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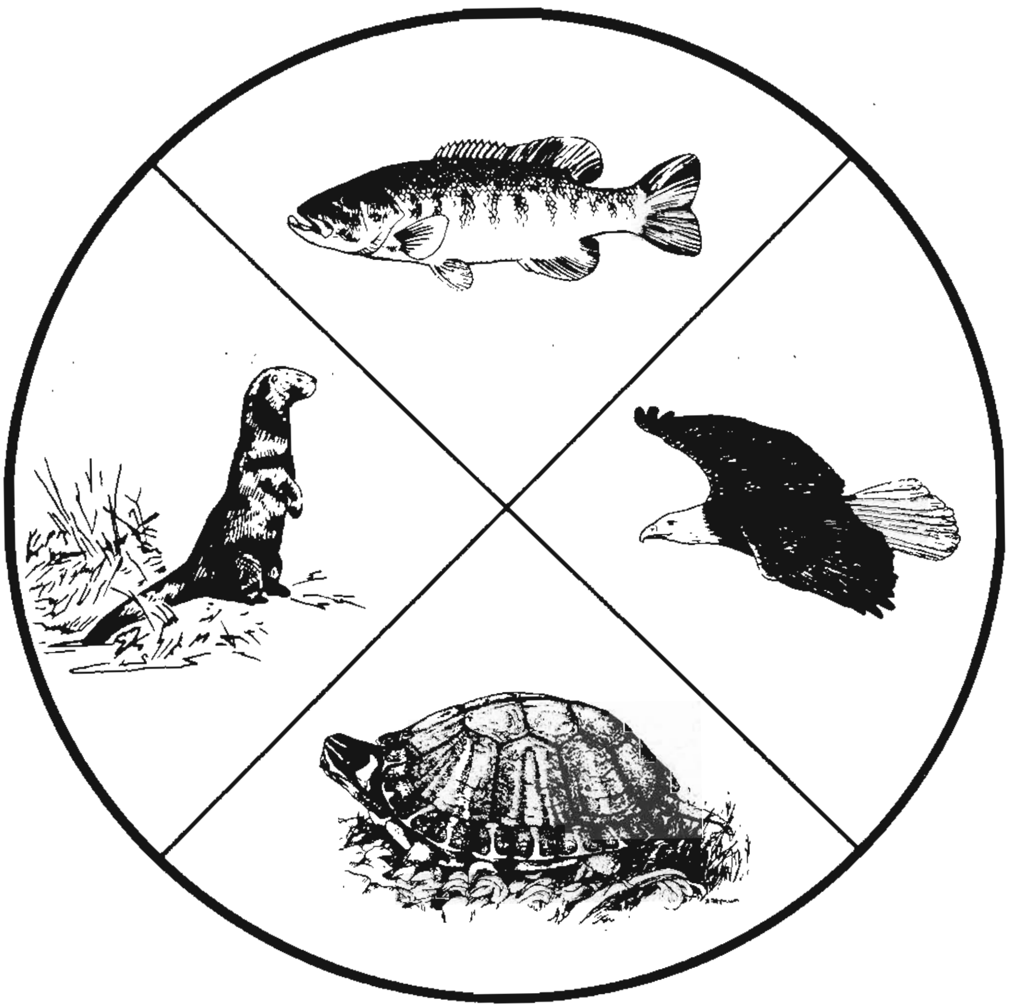
CONTAMINANTS REPORT
OCTOBER 1991

CONTAMINANTS IN BUFFALO LAKE NATIONAL WILDLIFE REFUGE, TEXAS



FISH AND WILDLIFE SERVICE

U.S. DEPARTMENT OF THE INTERIOR

Contaminants in Buffalo Lake National Wildlife Refuge, Texas

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EXECUTIVE SUMMARY/ABSTRACT

In response to eutrophication problems at Buffalo Lake National Wildlife Refuge, the U.S. Fish and Wildlife Service initiated a contaminants survey of the refuge and sites upstream in 1987. The study was conducted in cooperation with the Texas Water Commission, with Water Commission staff providing the collections and lab analyses of water data and the Fish and Wildlife Service providing the collections and laboratory analyses of tissues and sediments.

Residues of organochlorine, metallic, and nutrient contaminants were measured in triplicate sediment samples from 10 sites along Tierra Blanca Creek. Sample sites included the waterfowl impoundment in Buffalo Lake National Wildlife Refuge and various upstream sites.

The results indicate elevated concentrations of zinc, copper, strontium, and several nutrients in the sediments of feedlot ponds and in creek sediments apparently impacted by feedlot wastes. Water analyses of sites thought to be impacted by feedlot wastes revealed elevated concentrations of ammonia, calcium, chemical oxygen demand (COD), chlorophyll A, coliform bacteria, conductivity, magnesium, total kjeldahl nitrogen (TKN), sulfates, and volatile suspended solids (VSS). High concentrations of most of these same parameters have previously been documented in the literature as a characteristic of cattle feedlot runoff. In the current study, documentation that several of these pollution parameters were much more highly elevated at sites just downstream of cattle feedlots than at upstream sites is presented as evidence that feedlot wastes have been impacting Tierra Blanca Creek, the main source of water for Buffalo Lake National Wildlife Refuge.

Downstream of a site showing several signs of being impacted by a cattle feedlot, there was a shift toward lower ratios of total solids to volatile solids. This shift was seen as an additional indication that feedlot wastes had been leaking into the creek.

Tierra Blanca Creek is small enough that it does not take much feedlot runoff to have a major impact on water quality in the creek and on fish and wildlife values downstream. In the past, spills out of a few feedlot runoff retention ponds were implicated in fish kills in Buffalo Lake. At the time the current study was conducted, dissolved oxygen levels along Tierra Blanca Creek, especially at sites suspected of being impacted by feedlots, were below levels which would comfortably support a normal variety of aquatic life.

Texas Surface Water Quality Standards Section 307.5(b)(3) states that high quality waters within or adjacent to National Wildlife Refuges are considered Outstanding National Resource Waters. The quality of such waters is to be maintained and protected.

The potential effects upon shorebirds and waterfowl of ingesting unusually large amounts of various metals while feeding in feedlot impacted waters is a concern which has not yet been fully investigated.

Recommendations for additional studies, monitoring, and control measures are summarized.

Keywords-Feedlots, Cattle, Strontium, Copper, Zinc, Nutrients, Eutrophication, Buffalo Lake National Wildlife Refuge, Nitrogen, Phosphorus, Phosphates, Water Pollution, Birds, Sediments, Metals, Shorebirds, Waterfowl.

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INTRODUCTION

Buffalo Lake National Wildlife Refuge is located in Randall County of the Texas Panhandle (Fig.1). Buffalo Lake was created in 1939 with the completion of Umbarger Dam across Tierra Blanca Creek, the main water source for the lake. Tierra Blanca Creek drains about 525 square miles of land upstream of Buffalo Lake. The first spillway flows in June of 1941 nearly destroyed the dam and spillway, and in recent years the unsafe condition of the dam has resulted in the floodgates being kept open while studies to evaluate various alternative corrective actions have been in progress (Steve Jamieson, GEI Consultants, Engelwood, Colorado, personal communication).

When Buffalo Lake held water, it was an important migratory stop for numerous species of waterfowl, as well as a source of recreation for the people in this semi-arid region. Annual usage has exceeded 500,000 visitors in years when adequate water is available for boating, fishing, and recreation. Located on the Central Flyway, more than a million ducks and 40,000 geese have utilized the refuge as a feeding and rest stop on their annual migration. Information in Fish and Wildlife Service files indicates occasional usage of Buffalo Lake National Wildlife Refuge by endangered species such as bald eagles and whooping cranes and by various other rare migratory birds.

Historically, Buffalo Lake has had increasing problems associated with inadequate inflows and deteriorating water quality. During recent years, with the exception of major storms of unusual intensity, little or no water flows into the lake.

Water that does reach the refuge after a storm event has often been laden with nutrient rich runoff from numerous cattle feedlots located along the watershed. Heavy rainfall in 1967 resulted in an almost total fish kill in the lake; fecal coliform bacteria levels were elevated to the point that Federal and State health officials temporarily closed the lake to water contact sports. Information in Fish and Wildlife Service files indicate fish kills occurred in Buffalo Lake in 1959, 1964, 1967, 1968, 1969, 1970, 1971, and 1973.

According to a November 7, 1969, Texas Water Quality Board Inspection Report, rains of up to 6 inches on Tierra Blanca Creek during the week of May 5-8, 1969, resulted in most retention basins on feedlots being filled. One unpermitted discharge at Sugarland feedlot was found and ordered stopped. At Hereford Feedyards, 13 pens were flooded by the Creek and wastes were overflowing the spillway at the northeast retention basin. At least 68,000 pounds of BOD were spilled into the creek, and fish kills in Buffalo Lake were the result.

State and Federal safety concerns over the deteriorated condition of the dam and spillway led officials with the US Army Corps of Engineers, Bureau of Reclamation, and Texas Department of Water Resources to inspect the structures. The spillway was determined to be unsound and, in the event of a flood, spillway failure would endanger life and property downstream. The decision was made to drain the lake for safety reasons, although public outcry was strong to maintain the water level for recreation. The draining of the lake began in September of 1978. Buffalo Lake itself has been drained since 1979, but the Fish and Wildlife Service constructed a low level dike (Stewart Dike) at the upper end of the lake in 1975 to retain about 300 surface acres for winter waterfowl resting.

This region of the Texas Panhandle is characterized by a semiarid climate with low average annual rainfall (20 inches), large daily fluctuations in temperatures, and high wind conditions. Rainfall is often sporadic with intense storms causing runoff, and there are long periods of drying and heat. Soil distribution in the High Plains ranges from fine textured, semi-consolidated soil underlain by caliche to sandy soils and sand dunes. Soil type has been shown to have a significant relation to infiltration of surface

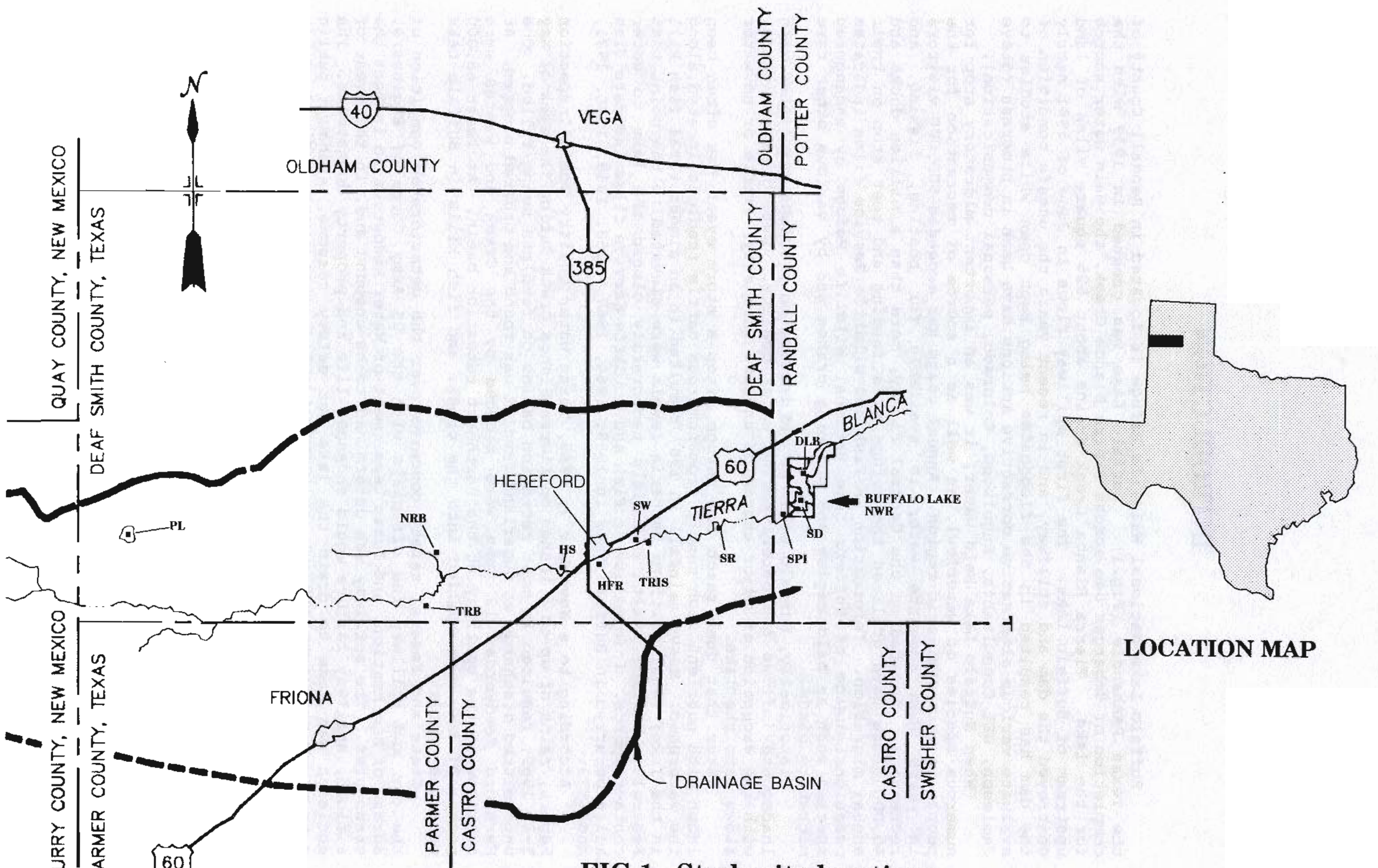

FIG 1. Study site locations

water and resulting groundwater quality [1]. Sandy soils allow greater infiltration than do the semi-consolidated fine textured clay and caliche soils found along Tierra Blanca Creek. The Ogallala Formation is the principal aquifer throughout this region, with depth-to-water ranges from a minimum of 10 feet in parts of Tierra Blanca Draw, to depths of 250-300 feet elsewhere in the High Plains. Most cattle feedlots are located on stream drainage or playa systems. Stream gradient (steepness of drop) ranges in this region are from 10 feet/mile to less than 5 feet/mile.

