0 barrels (7,770.0 gallons or 29,409.5 liters) of crude oil from a compromised tank battery were released into this stream, while on May 22, 1995, an estimated 50.0 barrels (2,100.0 gallons or 7,948.5 liters) of brine from a ruptured transfer pipeline were released into the stream (TNRCC, 1997; TPWD, 1997). A further 200.0 barrels (8,400.0 gallons or 31,794.0 liters) of crude oil were released into the stream on January 7, 1996 from a ruptured crude oil storage tank (TNRCC, 1997; TPWD, 1997).

Caney Creek is a perennial tributary of the Red River located approximately 29.0 miles (47.0 kilometers) east of the Refuge, in northwestern Fannin County, Texas (Figure 1). Its watershed encompasses approximately 50.7 square miles (131.2 square kilometers). This lotic system is characterized by steep banks, long runs and sparse riffle habitat. The substrate in this creek ranges from silt to coarse gravel. The stream is within the drainage of Texas Red River Segment No. 0202 (TNRCC, 1996b) and is located outside of the oil producing formation of the Big Mineral Oil Field. This creek has had no documented oil or brine contamination. In addition, no known permitted wastewater treatment facilities discharge effluent into this stream.

MATERIALS & METHODS

Three streams were selected for sampling within the Refuge for this study. Big Mineral Creek and Sandy Creek were selected as sampling sites because both streams contain perennial pools and both streams have experienced documented contamination from crude oil/brine releases. Beaver Creek was selected because it has oil pipelines within its watershed and contains perennial pools. Even though it is not within the confines of the Refuge, Caney Creek was selected as the control for the study because no known crude oil/brine production facilities were located within its watershed, it is within the Red River drainage, and like the other three streams it contains long runs with poorly defined riffle habitat. Three surface water and sediment sampling points were selected on each of these streams (Table 1; Figures 3A and 3B). One surface water grab sample and one composite sediment sample were collected at each of the 12 sampling points. Each stream water sample was collected by dipping a pre-cleaned 500.0 ml glass container immediately below the surface. Once collected, the container was sealed with a teflon lid, labeled, and placed on ice. Each composite sediment sample was collected using a sterile, disposable plastic scoop. After collection, each sample was placed in a 500.0 ml pre-cleaned glass container, sealed with a teflon lid, labeled, and placed on ice. In addition to the surface water and sediment samples, an aqueous brine sample was collected in a pre-cleaned 500.0 ml glass container directly from an outlet valve at a brine production unit located within the Refuge. All samples were transported to the Arlington, Texas, Field Office and remained chilled until submitted to a contract laboratory through the Service's Patuxent Analytical Control Facility for analyses.

Water samples, including the brine sample, were analyzed for sodium (Na), lithium (Li), bromide ($Br^{(-)}$),

Table 1. Surface Water and Sediment Collection Sites on One Stream in Fannin County, Texas, and Three Streams in Grayson County, Texas.		
Stream	**Site Identifier**	**Site Location**
Caney Creek	CC1753	Off Refuge, 115.0 feet (35.0 meters) upstream of Farm-to-Market Road (FM) 1753 in Fannin County, Texas.
	CCUSCR	Off Refuge, 115.0 feet (35.0 meters) upstream of County Road (CR) 1020 in Fannin County, Texas.
	CCDSCR	Off Refuge, 115.0 feet (35.0 meters) downstream of CR 1020 in Fannin County, Texas.
Big Mineral Creek	BMUS	Off Refuge, 33.0 feet (10.0 meters) upstream of Cordell Road in Grayson County, Texas.
	BMDSRR	On Refuge, 82.0 feet (25.0 meters) downstream of rip-rap low water crossing in Grayson County, Texas.
	BMDS	On Refuge, at the confluence with Martin's Branch in Grayson County, Texas.
Beaver Creek	BVUS	Off Refuge, 33.0 feet (10.0) meters upstream of Gage Road in Grayson County, Texas.
	BVRR	On Refuge, 66.0 feet (20.0 meters) upstream of Missouri-Kansas-Texas rail line in Grayson County, Texas.
	BVMID	On Refuge, 33.0 feet (10.0 meters) upstream of Refuge Service Road in Grayson County, Texas.
Sandy Creek	SOR	Off Refuge, 279.0 feet (85.0 meters) upstream of Old Sadler Road in Grayson County, Texas.
	SUSOS	On Refuge, 115.0 feet (35.0 meters) upstream of Old Sadler Road in Grayson County, Texas.
	SDSOS	On Refuge, 33.0 feet (10.0 meters) downstreamof Old Sadler Road in Grayson County, Texas.

Figure 3A. Surface Water and Sediment Sampling Points on Big Mineral Creek, Beaver Creek, and Sandy Creek, Hagerman National Wildlife Refuge, Grayson County, Texas (Maptech, 1998).

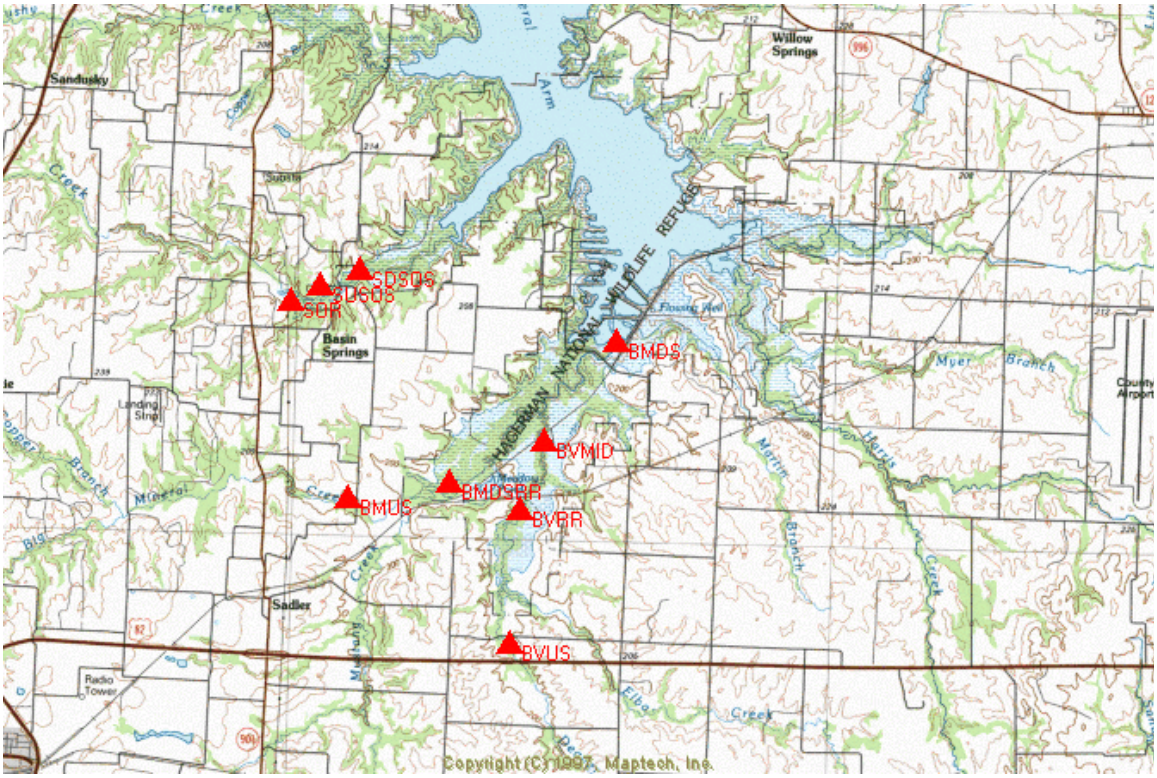
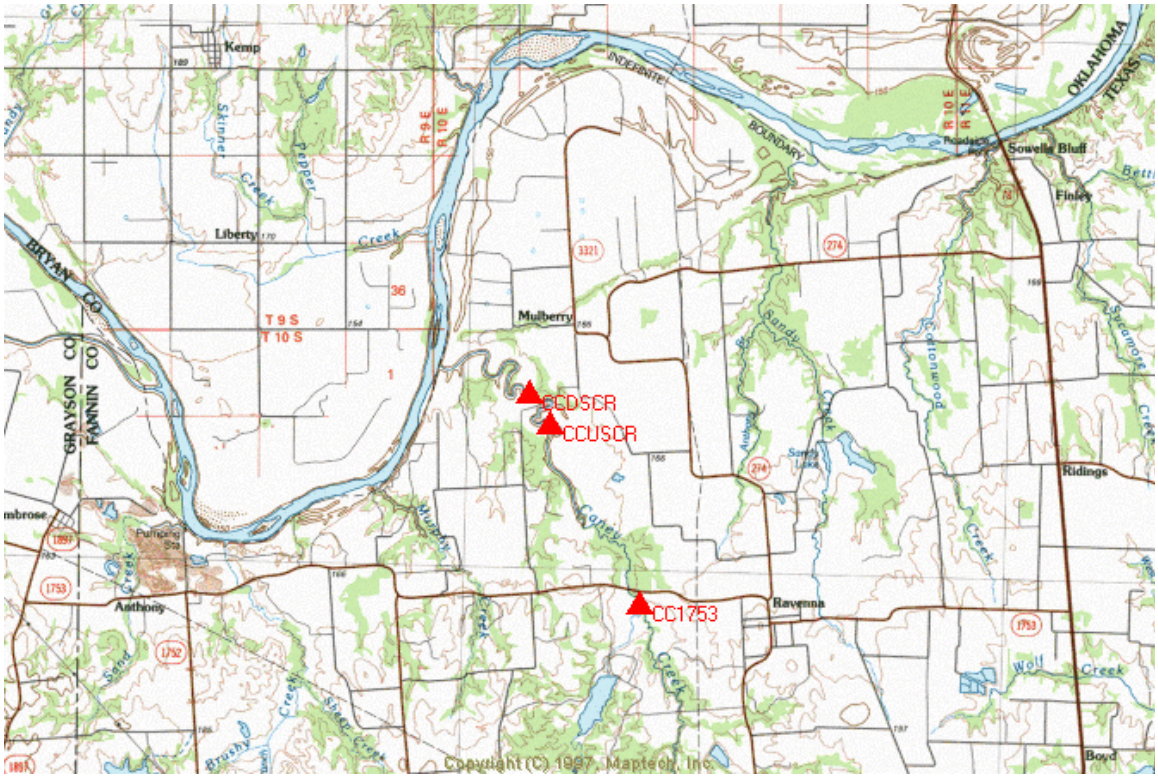


