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Environmental Contaminants Program

INITIAL CONTAMINANTS SURVEY OF  
HAGERMAN NATIONAL WILDLIFE  
REFUGE, TEXAS

by

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### Abstract

An initial contaminants survey was conducted at Hagerman National Wildlife Refuge (HNWR) in north central Texas. Contaminants from a variety of sources have the potential to reach and affect HNWR. Effluents from several wastewater treatment plants discharge into Myers Branch, Mineral Creek, and Mustang Creek, all of which flow through HNWR and into the Big Mineral Arm of Lake Texoma. Throughout HNWR, there are over 100 active oil and gas producing wells, pipelines, and associated storage and transfer facilities which could be sources of chronic oil pollution and also constitute the threat of potential spills. Sediment, soil, and whole fish samples were collected in 1991 from 12 locations within and adjacent to the HNWR. The samples were analyzed for metalloids (except soils), organochlorine pesticides (including polychlorinated biphenyls), aliphatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and nutrients (only sediment). Concentrations of metalloids, organochlorine pesticides, and nutrients in sediments were not high enough to pose risk to fish and wildlife health. Soil samples contained low concentrations of organochlorine pesticides. The hydrocarbon analysis scan was insufficient to make sound

conclusions of the effects to fish and wildlife resources. Few fish tissue samples contained concentrations of mercury and selenium at levels which have been associated with adverse biological effects in piscivorous predators that reside within the HNWR.

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## Introduction

Objectives of this study were to: 1) complete an initial contaminants survey at Hagerman National Wildlife Refuge (HNWR); 2) determine if there are any significant environmental contaminant issues that could pose a threat to fish and wildlife at HNWR. Significant contaminant issues indicated by this sampling would prompt a more definitive follow-up study.

A concern at the onset of this investigation was that contaminant concentrations in sediments, soils, and fish near oil and gas production sites (approximately 100 producing wells) on HNWR might be higher than in similar samples collected from reference sites both on and off HNWR. Contaminant levels determined at HNWR will also be compared with data collected during similar Fish and Wildlife Service (Service) contaminants studies in Region 2, i.e. Trinity River and Buffalo Lake National Wildlife Refuge.

Whole body predatory and bottom-feeding fish samples from Lake Texoma at HNWR have been monitored for contaminant residues as part of the National Contaminant Biomonitoring Program (NCBP) since 1976. Data from carp and bass from the lake have not indicated any problems attributable to metals, pesticides, or polychlorinated biphenyl (PCBs) contamination (Schmitt and Brumbaugh 1990, Schmitt et al. 1990). However, oil production is a potential source of contamination to fish and wildlife resources on the HNWR. The NCBP data did not include analyses for oil field contaminants such as aliphatic and polycyclic aromatic hydrocarbon (PAHs) compounds. This survey proposed to investigate the extent of aliphatic hydrocarbon and PAH contamination and provide a more comprehensive scan of metalloids and organochlorine pesticides (including PCBs) that might be present in sediments, soils, and fish throughout HNWR.

The HNWR manager, Jim Williams, identified three general areas of concern on HNWR: 1) soils and upland habitat that might be contaminated from oil field spills, 2) sediments and aquatic organisms potentially contaminated by the adjacent oil production facilities, and 3) sediments in Beaver Creek possibly contaminated by metals from an upstream steel wire manufacturing facility.

## Study Area

Hagerman National Wildlife Refuge is located in Grayson County, on the Big Mineral Arm of Lake Texoma, a flood control reservoir on the Red River on the Texas-Oklahoma state line (Figure 1). The Refuge was created by agreement between the Secretaries of the Interior and Army in 1946. Encompassing the ecotones of the Texas crosstimbers, the blackland prairie, and the Red River Valley, HNWR provides 4,585 hectares (ha) of varied wildlife habitat, including valuable wetland habitat for birds migrating through the Central Flyway. Recreational activities enjoyed by visitors include birdwatching, hiking, and fishing. Hunting is permitted during limited seasons in designated areas. Approximately 243 ha are cultivated

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in milo, corn, and green wheat. Cooperative farming, limited grazing, and controlled burns are among HNWR management strategies. Shallow marshes on the HNWR are periodically drained and managed to provide about 1,215 ha of wetland habitat.

Topography of the area is gently rolling, and soils are moderately deep, sandy and loamy. Annual precipitation averages 60 centimeters. The climate at HNWR is hot in summer and mild in winter with occasional surges of cold air masses. Land use around HNWR is primarily rangeland and agriculture. Crops grown in the watershed include sorghum, wheat, milo, soybeans, corn, and cotton. All facets of petroleum production, including drilling, pipelines and storage tanks, is prevalent throughout the watershed, as well as on HNWR.