Tierra Blanca Creek upstream of Buffalo Lake National Wildlife Refuge is notable for the high number of large cattle feedlots immediately adjacent to the creek. Feedlots have long been considered point-sources of wastes which can pollute streams [1,2,3,4,5]. The Federal Water Pollution Control Act Amendments of 1972 established the original guidelines and standards applicable to cattle feedlots. The Water Quality Act of 1987 continues these requirements. EPA's National Pollutant Discharge Elimination System (NPDES) regulations established under the Water Quality Act of 1987 dictate that there be no discharge of wastes from large cattle feedlots into navigable waters.

The Texas Water Commission has issued regulations, effective May 9, 1989, stating there shall be no discharge of waste and/or wastewater from concentrated animal feeding operations into the waters of the State. These rules are applicable under section 321 subchapter B of the Texas Administrative Code. Feedlot rules and surface water quality standards are both part of the Texas Administrative Code. All feedlot or concentrated animal operations are included; however, permits are required for feedlots of over 1,000 head or dairy operations of 250 head. Other cases for which a permit may be required include, but are not limited to, situations where: 1) the operation is located near surface and/or groundwater resources, 2) compliance with Standards in addition to those listed in subchapter B is necessary in order to protect freshwater from pollution, or 3) the operation is not in compliance with existing Standards. All feedlots, including those not required to obtain permits (less than 1,000 head), must locate, construct, and manage waste control facilities to protect surface and groundwaters. This requirement can be met by utilizing detention lagoons, ditches, dikes, berms, terraces or other such structures which prevent feedlot runoff from reaching a lake, creek, or river during the maximum rainfall expected to occur during 24 hours over a 25 year period, a "25-year, 24-hour rainfall event." The 25-year, 24-hour rainfall event for Randall and Deaf Smith counties is 4.5-5.0 inches, based on Weather Bureau Technical Paper No. 40.

Since the 1960's, an increase in cattle feedlots occurred in this region [1,6]. Many feedlots are now situated and operated such that some runoff drains into Tierra Blanca Creek. Even large feedlots regulated by permit for no discharge into the creek can discharge directly into the creek on days when the rainfall criteria has been exceeded. If the area receives substantial rainfall for several days in a row, or a brief torrential downpour, as often occurs in this region, the daily limitation is effectively bypassed. This study was conducted to determine the extent of contaminants entering and present in Tierra Blanca Creek, the watershed which provides water to the Buffalo Lake National Wildlife Refuge.

The relatively low amount of water flowing into Buffalo Lake National Wildlife Refuge in recent years and the apparently low quality of the inflow water have been a concern to the staff at the refuge. These two factors will be taken into account in any decision whether or not to repair the dam and allow Buffalo Lake to refill. Concern has increased over possible infiltration of nitrates and other ions into the groundwater beneath cattle feedlots, as well as the pollution of streams and surface waters from runoff and leaks from cattle feedlots [1,6,7,8,9,10]. In response to these concerns, field work for this preliminary contaminants survey was initiated in June of 1987.

MATERIALS AND METHODS

Study Design and Sample Collections

All samples were collected between June 2 and June 10, 1987. Triplicate sediment samples were collected at 10 sites along Tierra Blanca Creek (Fig. 1; Appendix 1 for collection site details) using standardized sediment collection procedures recommended by the Fish and Wildlife Service [11]. Water samples were collected from the same sites at the same time by Don Manning and his staff from the Amarillo Office of the Texas Water Commission using standardized water collection procedures recommended by the Texas Water Commission.

Except for the following samples, all samples were from Tierra Blanca Creek: Site PL was Garcia Lake, actually a "cattle tank" pit excavated in the middle of the lowest part of a large natural playa lake; site DLB, the dry soil lake bottom of what was formerly Buffalo Lake; and site SW, a feedlot wastewater retention basin adjacent to the creek.

Due to the high variability of species present at various sites, it was impossible to collect the same (single) vertebrate species at more than one or two sites. Therefore, a small number of tissue samples from a variety of species were collected from a number of sites. This was done as an initial screening step to get at least some anecdotal data on tissue residues. Tissue samples collected include the following:

1. Three composite whole-body black bullhead (total length 165-245 mm) samples from site SR.

2. Three composite whole-body crayfish samples from site SR.

3. Four (three organic, one inorganic) redwing blackbird samples (collected by shotgun) from site SPI. These were modified whole-body samples (the modification was that the beak, legs, and large feathers were removed).

4. Four (organic analyses) yellow mud turtle "fat-only" (the large fatty deposits under the carapace were dissected out to form the sample) samples from site SPI.

5. Four (inorganic analyses) yellow mud turtle liver samples from site SPI (dissected from the same SPI turtles the fat-only samples were taken from).

6. Four (three organic, one inorganic) composite whole-body black bullhead (total length 165-245 mm) samples from site SPI.

7. Three (organic analyses) coot samples (collected by shotgun) from site SPI. These were modified whole-body samples (the modification was that the beak, legs, skin, and G.I. tract were removed).

8. Three (inorganic analyses) coot liver samples from the same coots identified above in item 7.

9. Two (organic analyses) yellow mud turtle "fat-only" (the large fatty deposits under the carapace were dissected out to form the sample) samples from site PL.

10. Two (inorganic analyses) yellow mud turtle liver samples from site PL (dissected from the same PL turtles as the fat-only

samples, item number nine).

11. Three composite whole-body fathead minnow samples from site PL.

12. One composite whole-body red shiner (minnow) sample from site PL.

13. Three composite whole-body tiger salamander samples from site PL.

Laboratory Methods

Analyses for contaminants in sediments and tissues were conducted at laboratories under contract to the U.S. Fish and Wildlife Service. All contract laboratories were subjected to a rigorous evaluation process prior to the award of their contracts. The Patuxent Analytical Control Facility of the U.S. Fish and Wildlife Service closely monitored the performance of these laboratories during the analyses and has confidence in the accuracy of the data. Acceptable performance (recovery variation <20% for all chemicals detected) on spikes, blanks, and duplicates was documented in laboratory quality control reports.

Tissue concentrations in this report are stated as mg/kg (parts per million) wet weight and sediment concentrations are mg/kg dry weight, unless otherwise identified.

Chemical analysis for organochlorines and PCBs in 55 samples of fish, sediment, birds, crayfish, and turtles was accomplished by the Weyerhaeuser Analytical and Testing Services, Tacoma, Washington, using gas chromatography methods approved by the Patuxent Analytical Control Facility, U.S. Fish and Wildlife Service.

Versar Inc. (Springfield, Virginia) performed the analyses for metals. A graphite furnace technique was utilized for aluminum, cadmium, lead, nickel, and chromium. Mercury was determined with a cold vapor atomic absorption spectrophotometer. A hydride generation atomic absorption spectrophotometer was used for arsenic and selenium and the concentrations of all other metals were measured with an inductively coupled plasma atomic emission spectrophotometer (ICP).

In a cooperative interagency effort, the water samples were collected by the Texas Water Commission at the same time and place the senior author collected the sediment, soil, and tissue samples. Analyses for all water quality parameters were done by the Trinity River Authority Laboratory in Grand Prairie, Texas using standard Texas Water Commission water quality analyses procedures.

Analyses for organic matter, total phosphate phosphorus, TKN, ammonia, organic nitrogen, nitrate, and COD in soil and sediment samples were done by Versar Laboratories in Springfield, Virginia, using methods and quality control procedures approved by the Patuxent Analytical Control Facility, U.S. Fish and Wildlife Service.

Statistical Methods

A personal computer with Lotus 1-2-3 software was used for data entry and simple plots and scans; a Statgraphics program from STSC,Inc. was utilized for all statistical analyses. All references to "significantly lower" or "significantly higher" in this report refer to the accepted level of statistical significance ($P<0.05$) unless otherwise specified. The differences between independent samples were tested with the Mann-Whitney nonparametric statistical test (see the copper, strontium, and zinc sections).

RESULTS AND DISCUSSION

Low Level Contaminants/Contaminants Below Detection Limits

Buffalo Lake National Wildlife Refuge's rural location tends to isolate it somewhat from many contaminants that are more common in urban environments. Many contaminants were not found to be elevated in any samples. Most of the samples were free of elevated levels of organochlorine pesticides (mostly no longer used), organophosphate parent compounds (these tend to break down quickly), and carbamate parent compounds (these also break down quickly).

No elevations of PCB compounds (The Arolchlors) were found in any samples. Among organic contaminants, only beta-BHC, Dacthal, Dieldrin, Endosufan I, Tetradifon, and DDT and its breakdown products (DDE, DDD) were detected in any samples above the 0.01 mg/kg wet weight detection limit. The results for each of above listed contaminants is summarized below in separate sections listed under the contaminant name.

The following organic contaminants were below Weyerhaeuser Laboratory detection limits (0.01 mg/kg wet-weight for organochlorines and PCBS) in all samples:

Organochlorines and PCBs:

Aldrin
BHC:
- alpha-BHC
- gamma-BHC (Lindane)
- beta-BHC
- delta-BHC

Dicofol
Endosulfan II
Endosulfan Sulfate
Heptachlor
Hexachlorobenzene
Methoxychlor
PCBs (Arochlors 1016, 1221, 1232, 1242, 1248, 1254, and 1260)
Toxaphene

The following organophosphate contaminants were below Patuxent Analytical Control Facility detection limits (0.5 mg/kg wet-weight) in all samples:

Acephate
Azinphos-methyl
Chlorpyrifos (Dursban)
Coumaphos
Demeton
Diazinon
Dichlorvos
Dicrotophos
Dimethoate
EPN
Ethoprop
Famphur
Fensulfothion
Malathion
Methamidophos
Methyl Parathion
Mevinphos

Monocrotophos
Parathion
Phorate
Terbufos
Trichlorfon

The following carbamate contaminants were below Patuxent Analytical Control Facility detection limits (0.5 mg/kg wet-weight) in all samples:

Aldicarb
Carbaryl
Carbofuran
Methiocarb
Methomyl
Oxamyl

The only metallic contaminant below Versar Laboratory detection levels in all soil and sediment samples analyzed for metals was cadmium, which had a dry-weight detection limit of 0.50 mg/kg, and thallium, which had a dry-weight detection limit of 50 mg/kg (Note: cadmium was detected in some tissue samples).

Other Results

Appendix 2 contains tables listing all data for the major parameters studied. An interpretation of the data is summarized as follows for each parameter (alphabetical order):

Alkalinity:

Alkalinity is a measure of the buffering capacity of water to acids, resulting from the presence of bicarbonates, carbonates, hydroxides, and occasionally other substances such as volatile acids, salts, borates, silicates and phosphates. Alkalinity is expressed as concentration in mg/l of calcium carbonate with equivalent capacity to neutralize strong acids.

Some recent research has focused on the tendency of low-alkalinity (less than 50 μeq/l) waters to have a relatively high potential for acid deposition effects and increased bioaccumulation of mercury, lead and cadmium in fish [12]. Note: to convert μeq (micro equivalents) to mg/l, divide by 20, so 50 μeq/l equals 2.5 mg/l equals 2.5 ppm (James Wiener, Fish and Wildlife Service, personal communication). Edible fish tissue concentrations of mercury above the 0.5 to 1.0 μg/g wet weight values used for fish consumption advisories have been found in relatively pristine (but low alkalinity) waters [12].

Results: Water Concentrations and Gradient Monitoring:

The EPA "Gold Book" (water quality) criteria requires 20 mg/l or more (as $CaCO_3$) to provide enough buffering capacity for protection of aquatic life [3]. Alkalinity values found in this study were above 20 mg/l (as $CaCO_3$) and thus were within acceptable range (see above) for protection of fish and wildlife. The reduction of alkalinity to 38 mg/l in the upper creek might warrant investigation if this value decreases, or is found to be affected by land use or other impacts to the system.

The range of alkalinity in water samples was 38 to 260 mg/l as $CaCO_3$. The greatest alkalinity (260 mg/l) was measured at site TRIS below a large cattle feedlot. Alkalinity in the upper creek at site TRB was much less (38 mg/l), and below the municipal wastewater treatment plant in Hereford at site HFR was 93 mg/l. This variation in alkalinity is an indication there may be outside factors affecting various sites along this watershed.

Other than these anecdotal observations, no clear pattern is evident in the alkalinity data from Tierra Blanca Creek. Each sampling station has a different value, which indicates there are site specific characteristics which may alter/affect the local alkalinity. Alkalinity from U.S. Geological Survey data on Prairie Dog Town Fork of the Red River ranged from 84 to 158 mg/l.

Aluminum (Al)

Aluminum occurs in natural waters and appears in a wide array of forms [13]. Aluminum is a common soil and sediment component [19]. The toxicity of aluminum depends on how it is complexed [13]. Organically-bound forms of aluminum generally are less toxic than the inorganic forms [13]. The speciation of aluminum is pH-dependent, and higher aluminum toxicities occur at lower pH levels. Because of the many species of aluminum found in water, the precise relationships of aluminum concentrations to toxicity still are not well understood [13].

Aluminum has been implicated as a neurotoxic agent in a number of studies [14,15,16]. A primary mechanism for aluminum-induced toxicity is free-ion aluminum (Al^{3+}) substitution for magnesium at critical enzyme sites and resultant depressions in magnesium-dependent functions [17]. Much of the information about aluminum toxicity relates to human health research [18] or acid rain effects.

Tissue Concentration Results:

The significance of aluminum concentrations in tissues and sediments versus the welfare of fish and wildlife is not well understood. However, levels found in this study seemed unremarkable in comparison with concentrations found in other studies [19].