Figure 3B. Surface Water and Sediment Sampling Points on Caney Creek, Fannin County, Texas (Maptech, 1998).



and chloride ($Cl^{(-)}$) content to determine the presence of cations and anions associated with brine contamination. Na and Li concentrations were determined through graphite furnace atomic absorption and ion chromatography mass spectrometry measurements, while $Br^{(-)}$ and $Cl^{(-)}$ concentrations were determined through ion chromatography measurements (for a synopsis of analytical methods, see Appendix A, Method Codes 006, 012, 039, and 017).

Sediment samples were analyzed for total petroleum hydrocarbon (TPH), benzene, ethylbenzene, toluene, and ortho (o)-, meta (m)-, and para (p)-xylene (BETX) content to determine residual contaminants associated with possible crude oil contamination using gas chromatography and mass spectrometry (for a synopsis of analytical methods, see Appendix A, Method Codes 016 and 028). At the time of sampling, water temperature, dissolved oxygen (DO) content, pH, and conductivity were measured at each of the 12 stream sites using a Hydrolab Scout 2 submersible multi-parameter water quality instrument.

In addition to the surface water and sediment collection points, two sampling points were established on each stream for the collection of macroinvertebrate samples to determine the macroinvertebrate community structure (Table 2 and Figures 4A and 4B). Three benthic grab samples were collected at each sampling point in the upper 15.0 cm (6.0 inches) of sediment using a Petite Ponar Grab. According to Minshall (1984), based on the composition of the substratum in all four streams, it was not expected that macroinvertebrates would penetrate below this depth. Once collected, these samples were placed in polypropylene containers and preserved with 70% isopropyl alcohol. After the grab samples were collected, both margins at each of the sampling points were vigorously worked in an upstream direction for a distance of approximately 5.0 meters (16.0 feet) for a period of 15 minutes using fine-mesh dip nets. Once collected, these dip net samples were screened through a fine mesh box seine, placed in plastic zip lock bags, and placed on ice. All macroinvertebrate samples were transported to the Arlington, Texas, Field Office for sorting and identification. The grab samples remained chilled until processed, while the

Table 2. Macroinvertebrate Collection Sites on One Stream in Fannin County, Texas, and Three Streams in Grayson County, Texas.		
Stream	**Site Identifier**	**Site Location**
Caney Creek	CCUSCRB	Off Refuge, 66.0 feet (20.0 meters) upstream of County Road (CR) 1020 in Fannin County, Texas.
	CCDSCRB	Off Refuge, 66.0 feet (20.0 meters) downstream of CR 1020 in Fannin County, Texas.
Big Mineral Creek	BMDSRRB	On Refuge, 82.0 feet (25.0 meters) downstream of rip-rap low water crossing in Grayson County, Texas.
	BMDSB	On Refuge, at the confluence with Martin's Branch in Grayson County, Texas.
Beaver Creek	BVUSPLB	On Refuge, 650.0 feet (200.0 meters) upstream of Missouri-Kansas-Texas rail line and 66.0 feet (20.0 meters) upstream of old pipeline in Grayson County, Texas.
	BVDSPLB	On Refuge, 525.0 feet (160.0 meters) upstream of Missouri-Kansas-Texas rail line and 66.0 feet (20.0 meters) downstream of old pipeline in Grayson County, Texas.
Sandy Creek	SUSOSB	On Refuge, 115.0 feet (35.0 meters) upstream of Old Sadler Road in Grayson County, Texas.
	SDSOSB	On Refuge, 33.0 feet (10.0 meters) downstreamof Old Sadler Road in Grayson County, Texas.

Figure 4A. Macroinvertebrate Sampling Points on Big Mineral Creek, Beaver Creek, and Sandy Creek, Hagerman National Wildlife Refuge, Grayson County, Texas (Maptech, 1998).

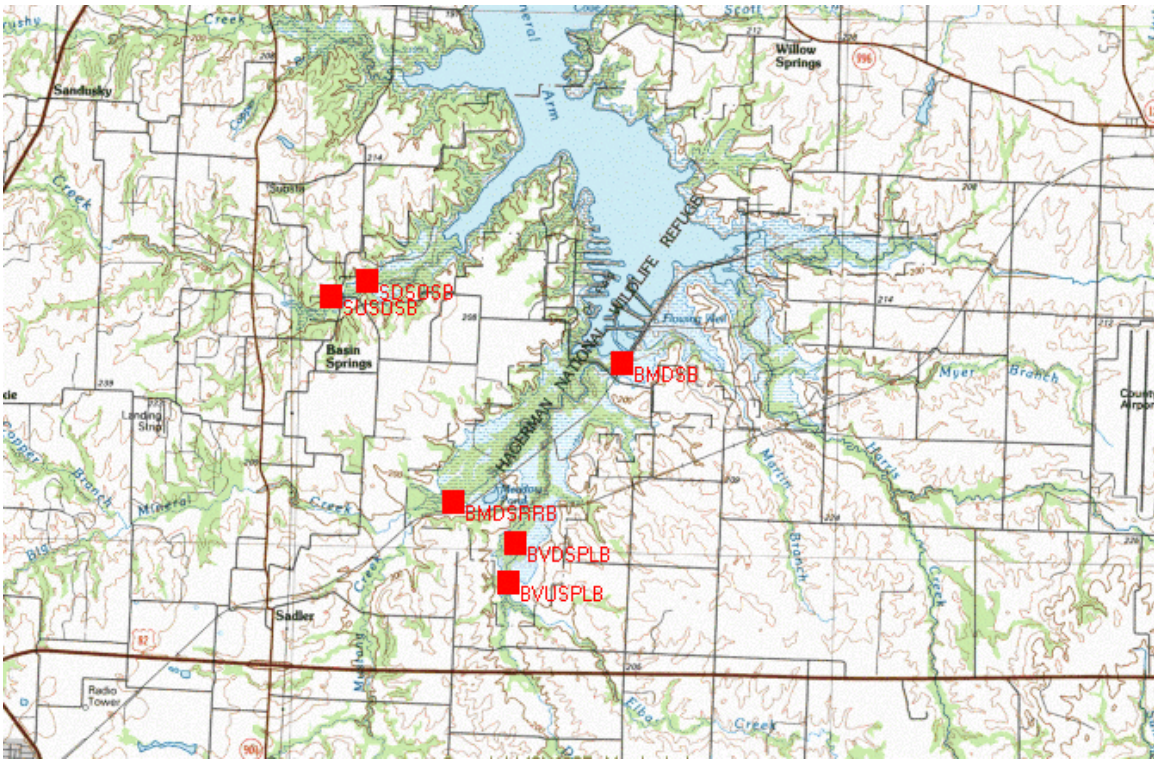


Figure 4B. Macroinvertebrate Sampling Points on Caney Creek, Fannin County, Texas (Maptech, 1998).

dip net samples were frozen until processed. The organisms collected were identified to the lowest taxonomic level practical utilizing Jaques (1951), Needham and Needham (1962), Brown (1976), McCafferty (1983), Thorp and Covich (1991), and Merrit and Cummins (1996).

RESULTS & DISCUSSION

WATER QUALITY

Water quality data measured at the time the surface water and sediment samples were collected from each of the 12 sites are presented in Table 3. The results of the surface water chemical analyses in parts per million (mg/L) are presented in Table 4. At the time of sampling, the water in all four streams was turbid, with an estimated visibility of 3.0 to 6.0 inches (7.6 to 15.2 cm) below the surface. Detected temperature, pH, and conductivity values from the four streams were within acceptable limits. DO concentrations were below the State criteria for Segment Nos. 0202 and 0203 in the downstream sample locations in Caney Creek, Big Mineral Creek and Beaver Creek and at all of the sites in Sandy Creek. These low DO concentrations may be attributed to time of sampling, depth of sampling, and/or negligible flow rates within these respective streams during the sampling period.