Contaminants from a variety of sources have the potential to reach and affect HNWR. Effluents from the wastewater treatment plants of the nearby towns of Denison, Whitesboro, and Sadler (Figure 1) discharge into Myers Branch, Mineral Creek, and Mustang Creek, respectively, all of which flow through HNWR and into the Big Mineral Arm of Lake Texoma. Throughout HNWR, there are over 100 active oil and gas producing wells, pipelines, and associated storage and transfer facilities which could be sources of chronic oil pollution and also constitute the threat of acute oil spills. Occasional spills from oil producing wells, pipelines, and associated storage and transfer facilities do occur, such as sites 10, 11, and 12 (Figure 1). Sites 10 and 12 are located on upland tracts well away from any water, therefore these spills have not contaminated aquatic resources. Production well site 10 is operated by Texaco Exploration and Production, Incorporated. Spills at this site represent poor equipment maintenance and have contaminated adjacent soils. Site 12 is a battery tank farm that consists of a diked area which contains frequent oil spills. The production well at site 11 is adjacent to the lake and is owned by Shell Oil Company. The one documented spill at this site occurred when a valve was inadvertently left open and discharged oil onto land and into water. The oiled areas were remediated by Shell Oil Company. As the oil field ages, wells proceed to secondary recovery, including processes in which fluids are injected under pressure into the oil bearing formations to facilitate oil

recovery.

### Methods and Materials

In July 1991, twelve locations were selected for the collection of sediment, soils and/or fish samples within and adjacent to HNWR (Figure 1). Ten composite sediment and nine whole fish samples of mosquitofish (*Gambusia* sp.) (Table 1) were collected from Dead Woman Pond Inflow Channel (site 1), Myers Branch (sites 2, 3, and 4), Scott Branch (sites 5 and 6), Sandy Creek (sites 7, 8, and 9), and Pad spill (site 11). Sites 1, 5, and 6 were selected to represent respective undisturbed areas on and off HNWR. Ten composite soil samples were collected from sites 2 through 6, Texaco Rig (site 10 n=2), and the Tank Farm spill area (site 12, n=3). Sediment and soil samples of apparently similar texture and particle-size were collected and composited into single samples at each site. They were not sieved.

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Fish were collected with a dipnet or a seine and composited for each sample. All sediment, soil, and fish samples were weighed following collection, stored on wet ice in the field, and later frozen in a commercial freezer.

Sediment samples were analyzed (Table 1) for metalloids (including grain size), methyl mercury, organochlorine pesticides (including PCBs), aliphatic hydrocarbons, PAHs, nutrients, and total organic carbon (TOC). Sediments submitted for nutrient analyses were insufficient in sample volume; therefore, nitrate analyses and sample-specific quality control was not accomplished. In addition, moisture analysis could not be performed for the site 5 sediment sample and an adjustment to a dry-weight sample basis was not possible. Therefore, for comparison purposes, all sediment sample results for organic nitrogen, soluble phosphorus, ammonia nitrogen, total kjeldahl nitrogen, and moisture content were reported on a wet sample basis.

Soil samples were analyzed for organochlorine pesticides (including PCBs), aliphatics, and PAHs, and also were assayed for TOC (Table 1). Fish were analyzed for metalloids, organochlorine pesticides (including PCBs), aliphatic hydrocarbons, and PAHs (Table 1).

Prior to the Exxon Valdez oil spill, requests for hydrocarbon scans were limited to the analyses of n-alkanes containing the n-C<sub>11</sub> to n-C<sub>20</sub> carbon atoms. Based on the Service's experience with analyses of the Exxon Valdez oil, it was recommended to specify the extended aromatic hydrocarbon scan (Robinson-Wilson, Everett 1991. Memorandum to Region 6, 8 May). The extended aromatic scan includes analysis of the n-alkanes containing the n-C<sub>21</sub> to n-C<sub>34</sub> carbon atoms and additional aromatic analytes, which are essential for

proper interpretation of hydrocarbon data to determine if samples have been oiled. We did not request the extended hydrocarbon scan for this study, thus only the n-alkanes containing the n-C<sub>11</sub> to n-C<sub>20</sub> carbon atoms and 24 aromatic analytes were analyzed.

All samples were submitted through the National Biological Service's Patuxent Analytical Control Facility (PACF) to its designated contract laboratories. Metalloids, organochlorine pesticides, aliphatic, PAHs, grain size, and TOC analyses were conducted by Geochemical and Environmental Research Group, Texas A&M University, Texas. Nutrient analyses were conducted by Versar Laboratories, Inc. of Springfield, Virginia. Methyl mercury analyses were conducted by Brooks Rand, Ltd. of Seattle, Washington. The PACF was responsible for assessing quality assurance and control (QA/QC) procedures for all contract labs and QA/QC met PACF standards.

Arsenic, selenium, cadmium, and lead concentrations in sediments and fish were determined by graphite furnace atomic absorption spectrometry (AAS) and mercury was determined by cold vapor AAS. All other elements were determined by atomic emission using argon plasma.

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Organochlorine pesticides, aliphatic hydrocarbon, and PAH concentrations in sediments and soils were detected by a Soxhlet extraction apparatus and in fish tissue concentrations were detected by capillary gas chromatography. Percent moisture was determined for sediment, soil, and fish tissue samples. Percent lipid was determined for fish samples.

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Metalloid concentrations in fish were compared with those reported in the NCBP for fish collected in 1976-1984 from 109 stations nationwide (Schmitt and Brumbaugh 1990). Concentrations of an element in whole fish were considered elevated when they exceeded the 85th percentile of the nationwide geometric mean. The 85th percentile concentration is a figure generally considered significantly elevated above national background concentrations.