Aluminum was detected (above 1.4 mg/kg) in all tissue samples analyzed for metals, except for the yellow mud turtle liver samples. The highest concentrations were at site PL (771 mg/kg dry weight or 100.23 mg/kg wet weight) in whole-body tiger salamanders from site PL. As was the case in the Trinity River [19], lowest concentrations were from a turtle sample.

Results for Sediment Samples:

In Tierra Blanca Creek sediments, aluminum ranged from 4,210 mg/kg dry weight at site HS to 14,900 mg/kg dry weight at sites SPI and SD. As was the case in the Trinity River [19], there appeared to be some tendency for aluminum to increase from upstream to downstream. There were four downstream sites (SRI, SPI, SD, DLB) exceeding a concentration of 10,000 mg/kg dry weight.

Ammonia Nitrogen (NH_3-N)

Ammonia is a biologically active nutrient present in most waters as a normal biological degradation product of nitrogenous organic matter [13]. It may also enter water as a byproduct of industrial wastes, as sewage effluent, or as agricultural runoff [13]. Ammonia is important to monitor in system productivity, eutrophication, or toxicity assessments [13].

Ammonia nitrogen is the amount of nitrogen (N) contributed by ammonia. Total ammonia (total ammonia nitrogen) is the sum of ammonia and ammonium [20]. Total ammonia and unionized ammonia are often discussed together because the monitoring for unionized ammonia is based on field measurements of pH, temperature, and total ammonia concentration. As pH increases, the concentration of unionized ammonia (NH_3) increases while that of the ammonium ion (NH_4+) decreases [20]. Temperature increase also favors the ammonia species, but to a lesser extent [20].

Unionized ammonia is the most toxic form of ammonia [20]. Unionized ammonia is acutely toxic to freshwater organisms at concentrations ranging from 0.083 mg/l for salmonid fish 96-hour LC_{50} to 22.8 mg/l for some invertebrate species (values uncorrected for pH) [3]. Unlike many heavy metals and priority pollutants, ammonia is more toxic to fathead minnows and some other fish species than to cladoceran invertebrate species; this is one clue which is sometimes used to help identify ammonia toxicity when the toxicant is unknown. Acclimation of fish to sublethal concentrations of ammonia resulting in increased resistance to later exposures has been reported by several authors [20].

Ammonia was determined to be an important sediment-associated toxicant in polluted sediments from the Lower Fox River and Green Bay Wisconsin [21]. The presence of ammonia can complicate the interpretation of results of sediment toxicity by masking the effects of other toxicants [21]. Some researchers have therefore recommended it would be prudent to routinely measure ammonia in any sediments that may have toxic amounts [21]. This is especially important in areas where sediments are anaerobic, since stress due to low oxygen can be exacerbated by toxicity of ammonia [21]. Also, anaerobic conditions prevent the oxidation/nitrification conversion of ammonia to nitrate, which can result in accumulation of ammonia in water. The decay of ammonia as part of the nitrification process may also contribute to the depression of oxygen levels (see Nitrogen/Nitrification discussion).

Many other factors also affect toxicity of ammonia, some of which include pH, temperature, fluctuating exposures, salinity, or the presence of other toxicants. Ammonia has been mentioned as having synergistic or additive effects when combined with metals and other contaminants. There is some evidence of ammonia having additive effects with copper and nitrate, and synergistic effects with hydrogen cyanide (HCN) [20]. A mixture of ammonia, zinc, and phenol exhibited toxicity greater than the sum of the individual toxicity of these three pollutants [20]. Ammonia toxicity is synergistically increased by elevated levels of copper and zinc [22]. The large number of times ammonia is included in examples of additive or synergistic effects makes it apparent that the toxicity of ammonia can be influenced by other toxics and that the toxicity of ammonia plus other pollutants can be synergistic [20]. Unionized ammonia has occurred in amounts toxic to fish in the main body of the Trinity River [19].

Water Data Results:

Range: Total ammonia concentrations ranged from 0.177 to 2.14 mg/l in this study (Fig. 2). The highest total ammonia concentration in water was 2.14 mg/l at site SR, Smith Ranch, a site impacted by runoff from a cattle feedlot. Conservatively, assuming the maximum temperature of 30 degrees centigrade, and a pH of 7.0, the average total ammonia concentration should not exceed 1.04 mg/l, for the purpose of maintaining an unionized ammonia concentration of <0.02 mg/l [3]. Three sites (HFR, NRB, and SR) had total ammonia concentrations (1.27, 1.46, and 2.14 mg/l, respectively) in excess of this value. Note: the results are presented as NH_3-N; when comparing ammonia data as NH_4+, the NH_4+ data can be converted to a NH_3-N ammonia nitrogen (ammonia as N) equivalent by multiplying it by 0.77777, a fraction reflecting the molecular weight ratio of 14 to 18.

Gradient Monitoring Levels: Total ammonia concentrations do not show an increasing tendency from upstream to downstream. Each site apparently has a distinct nitrogen fate/fractioning situation that is affected by ambient temperature and pH. Other factors such as dissolved oxygen concentration, localized land use practices, and other variables can also alter ammonia levels.

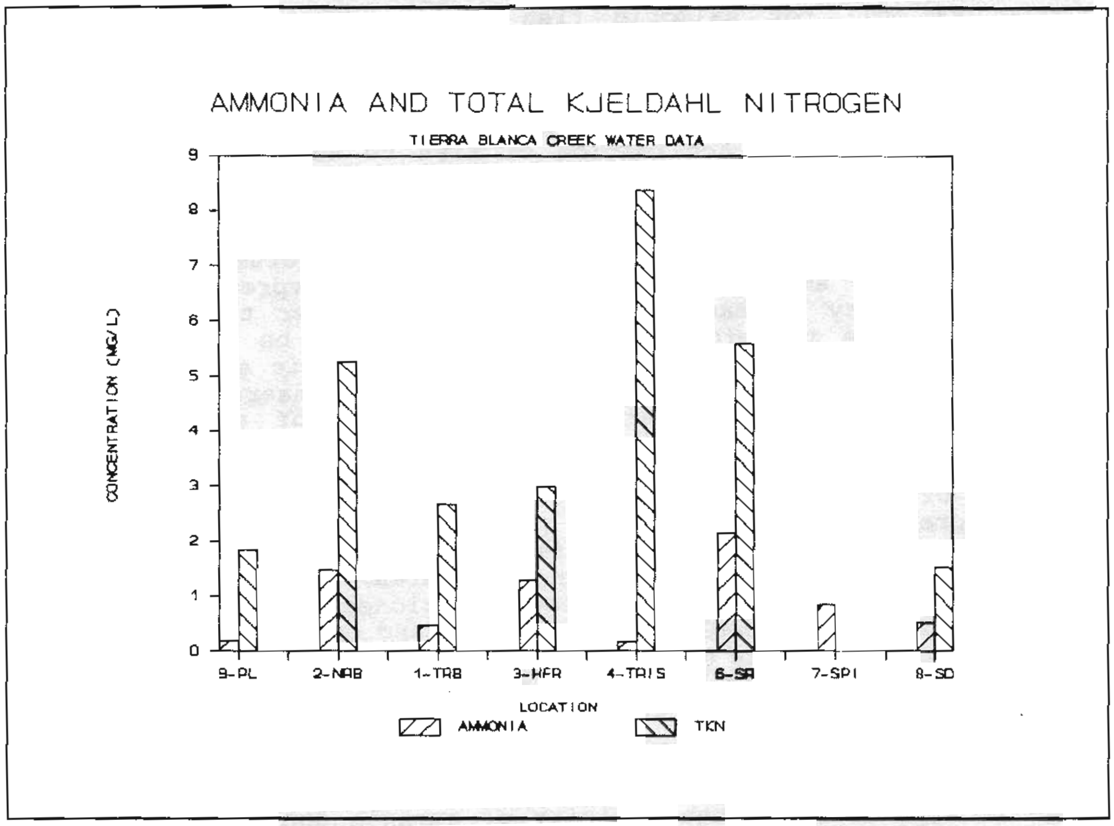

Fig. 2. Ammonia and Kjeldahl Nitrogen Concentrations

Discussion: Ammonia is likely having adverse impacts on aquatic life in the Tierra Blanca drainage where ammonia values exceeded EPA chronic effects levels for fish. Comparison values from the literature include the following:

> Typical ammonia nitrogen concentrations vary from 10 μg/l in some unpolluted surface and ground waters to 30 mg/l in some highly polluted wastewaters [23].
>
> The EPA ""Gold Book"" criteria for ammonia for protection of aquatic life is a site-specific calculation adjusted for temperature, type of species present, and pH [3]. The goal of this method is to provide a total ammonia limit which will result in less than 0.02 mg/l unionized ammonia.
>
>> For example, in a situation where sensitive coldwater species are absent, the temperature is 25 degrees centigrade, and the pH is 7.5, the water

quality criterion is that the 4-day average concentration for total ammonia should not exceed 1.49 mg/l. In the same circumstances except for a temperature of 30 degrees centigrade, the criterion is that the 4-day average concentration for total ammonia should not exceed 1.06 mg/l.

Sediment Data Results:

Range: The highest total ammonia concentrations found in stream sediments were 236 mg/Kg at Stewart Marsh (site SD, the final low-water impoundment downstream of all feedlots), and 215 mg/Kg at a site immediately adjacent to, and apparently impacted by, a large feedlot (site TRIS). Inside the feedlot, ammonia in the sediment of a manure-water lagoon (site SW) was 1830 mg/kg. This is significant because copper and zinc concentrations were elevated in feedlot impacted samples.

Gradient Monitoring Levels: No increasing or decreasing trend based on upstream/downstream locations was evident in ammonia concentrations in sediments.

General Discussion of Ammonia Results:

Ammonia has many acute and chronic toxic effects on freshwater fishes from diverse families such as minnows, catfish, sunfish and suckers. Ammonia is likely having adverse impacts to fish in the Tierra Blanca drainage where ammonia values exceeded EPA chronic effects levels for fish.

Arsenic

Arsenic analyses were done only on the 17 tissue samples. No arsenic above the 0.8 mg/kg detection limit was found in any of these samples.

Beryllium

Beryllium is a rare and quite toxic element [24]. Beryllium is listed by the Environmental Protection Agency as one of 129 priority pollutants [25], and is considered one of the 14 most noxious heavy metals [26]. Beryllium is also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at priority superfund sites [27]. Beryllium has been shown to be a carcinogen in rats and rabbits, to be teratogenic in a snail, and to cause developmental problems in salamanders [28,29]. All beryllium compounds are potentially harmful or toxic [26]. In the absence of a special source, river waters usually have very low or non-detectable concentrations of beryllium [30].

Sediment Concentration Results:

Sediment concentrations of beryllium ranged from 0.19 mg/kg dry weight at site SW to 1.2 mg/kg dry weight at site SPI. These values are well below the 6.0 mg/kg dry weight concentration which has been given as a normal soil concentration [26]. However, the SW value is above the 1.0 mg/kg dry weight soil level given as a 1987 soil criteria by the New Jersey Department of Environmental Protection [31].

Tissue Concentration Results:

The significance of beryllium concentrations in tissues and sediments versus the welfare of fish and wildlife is not well understood. However, levels found in this study seemed unremarkable in comparison with concentrations found in other studies [19].

Of the 17 tissue samples analyzed for metals, beryllium was found above detection limits (0.043 mg/kg dry weight) only in one tiger salamander sample from site PL (0.13 mg/kg dry weight or 0.017 mg/kg wet weight) and in two whole-body crayfish samples from site SR (0.11 and 0.19 mg/kg dry weight).

beta-BHC

Although not especially elevated, the presence of beta-BHC in some of the samples collected for this study is of anecdotal interest, since this compound has been associated with cattle production. In order to get levels below the maximum residue limit (MRL) for BHC in meat fat in New South Wales (Australia) of 0.3 mg/kg, cattle had to be taken off of BHC contaminated land and put on feedlots [126].

In the current study beta-BHC was detected ($\geq$ 0.01 mg/kg wet weight) in several tissue samples, including:

1) two fat-only samples of yellow mud turtles from station SPI (the concentration in each was 0.02 mg/kg wet weight).
2) one coot modified whole-body sample from station SPI (the concentration was 0.01 mg/kg wet weight).
3) one whole body composite sample of fathead minnows from station PL (the concentration was 0.04 mg/kg wet weight).

Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand measures the dissolved oxygen required by microorganisms during biodegradation of organic material. Biochemical oxygen demand determination does not reveal the concentration of a specific substance, but it does measure the effect of a combination of substances and conditions [13]. BOD is not a pollutant itself and causes no direct harm [13]. Only by lowering the dissolved oxygen content to levels threatening to fish life and other beneficial uses does BOD exert a potentially harmful effect [32]. High BOD loading to aquatic systems can create low oxygen conditions which may be responsible for fish kills.

The 5-day BOD test is a measurement of the depletion of dissolved oxygen in the water column (by degrading microbes) over a five-day (the accepted standard) incubation period. In some documents, a 5-day BOD measurement is referred to as a 5-d BOD or a BOD_5.

Very high BOD loads are known to come from cattle feedlots, usually much higher than from treated sewage or various types of nonpoint source runoff [5]. As mentioned in the introduction, high amounts of BOD have leaked from feedlot retention ponds into Tierra Blanca Creek in the past (see 1969 example) and contributed to fish kills in Buffalo Lake.

Water Data Results and Discussion:

Range: The range of 5-day BOD in water samples was 2-28 mg/l. The maximum 5-day BOD value (28 mg/l) occurred at station TRIS below a large cattle feedlot. This value was more than three times greater than any other 5-day BOD value in this study. High oxygen demand is also indicated at this site by the severe depression of dissolved oxygen (0.8 mg/l) and a high chemical oxygen demand (COD) value.

Gradient Monitoring Levels: No pattern is evident in 5-day BOD values from upstream to downstream with the exception of the noticeable increase in 5-day BOD below the cattle feedlot.