As would be expected, chloride, bromide, sodium, and lithium occur in much greater concentrations in oil field brines than in fresh groundwater and surface water (Morton, 1986). Still, chloride is one of the major inorganic anions in freshwater (APHA, 1985). Ambient water quality criterion protective of aquatic wildlife recommended by the State of Texas for chloride in Segment No. 0202 of the Red River is 375.0 mg/L, whereas due to natural halite deposition, the recommended water quality criterion for chloride in

Table 3. Measured water quality data from one stream in Fannin County, Texas, and three streams in Grayson County, Texas, compared with Surface Water Quality Standards from Texas Red River Segment Nos. 0202 and 0203. Note: m is meters; cm is centimeters; C is Celsius; DO is dissolved oxygen; and na is not applicable.

Stream	Site	Width m	Depth cm	Temperature C	DO mg/L	pH[1]	Conductivity[2] mhos/cm
Caney Creek	CC1753	7.0	45.7	29.08	6.9	7.5	567.0
	CCUSCR	10.0	61.0	29.75	4.7	7.7	579.0
	CCDSCR	11.0	76.2	29.59	4.0	7.6	529.0
Big Mineral Creek	BMUS	9.0	91.4	24.33	7.6	7.5	875.0
	BMDSRR	7.0	61.0	20.83	7.2	7.4	790.0
	BMDS	26.0	91.4	23.50	3.5	6.9	762.0
Beaver Creek	BVUS	8.0	45.7	21.94	7.6	7.4	330.0
	BVRR	3.5	45.7	20.64	7.6	7.3	436.0
	BVMID	20.0	91.4	20.87	4.2	7.1	445.0
Sandy Creek	SOR	14.0	45.7	21.29	4.5	7.0	1550.0
	SUSOS	9.0	76.2	21.38	4.3	7.0	1480.0
	SDSOS	12.0	45.7	21.52	4.2	7.0	1460.0
Segment 0202*	na	na	na	33.89	5.0	6.5	1167.5
Segment 0203*	na	na	na	33.33	5.0	6.5	1504.1

[1]Actual water quality standards for pH for both Segment Nos. 0202 and 0203 ranges from 6.5-9.0.
[2]Values presented for conductivity for Segment Nos. 0202 and 0203 represent reported values, not actual water quality standards.
*TNRCC, 1996b.

Table 4. Analytical results for surface water samples collected from three sites on Caney Creek (CC) in Fannin County, Texas, and from three sites each on Big Mineral Creek (BM), Beaver Creek (BV), and Sandy Creek (S) in Grayson County, Texas. Note: bdl is below detection limit.

Site	Bromide mg/L	Chloride mg/L	Lithium mg/L	Sodium mg/L
CC1753	bdl	9.7	bdl	27.1
CCUSCR	bdl	31.9	bdl	59.7
CCDSCR	bdl	28.1	bdl	54.6
BMUS	bdl	12.7	0.03	100.0
BMDSRR	bdl	92.4	0.04	73.6
BMDS	bdl	396.0	0.02	245.0
BVUS	bdl	15.6	bdl	14.2
BVRR	bdl	10.8	0.02	23.3
BVMID	bdl	20.3	0.02	19.0
SOR	1.58	299.0	0.02	114.0
SUSOS	1.51	318.0	0.02	115.0
SDSOS	1.30	220.0	0.03	112.0
Brine	668.0	116,000	3.53	58,670.0

Bromide detection limit = 0.01 mg/L
Chloride detection limit = 0.006 mg/L
Lithium detection limit = 0.01 mg/L
Sodium detection limit = 0.2 mg/L

Segment No. 0203 is 600.0 mg/L (TNRCC, 1996b). According to Morton (1986), degradation of water quality by brine is indicated where chloride concentrations are greater than 400.0 mg/L. The measured chloride concentration in the water sample collected from Big Mineral Creek at the confluence with Martin's Branch was the only sample that approached 400.0 mg/L; however, it was well below 600.0 mg/L. Morton (1986) also states that degradation of water quality by brine is indicated where bromide concentrations are 2.0 mg/L. The American Public Health Association (1985) further adds that bromide concentrations in some groundwater supplies have been ascribed to connate water; however, under normal circumstances, the bromide content of most fresh waters is negligible, seldom exceeding 1.0 mg/L. Bromide concentrations were below the analytical detection limits in Caney Creek, Big Mineral Creek, and Beaver Creek. Detected bromide concentrations in Sandy Creek were >1.0 mg/L but below 2.0 mg/L.

Currently, there are no surface water standards for sodium or lithium in Texas Red River Segment No. 0202 or No. 0203. Sodium is an alkali metal which is considered the third most abundant cation in freshwater systems after calcium and magnesium (Cole, 1983). In natural seawater, prior to evaporation, sodium concentrations can range up to 11,000.0 mg/L (Morton, 1986). In North America, the average sodium concentration in freshwater lotic systems is 9.0 mg/L (Goldman and Horne, 1994). The sodium levels detected in all four streams exceeded this concentration with the highest concentrations being detected in Big Mineral Creek; however, these detected concentrations were over 200 times less than the detected sodium concentration in the brine sample. Natural seawater contains approximately 0.2 mg/L of lithium which increases as evaporation increases (Morton, 1986). The detected lithium concentrations in Big Mineral, Beaver, and Sandy Creeks were 10 times less than this concentration and 100 times less than the detected concentration in the brine sample.

Morton (1986) states that degraded water quality attributable to brine intrusion can be ascertained by calculating the lithium to bromide ratio, the sodium to chloride ratio, the sodium to bromide ratio, and the bromide to chloride ratio provided that chloride levels are 400.0 mg/L and bromide concentrations are 2.0 mg/L. Morton (1986) further states that a lithium to bromide ratio of 0.01, a sodium to chloride ratio of ~ 0.46, a sodium to bromide ratio of ~ 92.0, and bromide to chloride ratio of ~ 0.0048 would all be indicative of brine contamination in freshwater. However, as previously stated, detected chloride levels were <400.0 mg/L and detected bromide concentrations were <2.0 mg/L; therefore, the aforementioned ratios were not calculated for this study.

SEDIMENTS

The results of the sediment chemical analyses in parts per million (mg/kg) dry weight are presented in Table 5. The TPH analysis was performed because it is an inexpensive screening mechanism useful in determining the possible presence of petroleum contaminated sediments (TNRCC, 1995). TPH concentrations were below the analytical detection limits (refer to Table 5) in the upstream sites at Caney Creek, Big Mineral Creek, and Sandy Creek; in the midstream sampling points at Beaver Creek and Sandy Creek; and at the downstream sample site on Big Mineral Creek. The detected TPH concentrations in sediments from the remaining sites at Caney Creek, Big Mineral Creek, and Beaver Creek were <50.0 mg/kg. These detected concentrations may be attributed to the incidental breakdown of hydrocarbons within these respective streams. The detected TPH value at the downstream sampling point in Sandy Creek was elevated; however, this may be attributed to run-off from the asphalt bridge discharging into the stream.

Benzene, ethylbenzene, toluene, and xylene are all components of crude oil (USEPA, 1980a; USEPA,1980b; Verschueren, 1983; Shineldecker, 1992). Benzene is a known human carcinogen (USEPA, 1980a). In freshwater, the recommended ambient water quality chronic criterion for benzene protective

Table 5. Analytical Results in mg/kg dry weight of Sediment Samples Collected from Caney Creek (CC), Big Mineral Creek (BM), Beaver Creek (BV), and Sandy Creek (S). Note: TPH is total petroleum hydrocarbons; dw is dry weight; dl is analytical detection limit in mg/kg dry weight; and bdl is below detection limit.

Sample	% Moisture	TPH (mg/kg dw)	dl	Benzene (mg/kg dw)	dl	Ethylbenzene (mg/kg dw)	dl	Xylene (m,p,o) (mg/kg dw)	dl	Toluene (mg/kg dw)	dl
CC1753S	22.9	bdl	1.3	bdl	0.06	bdl	0.06	bdl	0.06	0.31	0.06
CCUSCRS	24.3	8.6	1.3	bdl	0.07	bdl	0.07	bdl	0.07	0.31	0.07
CCDSCRS	29.9	21.0	1.4	bdl	0.07	bdl	0.07	bdl	0.07	0.34	0.07
BMUSS	22.2	bdl	1.3	bdl	0.06	bdl	0.06	bdl	0.06	0.13	0.06
BMDSRRS	29.8	45.3	1.4	bdl	0.07	bdl	0.07	bdl	0.07	0.13	0.07
BMDSS	35.2	bdl	1.5	bdl	0.08	bdl	0.08	bdl	0.08	0.15	0.08
BVUSS	28.5	25.1	1.4	bdl	0.07	bdl	0.07	bdl	0.07	0.14	0.07
BVRRS	18.6	bdl	1.2	bdl	0.06	bdl	0.06	bdl	0.06	0.11	0.06
BVMIDS	33.2	44.6	1.5	bdl	0.07	bdl	0.07	bdl	0.07	0.14	0.07
SORS	26.2	bdl	1.4	bdl	0.07	bdl	0.07	bdl	0.07	0.13	0.07
SUSOSS	29.9	bdl	1.4	bdl	0.07	bdl	0.07	bdl	0.07	0.13	0.07
SDSOSS	23.6	1,666.0	1.3	bdl	0.07	bdl	0.07	bdl	0.07	0.13	0.07