Results reported for metalloid, methyl mercury, organochlorine pesticide, aliphatic hydrocarbon, and PAH analyses in sediment and soil samples are in  $\mu\text{g/g}$  (parts per million) dry weight basis. Results for sediment analyses of organic nitrogen, soluble phosphate, ammonia nitrogen, total kjeldahl nitrogen, and percent moisture are reported in  $\mu\text{g/g}$  wet weight basis; in  $\mu\text{g/g}$  oven-dried basis for total phosphorous and percent organic matter; and  $\mu\text{g/g}$  air-dried basis for chemical oxygen demand. For fish, results are reported in  $\mu\text{g/g}$  wet weight basis.

## Results and Discussion

## Metalloids

Sediment - Sixteen of the 19 metalloids including methyl mercury tested for were detected in sediment samples from most of the sites (Table 2). Mercury, molybdenum, and selenium were not detected in the sediment samples. The highly sandy soils are probably the reason for the low detection of these elements (Table 2). Nine of the highest concentrations of the 16 elements detected were found at site 11. The following potentially toxic inorganic elements are discussed below: arsenic, cadmium, chromium, copper, lead, and zinc.

Arsenic - Large quantities of arsenic are released into the environment as a result of industrial and agricultural activities (Eisler 1988a). The International Joint Commission (IJC 1988) considered 1.1  $\mu\text{g/g}$ , dry weight to be the background level in sediments. Sediments with arsenic concentrations below 3.0  $\mu\text{g/g}$  were classified as non-polluted in the Great Lakes harbor by Beyer (1990). Sediments collected from areas contaminated by arsenical herbicides contain concentrations of arsenic ranging from 198 to 3,500  $\mu\text{g/g}$  (Eisler 1988a). Arsenic was recovered in sediment samples from HNWR at concentrations of 3.8 to 9.9  $\mu\text{g/g}$  (Table 2). However, the concentrations found are not at levels harmful to fish or wildlife.

Cadmium - Anthropogenic sources of cadmium include smelter fumes and dusts, the products of incineration of cadmium-bearing materials and fossil fuels, fertilizers, and municipal wastewater and sludge discharges; concentrations are most likely highest in the localized regions of smelters or in urban industrialized areas (Eisler 1985). Background

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levels of cadmium in uncontaminated riverine and lake sediments have been reported at 5  $\mu\text{g/g}$  (Eisler 1985). Cadmium was recovered at 0.2  $\mu\text{g/g}$  in few samples (Table 2), but the cadmium levels detected would not be harmful to fish or wildlife.

Chromium - Chromium concentrations in sediments tend to be elevated in the vicinity of industrial operations and municipal waste treatment facilities where chromium is a significant component of wastes discharged into the environment (Eisler 1986a). It is generally agreed that most chromium in soil and sediment is unavailable to living organisms; adsorption and bioaccumulation are relatively minor. Sediments with chromium concentrations below 25  $\mu\text{g/g}$  dry weight were classified as non-polluted in the Great Lakes harbor by Beyer (1990). Background concentrations of chromium in freshwater sediments have been reported at 140  $\mu\text{g/g}$  (Eisler 1986a). Chromium concentrations in sediments collected from HNWR ranged from 8.2 to 43  $\mu\text{g/g}$  (Table 2). Based on these results the chromium concentrations are unlikely to be harmful to fish or wildlife.

Copper - Elevated concentrations of copper are often recovered in the vicinity of municipal and industrial outfalls, particularly from smelting, refining, or metal plating industries (USEPA 1983). Concentrations of copper ranged from 3.1 to 22.4  $\mu\text{g/g}$  in sediments collected from HNWR (Table 2). Copper in sediments from the site 11 sample slightly exceeded the IJC (1988) background level of 20.8  $\mu\text{g/g}$ . Other locations on and off the refuge appear to be free from anthropogenic related inputs of copper. Copper levels observed in sediments at HNWR would not be harmful to fish or wildlife.

Lead - Elevated lead concentrations in sediments come from sources as diverse as steelworks, shipyards, crude oil refineries, cement and ceramic factories, lead storage battery recycling plants, and heavy automobile traffic (Eisler 1988b). Sediments in the upper Mississippi River had recovered lead concentrations of 86  $\mu\text{g/g}$ , whereas the southeastern Missouri Big River sediments contained concentrations of lead as high as 2,200  $\mu\text{g/g}$  downstream from a lead mining area (Eisler 1988b). Lead concentrations in sediments from HNWR (Table 2) were below the IJC (1988) background level of 27.5  $\mu\text{g/g}$ . Lead concentrations in sediments do not present a risk to fish or wildlife at HNWR.

Methyl mercury - Methyl mercury is the most hazardous form of mercury due to its high stability, lipid solubility, and possession of ionic properties that lead to a high ability to penetrate membranes in living organisms (Eisler 1987a). In the aquatic environment, mercury may become methylated by biological or chemical process or both. Mercury in bottom sediments can be re-suspended during floods and carried further downstream. The statewide 90th percentile value for mercury in sediments was 0.32  $\mu\text{g/g}$  dry weight (Davis 1987). Methyl mercury concentrations recovered in sediments collected from HNWR ranged from 0.00003 to 0.00129  $\mu\text{g/g}$  (Table 2). These recorded mercury levels would not be a risk to the health of fish or wildlife.