United States Geological Survey data for the Prairie Dog Town Fork of the Red River in 1987 shows no 5-day BOD value in excess of 2.0 mg/l. In 1985 during a high-flow event, the greatest 5-day BOD value recorded in Prairie Dog Town Fork of the Red River was 16 mg/l. Tierra Blanca Creek has relatively high 5-day BOD loading even at low-flow conditions, so it may be safe to assume a high-flow event could produce a slug of extremely elevated-BOD laden water and sediment that would impact oxygen concentrations downstream, as occurred in the fish kills of 1967,1968, 1969 and 1973 in Buffalo Lake.

Discussion: No water quality criteria related to fish and wildlife protection have been established for 5-day BOD [3]. The Texas Water Commission has a computer program which alerts them to check for possible errors when a 5-day BOD value greater than 50 mg/l is entered in their computer system. A true instream 5-day BOD value in excess of 50 mg/l is very high (Charlie Howell, EPA, personal communication). A value this high might indicate a source of pollution that could result in depletion of available oxygen and concern for fish and aquatic life (Jim Thompson, Texas Water Commission, personal communication).

The sharp increase in 5-day BOD (28.3 mg/l) below the feedlot is significantly greater than 5-day BOD values at all other sites. Increased BOD levels are a concern due to oxygen problems in the stream. General BOD standards for effluent discharge will vary depending upon the condition of the receiving water [13]. In a slow-moving stream, a 5-day BOD of 5 mg/l may be enough to produce deoxygenation, which results in anaerobic conditions [13].

The net result of excessive BOD loading is depletion of dissolved oxygen. At the time of this study, Tierra Blanca Creek had a severe dissolved oxygen problem, a condition that was unacceptable according to State and EPA Federal water quality criteria (see dissolved oxygen section).

Cadmium (Cd)

The chemical element cadmium has no known essential biological function [12] and is very toxic to a variety of species of fish and wildlife. Cadmium causes behavior, growth, and physiological problems in aquatic life at sublethal concentrations [33]. Cadmium tends to bioaccumulate in fish [33], clams [34,35], and algae [35], especially in species living in close proximity to sediments contaminated by cadmium [35]. Cadmium ions are extremely poisonous; their action is similar to those of mercury [36].

Cadmium acts as a cumulative poison [26] and is listed by the Environmental Protection Agency as one of 129 priority pollutants [25]. Cadmium is also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at priority superfund sites [27]. All cadmium compounds are potentially harmful or toxic [26].

Cadmium is also a suspected carcinogen [29,37] and has been shown to cause birth defects in mammals [37]. Mammals and birds consuming cadmium-contaminated food have experienced lowered sperm counts, kidney damage, increased mortality of young, elevated blood sugar, and anemia [33].

Sediment Concentration Results:

No cadmium was detected (above 0.5 mg/kg dry weight) in any soil or sediment samples.

Tissue Concentration Results:

Cadmium whole-body levels above 0.5 mg/kg are considered to be harmful to fish and predators [38]. That level was exceeded in the present study in one whole-body sample of black bullheads from site SPI (0.58 mg/kg dry weight or 0.132 mg/kg wet weight). This concentration also seems high in comparison to figures given in a recent (1976-1984) NCBP survey report, which gave the nationwide geometric mean wet-weight concentration of cadmium in composite samples of whole fish as 0.03 mg/kg wet weight [39], the maximum level ever recorded as 0.22 mg/kg, and the 85th percentile level as 0.05 mg/kg [39].

Dry weight concentrations above 0.5 mg/kg were also found in the following dissected samples: three yellow mud turtle liver samples from sites SPI and PL (0.64 to 1.7 mg/kg), and two coot liver samples from site SD (0.8 to 2.1 mg/kg dry weight). In the absence of detections in the sediments, the source of the cadmium is unclear.

<u>Calcium: see Hardness</u>

<u>Carbon (Total Organic Carbon, TOC)</u>

Like dissolved organic carbon (DOC), total organic carbon is a measure of the total organic material in a sample, the total carbon from organic sources present in the system [30]. Organic carbon is "fixed" by primary producers via photosynthesis and is available through the food chain, which includes detritus. Outside additions or enrichments of organic material (carbon) can alter aquatic carbon cycles. Organic material from outside sources is often enriched with nutrients, stimulating eutrophication and increasing sedimentation in the system.

When taking sediment samples for toxic organics such as PCBs, PAHs, and organochlorines, one should also routinely ask for total organic carbon analyses so sediment values may be normalized for carbon. This will allow comparison with the newer EPA interim criteria [40,41].

Total organic carbon in a freshwater wetland receiving highway runoff increased with distance from the inlet [42].

<u>Water Data Results</u>:

<u>Range</u>: The range of total organic carbon (TOC) in this study was 10 mg/l (as C) below the municipal wastewater treatment plant at Hereford to 34.5 mg/l below the large cattle feedlot.

<u>Gradient Monitoring Levels</u>: No pattern is evident in TOC levels from upstream to downstream, although organic inputs to the creek are reflected by a three-fold increase in TOC below the cattle feedlot.

<u>Discussion:</u> Apparently, no national water quality criteria have been established for TOC [3]. However, one result of excessive organic loading is oxygen depletion; and severe oxygen depletion was seen along most of Tierra Blanca Creek.

<u>Chemical Oxygen Demand (COD)</u>

Like BOD, COD is a measure of the oxygen requirement for degradation of a material. However, COD is a measure of the total chemical oxygen demand rather than just the biological portion of oxygen demand. The procedure to measure COD includes a rigorous digestion with heat and strong acid. COD requirement of oxygen is greater than BOD because, theoretically, the rigorous digestion with heat and acid chemically degrades substances that microbes cannot. Very high COD loads are known to come from cattle feedlots, usually much higher than from treated sewage or various types of nonpoint source runoff [5].

Water Data Results:

Range: The range of COD in water samples was 38 mg/l to 182 mg/l. The highest COD value (182 mg/l) occurred below a large cattle feedlot (site TRIS) and was almost twice the nearest value (95 mg/l). This is further evidence there is an inflow of waste from the feedlot to the creek.

Gradient Monitoring Levels: No pattern or trend is evident for COD values along Tierra Blanca Creek, with the exception of a significant increase below the feedlot. Localized activity may be impacting different sites.

Discussion: No national water quality criteria have been established for COD [3]. A very high COD level, 182 mg/l, was recorded at site TRIS impacted by the cattle feedlot. Texas Water Commission is alerted when a COD in excess of 150 mg/l is observed on computer records (Jim Thompson, Texas Water Commission, personal communication). This alert is for the purpose of identifying high values which might be data input or laboratory errors; an actual concentration of COD in excess of 150 mg/l would be considered to be very highly elevated and would suggest a pollution source (Steve Twidwell, Texas Water Commission, personal communication). Coupled with elevated BOD and 0.8 mg/l dissolved oxygen, a COD value of 182 mg/l represents a cause of concern for fish and wildlife.

Chlordane

Chlordane components cis (alpha)-Chlordane, trans (gamma)-Chlordane, cis-Nonachlor, and trans-Nonachlor were found to be above detection limits (0.01 mg/kg dry weight) only in yellow mud turtle fat samples from site SPI; none of these samples had concentrations of these compounds higher than 0.02 mg/kg.

Chloride/chlorides

Chloride concentrations in water were especially low (2.5 mg/l) at the upper sites, but sites impacted by feedlot runoff showed ten-fold increase in chlorides (36.3 and 22.0 mg/l). See Appendix 2 for a list of the values and the salinity section for a more detailed discussion of the values.

Chlorophyll-a/Pheophytin-a

Chlorophyll is the photosynthetic compound found in plants. Since algae contain it, measurement of chlorophyll-a in water is one method of quantifying algal biomass in the water column [45]. Pheophytin is a degradation compound of chlorophyll-a and can be useful in determining the growth rate/phase of the photosynthetic community. In some cases, satellite data can be used to map chlorophyll-a ranges (Jerry Miller, U.S. Bureau of Reclamation, personal communication).

Water Data Results:

Range: The greatest chlorophyll-a value (319 $\mu g/l$) occurred below the cattle feedlot (site TRIS) and was an order of magnitude higher than all other values (1-32 $\mu g/l$) found along the creek (see Appendix 2 for all chlorophyll A and pheophytin A concentrations). The greatest pheophytin-A value (49.8 $\mu g/l$) also occurred below the cattle feedlot

(site TRIS)

Gradient Monitoring Levels: Chlorophyll was low in the upper Tierra Blanca Creek site TRB (average value 1.1 μg/l), with only a slight increase below the municipal wastewater treatment plant HFR (16.5 μg/l). A significant increase (319 μg/l) in chlorophyll is seen at site TRIS below the cattle feedlot, where nutrients were plentiful enough to support an algal bloom. Proceeding downstream from this site, chlorophyll values showed a decreasing trend (32.5, 21.7, and 2.5 μg/l).

Discussion: A literature search done for this study revealed no water quality criteria or other concern levels for protection of fish and wildlife which have been suggested for chlorophyll A [3]. However, algal blooms are associated with nutrient enrichment, and often cause a decline in water quality both from aesthetics and from altering other physical and chemical parameters within the system such as light penetration, alkalinity, and dissolved oxygen concentration. Vollenweider classified lakes with chlorophyll values ranging 1-15 ug/l as mesotrophic and lakes with values 5-140 ug/l as eutrophic [137]. The very high value (319 μg/l) at site TRIS indicates the existence of an algal bloom at the site and corresponds with elevated nutrient levels found at this same site.

Chromium (Cr)

Chromium is a metallic element which is listed by the Environmental Protection Agency as one of 129 priority pollutants [25]. Chromium is considered one of the 14 most noxious heavy metals [26]. Chromium is also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at priority superfund sites [27].

Sediment Concentration Results:

Sediment concentrations of chromium ranged from 4.8 mg/kg dry weight at site HS to 14 mg/kg dry weight at site SPI. These are well below concentrations thought to be elevated and/or of concern to fish and wildlife [44,46,47,48].

Tissue Concentration Results:

Little is known about the effects of elevated tissue levels of chromium on fish and wildlife. Apparently, the only chromium level that has been proposed as a protective standard for animal tissues is 0.20 mg/kg [49]. Based on a review of data from several U.S. Fish and Wildlife Service studies in the southwest, chromium levels above 0.8 mg/kg wet weight in fish and wildlife tissues may tentatively be considered to be elevated [19,50,51,52]. That level was not exceeded in any of the 17 tissue samples analyzed for metals in this study.

The highest wet concentrations were in three tiger salamander samples from site PL (1.8 to 2.0 mg/kg dry weight or 0.234 to 0.254 mg/kg wet weight), three whole-body crayfish samples from site SR (1.7 to 1.9 mg/kg dry weight or 0.408 to 0.486 mg/kg wet weight), one red wing blackbird sample from site SPI (1.3 mg/kg dry weight or 0.386 mg/kg wet weight), and one black bullhead sample from site SPI (1.1 mg/kg dry weight or 0.250 mg/kg wet weight).

Coliform Bacteria

Coliform bacteria are considered to be the primary indicators of fecal contamination, and as such are some of the most frequently applied indicators of water quality [3,13]. Although harmless to humans, they are normally used as indicators of the potential presence of other bacteria and viruses that can cause disease.

Researchers have found that the presence of cattle directly affects fecal coliform densities in adjacent streams and that feedlot runoff may contain pathogens which are harmful to humans and animals [8]. Bacteriological concerns involving fish and wildlife include outbreaks of Avian Botulism (Clostridium botulinum type C) and Avian Cholera (Pasteurella multocida), which annually kill thousands of migratory waterfowl. Avian cholera occurring in the Texas High Plains has often been discovered in ponds or playa lakes located at or near animal feeding centers. The first case reported was at a chicken feeding operation (Harvey Miller, U.S. Fish and Wildlife Service, personal communication). In recent years, avian cholera outbreaks in the Texas High Plains are most frequently found at cattle feedlot ponds. Other bacterial diseases can affect both birds and mammals, such as bacteria of the genus Salmonella, Staphylococcus, and Streptococcus. Human health concerns surrounding bacterial contamination must also be addressed when considering contact recreation in Buffalo Lake.

Typical Freshwater Concentrations:

USGS 1974-1981: the 50th percentile for fecal coliform bacteria of 305 (not especially clean) NASQWAN and NWQSS river sites in the U.S. was 355 colonies per 100 ml; the 25th percentile was 92 colonies per 100 ml, and the 75th percentile was 1222 colonies per 100 ml [55]. These riverine sites in the USGS study were mostly in (or downstream of) agricultural and urban areas [55].

Other Concern levels for water concentrations:

Water Quality Standards: Various states have set the following water quality standards for fecal coliforms for waters having aquatic life propagation as a use: South Carolina (best trout streams), 200/100 ml secondary upper limit and 400/100 ml upper value; and Tennessee, 1000/100 ml secondary upper limit and 5000/100 ml upper value [56]. Though state standards vary, fecal coliform limitations for non-contact recreational waters generally range from a geometric mean of 100 to 1000 organisms per 100 ml, with not more than 10% of the samples exceeding twice the adopted standard [13, US EPA 1979 Drinking Water Regulations].

Drinking Water: Drinking water standards are based on total coliform bacteria and are usually regulated by the state [13]. The National Academy of Science [57] recommended a limit of 2000 coliform/100 ml for raw water prior to treatment. Drinking water must be free of coliform organisms at the time of consumption [13]. Normally this is accomplished via disinfection (chlorine, ozonation, etc.) as part of the water treatment process [13].

Water Data Results:

Range: The sample with the highest coliform growth was found at site TRIS, the location just below a cattle feedlot. The plate had confluent bacterial growth, which means bacteria completely covered the medium, and individual colonies were unable to be counted. Counts on other samples ranged from <1 per 100 ml at site HFR, to 1600 per 100 ml at site SR.