of aquatic wildlife is 0.046 mg/L (TNRCC, 1996a). For sediments, the recommended criterion is 0.057 mg/kg (TNRCC, 1996a). None of the sediment samples collected from Caney Creek, Big Mineral Creek, Beaver Creek, or Sandy Creek contained benzene concentrations above the analytical detection limits (Table 5). In freshwater, acute toxicity to aquatic organisms occurs at ethylbenzene concentrations of 32.0 mg/L (USEPA, 1986). The ambient water criterion is 1.4 mg/L for the protection of human health from the toxic properties of ethylbenzene ingested through water and contaminated aquatic organisms, (USEPA, 1986); however, the recommended ambient water quality chronic criterion protective of aquatic wildlife is 0.29 mg/L (TNRCC, 1996a). In sediments, the recommended criterion is 3.6 mg/kg (TNRCC, 1996a). None of the sediment samples collected from Caney Creek, Big Mineral Creek, Beaver Creek, or Sandy Creek contained ethylbenzene concentrations above the analytical detection limits. Toluene concentrations of 17.5 mg/L in freshwater are acutely toxic to aquatic organisms (USEPA, 1986). For the protection of human health against the toxic properties of toluene ingested through water and contaminated aquatic organisms, the ambient water criterion is 14.3 mg/L (USEPA, 1986); whereas, the recommended ambient water quality chronic criterion protective of aquatic wildlife is 0.13 mg/L (TNRCC, 1996a). In sediments, the recommended criterion is 0.67 mg/kg (TNRCC, 1996a). Toluene concentrations were detected above the analytical detection limits in all of the sediment samples collected from Caney Creek, Big Mineral Creek, Beaver Creek, and Sandy Creek, with the highest concentrations detected in Caney Creek. None of the detected concentrations from any of the four streams approached or exceeded 0.67 mg/kg. Xylene exists in three isomeric forms, ortho-, meta-, and para-xylene (Fishbein, 1985). In freshwater, the recommended ambient water quality chronic criterion protective of aquatic wildlife is 0.0018 mg/L (TNRCC, 1996a). For sediments, the recommended criterion is 0.025 mg/kg (TNRCC, 1996a). None of the sediment samples collected from Caney Creek, Big Mineral Creek, Beaver Creek, or Sandy Creek contained meta-, para-, or ortho-xylene concentrations above the analytical detection limits.

MACROINVERTEBRATES

According to Hynes (1984), in addressing aquatic invertebrate communities, family boundaries typically define ecological niches. In turn, community structure of benthic macroinvertebrate populations can be used to evaluate conditions in streams receiving organic wastes (Wilhm, 1967). The results of the macroinvertebrate sampling from the four streams are presented in Tables 6A-6E. Using these results and employing the equation:

$$\frac{(s - 1)}{\ln} \qquad \text{where: } s = \text{number of species}$$
$$= \text{number of individuals}$$

diversity indices were calculated for the macroinvertebrate populations for each stream (Figure 5). Chronic exposure to petroleum hydrocarbons can reduce both diversity and abundance of macroinvertebrates (Wiederholm, 1984). According to Harrel (1985), the responses of the macroinvertebrate community to a crude oil release in a southeast Texas stream included an increase in density of oligochaetes, a decrease in numbers and taxa of chironomids, and overall low community diversity. This was not the case in any of the streams sampled. The most abundant family of macroinvertebrates found in all four streams were chironomids. Oligochaetes were present in all four streams, but in low numbers. Gatherers/collectors dominated the trophic levels within Caney, Big Mineral, and Beaver Creeks (Figure 6). The second most abundant trophic groups in Big Mineral and Beaver were predators, whereas scrapers were the second most abundant group in Caney Creek (Figure 6). Sandy Creek demonstrated more of an evenness in distribution between gatherers/collectors and predators, 46% verses 39%, respectively, than the other three streams (Figure 6). In comparison to the control stream, Caney Creek, the macroinvertebrate communities within the three streams from the Refuge exhibited equivalent or greater diversity indices. Caney Creek had an overall diversity index of 3.58, whereas the calculated diversity indices for Big Mineral, Beaver,

Table 6A. Groups of Invertebrates and Corresponding Number of Individuals Collected from One Stream in Fannin County, Texas, and Three Streams in Grayson County, Texas.								
Invertebrate Group	**Caney Creek**		**Sandy Creek**		**Big Mineral Creek**		**Beaver Creek**	
	Number of Individuals	% of Total	Number of Individuals	% of Total	Number of Individuals	% of Total	Number of Individuals	% of Total
Diptera	1479	59.6	853	26.0	1037	51.0	337	60.9
Coleoptera	71	2.9	558	17.0	88	4.3	36	6.5
Odonata	18	0.7	177	5.4	28	1.4	3	0.5
Ephemeroptera	174	7.0	662	20.2	53	2.6	35	6.3
Trichoptera	7	0.3	10	0.3	2	0.1	1	0.2
Plecoptera	10	0.4	0	0	0	0	0	0
Hemiptera	87	3.5	502	15.3	440	21.7	29	5.2
Megaloptera	1	0.04	22	0.7	1	0.05	0	0
Lepidoptera	0	0.0	0	0.0	0	0.0	2	0.4
Oligochaeta	58	2.3	63	1.9	66	3.2	15	2.7
Nematoda	4	0.2	2	0.06	1	0.05	4	0.7
Gastropoda	484	19.5	424	12.9	284	14.0	52	9.4
Bivalvia	63	2.5	0	0	14	0.7	3	0.5
Collembola	1	0.04	6	0.2	2	0.1	2	0.4
Decapoda	27	1.1	0	0	17	0.8	40	7.2
Total Number of Individuals	2484		3279		2033		559	

and Sandy Creeks were 4.86, 3.32, and 4.70 respectively.

Macroinvertebrates may also be used as bio-indicators of water quality based on their tolerance to contamination (Kolbe and Luedke, 1993). In general, tolerant organisms are found in polluted streams; whereas, due to their sensitivity, intolerant organisms would not be found in contaminated streams. However, water quality is not always the limiting factor in the presence or absence of aquatic organisms and the lack of suitable habitat (i.e., riffles, deep margins, etc.) can be just as limiting a factor as poor water quality (Sheldon, 1984; Kolbe and Luedke, 1993). Kolbe and Luedke (1993) further state that degraded streams are typically dominated by dipterans (maggot, cranefly, horsefly, and midge (chironomid) larvae), hirudineans (leeches) and pulmonate gastropods (snails). Moderately impacted streams exhibit macroinvertebrate communities with increased numbers of odonates (dragonflies and damselflies), simuliids (blackflies), decapods (crayfish and shrimp), and bivalves (mussels) (Kolbe and Luedke, 1993). Megalopterans (hellgramites), coleopterans (beetles), plecopterans (stoneflies), ephemeropterans (mayflies), and tricopterans (caddisflies) are considered sensitive groups and would not be expected to be present in contaminated systems (Kolbe and Luedke, 1993). According to Barbour *et al*. (1999), without relatively

Table 6B. Macroinvertebrates with Corresponding Trophic Groups Collected from Caney Creek, Fannin County, Texas.

Group	Family	Genus	Trophic Group*	No. of Individuals
Oligochaeta			Gatherers/Collectors	58
Diptera	Chironomidae		Gatherers/Collectors	1387
	Ceratopogonidae	*Atrichopogon sp.*	Predators	1
			Predators	86
	Chaoboridae	*Chaoborus sp.*	Predators	1
	Culicidae		Gatherers/Collectors	1
	unknown			3
Coleoptera	Dytiscidae		Predators	18
	Hydrophilidae	*Berosus sp.*	Predators	6
	Curculionidae			17
	Haliplidae	*Peltodytes sp.*	Shredders	25
	Elimidae		Gatherers/Collectors	4
	Scirtidae		Scrapers	1
Odonata	Gomphidae	*Arigomphus sp.*	Predators	3
	Coenagrionidae		Predators	15
Ephemeroptera	Caenidae		Gatherers/Collectors	170
Trichoptera	Hydroptilidae		Scrapers	1
	Leptoceridae		Gatherers/Collectors	1
	unknown			5
Plecoptera	Perlidae	*Perlesta sp.*	Predators	10
Hemiptera	Corixidae		Predators	87
Megaloptera	Sialidae	*Sialis sp.*	Predators	1
Decapoda	Cambaridae		Gatherers/Collectors	3
	Palaemonidae		Shredders	24
Nematoda			Parasites	4
Bivalva			Filer/Collectors	63
Gastropoda	Ancylidae		Scrapers	2
			Scrapers	482
Collembola			Gatherers/Collectors	1

*Organisms were classified in trophic groups in accordance with Barbour *et al.*, 1999.