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Zinc - Major sources of anthropogenic zinc in the environment include electroplaters, smelting and ore processors, mine drainage, domestic and industrial sewage, combustion of solid wastes and fossil fuels, road surface runoff, corrosion of zinc alloys and galvanized surfaces, and erosion of agricultural soils (Eisler 1993). Background concentrations of zinc in sediments seldom exceed 200  $\mu\text{g/g}$  (Eisler 1993). Anthropogenic sources of zinc surrounding the refuge could be limited to agricultural runoff and a future electroplating facility south of HNWR. Analytical results from zinc concentrations in sediments collected at HNWR (Table 2) are not a risk to fish or wildlife.

Fish All 19 inorganic elements tested were recovered in mosquitofish tissue (Table 3). Cadmium and lead recovered in fish tissue were below the NCBP 85th percentiles and will

not be included further in this discussion. Arsenic, copper, mercury, selenium, and zinc concentrations in several mosquitofish exceeded the NCBP 85th percentile concentrations (Schmitt and Brumbaugh 1990) at sites 1, 5, and 6.

**Arsenic** - Arsenic whole-body levels above 0.5  $\mu\text{g/g}$  were considered harmful to fish and predators by Walsh et al. (1977). Only the mosquitofish sample from Site 1 (Table 3), slightly exceeded the 1990 NCBP 85th percentile of 0.27  $\mu\text{g/g}$  (Schmitt and Brumbaugh 1990). Results were below the level considered harmful to fish; therefore, we conclude that minimal arsenic-related health risk exists for fish or wildlife.

**Copper** - Copper concentrations in mosquitofish equalled or exceeded the 1990 NCBP 85th percentile concentration of 1.0  $\mu\text{g/g}$  as reported by Schmitt and Brumbaugh (1990) in sites 1, 5, and 6 (Table 3). We are not aware of any proposed or suggested action levels of copper in tissues of fish or wildlife. However, copper does not appear to pose any risk to fish or wildlife species on the refuge.

**Mercury** - Mercury and its compounds have no known biological function. The presence of the metal in cells of living organisms is undesirable and potentially hazardous (Eisler 1987a). The predator protection limit for mercury is 0.1  $\mu\text{g/g}$  for fish-eating waterfowl (National Academy of Sciences and National Academy of Engineering (NAS/NAE) 1973). Eight of the nine fish samples had concentrations below that level (Table 3). The mosquitofish sample from site 6 slightly exceeded the predator protection limit, as well as the 1990 NCBP 85th percentile concentration of 0.17  $\mu\text{g/g}$ . Because the percentage of detection among samples was low, mercury does not appear to pose any risk to the populations of fish or fish-eating birds foraging at HNWR.

**Selenium** - The whole body toxic effect threshold of selenium for health and reproduction of freshwater fish is 4  $\mu\text{g/g}$  dry weight and the toxic threshold for selenium transferred to consumer species of fish and wildlife through aquatic food-chains is 3  $\mu\text{g/g}$  dry weight (Lemly 1993). Selenium was detected in seven of the nine fish samples (Table 3). Site 6 sample exceeded both toxic effect thresholds and the 1990 NCBP 85th percentile concentration of 0.73  $\mu\text{g/g}$ . Based on these analytical findings, selenium could present some

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threat to the health and reproduction of fish and wildlife at HNWR. However, since the percentage of detection among samples was low, selenium does not appear to pose any risk to the overall population of fish or the food base of fish and wildlife.

**Zinc** - Zinc was detected in all mosquitofish samples at concentrations of 9.2 to 116  $\mu\text{g/g}$  (Table 3). The 116  $\mu\text{g/g}$  in the site 6 sample greatly exceeded the 1990 NCBP 85th

percentile concentration of 34.2 µg/g. Insufficient information is available to determine a threshold concentration in fish. The recommended maximum zinc limit in bird diets is 178 µg/g dry weight to prevent marginal sublethal effects (Eisler 1993). The zinc concentration at site 6 did not exceed that dietary limit. Given the low residue levels in fish tissue, zinc does not appear to pose any risk to fish and wildlife.

#### Organochlorine Pesticides

Sediment/soil/fish - No organochlorines were detected (< 0.01 µg/g) in sediments and only three organochlorines were detected in soil or mosquitofish. Total chlordane (0.01 µg/g), total p,p'DDT (0.01 µg/g), and aldrin (0.04 µg/g) were recovered in soil sample 1 from site 10. Total organic carbon for this sample was 2.9 percent. DDT compounds (primarily p,p'DDE) were recovered in fish samples at 0.01 µg/g from sites 2, 6, and 11. The level in the fish samples is below the NAS/NAE (1973) DDT and metabolites criterion of 1.0 µg/g, for the protection of wildlife. Concentrations recovered in soil and fish tissue samples do not indicate a risk to the health of fish and wildlife.

A few sediment, soil, or fish samples contained detectable levels of PCBs. Sediments in the Great Lakes with PCB concentrations below 1 µg/g were classified as non-polluted by the Environmental Protection Agency according to Beyer (1990). Sediments from site 6 had a PCB concentration of 0.01 µg/g and the TOC was below 1 percent. PCBs in soils were recovered at concentrations 0.06 µg/g from all soil samples except sample 1 at site 10. This sample contained 0.59 µg/g, but this concentration would be considered unpolluted.