Gradient Monitoring Levels: Coliform bacteria were high in the upper Tierra Blanca Creek site TRB (900/100 ml), as well as a stock watering pit (1100/100 ml, site PL). No increasing or decreasing trend was evident along the stream. Subsequent bacteriological sampling at Stewart Dike in 1988 has produced coliform counts as high as 70,000 colonies per 100 ml.

Discussion: There is no national water quality criteria for coliforms for protection of fish and wildlife [3]. For protection of human health (bathing or contact recreation, the Texas Water Quality Standards limit is not more than 200 fecal coliform colonies per 100 ml in a geometric mean of at least five samples. Noncontact limits are 2000 colonies per 100 ml. The majority of Tierra Blanca Creek samples reviewed in this study exceeded the 200 coliform/100 ml criterion. Samples of influent to Buffalo Lake Wildlife Refuge in the summer of 1988 had coliform readings of 23,000, 40,000, and 70,000 coliform/100 ml. One sample, taken June 2, 1988, revealed a population too numerous to count (TNTC).

Some of the coliform bacteria probably come from rangeland cattle not confined to feedlots, other animal sources, general agriculture, and urban runoff from the city of Hereford. However, extremely high values (such as the concentrations of 40,000, and 70,000 coliform/100 ml flowing into Buffalo Lake in 1988) would not be expected from such sources.

Coliform values from creeks and rivers running through open pasture land are usually not so highly elevated if rangeland cattle and other animals are the main source. Concentrations of fecal coliform (FC) and fecal streptococcus (FS) measured weekly in stream water of 13 wildland watersheds in Oregon were not significantly different in areas with no cattle grazing than in areas grazed with management for livestock distribution [135]. Although there is typically some elevation of coliforms immediately after important precipitation events from cattle grazing on pasturelands, creeks going through grazed pasturelands typically have relatively low levels of coliforms during dry periods (Bill Platts, Don Chapman Consultants, Boise, Idaho, personal communication). At the time of field collections done for the Buffalo Lake study, it had been a while since there was significant rain fall, and the creek was relatively dry in most places. Note: also at the time of field collections, several of the retention lagoons at the sewage plant in Hereford were dry; this extra capacity was seen as a clue that there had probably been no recent releases from these ponds into the creek.

The following data confirms that general farming and grazed rangeland areas of the Texas High Plains do not consistently have highly elevated levels of coliforms: Fecal coliform counts from the Canadian River Basin (segment 101, north of the study area), average 61 coliform/100 ml; the highest concentration in 37 samples in this segment was 652 coliform/100 ml [134]. Tierra Blanca Creek, the study area, is in the Red River Basin. Fecal coliform counts from Segment 0222 of the Red River Basin (east of the study area) average 40 coliform/100 ml [134]. Fecal coliform counts from two sites on Red River Basin segment 0227, (south of the study area) were higher at 455 and 15,600 coliform/100ml [134]. Although the latter concentration was high enough to suspect a specific point source, it was still lower than the coliform counts in the influent water at Buffalo Lake National Wildlife Refuge in the summer of 1988 (23,000, 40,000, and 70,000 coliform/100 ml). For additional contrast, in the Prairie Dog Town Fork of the Red River, the highest fecal coliform found by the U.S. Geological Survey in 1987 was 540 colonies/100 ml [54].

Summary: Although extremely high coliform counts of the magnitude found in 1988 inflows into Buffalo Lake National Wildlife Refuge have been associated with feedlot runoff [136], such high values are usually not found in Texas creeks in areas of general farming and grazed pasture lands [134]. The very high coliform levels in some of the Buffalo Lake influent samples are seen as one of several clues that feedlot wastes are influencing the water quality of Tierra Blanca Creek.

Conductivity (Specific Electrical Conductance)

Conductivity (also referred to as specific conductance) measures the ability of water to conduct an electric current [23]. It is the reciprocal of resistance, for which the unit is ohm; therefore the unit of conductance is termed mho, or for most low-conductivity natural waters is termed a micromho (μmho). Measurement is usually made using two electrodes 1 cm apart, and is generally reported as micromhos per centimeter (μmhos/cm) [23]. In the international system of units (SI), conductivity is reported as millisiemens per meter (mS/m); 1mS/m = 10 μmhos/cm.

Conductivity is related to salinity and total dissolved solids because the ions in solution are what allows electrical current to be transmitted through water. Temperature of the solution alters the ion velocity, and therefore the specific conductance increases with temperature for both salinity and conductivity. Conductivity increases about 2% per degree Celsius. In Texas, total dissolved solids are limited by State standards, but calculated by halving conductivity measurements (Dave Buzan, Texas Water Commission, personal communication).

A table for the conversion of conductivity to salinity is given in Appendix 3. Greater conductivity would correspond with higher salinity and greater total dissolved solids. This is important to fish and other aquatic life because substances in solution exert osmotic pressure on aquatic organisms [32]. When osmotic pressure becomes too high it can draw water out of vital body organs and cause cellular damage or death. Most aquatic life can adapt to minor or slow changes, but wide or sudden variations (such as a sudden intrusion of oil field brine into a freshwater ecosystem) can be too severe for adaptation and result in elimination of species from impacted areas [32,58,59].

Specific conductance in a freshwater wetland receiving highway runoff decreased with distance from the inlet and also decreased during storm flows (dilution) [42]. In intermittent streams, high levels of conductance can occur during periods of low flow (lack of dilution) [60]. However, the drainage area soil type is also an important factor affecting conductivity levels (Dave Buzan, Texas Water Commission, personal communication).

Water Data Results:

Range: The range of conductivity in this study was 177-667 μmhos/cm. The greatest conductivity reading along Tierra Blanca Creek was taken just below a cattle feedlot (667 μmhos/cm at Site TRIS). Conductivity is related to the types and amounts of ions in solution, and the high level at site TRIS corresponded with elevated levels of individual ions at this same site, a site suspected of being impacted by a cattle feedlot.

Gradient Monitoring Levels: No increasing or decreasing trend is seen along the creek. However, a significant increase in conductivity was observed below the cattle feedlot.

Discussion: No national fish and wildlife protection criteria have been established for conductivity [3], but most of the levels found in this study are not high enough to cause undue concern for fish and wildlife. The literature related to effects on fish and wildlife is usually expressed in related measures (salinity, total dissolved solids, etc.) rather than as conductivity. Comparison data from other sources is provided as follows:

> Good mixed fish fauna have not often been found in waters with a specific conductance greater than 2000 μmhos at 25°C [13]. A specific conductance of 4000 μmhos at 25°C is the approximate upper limit of ionizable salts tolerated by fish in mixtures of sodium, magnesium, and calcium compounds [13]. It has been reported that in U.S. waters supporting a good fish fauna, approximately 95% have a conductivity reading (at 25°C) of under 1100 μmhos [32].
>
> Conductivity measured by the U.S. Geological Survey in the Prairie Dog Town Fork of the Red River was much higher than in Tierra Blanca Creek, ranging from 10100 to 35700 μmhos/cm, However, this is not considered as important as the data in the current study showing elevations at certain sites (like below the feedlot) in Tierra Blanca Creek, since the Red River is known to have natural seeps of salty water which degrade the water quality in that system.

Copper (Cu)

The chemical element copper is widely distributed in nature in the elemental state, in sulfides, arsenites, chlorides, and carbonates [18]. Copper is listed by the Environmental Protection Agency as one of 129 priority pollutants [25]. One important effect of copper is its greater toxicity to younger fish [3]. Copper is a toxic pollutant designated pursuant to section 307(a)(1) of the Clean Water Act and is subject to effluent limitations [18].

Some researchers believe negative effects of copper on fish are more likely the result of toxicity of high concentrations in water than toxicity from intake of prey containing copper [64]. However, in all animals studied, continued ingestion of copper in excess of dietary requirements led to some accumulation in tissues, particularly the liver and kidneys [62]. Excess copper accumulation can lead to copper toxicosis and cell damage [62]. Fish living or foraging in contaminated sediments may accumulate it directly from the sediments [35].

In water, copper acts synergistically with other common contaminants such as ammonia, cadmium, mercury, and zinc to produce an increased toxic effect on fish [22,65]. Sublethal concentrations adversely affect minnow fry survival and growth [33].

Minute amounts of copper in the diet are needed for human, plant, and animal enzymes [61,62,63], and copper poisoning or deficiency problems are rare in humans [61]. However, high concentrations of copper in water can be toxic to fish [26,64], plants [66], and many other aquatic species [18]. Elevated concentrations of copper in water are particularly toxic to many species of algae, crustaceans, annelids, cyprinids, and salmonids [62]. A water's alkalinity directly affects the toxicity of copper to aquatic life, which generally is augmented at lower alkalinities [12,13].

More research needs to be done on the toxicity, mobilization, and bioavailability of copper in low alkalinity and/or low pH waters [12]. Preliminary data suggests the potential for bioaccumulation or bioconcentration of copper is high to very high for the following biota: mammals, birds, fish, mosses, lichens, algae, mollusks, crustacea, lower animals, and higher plants [26]. The best potential mediums for biological monitoring (including gradient monitoring) appear to include clams, lichens, mosses, algae, and higher plants [26]. As mentioned above, continued ingestion of copper by animals in excess of dietary requirements led to some accumulation in tissues, particularly the liver and kidneys [62].

Sediment Concentration Results:

Sediment concentrations of copper ranged from 9.3 mg/kg dry weight at site PL to 90 mg/kg dry weight at site SW. Copper concentrations in three sediment samples from the upstream Tierra Blanca Creek site (NRB) and three sediment samples from the playa lake (PL) off-stream site were low, all samples being at or below 11 mg/kg dry weight. These are well below concentrations thought to be elevated and/or of concern to fish and wildlife [26,46,67].

For contrast, three samples from the Tierra Blanca Creek site (TRIS) suspected of being polluted by a large feedlot had significantly higher copper concentrations (from 25-29 mg/kg dry weight) and the waste water pond in the feedlot had highly elevated copper concentrations (81-90 mg/kg). Freshwater sediment concentrations which various parties have considered to be elevated or concern levels have included the following:

Texas: The statewide 90th percentile value for copper in freshwater sediments was 40 mg/kg dry weight [43]. Concentrations above 17.0 mg/kg and 33.0 mg/kg are higher than 50% and 85% of lake samples statewide, respectively [124].

Great Lakes Harbors, EPA 1977: Sediments having concentrations higher than 50 mg/kg dry weight were classified as "heavily polluted" [46]. Twenty five to fifty is considered moderately polluted [31,68].

Illinois EPA, 1984: Sediments having concentrations higher than 60.0 mg/kg dry weight were classified as "elevated" [46].

EPA Region 6, 1973: The concentration proposed by EPA Region 6 as a guideline for determining acceptability of dredged sediment disposal was 50 mg/kg [44].

Ontario, 1978: The concentration proposed by the Ontario Ministry of the Environment as a threshold for evaluations of dredging projects was 25.0 mg/kg [46].

International Joint Commission, 1988: The IJC suggested sediment concentrations not exceed background levels of 21.0 mg/kg [46].

An anecdotal note of interest on copper concentrations in the Texas Panhandle is that one high level of copper (61 mg/kg) has been reported from Lake Meredith sediments (Don Manning, Texas Water Commission, personal communication). The source of high metals in Lake Meredith is unknown, but may include soils or unknown sources in the large river basin impounded by the lake. The Canadian River is impacted upstream of the lake by heavy (over) grazing (Joan Glass, Texas Parks and Wildlife, personal communication) and by a major brine artisan aquifer in the vicinity of Logan, New Mexico [134].

However, the data reviewed to date for this study does not suggest widespread natural elevations of copper in the Texas High Plains. Upstream samples in Tierra Blanca Creek did not show elevations of copper. Copper compounds are known to be used as feed additives at some feedlots. Feedlot samples had copper concentrations (81-90 mg/kg), even higher than the Lake Meredith concentration mentioned above. A Mann-Whitney statistical test showed copper concentrations from the six upstream samples in Tierra Blanca Creek to be significantly lower than the six samples in the study area known or suspected of being influenced by feedlot wastes (significance level of 0.0051).

Tissue Concentration Results:

Copper was detected in all 17 tissue samples. The concentrations ranged from 3.1 mg/kg dry weight (0.704 mg/kg wet weight) in whole body samples of black bullhead catfish from site SPI to 68 mg/kg dry weight (16.796 mg/kg wet weight) in a coot liver sample from site SD. All samples had concentrations lower than 10 mg/kg dry weight copper except for three whole-body samples of crayfish from site SR (40 to 53 mg/kg dry weight or 9.6 to 13.14 mg/kg wet weight) and three coot liver samples from site SD (59 to 68 mg/kg of copper, dry weight, or 15.9 to 16.8 mg/kg wet weight).

There is limited data available for interpreting the meaning of the tissue concentration results. No predator protection levels for copper were found in a literature search done for this study. However, the concentration of copper in earthworms is correlated with soil concentrations [69], which may be a consideration relative to birds feeding on other worms and midges in copper-polluted soils or sediments [69]. Wet-weight legal limits for concentrations of copper in fish and fishery products include:

> The lowest legal limit is 10 mg/kg (Venezuela, India, Ecuador, Chile) [70,71]. Nine countries have limits less than or equal to 70 mg/kg, but the U.S. apparently has no limit [70,71]. The Australian National Health and Medical Research Council recommends 30 mg/kg copper as a maximum content for seafood products [72].

The anecdotal tissue data from the study showed only two whole body samples (crayfish from site SR) above 10 mg/kg wet weight. The coot livers were higher, but liver samples would be expected to have more copper than whole-body samples.