Table 6C. Macroinvertebrates with Corresponding Trophic Groups Collected from Beaver Creek, Hagerman National Wildlife Refuge, Grayson County, Texas.				
Group	**Family**	**Genus**	**Trophic Group***	**No. of Individuals**
Oligochaeta			Gatherers/Collectors	15
Diptera	Chironomidae		Gatherers/Collectors	314
	Ceratopogonidae		Predators	14
	Culicidae		Gatherers/Collectors	2
	unknown			7
Coleoptera	Dytiscidae		Predators	30
	Hydrophilidae	*Berosus sp.*	Predators	1
	Helophoridae	*Helophorus sp.*	Shredders	3
	Curculionidae			2
Odonata	Coenagrionidae		Predators	3
Ephemeroptera	Caenidae		Gatherers/Collectors	32
	Baetidae		Gatherers/Collectors	2
	Ephemeridae	*Hexagenia sp.*	Gatherers/Collectors	1
Trichoptera	unknown			1
Hemiptera	Corixidae		Predators	29
Megaloptera	Sialidae	*Sialis sp.*	Predators	1
Lepidoptera	Tortrichidae	*Archips sp.*	Shredders	2
Decapoda	Cambaridae		Gatherers/Collectors	40
Nematoda			Parasites	4
Bivalva			Filer/Collectors	3
Gastropoda			Scrapers	52
Collembola			Gatherers/Collectors	2

*Organisms were classified in trophic groups in accordance with Barbour *et al.*, 1999.

stable trophic dynamics in a freshwater lotic system, an imbalance in functional feeding groups will result, reflecting stressed conditions in the stream. As previously stated, Caney, Big Mineral, and Beaver Creeks were dominated by gatherers/collectors. This type of generalist feeding strategy allows for a broad range of acceptable food materials, and thus, these organisms tend to be more tolerant to pollution which might alter the availability of certain food items (Barbour *et al.*, 1999). Specialized feeders such as scrapers, shredders, and predators rely on more specific food items and would be detrimentally impacted by contaminants which affect these food sources (Barbour *et al.*, 1999). Filter feeders are thought to be sensitive in low gradient streams (Barbour *et al.*, 1999).

Table 6D. Macroinvertebrates with Corresponding Trophic Groups Collected from Big Mineral Creek, Hagerman National Wildlife Refuge, Grayson County, Texas.

Group	Family	Genus	Trophic Group*	No. of Individuals
Oligochaeta			Gatherers/Collectors	66
Diptera	Chironomidae		Gatherers/Collectors	918
	Ceratopogonidae	*Atrichopogon sp.*	Predators	2
			Predators	19
	Chaoboridae	*Chaoborus sp.*	Predators	13
	Tabanidae		Predators	1
	Tipulidae		Shredders	1
	Stratiomyidae	*Stratiomys sp.*	Gatherers/Collectors	1
	Simuliidae		Filter/Collectors	81
	Culicidae		Gatherers/Collectors	1
Coleoptera	Dytiscidae		Predators	38
	Gyrinidae	*Gyrinus sp.*	Predators	2
		Dineutes sp.	Predators	1
	Hydrophilidae	*Berosus sp.*	Predators	9
		Tropisternus sp.	Predators	7
	Curculionidae		Shredders	2
	Haliplidae	*Peltodytes sp.*	Shredders	25
	Chrysomelidae		Shredders	1
	Elimidae		Gatherers/Collectors	1
Odonata	Gomphidae	*Dromogomphus sp.*	Predators	1
	Aeshnidae	*Anax sp.*	Predators	4
	Coenagrionidae		Predators	23
Ephemeroptera	Caenidae		Gatherers/Collectors	50
	Baetidae		Gatherers/Collectors	3
Trichoptera	unknown			2
Hemiptera	Corixidae		Predators	365
	Gerridae		Predators	44
	Belostomatidae		Predators	2
	Notonectidae		Predators	21
	Pleidae	*Neoplea sp.*	Predators	1
	Hydrometridae	*Hydrometra sp.*	Predators	7
Megaloptera	Corydalidae	*Chauloides sp.*	Predators	1
Decapoda	Cambaridae		Gatherers/Collectors	1
	Palaemonidae		Shredders	16
Nematoda			Parasites	1
Bivalva			Filer/Collectors	14
Gastropoda			Scrapers	284
Collembola			Gatherers/Collectors	2

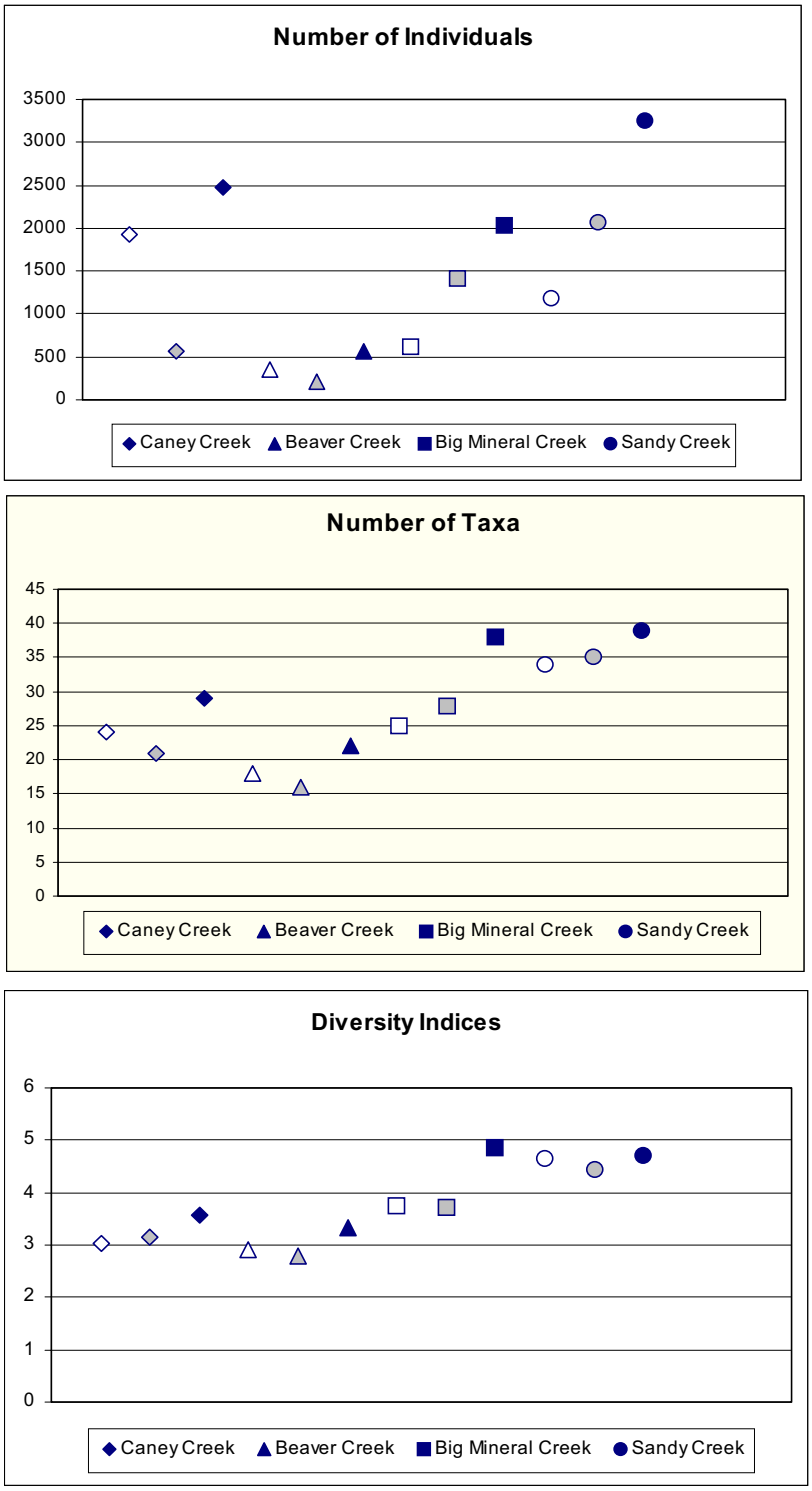
*Organisms were classified in trophic groups in accordance with Barbour *et al.*, 1999.

Table 6E. Macroinvertebrates with Corresponding Trophic Groups Collected from Sandy Creek, Hagerman National Wildlife Refuge, Grayson County, Texas.

Group	Family	Genus	Trophic Group*	No. of Individuals
Oligochaeta			Gatherers/Collectors	63
Diptera	Chironomidae		Gatherers/Collectors	740
	Ceratopogonidae		Predators	98
	Tabanidae		Predators	1
	Tipulidae		Shredders	1
	Stratiomyidae	*Stratiomys sp.*	Gatherers/Collectors	4
	Psychodidae		Gatherers/Collectors	3
	unknown			6
Coleoptera	Dytiscidae		Predators	246
	Gyrinidae	*Gyrinus sp.*	Predators	19
		Dineutes sp.	Predators	5
	Hydrophilidae	*Berosus sp.*	Predators	223
		Tropisternus sp.	Predators	5
	Hydrochidae	*Hydrochus sp.*	Shredders	6
	Haliplidae	*Peltodytes sp.*	Shredders	39
		Haliplus sp.	Shredders	8
	Scirtidae		Shredders	4
Odonata	Libellulidae	*Sympetrum sp.*	Predators	2
		Pachydiplax sp.	Predators	1
	Corduliidae		Predators	5
	Aeshnidae	*Anax sp.*	Predators	20
			Predators	6
	Coenagrionidae		Predators	123
Ephemeroptera	Caenidae		Gatherers/Collectors	620
	Baetidae		Gatherers/Collectors	36
	Ephemeridae	*Hexagenia sp.*	Gatherers/Collectors	6
Trichoptera	Leptoceridae		Gatherers/Collectors	2
	unknown			8
Hemiptera	Corixidae		Predators	434
	Gerridae		Predators	8
	Belostomatidae		Predators	21
	Nepidae	*Ranatra sp.*	Predators	2
	Pleidae	*Neoplea sp.*	Predators	5
	Hydrometridae	*Hydrometra sp.*	Predators	30
Megaloptera	Corydalidae	*Chauloides sp.*	Predators	12
	Sialidae	*Sialis sp.*	Predators	10
Nematoda			Parasites	2
Gastropoda			Scrapers	424
Collembola			Gatherers/Collectors	6