Whole body PCB concentrations of 0.4 µg/g wet weight are associated with reproductive toxicity in rainbow trout (Eisler 1986b). PCBs recovered in fish from site 2 (0.03 µg/g) are below the predator protection limit of 3 µg/g wet weight for total PCBs as whole body residue to protect fish-eating birds and mammals, and even below the limit associated with reproductive toxicity in fish (Eisler 1986b). The concentration of PCBs recovered in the fish tissue sample does not indicate a significant risk to the health of fish and wildlife.

Aliphatic and Aromatic (PAHs) Hydrocarbons - Hydrocarbons include a wide variety of naturally-occurring and biologically synthesized substances. Petroleum hydrocarbons can be generally subdivided into two groups: aliphatic and aromatic. Aliphatic compounds are carbon-based straight chain and branched chain (i.e. pristane and phytane) structures, whereas aromatic compounds are carbon-based rings (i.e. benzene). Aliphatic hydrocarbons are comprised of 3 subgroups: 1) paraffins (alkanes), all of which are saturated and comparatively unreactive; 2) olefins (alkenes or alkadienes) which are unsaturated and quite

reactive; and 3) acetylenes (alkynes) which contain a triple bond and are highly reactive (Sax and Lewis 1987). Most aliphatics and paraffins are insoluble in water, so their toxicity to aquatic life is low at levels commonly found in sediment and water samples. Hydrocarbons of recent biological origin tend to have aliphatic compounds with odd-numbers of carbons dominant, whereas petroleum compounds have nearly equal concentrations of odd- and even-numbered aliphatics (Hall and Coon 1988). The ratio of pristane to phytane serves as a useful indicator of the presence of petrogenic hydrocarbons. If the ratio is near one, then the oil is of petroleum derived hydrocarbons (Broman et al. 1987). Interpretation of hydrocarbon residues in fishes is more complicated than for sediments because fish metabolize aromatic compounds (Eisler 1987b).

Hydrocarbon analyses did not include an extended scan for n-alkanes containing the 21 to 34 carbon atoms (n-C<sub>21</sub> to n-C<sub>34</sub>), which are essential for proper interpretation of hydrocarbon data to determine if samples have been oiled (Robinson-Wilson, Everett. 1991. Memorandum to Region 6, 8 May). Because of insufficient hydrocarbon analyses, interpretation of hydrocarbon data is limited and sound conclusions of the effects on fish and wildlife resources can not be made. However, the data will be presented for information purposes.

Sediment/soil - Total aliphatic concentrations in sediments ranged from 4.03 to 146.2 µg/g (Table 4) and concentrations in soil ranged from 0.035 to 107 µg/g (Table 5). Twenty-four aromatics were detected in nearly all sediment (Table 6) and soil samples (Table 7). The greatest PAH concentration in sediments occurred at site 11(1.27 µg/g, Table 6) and is possibly associated with the documented oil spill. Total PAH concentrations in soil samples from sites 10 and 12 were among the highest levels. Sites 10, 11, and 12 are just a few of the many areas on the refuge that have active oil pumping wells, where higher concentrations of PAHs would be expected to occur.

Fish - Total aliphatic concentrations recovered in mosquitofish ranged from 0.17 to 1.96 µg/g (Table 8). Published literature on the biological effects of aliphatic compounds upon fish is sparse and prevents a more accurate assessment of the effects of the concentrations observed. Some aromatic compounds, i.e. long chain aromatics, are documented carcinogens in fish and have been associated with fish tumors (Baumann et al. 1982, Baumann 1984, Baumann and Whittle 1988). Fish tumors have been documented in the Great Lakes Region since the mid 1970s and include liver, thyroid, gonad, and skin. Total PAH concentrations in fish (Table 9) were below the total PAH concentrations detected in Trinity River fish (0.02 to 60.79 µg/g) reported by Irwin (1988).

Nutrients - Major sources of nitrogen and phosphorus pollution in aquatic areas generally result from agricultural fertilizer runoff or effluent discharges from wastewater treatment plants (Connell and Miller 1984). Several tributaries, including Mineral Creek, Mustang Creek, and Myers Branch, receive wastewater effluent discharges from respective wastewater

treatment plants in Sadler, Whitesboro, and Denison, Texas.

Major point-sources of nitrogen enter into water bodies from wastewater treatment plants, septic tanks, and animal feedlots. Irwin (1991) reported average sediment organic nitrogen concentrations from 1,065 to 22,233  $\mu\text{g/g}$  dry weight upstream from the Buffalo Lake National Wildlife Refuge. Concentrations of organic nitrogen in sediments collected from HNWR (Table 10), were generally well below the levels at Buffalo Lake National Wildlife Refuge found by Irwin (1991). There are no fish and wildlife protection criteria for organic nitrogen, but we believe that there would be no detrimental effects from nitrogen on fish or wildlife.