Copper whole-body levels above 0.9 mg/kg wet weight were higher than the concentrations of 85% of all fish samples in a (NCBP) national survey [73]. A more recent (1976-1984) NCBP survey report gave the nationwide geometric mean concentration of copper in composite samples of whole fish as 0.65 mg/kg wet weight [39]. The only whole body fish tissue sample collected in this study which is directly comparable with these figures was a black bullhead whole body sample from site SPI, which had 0.704 mg/kg wet weight of copper.

Dacthal (DCPA)

Low levels of DCPA were detected ($\geq$ 0.01 mg/kg wet weight) in several tissue samples, including:

1) three whole body samples of black bullhead from station SR (the concentration in each was 0.01 mg/kg wet weight).
2) two whole body samples of crayfish from station SR (the concentration in each sample was 0.09 mg/kg wet weight).
3) two whole body samples of fathead minnows from station PL (the

concentration in each sample was 0.09 mg/kg wet weight).

DDD

PP'DDD, a breakdown product of DDT and dicofol, was detected (≥ 0.01 mg/kg wet weight) in relatively low concentrations (≤ 0.04 mg/kg) at various sites, including sediments from site HFR, yellow mud turtle fat from sites PL and SPI, and whole-body black bullhead samples from sites SPI and SR. OP'DDD, another breakdown product of DDT, was detected (≥ 0.01 mg/kg wet weight) in relatively low concentrations (≤ 0.03 mg/kg) in sediments from site SW and yellow mud turtle fat from site SPI.

DDE

PP'DDE, a breakdown product of DDT and dicofol, was detected (≥ 0.01 mg/kg wet weight) in relatively low concentrations (≤ 0.08 mg/kg) at various sites, including sediments from sites HFR and TRIS. The following anecdotal data suggested some elevations of DDE in the following samples:

1) two sediment samples from site SR (the concentrations were 0.11 and 0.49 mg/kg dry weight).
2) two red-winged blackbird samples from site SPI (the concentrations were 0.13 and 0.19 mg/kg wet weight).
3) two fat samples from yellow mud turtles (the concentration in the sample from site PL was 0.23 mg/kg wet weight, and the concentration in the sample from site SPI was 1.4 mg/kg wet weight).

DDT

PP'DDT, an organochlorine insecticide which has long been banned in the U.S. except as a contaminant in some formulations of dicofol, was detected (≥ 0.01 mg/kg wet weight) in relatively low concentrations (≤ 0.03 mg/kg) in tissues from various sites, including yellow mud turtle fat samples from sites PL and SPI, whole-body black bullhead samples from site SR, and one coot modified whole-body sample from SPI. OP'DDT was detected (≥ 0.01 mg/kg wet weight) in relatively low concentrations (≤ 0.02 mg/kg) in only two samples: yellow mud turtle fat from site SPI and black bullhead whole body samples from site SR.

Dieldrin

Dieldrin, another banned organochlorine insecticide, was detected (≥ 0.01 mg/kg wet weight) in relatively low concentrations (≤ 0.06 mg/kg) in tissues from various sites, including yellow mud turtle fat samples from sites PL and SPI, whole-body black bullhead samples from site SR, whole body black bullhead samples from sites SR and SPI, a red shiner sample from site PL, and sediment samples from sites HFR and SW.

Endosulfan 1

Endosulfan 1 was detected (≥ 0.01 mg/kg wet weight) in this study in only four sediment samples. Three of these four were in the waste pond at the cattle feedlot (station SW) and one was at a site downstream of some feedlots (station SR). In all four cases, the concentration detected in the sediment samples was 0.01 mg/kg wet weight.

FIFRA has residue tolerances for endosulfan in meat byproducts of cattle [18]. Silage and other plant materials consumed by cattle are among the things which have at times been sprayed with endosulfan [18]. However, the levels detected in the current study were not especially high and endosulfan has also been detected in rain and snow [18]. The levels detected were barely above the detection limit and are below most concern levels or levels considered in the literature to "elevated."

However, it is interesting that only endosulfan I and not the metabolite endosulfan sulfate was present in the sediment samples. Another anecdotal note of interest is that three of four occurrences were in the wastewater lagoon of a feedlot.

Endrin

Like DDT, endrin is a now banned organochlorine insecticide. It was detected ($\geq$ 0.01 mg/kg wet weight) in only one sample:(0.03 mg/kg wet weight) in a yellow mud turtle fat sample from site SPI.

Eutrophication

Eutrophication is the gradual aging process in a lake, reservoir, pond or stream that is characterized by numerous undesirable changes in the water body, such as decreased mean depth, decreased water clarity and quality, and increased algal/plant growth. Nutrient enrichment primarily associated with nitrogen and phosphorus input has been shown to be causative in accelerating the natural processes, and man's influence is often termed cultural eutrophication [2].

Although the term eutrophication is most often associated with lakes or ponds, eutrophication is obviously occurring in the pools behind low water dams in Tierra Blanca Creek, including the waterfowl impoundment in Buffalo Lake National Wildlife Refuge. Eutrophication was a major problem when Buffalo Lake was full. Nutrient analyses, primarily for forms of nitrogen and phosphorus, are helpful in determining potential problems associated with increased productivity and eutrophication. Although no separate measure of eutrophication was done for this report, evidence of eutrophication at the sites sampled is provided in the nitrogen, phosphorus, and chlorophyll sections.

Hardness (Water Hardness)

In simple terms, hardness is mostly the amount of calcium, magnesium, and ferric carbonate in freshwater [74]. Hardness can effect the toxicity of many inorganic contaminants, and many concern levels or standards are therefore expressed as dependent of specific hardness ranges [74]. Data from some studies have indicated that the presence of carbonate hardness may reduce toxicity of some metals [2]. However, others have stated that hardness may limit the growth of fish [13]. The effects of hardness on freshwater fish and other aquatic life appear to be related to the ions causing the hardness rather than the hardness itself [3].

In technical terms, hardness of water represents the total concentration of polyvalent metallic ions (primarily calcium and magnesium ions in freshwater), expressed as an equivalent concentrations of $CaCO_3$ in milligrams per liter [3]. Historically, hardness was the ability of water to precipitate soap, or the ability, upon evaporation, to leave mineral deposits. There has been much interest in hardness related to potential positive benefits to human health [30].

Hardness in freshwater is frequently distinguished as carbonate and non-carbonate fractions [3]. The carbonate hardness is considered equal to the alkalinity, since bicarbonates are generally measured as alkalinity [3].

In intermittent streams, high levels of hardness can occur during periods of low flow (lack of dilution) [60]. However, the drainage area soil type is also an important factor affecting water hardness (Dave Buzan, Texas Water Commission, personal communication).

Water Data Results:

Range: Calcium concentrations ranged from 17.2 to 43.6 mg/l.

Magnesium concentrations ranged from 3.8 to 15.5 mg/l. The highest concentration of both calcium (43.6 mg/l) and magnesium (15.5 mg/l) occurred at site TRIS below the cattle feedlot.

Gradient Monitoring Levels: There is no evidence of increasing trends in calcium or magnesium along this system, with the exception of an increase in both ions at the site below the feedlot. United States Geological Survey data for Prairie Dog Town Fork of the Red River are ten times higher for both calcium and magnesium than in Tierra Blanca Creek.

Discussion: Hardness classifications are defined in EPA's recent water quality criteria document, but hardness has fallen out of favor as a stand-alone criterion for protection of aquatic life [3]. Just as reviewers of the EPA "Red Book" recommended against the use of the term hardness in favor of inclusion of the concentrations of the specific ions [75], EPA's more recent water quality criteria summary states that the effects of hardness on freshwater aquatic life appear to be related to the ions causing the hardness rather than the hardness itself [3].

Heptachlor epoxide

This compound was detected (≥ 0.01 mg/kg wet weight) in low concentrations (≤ 0.05 mg/kg) in the following samples: two red winged blackbird samples from site SPI, and five yellow mud turtle fat samples from SPI and PL.

Iron

Iron is the fourth most abundant element in the earth's crust and is an essential trace element required by both plants and animals [3]. Another reference says iron is the second most abundant metal in the earth's crust after aluminum; about 5% of the earth's core is believed to consist mainly of iron [18,76].

The primary sources of iron in rivers include soil erosion, urban runoff, and industrial discharges. Iron is also present in the leachate of some municipal landfills [77].

Environmental Considerations Related to Iron:

Many iron compounds are ubiquitous and are not especially toxic. The literature on iron as a contaminant is not extensive; references are found to relatively minor effects, such as the fact that rust rings have been produced by implanting iron particles in guinea pig corneas [18].

Body burden issues are not well understood. Little is known about the effects of predators consuming fish carrying excess iron. Iron tends to accumulate in the brains of rats as they age and may play a role in oxidative damage to brain tissues [78].

In some waters, iron may be a limiting factor in growth of algae and plants [3]. Iron plays an essential role in oxygen transport in all vertebrates and some invertebrates [3]. In localities where it is elevated, iron is an important freshwater quality ion which contributes to water "hardness" [3].

Iron oxide precipitates have been postulated as factors in riverine impacts. The episodic (flood related) contamination of food by red ferric precipitates, probably ferric hydroxide, and other metallic oxides was thought to be playing a role in toxicity to benthic macroinvertebrates in the Trinity River below Dallas/Fort Worth, perhaps in conjunction with stresses from pesticides and low oxygen; since non-ferric metals are known to strongly adsorb to hydrous oxides of iron and manganese, other metallic oxides may have been primarily responsible for most of the damage to macrobenthic organisms (Jack Davis, Texas Water Commission, personal communication). Possible sources of excess iron were thought to include soil and sewage discharges or overflows; a red precipitate was seen on the bank and on benthic organisms following flood events. Note: Jack Davis believes low oxygen may cause anaerobic conditions at or just below the sediment surface and that these conditions may then mobilize iron and/or other metallic compounds which precipitate out downstream when oxygen is higher. The precipitates can cause problems simply by physically covering invertebrates and in some cases, contact or oral toxicity and/or gill impacts may also be involved (Jack Davis, Texas Water Commission, personal communication). Note from Roy Irwin: lower pH caused by chlorine or other localized factors can also cause mobilization of metals which later precipitate back to the bottom.

Sediment Concentration Results:

Sediment concentrations of iron ranged from 7390 mg/kg dry weight at site TRIS to 13800 mg/kg dry weight at site SPI. The only bit of (even remotely) comparable information located in the literature is provided as follows:

> Unpublished guidelines for the pollution classification of Great Lakes Harbors in Region 3 of EPA, Chicago, Illinois, included dry weight (mg/kg) sediment concentrations of iron of: <17,000 for non polluted waters, 17,000 to 25,000 for moderately polluted waters, and greater than 25,000 for heavily polluted waters [31].

Tissue Concentration Results:

Iron was detected in all 17 tissue samples. The concentrations ranged from 71 mg/kg dry weight (16.117 mg/kg wet weight) in whole body samples of black bullhead catfish from site SPI to 2250 mg/kg dry weight (699.75 mg/kg wet weight) in a yellow mud turtle liver sample from site SPI.

In a previous study of the Trinity River, the senior author found the highest level of iron (1820 mg/kg wet weight) was in a fatty composite sample of three Mississippi map turtles; the 12 highest values (230-1820 mg/kg) were all from samples of turtles or mosquitofish from polluted areas [19]. In a third study, mosquitofish from rural sites on the Rio Grande River at Big Bend National Park had iron concentrations ranging from 33 to 66 mg/kg wet weight [50].

Lead (Pb)

Lead is a heavy metal which is very toxic to aquatic organisms, especially fish [33]. It tends to bioaccumulate in mussels and clams [34,35]. Benthic fish may accumulate lead directly from the sediments [35]. Some salts of this element are carcinogenic [29]. Like cadmium, lead has no known essential biological function [12], and all lead compounds are potentially harmful or toxic, especially tetraethyl lead [26]. Lead functions as a cumulative poison [26] and is listed by the Environmental Protection Agency as one of 129 priority pollutants [25]. Lead is also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at priority superfund sites [27].

All measured effects of lead on living organisms are adverse, including those negatively affecting survival, growth, learning, reproduction, development, behavior, and metabolism [79]. There is fairly good correlation between degree of lead intoxication and body burden of lead, the main exception being where there has been high exposure over a short period [18]. Effects of sublethal concentrations of lead include increased mucous formation, delayed embryonic development, suppressed reproduction, inhibition of growth, and fin erosion [33]. In vertebrates, sublethal lead poisoning is characterized by neurological problems (including blockage of acetylcholine release), kidney disfunction, enzyme inhibition, and anemia [62]. Animal studies indicate relatively high levels of lead exposure interfere with resistance to infectious disease [18].

Sediment/Soil Concentration Results:

Sediment concentrations of lead ranged from 5.2 mg/kg dry weight at site SW to 22 mg/kg dry weight at site SPI. These concentrations are below known concern levels or levels considered to be elevated [18,42,43,44,45,46,47,48]. Soil concentrations from site DLB (13-17 mg/kg dry weight) were not highly elevated compared to other published values [18,31].

Tissue Concentration Results:

The concentrations of lead ranged from <0.58 mg/kg dry weight in several tissue samples to 221 mg/kg dry weight (65.63 mg/kg wet weight) in a whole body sample of redwinged blackbirds from site SPI. The only elevations above 0.6 mg/kg dry weight were from blackbird and coot samples, which may have been influenced by lead shot. The principal source of exposure to ducks and waterfowl is from lead shot which is ingested by the birds in search of gravel [18]. The non-bird aquatic samples were not highly contaminated with lead in comparison to aquatic samples from urban areas [19].

Manganese (Mn)

The chemical element manganese is a silver gray transition metal [80]. Manganese occurs in nature in various salts and oxides and it is used in various industrial and agricultural applications [3]. Manganese is a widely distributed, abundant element; it constitutes 0.085% of earth's crust [76].

In localities where it is elevated, manganese is an important freshwater quality ion which contributes to water "hardness" [3]. Body burden issues are less well understood. Manganese is a required trace element for both plants and animals [3]. Beef cattle fed corn may require manganese supplements [3]. Fish and other organisms have some ability to excrete excess manganese [18,35] but the precise significance of excess body burdens of manganese is unclear for most species of fish and wildlife. Manganese tends to accumulate in bone, skin, and scales [81].