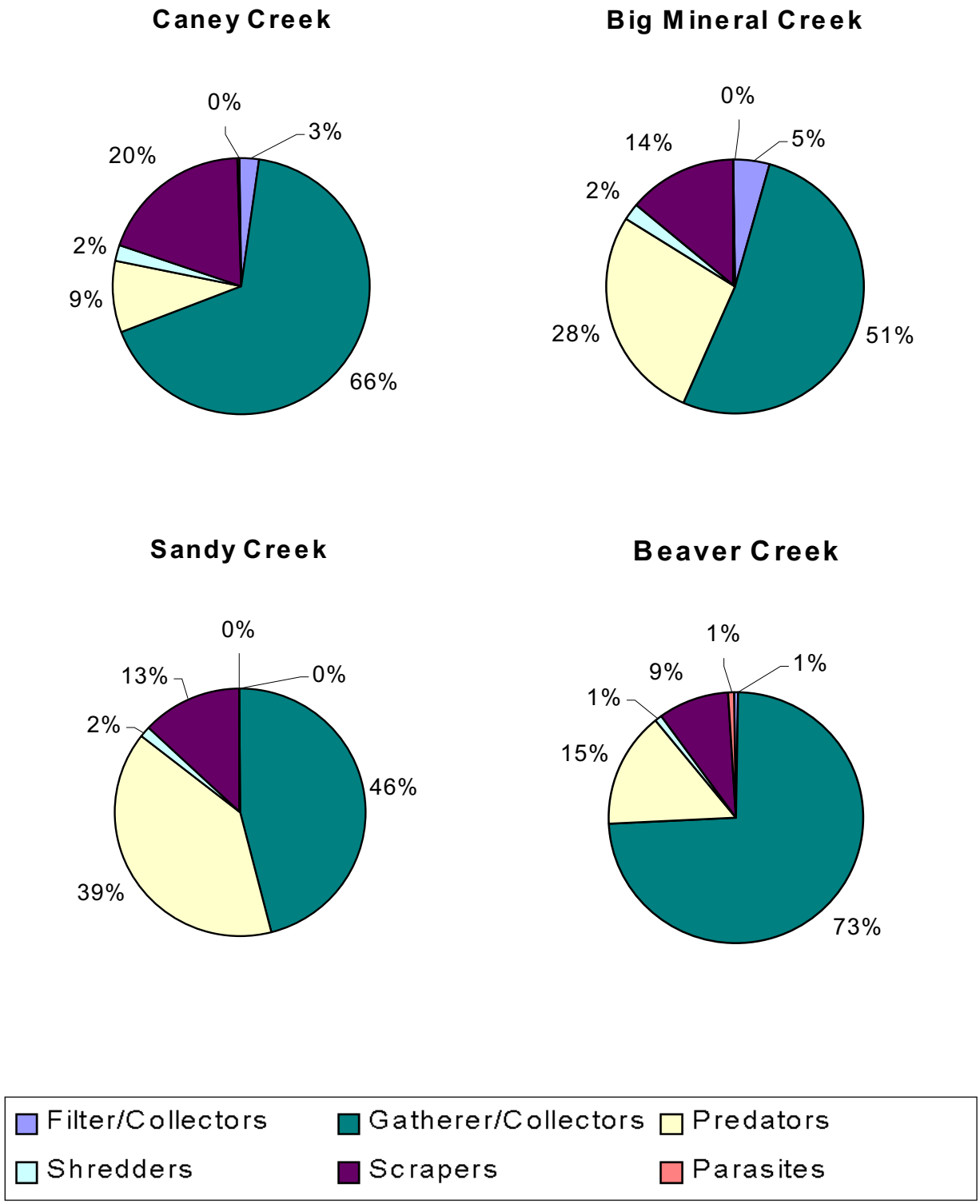
*Organisms were classified in trophic groups in accordance with Barbour *et al.*, 1999.

Figure 5. Number of Individuals, Number of Taxa, and Diversity Indices for Caney Creek, Beaver Creek, Big Mineral Creek, and Sandy Creek.



Note - clear figure represents upstream site, lightly shaded figure represents downstream site, while darkly shaded figure represents total number for the given stream.

Figure 6. Macroinvertebrate Trophic Group* Composition for Caney Creek, Beaver Creek, Big Mineral Creek, and Sandy Creek *(from Barbour *et al.*, 1999).



Based on sensitivity, pollution tolerance values have been assigned to certain aquatic macroinvertebrates to assist in assessing the water quality of a stream (Plafkin *et al.,* 1989; Kolbe and Luedke, 1993). These tolerance values range from 0 to 10 with 0 being the least tolerant and 10 being the most tolerant (Plafkin *et al.*, 1989). Using the results from the four streams the corresponding tolerance values for the organisms collected are as follows: for megalopterans collected, the range is from 3 to 4; for dipterans, from 3 to 8 (simuliids have a value of 6; chironomids have a value ranging from 6 to 8; and tipulids have a value of 3); for plecopterans, from 1 to 2; for ephemeropterans, from 4 to 7; for odonates, 1 to 9 (the Family Aeshnidae has a value of 3; the Family Gomphidae has a value of 1; and the Family Coenagrionidae has a value of 9); tricopterans have a value of 4; and hemipterans and coleopterans have a value of 5 (Plafkin *et al.,* 1989; Kolbe and Luedke, 1993). Based on the assigned tolerance values of the macroinvertebrate organisms inhabiting the Refuge streams sampled, it appears that overall water quality in these streams ranges from fair to good and that the chronic impact from crude oil and brine releases to the macroinvertebrate communities appears to be negligible.

CONCLUSIONS & RECOMMENDATIONS

The water chemistry analyses from this study indicated that residual brine did not appear to be present in any of the streams sampled on the Refuge. Residual TPH, benzene, ethylbenzene, toluene, and xylene concentrations in sediments within Big Mineral Creek, Beaver Creek, and Sandy Creek from previous crude oil spills did not appear to be at levels that represent an ecological concern at the time the study was conducted. Considering that the streams sampled within the Refuge contained as diverse macroinvertebrate communities as an un-impacted off-refuge stream, it appears that in the Refuge streams sampled, the impact of residual crude oil and brine contamination on the macroinvertebrate communities was negligible. Furthermore, based on the macroinvertebrate organisms inhabiting the streams sampled within the Refuge, overall water quality within these streams appeared to range from fair to good.

Since the downstream sampling site at Sandy Creek apparently did not incorporate enough distance to be out of the influence from direct run-off from the asphalt road, it is recommended that any future sampling at Sandy Creek be conducted in a manner to include a greater distance between sampling points. In addition, based on historical contamination from crude oil and brine releases, and current releases from crude oil production units (see Appendix B), intensive water, sediment, and macroinvertebrate sampling should be conducted at Harris Creek.

REFERENCES

American Public Health Association (APHA). 1985. Standard Methods for the Examination of Water and Wastewater, 16th Edition. American Public Health Association. Washington, D.C. 1268 pp.

Baker, D.L., R. Irwin, and S. Dodson. 1995. Initial Contaminants Survey of Hagerman National Wildlife Refuge, Texas. U.S. Fish and Wildlife Service. Arlington, Texas. 26 pp.

Barbour, M.T., J. Gerritsen, B.D. Snyder, and J.B. Stribling. 1999. Rapid Bioassessment Protocols for Use in Streams and Wadeable Rivers: Periphyton, Benthic Macroinverterbrates, and Fish (2nd Edition). U.S. Environmental Protection Agency. Washington, D.C.

Brown, H.P. 1976. Aquatic Dryopid Beetles (Coleoptera) of the United States. Wat. Poll. Res. Ser. U.S. Environmental Protection Agency. Washington, D.C. 82 pp.

Cole, G.A. 1983. Textbook of Limnology, 3rd Edition. C.V. Mosby Company. St. Louis, Missouri. 401 pp.

Fishbein, L. 1985. An Overview of Environmental and Toxicological Aspects of Aromatic Hydrocarbons III. Xylene. The Science of the Total Environment, 43. Elsevier Scince Publishers. Amsterdam, The Netherlands. pp 165-183.

Goldman, C.R. and A.J. Horne. 1994. Limnology, 2nd Edition. McGraw-Hill, Incorporated. St. Louis, Missouri. 576 pp.

Harrel, R.C. 1985. Effects of a crude Oil Spill on Water Quality and Macrobenthos of A Southeast Texas Stream. Hydrobiologia 124. pp 223-228.

Hynes, H.B.N. 1984. The Relationships Between the Taxonomy and Ecology of Aquatic Insects. In V.R. Resh and D.M. Rosenberg, eds. The Ecology of Aquatic Insects. Praeger Publishers. New York, New York. pp 9-23.

Jaques, H.E. 1951. How to Know Beetles. W.C. Brown. Dubuque, Iowa. 372 pp.

Kolbe, C.M. and M.W. Luedke. 1993. A Guide to Freshwater Ecology. Texas Natural Resource Conservation Commission. Austin, Texas. 138 pp.

Maptech. 1998. Terrain Navigator Dallas-Fort Worth (Sherman). Maptech. Greenland, New Hampshire.