Total phosphate phosphorus refers to the total phosphorus portion of phosphates, expressed as P. Total phosphorus is meant to be a measure of most forms of phosphorus, since in nature and in natural waters, almost all the phosphorus is in the form of phosphates (Irwin 1991). Phosphorus is often adsorbed to sediment particulates. As reported by Irwin (1991) average dry weight total phosphate phosphorus concentrations in sediments ranged from 303 to 15,000  $\mu\text{g/g}$  upstream from the Buffalo Lake Refuge. The statewide 90th percentile value for this compound in sediments is 1,571  $\mu\text{g/g}$  dry weight (Davis 1987). Total phosphorus in sediments collected from HNWR was recovered at concentrations ranging from 114 to 642  $\mu\text{g/g}$  (Table 10). Soluble phosphorus in sediments collected from HNWR ranged from 0.19 to 1.43  $\mu\text{g/g}$  (Table 10). There are no fish and wildlife criteria for total phosphate phosphorus and soluble phosphorus concentrations in sediments. The total phosphate phosphorus concentrations were below the Texas 90th percentile for sediments. We believe this nutrient and soluble phosphorus in sediments is unlikely to result in direct adverse effects upon fish and wildlife.

Ammonia enters water as a byproduct of industrial wastes as sewage effluent or as agricultural runoff. The amount of nitrogen contributed by ammonia is ammonia nitrogen. Ammonia was determined to be an important sediment-associated toxicant in polluted sediments from the Lower Fox River and Green Bay Wisconsin (Irwin 1991). Irwin (1991) reported total average ammonia concentrations of in-stream sediments from 25 to 236  $\mu\text{g/g}$  dry weight upstream from Buffalo Lake Refuge. Ammonia nitrogen concentrations in sediments collected from HNWR ranged from 7.08 to 82.7  $\mu\text{g/g}$  (Table 10). No fish and wildlife protection criteria for ammonia nitrogen concentrations in sediments exists. The low ammonia nitrogen levels in HNWR sediments suggest that there should be no effects on fish or wildlife health.

Total Kjeldahl Nitrogen (TKN) reflects the technique used to measure all forms of organic nitrogen together with ammonia present in a sample. Nitrogen of this type is most readily

available to, and associated with, biota. The statewide 90th percentile for TKN in sediments was 2,816  $\mu\text{g/g}$  dry weight (Davis 1987). Irwin (1991) reported average in-stream sediment TKN concentrations from 1,093 to 7,720  $\mu\text{g/g}$  dry weight upstream from the Buffalo Lake Refuge. A TKN value greater than 2,400  $\mu\text{g/g}$  dry weight is considered high. Recovered TKN concentrations in sediments collected from HNWR (Table 10) were below the Texas 90th percentile and the observed concentrations in the Buffalo Lake Refuge study. There are

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no fish and wildlife criteria for TKN concentrations in sediments. However, we believe that TKN levels would not affect the health of fish or wildlife at HNWR.

Chemical oxygen demand (COD) is the measure of the oxygen requirement for degradation of a material. Very high COD loads are known to come from cattle feedlots, usually much higher than from treated sewage or various types of non-point source runoff. Average dry weight concentrations of COD from in-stream sediments upstream from Buffalo Lake Refuge ranged from 23,166 to 147,666  $\mu\text{g/g}$  (Irwin 1991). Chemical oxygen demand in sediments from HNWR ranged from 6,840 to 80,500  $\mu\text{g/g}$  (Table 10). There are no fish and wildlife criteria for COD concentration in sediments.

### Conclusions

Metalloids, methyl mercury, and organochlorine pesticide (including PCBs) concentrations in sediments do not present a threat to fish or wildlife at the Hagerman National Wildlife Refuge. Nine metalloids recovered in sediments had the highest concentrations at site 11. However, only copper exceeded the IJC background level.

Concentrations of organochlorine pesticides (including PCBs) in soil samples were below levels considered harmful to wildlife. Soil sample 1 from site 10 had the highest concentration of PCBs.

Metalloid (except mercury and selenium) and organochlorine (including PCBs) compounds in fish tissue were present in amounts that should not cause adverse biological effects to fish and wildlife. Fish from site 1 had arsenic and copper concentrations exceeding the NCBP 85th percentile. Fish tissue representative of site 6 had the highest concentrations of copper, mercury, selenium, and PCBs. The mercury and selenium levels exceeded the predator protection and toxic effects threshold limits for fish-eating waterfowl and fish health. Repeated foraging at site 6 (Scott Branch) by fish-eating waterfowl may present a threat to their health. Resident fish populations in this area may have impaired reproduction. Low concentrations of DDE were found in fish tissues from sites 2, 6, and 11. Nutrients in

sediments were within normal sediment levels. Sites 1, 5, and 6 were selected to represent relatively clean areas on and adjacent to HNWR; however, results of fish tissue data did not reflect this intent.

Analyses of hydrocarbons were insufficient to make sound conclusions on the effects to fish and wildlife resources at HNWR.

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### Recommendations

Because of the insufficient hydrocarbon analyses and the difficulty in making sound conclusions of the effects of hydrocarbons on fish and wildlife resources, it is recommended that a new set of sediment and soil samples be collected and analyzed for an extended hydrocarbon scan. It is also recommended that bile from fish be collected and analyzed for hydrocarbons. Analysis for aromatic hydrocarbons in fish tissue do not provide useful information about the exposure of fish to hydrocarbons because they are rapidly metabolized (Krahn et al. 1986 and Krahn et al. 1987). Estimating the exposure of fish to hydrocarbons can be done effectively by measuring the concentration of metabolites in fish bile. An extended hydrocarbon scan and analysis of bile should provide sufficient information to determine if there are any significant environmental contaminants related to the oil fields that may pose a threat to fish and wildlife resources at HNWR.