Poisonings from excess levels have occurred in humans but are rare [3,33].

The most frequently occurring valence of manganese is +2, but +4, +6, and +7 are also common, and +1, +3, and +5 are known [80].

Some have recommended that more research needs to be done on the toxicity, mobilization, and bioavailability of manganese in low alkalinity and or/low pH waters [12].

Pure manganese is rarely used, as it is a moderately reactive and brittle metal [80]. However, manganese occurs naturally in surface waters from soil erosion. Other sources include air pollution deposition from power plants, sewage treatment plant effluents, and leachates from municipal landfills [77]. Fish and Wildlife Service files contain unpublished lab reports of elevated levels of manganese in ground water monitor wells for a municipal landfill in the Dallas/Fort Worth area.

The earth's crust contains 850 ppm manganese in chemically bonded form. By far the most important manganese mineral is pyrolusite, which consists largely of manganese dioxide [80]. About 95% of the world's annual production of manganese is used by the iron and steel industry [80]. In alloys, manganese increases the durability and corrosion resistance of iron and steel and makes steel more malleable when forged [80].

Manganese is an important metal from a water toxicity standpoint in metal mine drainage areas of the Rocky Mountains (Jim Lazorchak, U.S. E.P.A., Cincinnati, personal communication). There is little information available in the open literature concerning the general aquatic toxicity of manganese (Bill Stubblefied, ENSR Consulting, Fort Collins, Colorado, personal communication).

Fish or wildlife ingesting moderate levels of manganese as part of their diet or accidental ingestion of sediment does not appear to be very harmful [18]. Concentrations are regulated by excretion [18,35], but manganese also collects in various organs [18].

Sediment/Soil Concentration Results:

Sediment concentrations of manganese ranged from 206 mg/kg dry weight at site TRIS to 420 mg/kg dry weight at site SD. A search of the literature for information which might be helpful in interpreting the meaning of these sediment levels produced the following:

> Unpublished guidelines for the pollution classification of Great Lakes Harbors in Region 3 of EPA, Chicago, Illinois, included dry weight (mg/kg) sediment concentrations of: <300 for non polluted waters, 300-500 for moderately polluted waters, and greater than 500 for heavily polluted waters [31].
>
> From the standpoint of exposures precipitating chronic manganese disease, repeated oral administration of manganese to animals... for prolonged periods gave no evidence of injury in moderate doses; manganese stimulated growth when present in diet up to 100 ppm but proved deleterious at 600 ppm. [18, Clayton, G. D. and F. E. Clayton (eds.). Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology. 3rd ed. New York: John Wiley Sons, 1981-1982. 1756].

Soil concentrations from site DLB (13-17 mg/kg dry weight) were not highly elevated compared to other published values [31]. Much of the literature on soil concentrations seems to concentrate on effects of manganese deficiencies on plants.

Magnesium (Mg)

Magnesium is a divalent alkaline earth metal (a common component of the earth's crust) [30]. Along with calcium, magnesium is one of the two most common polyvalent metallic ions in freshwater and a major contributor to water "hardness" [3].

Magnesium has some useful physiological functions and small amounts of magnesium in the diet are necessary to control cell metabolism [61]. Magnesium cations (positively charged ions) play an important role in various biological processes. Like calcium, magnesium ions play major roles in human nerve conduction, muscle contraction, and bone formation [61]. Magnesium ions also play important roles in enzyme activation and protein metabolism [61]. Also like calcium, magnesium is often used as a dietary supplement in multi-mineral pills consumed by humans.

Little is known concerning whether or not highly elevated levels of magnesium in animal tissues might be harmful to the organism or fish and wildlife species which consume the organism. In humans, most magnesium is stored in bones and teeth. Excess magnesium intake in humans has led to heart damage and respiratory failure [61]. Magnesium is considered relatively nontoxic to humans since it becomes unpalatable before dangerous concentrations are reached [13.32].

The following paragraph concerning the biological significance of magnesium is quoted from reference [82]:

Magnesium is one of the most important metals in both plants and animals. The body of an average adult contains about 25 g (0.9 oz) of magnesium; however, the specific actions of magnesium in the human body are still unknown. Magnesium is known to be an activator of many enzyme systems and acts as a depressant of the central nervous system when it is injected intravenously. For this reason, magnesium and some of its compounds are used to control convulsions resulting from tetanus and childbirth. Magnesium is found in many foods, such as meats, cereals, vegetables, and milk. The average adult ingests about 300 mg (0.01 oz) of magnesium per day. Magnesium deficiency results in weakness, dizziness, and convulsions. The kidneys regulate the amount of magnesium in the body, and magnesium overdose may result from kidney failure, hormonal disruption, or use of too much magnesium as a drug.

Water Data Results:

Range: As mentioned in the hardness section, magnesium concentrations in water ranged from 3.8 to 15.5 mg/l. The highest concentration of magnesium (15.5 mg/l) occurred at site TRIS below the cattle feedlot.

Gradient Monitoring Levels: There is no evidence of increasing trends in magnesium in water along this creek, with the exception of an increase in magnesium ions at the site below the feedlot. United States Geological Survey data for Prairie Dog Town Fork of the Red River are ten times higher for magnesium than in Tierra Blanca Creek.

Sediment/Soil Concentration Results:

Sediment concentrations of magnesium ranged from 5800 mg/kg dry weight at site SPI to 19100 mg/kg dry weight at site SR. Higher values (16400 and 17400 mg/kg dry weight) were also found in soil samples from two sites in the dry lake bed (DLB). The literature surveyed for this study had very little information relevant to interpreting the meaning of these values as they relate to potential impacts to fish and wildlife.

Mercury (Hg)

Mercury is a cumulative poison [26] and is the heavy metal most toxic to fish [83]. Elevated concentrations of mercury in water are particularly toxic to many species of algae, crustaceans, and salmonids [62]. Mercury is listed by the Environmental Protection Agency as one of 129 priority pollutants [25]. Methyl and alkyl mercury compounds are two of the most toxic classes of mercury compounds [26]. Mercury deposits in the brain cause many disorders and sometimes dementia in humans [61]. Mercury deposits in human kidneys may lead to renal failure [61].

Mercury is one of the few metals which strongly bioconcentrates and biomagnifies; has only harmful effects with no useful physiological functions when present in fish and wildlife; is a carcinogen, mutagen, and teratogen; and is easily transformed from a less toxic inorganic form to a more toxic organic form in fish and wildlife tissues [83]. It is a metal whose use should be curtailed as much as possible to prevent impacts to fish and wildlife [83].

Results: Sediment Concentrations:

None of the sediment samples had mercury concentrations which exceeded the detection limit (0.1 mg/kg dry weight).

Results: Tissue Concentrations:

Mercury was detected in all 16 tissue samples containing adequate volume for analyses. The concentrations ranged from 0.027 mg/kg wet weight in whole body samples crayfish from site PL and blackbullhead from site SPI to 0.560 mg/kg wet weight in a liver sample from yellow mud turtles from site SPI.

A recommended level for the protection of avian predators which consume fish and other aquatic organisms is that total mercury in these food items should not exceed 0.1 mg/kg [83]. One whole-body sample in this study, a sample of tiger salamanders from site PL, had a mercury concentration of 0.114 mg/kg wet weight. With the exception of this one salamander sample, none of the whole body samples had notably elevated mercury levels. Actually, the 0.1 mg/kg alert level may be inadequate to protect fish and wildlife, since concentrations of 0.1 mg/kg fed to ducks reduced fertility and inhibited food conversion [84]. However, with the exception of the liver samples and the one previously mentioned salamander sample, all tissue had concentrations lower than 0.064 mg/kg wet weight mercury.

The coot liver samples from site SD ranged from 0.08 to 0.39 mg/kg wet weight. These are not especially high compared to other coot liver data collected by the Fish and Wildlife Service in other parts of the country. The liver samples had generally higher concentrations than whole-body samples, as might be expected [18].

There is limited data available for interpreting the meaning of the tissue concentration results, especially for the samples which were not whole body samples. Wet-weight legal limits for concentrations of mercury in fish and fishery products include a legal limit of 0.1 mg/kg (Venezuela) [70,71]. Eighteen countries have limits less than or equal to 0.5 mg/kg, but the U.S. limit is 1.0 mg/kg total mercury [70,71].

The recent (1976-1984) NCBP survey report gave the nationwide maximum mercury level as 0.37 mg/kg wet weight, the 85th percentile level as 0.17 mg/kg, and the geometric mean level as 0.10 mg/kg [39]. In the Buffalo Lake samples, the only whole body fish tissue sample was a black bullhead whole body sample from site SPI, which had a mercury concentration of 0.027 mg/kg wet weight.

Summary Discussion of Mercury Data:

In general, the mercury concentrations found in this study were not especially high.

Nickel (Ni):

Nickel is a hard metal which is also abundant in the earth's crust [30]. Divalent nickel is the primary aqueous form [30]. Nickel is a toxic pollutant designated pursuant to section 307(a)(1) of the Clean Water Act and is subject to effluent limitations [18],[40 CFR 401.15 (7/1/87)]. Nickel is listed by the Environmental Protection Agency as one of 129 priority pollutants [25], and is considered to be one of the 14 most noxious heavy metals [26]. Nickel is also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at priority superfund sites [27].

Little information is available on the effects of nickel body burdens on fish and wildlife, but experimental doses of nickel have induced cancer in rats, guinea pigs, and rabbits [85]. Some salts of this element are carcinogenic [29]. Nickel is present in asbestos and may play a role in asbestos carcinogenicity [85]. Mixtures of nickel, copper, and zinc produced additive toxicity effects on rainbow trout [33].

Although water soluble nickel salts have not been shown to initiate carcinogenesis in rodents, the soluble nickel salts are evidently effective as cancer promoters following initiation of tumorigenesis by aromatic hydrocarbons and nitrosoamines [18]. Growing evidence suggest that the nickel(III)/nickel(II) redox couple facilitates oxygen free radical reactions, which may represent one of the molecular mechanisms for genotoxicity and carcinogenicity of nickel compounds [18].

In addition to numerous references on harmful properties of nickel, the literature contains quite a few references to its bionecessity [18]. Nickel deficiency leads to iron deficiency, impairs iron absorption, and has been documented in birds [18]. Nickel deprivation has an effect on body weight, reproductive capability, viability of offspring, and induction of anemia through reduced absorption of iron [18]. Deficiency is unlikely in humans taking a conventional diet; the margin between required and toxic concentration is wide [18].

Preliminary data suggests the potential for bioaccumulation or bioconcentration of nickel is moderate for the following biota: mammals, birds, and fish. It appears to be high to very high for mollusks, crustacea, lower animals, mosses, lichens, algae, and higher plants [26]. The best potential mediums for biological monitoring (including gradient monitoring) appear to include higher plants, mosses, and lichens [26]. Irwin found mosquitofish to be acceptable for gradient monitoring of nickel [19]. In some animal tissues, nickel levels are similar to levels in plants that the animals are eating [18].

<u>Sediment/Soil Concentration Results:</u>

Sediment concentrations of nickel ranged from 5.8 mg/kg dry weight at site SW to 15.0 mg/kg dry weight at site SPI. These concentrations are below known concern levels or levels considered to be elevated [18,43,44,46,47,48,86]. Soil concentrations from site DLB (11-12 mg/kg dry weight) were not highly elevated compared to other published values [18,26].

<u>Tissue Concentration Results:</u>

Nickel was detected in all 17 tissue samples. The concentrations ranged from 0.23 mg/kg dry weight (0.073 wet weight) in a yellow mud turtle sample from site SPI to 1.5 mg/kg dry weight (0.372 mg/kg wet weight) in a whole body sample of crayfish from site SR. Fish concentrations above 0.9 mg/kg wet weight nickel appear to be elevated values in relationship to relatively unpolluted sites in the Southwest studied by the Fish and Wildlife Service; none of the wet weight values in this study exceeded this level or seemed high in comparison with other studies [19,50].

<u>Nitrate Nitrogen (NO_3-N) and Total Nitrate Nitrogen (T-NO_3-N)</u>

Nitrate nitrogen is a measure of nitrate expressed as N (a measure of the nitrogen contributed by nitrates). Most monitoring and standards related to nitrates utilize nitrate nitrogen (Bill Cyrus, Trinity River Authority, personal communication).

Large inputs of nitrate into river systems usually relate to agricultural activities [55]. Very high total nitrate nitrogen loads are known to come from animal feedlots, usually much higher than from treated sewage or various types of nonpoint source runoff [5].

Nitrate is much less toxic to fish than nitrites or ammonia [20]. In fact, many fish LC50's for nitrate exceed 1000 mg/l, and nitrate is often the anion of choice in toxicity studies of various cations, the assumption being that nitrate will not add much to the toxicity [20]. Except for human health issues, most aquatic problems related to nitrates are therefore related to eutrophication and algae blooms rather than direct toxicity [20]. High concentrations of nitrates may suggest pollution, may encourage growth of algae and various undesirable organisms, and may cause methemoglobinemia in human infants [138].

Nitrogen is assimilated by plants and used to synthesize proteins. Nitrates are the relatively stable end products of the nitrification process. Under aerobic conditions, ammonia is oxidized into nitrites by Nitrosomas bacteria and then into nitrates by Nitrobacter bacteria, in the "nitrification" process [20]. However, the process can also be reversed in certain circumstances. Under the anaerobic conditions found in feedlot ponds and playas, nitrates are reduced to nitrites, ammonium is fixed by nitrogen-fixing bacteria, and considerable amounts of ammonium are volatized into the atmosphere [133].