McCafferty, P.W. 1983. Aquatic Entomology. Jones and Bartlett. Boston, Massachusetts. 448 pp.

Merrit, R.W. and K.W. Cummins (eds). 1996. An Introduction to the Aquatic Insects of North America, 3rd Edition. Kendall/Hunt. Dubuque, Iowa. 862 pp.

Minshall, G.W. 1984. Aquatic Insect-Substratum Relationships. In V.R. Resh and D.M. Rosenberg, eds. The Ecology of Aquatic Insects. Praeger Publishers. New York, New York. pp 358-400.

Morton, R.B. 1986. Effects of Brine on the Chemical Quality of Water in Parts of Creek, Lincoln, Okfuskee, Payne, Pottawatomie, and Seminole Counties, Oklahoma. Oklahoma Geological Survey.

Oklahoma City, Oklahoma.

Needham, J.G. and P.R. Needham. 1962. A Guide to the Study of Freshwater Biology, 5th Edition. Holden-Day. San Francisco, California. 108 pp.

Plafkin, J.L., M.T. Barbour, K.D. Porter, S.K. Gross, and R.M. Hughes. 1989. Rapid Bioassessment Protocols for Use in Streams and Rivers: Benthic Macroinvertebrates and Fish. U.S. Environmental Protection Agency. Washington, D.C.

Sheldon, A.L. 1984. Colonization Dynamics of Aquatic Insects. In V.R. Resh and D.M. Rosenberg, eds. The Ecology of Aquatic Insects. Praeger Publishers. New York, New York. pp 401-429.

Shineldecker, C.L. 1992. Handbook of Environmental Contaminants: A Guide for Site Assessment. Lewis Publishers. Ann Arbor, Michigan. 371 pp.

Texas Natural Resource Conservation Commission (TNRCC). 1995. Guidance for Risk-Based Assessments at LPST Sites in Texas (RG-175). Texas Natural Resource Conservation Commission. Austin, Texas. 23 pp.

Texas Natural Resource Conservation Commission (TNRCC). 1996a. Guidance for Conducting Ecological Risk Assessments Under the Texas Risk Reduction Program. Texas Natural Resource Conservation Commission. Austin, Texas. 80 pp.

Texas Natural Resource Conservation Commission (TNRCC). 1996b. The State of Texas Water Quality Inventory, 13th Edition, Volume 2 (SFA-50). Texas Natural Resource Conservation Commission. Austin, Texas. 758 pp.

Texas Natural Resource Conservation Commission (TNRCC). 1997. Emergency Response Database for Grayson County, Texas. Texas Natural Resource Conservation Commission. Austin, Texas.

Texas Parks and Wildlife Department (TPWD). 1997. Pollution Response Inventory and Species Mortality (PRISM) Database. Compiled by Texas Parks and Wildlife Department Kills and Spills Team, Resource Protection Division. Austin, Texas.

Texas Water Commission (TWC). 1989. Groundwater Quality of Texas (Reports 89-01). Texas Water Commission. Austin, Texas. 197 pp.

Thorp, J.H. and A.P. Covich (eds). 1991. Ecology and Classification of North American Freshwater Invertebrates. Academic Press. San Diego, California. 911 pp.

U.S. Environmental Protection Agency (USEPA). 1980a. Ambient Water Quality Criteria for Benzene (EPA 440/5-80-018). U.S. Environmental Protection Agency. Washington, D.C.

U.S. Environmental Protection Agency (USEPA). 1980b. Ambient Water Quality Criteria for Ethylbenzene (EPA 440/5-80-048). U.S. Environmental Protection Agency. Washington, D.C.

U.S. Environmental Protection Agency (USEPA). 1986. Quality Criteria for Water (EPA 440/5-86-001). U.S. Environmental Protection Agency. Washington, D.C.

U.S. Fish and Wildlife Service (USFWS). 1989. Hagerman National Wildlife Refuge (RF-21580-1). U.S. Fish and Wildlife Service, Hagerman National Wildlife Refuge. Sherman, Texas.

U.S. Fish and Wildlife Service (USFWS). 1997. Contaminant Assessment Process Database for Hagerman National Wildlife Refuge. U.S. Fish and Wildlife Service. Arlington, Virginia.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Company. Cincinnati, Ohio. 1310 pp.

Wiederholm, T. 1984. Response of Aquatic Insects to Environmental Pollution. In V.R. Resh and D.M. Rosenberg, eds. The Ecology of Aquatic Insects. Praeger Publishers. New York, New York. pp 508-558.

Wilhm, J.L. 1967. Comparison of Some Diversity Indices Applied to Populations of Benthic Macroinvertebrates in a Stream Receiving Organic Wastes. Journal WPCF, Vol. 39, No. 10, Part 1. pp 1673-1683.

APPENDIX A
(Analytical Methods)

Method Codes: 006, 012, 039, and 017
Laboratory: Research Triangle Institute

For Samples: BMDS, BMDSRR, BMUS, BVMID, BVRR, BVUS, SDSOS, SOR, and SUSOS

Method Code 006/039: Measurement by ICP and ICP-MS.
ICP measurements to determine lithium and sodium concentrations in water were made using a Leeman Labs Plasma Spec I sequential or ES2000 simultaneous spectrometer.

Method Code 012: Digestion for Graphite Furnace Atomic Absorption (GFAA) Measurement.
Using a CEM microwave oven, 50.0 ml of water sample were heated in a capped 120.0 ml Teflon vessel in the presence of 5.0 ml of Baker Instra-Analyzed nitric acid for 15 minutes at 300 watts. The sample was then diluted to 50.0 ml with laboratory pure water to determine calcium, potassium, lithium, sodium, and rubidium concentrations in water.

Method Code 017: IC Measurement of Water Samples.
Bromide and chloride anions in water were determined by ion chromatography.

Method Codes: 003, 016, and 028
Laboratory: Geochemical & Environmental Research Group, Texas A&M

For Samples: CC1753S, CCDSCRS, CCUSCRS, BMDSRRS, BMDSS, BMUSS, BVMIDS, BVRRS, BVUSS, SDSOSS, SORS, and SUSOSS

Method Code 003: Determining % Moisture in Sediment.
Approximately 1.0 gram of wet sample was weighed into a clean, labeled, pre-weighed 10.0 ml beaker. The Beaker was placed in a forced air oven at approximately 75.0 C for 24 hours. The beaker was then weighed and the % dry weight was calculated by the formula:

$$\frac{\text{(wt. dry sample and beaker) - (wt. beaker) (100)}}{\text{(wt. wet sample and beaker) - (wt. beaker)}}$$

Method Code 016: Determination of Benzene, Toluene, Ethylbenzene, and M,P,O-Xylene by Gas Chromatography/Mass Spectrometry (GC/MS)
The method described quantitatively determines Benzene, Toluene, Ethylbenzene, and M,P,O-Xylene (BTEX) in a variety of matrices. This method is applicable to nearly all types of samples including water, sediments, soils, waste solvents, sludges, and industrial wastes. Quantitation is performed by gas chromatography/mass spectrometry in the full scan mode. The BTEX compounds are introduced into the GC by a purge and trap technique and detected using MS which provides both qualitative and quantitative information. The GC/MS system is operated to obtain separation of the analytes of interest from any interferences. In sample preparation, the sample was drawn into a syringe and the volume was adjusted to either 5.0 or 25.0 ml. Once the volume was adjusted, the surrogate and internal standards were added. A second aliquot was removed at that time to protect the integrity of the sample. The sample was then introduced into the purging device, while the second sample was maintained only until such time when the first sample had been properly analyzed. After the sample and appropriate standards were transferred to the purging device, the purging program was initiated. The samples were purged with purified helium at a flow of 40.0 ml/minute for 11 minutes at a temperature of 75.0 C. The purged analytes were trapped on a 0.31 x 25.0 cm stainless steel column packed with 8.0 cm each of Tenax-GC, Silican gel, and charcoal. The trap was held at ambient temperatures (25.0 C). After purging was completed the analytes were backflushed for two minutes from the trap to the head of the analytical capillary column which had

been cooled to -160.0 C. After the desorb step was completed the analytes were analyzed by GC/MS.