A review and coordination with the Shell Oil Company's oil spill contingency plan for HNWR should be done. In addition, an oil spill contingency plan should be prepared for the Texaco Oil Company's operations. These plans should provide for minimized exposure of trust resources on the Refuge to an oil spill that might occur in the Big Mineral Arm of Lake Texoma at any of the several oil production facilities.

Because the relatively clean sites had elevated metal concentrations in fish tissue, we recommend routine monitoring at all 12 sites on a three-year basis to address the presence of elevated levels of mercury and selenium in sediments, soils, and fish tissue.

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Site Number	Station Location	Metalloids <sup>1</sup>	Organo-chlorines <sup>2</sup>	PAHs <sup>3</sup> & Aliphatics <sup>4</sup>	Nutrients <sup>5</sup>
1	Dead Woman Pond Inflow Channel	Sed, F	Sed, F	Sed, F	Sed
2	Myers Branch near Confluence	Sed, F	Sed, Soil, F	Sed, Soil, F	Sed
3	Myers Branch at Gravel Road	Sed, F	Sed, Soil, F	Sed, Soil, F	Sed
4	Myers Branch at Enterprise Road	Sed, F	Sed, Soil, F	Sed, Soil, F	Sed
5	Scott Branch near Bridge	Sed, F	Sed, Soil, F	Sed, Soil, F	Sed
6	Scott Branch near Confluence	Sed, F	Sed, Soil, F	Sed, Soil, F	Sed
7	Sandy Creek at Hwy 901	Sed, F	Sed, F	Sed, F	Sed
8	Sandy Creek at HNWR	Sed, F	Sed, F	Sed, F	Sed
9	Sandy Creek at Pipeline	Sed	Sed	Sed	Sed
10	Texaco Rig Site		Soil (2)	Soil (2)	
11	Pad Spill Site	Sed, F	Sed, F	Sed, F	Sed
12	Tank Farm Spill		Soil (3)	Soil (3)	

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<sup>1</sup>Metalloids - includes methyl mercury and 19 elements.

$\gamma$ OC - organochlorine pesticide scan - includes 20 pesticides and total PCBs.

[sup]3PAH - Polycyclic aromatic hydrocarbons - includes 24 compounds.

[sup]4Aliphatics - Aliphatic hydrocarbons - includes 11 compounds.

[sup]5Nutrients - includes eight parameters.

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Table 2. Metalloid concentrations in sediment ( $\mu\text{g/g}$  dry weight) and sediment properties from Hagerman National Wildlife Refuge, Texas, 1991.

Site

Element <sup>1</sup>	1	2	3	4	5	6	7	8	9	11
Al	20700	15700	11300	19300	12300	14200	5000	5330	2930	24300
As	4.2	5.1	7.1	4.5	4.1	3.8	5.6	7.3	9.9	5.3
B	14.9	15.3	17.5	22.8	14.2	16.3	17.4	19.1	4.6	21.3
Ba	139	153	108	147	69.8	95.4	118	83.1	31.2	153
Be	1.0	0.9	0.06	1.0	0.5	0.6	0.3	0.5	<0.1	1.2
Cd	0.2	0.2	0.2	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2
Cr	33	26.9	21.8	37.9	22	25	14.2	25.1	8.2	43
Cu	19.9	18.4	12.7	17.2	8.5	10.1	8.5	11.1	3.1	22.4
Fe	3140	29300	28900	30200	23400	25900	37600	40700	10600	37500
Pb	17.3	14.4	21.5	14.6	9.9	8.9	6.7	7.7	5.0	20.7
Mg	4150	3750	2700	4000	2230	2630	1240	1240	578	4590
Mn	321	319	667	326	237	283	1800	1720	474	599
Ni	26.3	24.8	24.5	27.8	13.3	16.7	15.7	21.2	4.6	28.3
Sr	82.2	121	72.8	111	53.8	74.7	87.4	63.7	21.6	121
V	49.6	38.4	36.6	51.9	36.7	41	34	48.1	12.9	65.6
Zn	63.5	52.5	40.2	58.5	26	33.8	27.8	38.7	7.6	71.5
CH <sub>3</sub> Hg	0.00075	0.00129	0.00018	0.00021	0.00022	0.00099	0.00007	0.00004	0.00003	0.00072
Clay (%)	26	23	12	28	16	24	12	5	4	14
Silt (%)	73	74	45	52	40	46	30	31	23	78
Sand (%)	1	3	43	20	44	30	58	64	74	8

<sup>1</sup>Mercury, molybdenum, and selenium were not detected in any samples.

Table 3. Metalloid concentrations in fish (æg/g wet weight) and percent moisture from Hagerman National Wildlife Refuge, Texas, 1991.

	Site									
Element/	1	2	3	4	5	6	7	8	11	
% moisture										
Al	1750	663	73.4	131	31.7	<1.0	620.8	50.3	36.3	
As	0.3	<0.1	<0.1	<0.1	0.1	<0.1	0.1	<0.1	<0.1	
B	1.7	1.6	<0.4	<0.4	0.8	<0.4	0.8	0.9	<0.4	
Ba	14.1	1.5	3.2	1.3	1.5	13.7	3.6	1.9	3.6	
Be	0.1	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	
Cd	<0.02	<0.02	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	
Cr	3.1	1.5	<0.1	0.4	<0.1	4.8	1.5	0.4	<0.1	
Cu	1.9	0.9	0.7	0.3	1.0	2.1	0.8	0.9	0.7	
Fe	1720	403	44.7	52.1	67.1	73.1	134	177	60.2	
Hg	0.05	0.06	0.05	<0.02	0.05	0.2	0.04	0.05	0.04	
Pb	2.1	3.5	<0.1	<0.1	0.1	13.2	0.7	<0.1	0.1	
Mg	613	412	206	60.7	253	160	199	278	175	
Mn	29.4	19.3	13.2	1.4	15.3	83.8	95	30.8	13.3	
Mo	6.3	<0.4	0.7	<0.4	0.7	24.9	<0.4	<0.4	0.6	
Ni	1.8	1.2	0.2	<0.1	0.3	1.6	0.9	0.3	0.3	
Se	0.3	0.2	0.3	0.3	<0.1	1.1	0.2	<0.1	0.1	
Sr	19.7	16.6	15.1	5.9	18.7	96	28.6	21.7	22	
V	4.3	<0.1	<0.1	<0.1	<0.1	<1.3	<0.1	0.3	0.1	
Zn	34	31.1	25.9	9.2	24.3	116	19.2	28.3	25.4	
% moisture	78.71	77.88	76.92	78.88	78.41	31.75	75.36	75.68	71.95	

Table 4. Aliphatic hydrocarbon concentrations in sediments (æg/g dry weight) from Hagerman National Wildlife Refuge, Texas, 1991.

	Site										
Aliphatic Hydrocarbons	1	2	3	4	5	6	7	8	9	11	

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N-dodecane	1.168	2.575	2.96	1.188	1.912	3.197	33.61	3.044	2.408	8.022
N-tridecane	1.507	3.348	3.54	1.313	2.215	3.938	43.32	3.783	2.934	9.778
N-tetradecane	0.926	2.072	2.13	0.854	1.306	2.454	29.44	2.521	1.913	6.227
N-pentadecane	0.442	1.099	0.994	0.408	0.557	1.088	20.16	1.347	0.975	3.858
N-hexadecane	0.119	0.218	0.292	0.115	0.164	0.322	5.946	0.437	0.31	0.966
N-heptadecane	0.221	0.765	0.115	0.087	0.058	0.124	8.587	1.492	0.629	3.361
Pristane	0.053	0.094	0.086	0.025	0.065	0.099	1.319	0.082	0.066	0.356
N-octadecane	0.03	0.034	0.028	0.01	0.018	0.029	0.794	0.034	0.026	0.158
Phytane	0.07	0.111	0.05	0.008	0.018	0.028	0.72	0.03	0.024	0.227
N-nonadecane	0.04	0.053	0.021	0.007	0.014	0.019	0.985	0.04	0.014	0.176
N-eicosane	0.028	0.029	0.018	0.012	0.012	0.018	1.289	0.03	0.009	0.058
Total Residue	4.60	10.40	10.23	4.03	6.34	11.32	146.2	12.84	9.31	33.19

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Table 5. Aliphatic hydrocarbon concentrations in soils(µg/g dry weight) from Hagerman National Wildlife Refuge, Texas, 1991.

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## Site

## Aliphatic

Hydrocarbons	2	3	4	5	6	10-1	10-2	12-1	12-2	12-3
N-dodecane	3.877	0.003	0.004	4.925	29.20	1.46	0.019	0.075	1.023	0.086
N-tridecane	4.635	0.002	0.001	5.855	34.88	2.40	0.086	0.348	1.227	0.151
N-tetradecane	3.087	0.003	0.003	3.77	24.12	2.86	0.236	0.856	0.908	0.245
N-pentadecane	1.585	0.004	0.002	1.939	11.97	4.12	0.482	1.445	0.447	0.408
N-hexadecane	0.495	0.003	0.003	0.655	3.88	4.42	0.794	1.753	0.145	0.64
N-heptadecane	0.204	0.018	0.004	0.221	0.3	8.58	1.432	2.322	0.182	1.179
Pristane	0.137	0.001	0.001	0.136	0.81	8.69	0.813	1.271	0.078	0.714
N-octadecane	0.052	0.008	0.003	0.053	0.3	8.17	1.397	2.007	0.048	1.233
Phytane	0.007	0.002	0.002	0.035	0.21	7.91	0.774	1.179	0.084	0.765
N-nonadecane	0.036	0.011	0.004	0.023	0.14	10.24	1.526	2.272	0.076	1.527
N-eicosane	0.028	0.013	0.008	0.036	0.19	10.28	1.463	2.036	0.085	1.462
Total Residue	14.21	0.068	0.035	17.65	107.0	69.14	9.025	15.57	4.30	8.41

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