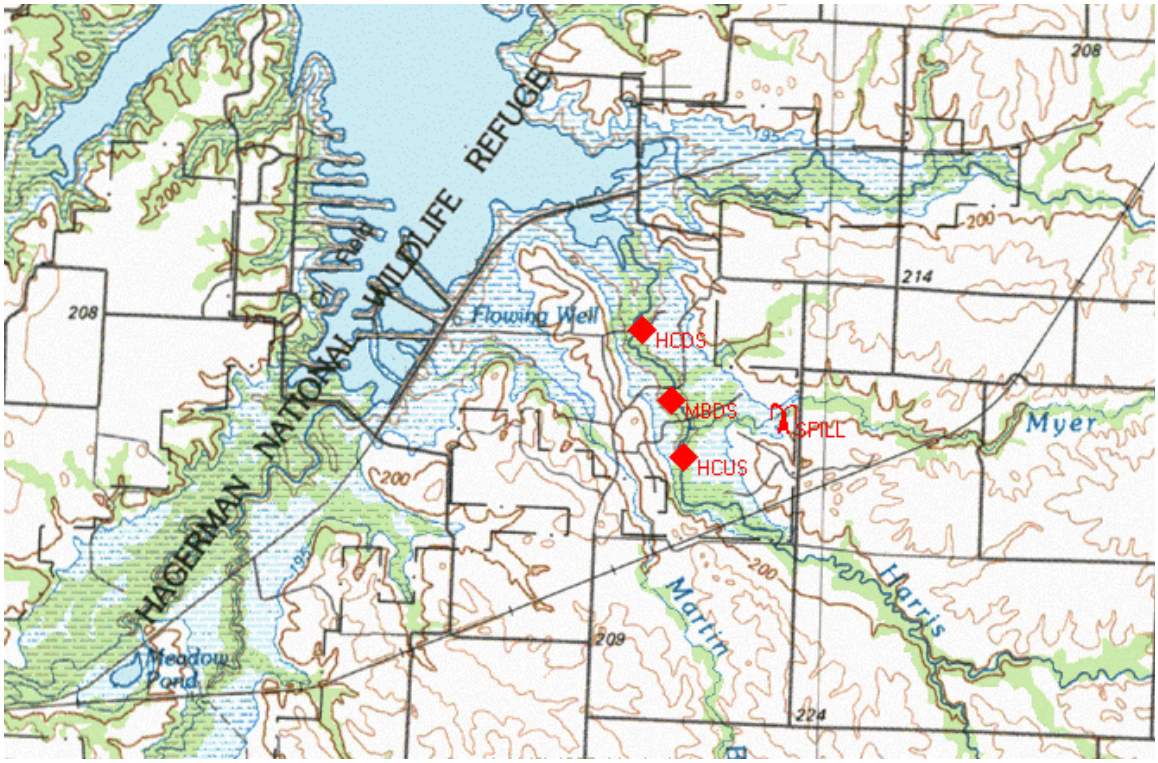
Method Code 028: Determining Total Petroleum Hydrocarbons (TPH) in Sediments.
The sediment samples were freeze-dried and extracted in a Soxhlet extraction apparatus. The freeze-dried sediment samples were homogenized and a 15.0 gram sample was weighed into the extraction thimble. Surrogate standards and methylene chloride were added and the samples extracted for 12 hours. The extracts were treated with copper to remove sulfur. Extract was rotovaped to 5.0 ml and then brought to dryness under a clean nitrogen stream. GC internal standards were added and the extract was run on GC with flame ionization detector. TPH was determined by summing the total unresolved complex mixture and the total resolved (all peaks in the chromatogram). The concentration was based on an average of the response factors for alkanes from n-C10 through n-C-34.

APPENDIX B
(1999 Crude Oil Release into Harris Creek)

Crude Oil Release in Harris Creek, May, 1999

After sampling was conducted for the Hagerman National Wildlife Refuge macroinvertebrate study, a crude oil release occurred in Harris Creek on May 28, 1999. Approximately 60 barrels (2,520.0 gallons or 9,525.6 liters) of crude oil and brine were released into Harris Creek via Myer's Branch from a crude oil production well located east of the Refuge (Figure B1).

Figure B1. Sample Points on Harris Creek, Grayson County, Texas (Maptech, 1998).



In June, 1999, the U.S. Fish and Wildlife Service collected sediment samples from Harris Creek above the confluence with Myer's Branch-South (HCUS), below the confluence with Myer's Branch-South (MBDS), and from an area approximately 250.0 meters downstream of the confluence with the Myer's Branch-South (HCDS) (Figure B1). These samples were analyzed for total petroleum hydrocarbons, benzene, ethylbenzene, toluene, and xylene content through the U.S. Fish and Wildlife Service's Patuxent Analytical Control Facility. The results in parts per million (mg/kg) dry weight are presented in Table B1.

The well was operated by a representative of Laguna Oil Company. The release occurred off-Refuge; however due to an initial lack of response by the responsible party and a significant rainfall event, the product flowed down Myer's Branch-South and impacted Harris Creek within the confines of the Refuge. The operator of the oil production unit did not notify the National Response Center until five days after the release occurred; however, once the significance of the release was determined, the responsible party deployed an emergency response contractor to remediate the release (Figures B2-B5). The release did not reach the Big Mineral Arm of Texoma Reservoir. No dead or dying fish or wildlife were observed. By July 17, 1999, clean-up operations were complete. Adsorbent booms were left in place on Harris Creek downstream of the impacted area to retain residual petroleum contaminants which could be washed out of impacted sediments and vegetation (refer to National Response Center Report No. 485948).

Table B1. Analytical results in mg/kg dry weight of sediments collected from Harris Creek from upstream of the confluence with Myer's Branch-South (HCUS), from downstream of the confluence with Myer's Branch-South (MBDS), and 250 meters downstream of the confluence with Myer's Branch-South. (Note: bdl is below detection limit and dw is dry weight)

Analyte	HCUS	MBDS	HCDS
% Moisture	35.9	29.0	25.3
Total Petroleum Hydrocarbons (in mg/kg dw)	71.5	270.0	2455.0
detection limit (in mg/kg dw)	1.6	1.4	1.3
Benzene (in mg/kg dw)	bdl	bdl	bdl
detection limit (in mg/kg dw)	0.08	0.07	0.07
Ethylbenzene (in mg/kg dw)	bdl	bdl	bdl
detection limit (in mg/kg dw)	0.08	0.07	0.07
Toluene (in mg/kg dw)	0.37	0.34	0.33
detection limit (in mg/kg dw)	0.08	0.07	0.07
m-, p-, and o-Xylene (in mg/kg dw)	bdl	bdl	bdl
detection limit (in mg/kg dw)	0.08	0.07	0.07

Figure B2. Harris Creek at Hagerman National Wildlife Refuge, June 1999.

Figure B3. Harris Creek at Hagerman National Wildlife Refuge, June 1999.

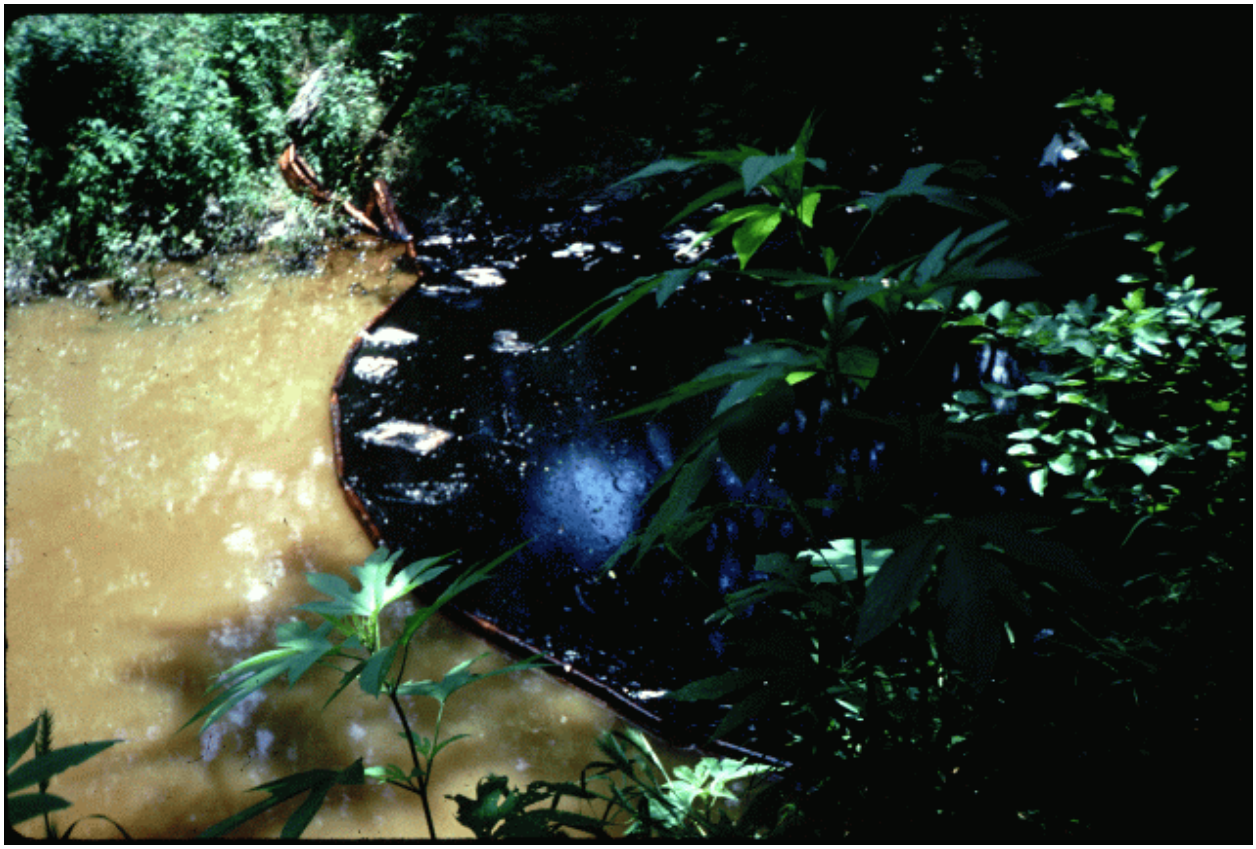


Figure B4. Harris Creek at Hagerman National Wildlife Refuge, June 1999.

Figure B5. Harris Creek at Hagerman National Wildlife Refuge, June 1999.