Nitrates are water soluble and therefore can be transported to groundwaters. Concentrations of nitrates in excess of 10 mg/l have been found in some shallow farm and rural wells, often as a result of inadequate treatment of septic tanks or barnyard drainage [3]. Nationwide studies have indicated nitrate concentrations were trending upward more often than downward in the West, with increases in nitrates strongly associated with the following nonpoint source variables: fertilized acreage, livestock density, and feedlot activity [55].

Nitrate transport in rivers is much less dependent on the movement of suspended sediment than is phosphorus transport [55]. This is because nitrates are less apt to be bound to bottom sediments or soil particles than phosphorus and are therefore not as easily trapped by sedimentation [55]. Nitrate is naturally present in water at low concentrations. However, in some wetlands nitrate nitrogen is a smaller portion of the total nitrogen than organic nitrogen [42].

Water Data Results and Discussion:

Range and Comparisons: The highest concentration of nitrates in surface water was 1.38 mg/l found at site PL in Garcia Lake, a playa lake in the upper drainage basin of Tierra Blanca Creek. Garcia Lake had mostly dried when the samples for this study were collected, and the remaining water was heavily used and polluted by rangeland cattle. However, Garcia Lake was separated from Tierra Blanca Creek and also had the highest dissolved oxygen concentration. Therefore, nitrates probably would not be biologically or chemically reduced as may have happened in Tierra Blanca Creek proper where oxygen concentrations were low at most sites.

Except for site TRB, where nitrates were 0.88 to 0.92 mg/l, nitrate concentrations in water elsewhere along the creek were not high in comparison with riverine samples around the country, ranging from 0.010 to 0.18 mg/l. Background or natural (non-polluted) waters usually contain nitrogen (parameters) in concentrations below 0.3 mg/l [2]. For additional comparison, the 50th percentile of nitrate (total nitrate as N) at 383 (not especially clean) NASQWAN and NWQSS river sites in the U.S. was 0.41 mg/l; the 25th percentile was 0.20 mg/l, and the 75th percentile was 0.89 mg/l [55]. These riverine sites in the USGS study were mostly in (or downstream of) agricultural and urban areas [55]. Another note concerning nitrate levels: most National Park Service waters are accorded the highest degree of protection. An example is Everglades National Park, which has a maximum nitrate standard of 0.7 mg/l [13].

Gradient Monitoring Levels: Sites (2-TRB and TRIS) having low dissolved oxygen concentrations (<1.0 mg/l) also have low nitrate levels (<0.03), despite having a TKN greater than 5.2 mg/l. Anaerobic conditions in the stream may stimulate denitrification by facultative anaerobes when microorganisms utilize other reducible compounds, such as nitrate, for respiratory oxygen. Nitrate levels found in this study were somewhat lower than might be expected, given the TKN; therefore denitrification may be occurring, given the anaerobic conditions.

Discussion of Nitrate Water Results: There is no EPA water quality criterion for nitrates for protection of fish and wildlife [3]. Nitrates are not very toxic to most fish or other aquatic life and are therefore not considered very hazardous to them except indirectly (as a potential source of nitrites and ammonia under conditions which are favorable to denitrification or as a source of excess nutrients) [20]. A study of cattle feedlot drainage infiltration in the Texas High Plains indicated some existing feedlots have contributed nitrate to groundwater at levels approaching or exceeding the recommended limits [1]. Groundwater in the study area is within the Ogallala Formation, with depth-to-water ranges from a minimum of 10 feet in parts of the Tierra Blanca Creek, to depths of 250-300 feet elsewhere in the Ogallala beneath the Texas High Plains [1]. Groundwater quality varies significantly in the Ogallala aquifer within short distances (a few hundred feet), regionally north to south, and in other localized geographic regions [1]. Concentration of nitrates and other dissolved solids in groundwater as a result of runoff from feedlots is related to soil type patterns [1]. Feedlot water quality data show higher infiltrate concentrations in groundwater beneath sandy soils than in the hardland region [1].

Historically, nitrate nitrogen was often high in Buffalo Lake before it was drained [119]. A nitrogen level of 0.8 mg/l is considered a eutrophic level which will produce algal blooms and nuisance weed growths [119]. The average of all past values in Buffalo Lake was 0.81 mg/l, and in August of 1984 (presumably creek inflow waters) a concentration of 6.6 mg/l nitrate nitrogen was recorded [119]. Most of the nitrogen probably originated in feedlots. However, one estimate was that up to 33,000 pounds per year may have been contributed by migratory waterfowl [119].

Sediment Data Results and Discussion:

Range: Nitrates in sediments ranged from 0.57 mg/Kg at site PL, an upstream site, to 44.0 mg/Kg at site TRIS, a site impacted by a large cattle feedlot. It is interesting that nitrates in sediments are elevated at this site in spite of low concentrations of dissolved oxygen and nitrates in the water. Nitrates in the sediments of the cattle wastewater lagoon, site SW, were only 1 mg/kg despite a TKN of 24000 mg/kg, which is probably due to lack of oxygen causing denitrification in that system. Other researchers have found significant nitrate and ammonia losses due to ammonia volatilization and denitrification [87].

Gradient Monitoring Levels: Nitrates show an increasing trend (0.57-44.0 mg/Kg) in sediments along Tierra Blanca Creek in the upper four sampling sites, reaching the maximum at site TRIS, the site most directly impacted by a large cattle feedlot. Sites downstream from the feedlot show a decrease ranging from 1.0-11.3 mg/kg.

Discussion: No recommended fish and wildlife protection criteria for nitrate concentrations in sediment were located in the literature search done for this study. Nitrate nitrogen concentrations above 20 mg/kg are considered very high for soils in Texas cotton farms [138]. The very high nitrate concentrations in creek sediments at site TRIS (44.0 mg/Kg) have potential to pose concern as a source of excess nutrients and as a potential source of nitrate infiltration into groundwater [1,6]. Nitrate and nitrite levels should probably be more closely monitored throughout this drainage and associated groundwater.

Nitrite Nitrogen (NO_2-N)

The word nitrite in the literature most often refers to nitrite nitrogen rather than nitrite as the nitrite anion. Nitrite is formed from the nitrate or ammonium ion as an intermediate product of the nitrification-denitrification processes by certain microorganisms found in water, soil, sewage or digestive tracts. In (aerobic) water, ammonia is oxidized into nitrites by Nitrosomas bacteria and then into nitrates by Nitrobacter bacteria in the "nitrification" process [20]. In oxygenated natural waters, nitrite is often less of a problem than ammonia since nitrite is usually so rapidly converted to nitrate [20].

Nitrite toxicity reduces the tolerance of fish to low oxygen [20,88]. Toxic effects of nitrites which have been observed in fish include: 1) oxidation of hemoglobin to methemoglobin, a form incapable of binding oxygen, and 2) reduced swimming performance [20,88]. Nitrite is particularly hazardous to warm-blooded animals because of it's ability to bind to the hemoglobin, impairing oxygen transport and producing methemoglobinemia.

Nitrite presence has been implicated with the formation of N-nitroso compounds which are carcinogenic to various fish species [20]. Within a human intestine, nitrites are converted to nitrosamines, compounds which are carcinogenic to laboratory animals [61].

Water Data Results:

Range: The highest nitrite concentration in water was 0.106 mg/l (as N) found in the upper Tierra Blanca Creek (site TRB). Nitrite ranged from 0.006 to 0.093 mg/l at other study sites.

Gradient Monitoring Levels: Nitrite in water was highest at the uppermost location on Tierra Blanca Creek (site TRB) with a concentration of 0.106 mg/l. Site SR had 0.092 mg/l nitrite, and all other sites had nitrite less than 0.02 mg/l. There is no apparent pattern to nitrite concentrations along the stream gradient.

Discussion: The water levels observed were not highly elevated in comparison with various concern levels and standards:

Concern Levels in Water

Acute toxicity of nitrite is pH and water chemistry related. For example, as pH increases over 6.4, the toxicity of total nitrite decreases, and as chloride concentrations increase, nitrite toxicity decreases. Given these factors, representative LC50 values for trout and salmon ranged from 0.1 to 0.9 mg/l, [20]. Other representative LC50 values included the following: mosquitofish, 1.6 mg/l and channel catfish, 7.5-13 mg/l [20]. Other concentrations of nitrites which have been associated with impacts upon aquatic organisms include LC_{50} of 2.4 mg/l in bluegills and other warmwater species (lower for salmonids and sensitive coldwater species) [89], and decreased swimming performance in channel catfish at 0.5 mg/l [88].

Water Quality Standards

State water standards in Oklahoma recommend 0.15 mg/l level for nitrite criteria.

Most National Park Service waters are accorded the highest degree of protection. An example is Everglades National Park, which has a maximum nitrite standard of 0.04 mg/l [13].

Water Quality Criteria

Apparently, there is no EPA water quality criteria that have been established for nitrite [3].

Other Concern Levels for Water

Few other concern levels have been named in the literature. However, it should be kept in mind that nitrite toxicity reduces the tolerance of fish to low oxygen [88] and that elevated levels of nitrites have been observed during riverine fish kills thought to be oxygen related [90].

Nitrogen/Nitrification

Nitrogen is present in water in several forms and originates from various sources. Very high total nitrogen loads are known to come from cattle feedlots, usually much higher than from treated sewage or various types of nonpoint source runoff [5].

Atmospheric fallout, ammonia, organic sources, leachate from rocks and soils, and nitrogen fixation by blue-green algae also contribute to the total nitrogen available. Major point-sources of nitrogen entry to water bodies are wastewater treatment plants, septic tanks and animal feedlots [3]. Nitrogen is an essential macronutrient for metabolism. Organic nitrogen is present in amino acids, a major constituent of proteins, peptides, nucleic acids, enzymes, and other plant and animal tissues. Animal wastes contain organic nitrogen in many forms, such as urea. Microbes degrade organic material producing inorganic nitrogen upon degradation. The nitrogen cycle is complex.

The first step of nitrification, or the biological conversion of nitrogenous compounds from a reduced state to a more oxidized state, is the oxidation of unionized ammonia (NH_3) to the ammonium ion (NH_{4+}). In the presence of oxygen, the ammonium ion is next oxidized by microbes, principally the bacteria Nitrosomonas, to nitrite (NO_2). Nitrites are usually an intermediate state which exist only briefly. Further oxidation by Nitrobacter bacteria converts nitrites to nitrates (NO_3), the relatively stable end products.

The oxygen demand for nitrification is approximately 4.57 mg/l oxygen per 1 mg/l Total Kjeldahl Nitrogen (TKN). In anaerobic environments where oxidizable organic substrates or nitrates are abundant, a process known as denitrification occurs. In denitrification, the nitrification steps are reversed and nitrate is reduced to ammonia and to nitrogen gas. Typical anaerobic environments which produce denitrification include the anoxic hypolimnion or sediments of eutrophic lakes, and nitrate removal from water occurs at the water-mud interface in wetlands.

Fractioning of nitrogenous compounds and their cyclic dynamics are complex and not completely understood. Plants often require more nitrogen than is available for growth. This "limiting" nutrient concept is also known as Leibeg's "Law of the Minimum". The law of the minimum has been used to explain increases in productivity and accelerated eutrophication in aquatic systems which receive nutrient inputs from outside sources. Various measures of nitrogen in water and sediment are discussed in separate sections of this report (TKN, Nitrate, Nitrite, Ammonia, etc.).

Nitrogen/Kjeldahl (Total Kjeldahl Nitrogen, TKN)

Total Kjeldahl Nitrogen (TKN) reflects the technique used to measure all forms of organic nitrogen together with ammonia present in a sample after vigorous digestion with heat and strong acid. Since nitrogen in the form of ammonia is the form most readily available to biota and since organic nitrogen is cycled through biota and released into the environment by decomposing plants and animal wastes, TKN is often thought of as the form of nitrogen most readily available to, and associated with, biota. Elevated levels of TKN can be an indication of nitrogen over-enrichment with potential problems associated with eutrophication.

Although the word total is in its name, TKN is not really a comprehensive total measure of nitrogen since nitrates and nitrites are lost in the digestion process (Bill Cyrus, Trinity River Authority, personal communication). Nitrogen species are subject to change (see nitrogen section). Some investigators report both dissolved (filtered) and total (not filtered) TKN [42].

Kjeldahl nitrogen was the dominant nitrogen species present in the sediments of detention ponds and wetlands receiving runoff from highways, although the concentrations were variable and not well related to runoff [42]. Unlike several heavy metals, the highest TKN level in sediments was in a wetland rather than in a highway detention pond upstream of the wetland [42].

Water Data Results:

Range: Water TKN values ranged from 1.5 mg/l (as N) at Stewart Marsh in the Refuge (site SD), to 8.3 mg/l at site TRIS, the location most impacted by a large cattle feedlot (See Fig 2 in Ammonia section for a graphic display which includes TKN values). The second highest value for TKN was 5.6 mg/l at Smith Ranch (site SR), another site impacted by nonpoint source runoff from a feedlot.

Gradient Monitoring Levels: At most sites, the concentration of TKN in water was paralleled by the ammonia concentration, ammonia making up about 30% of the TKN. However, the highest TKN concentration (site TRIS) corresponded with the lowest ammonia concentration. The low ammonia concentration may be due to climatic factors such as high winds and temperatures combined with low moistures allowing the ammonia to volatilize to the atmosphere. Another theory is that the nitrogen is bound in organic compounds or living organisms (algae, bacteria). Again, the chemistry of the different forms of nitrogen in natural waters is complex.

Otherwise, TKN concentrations do not show a clear pattern/trend along this creek. Rather than increasing or decreasing with gradient, TKN concentrations at various sites seem to reflect independent (site-specific) nitrogen fractioning dynamics.

Discussion: No water quality criteria for protection of fish and wildlife has been established for TKN [3]. Three of the sites in this study had TKN water concentrations greater than 5.2 mg/l. For comparison, data from 904 nonpoint source type watersheds indicate areas of >90% agriculture have the highest stream total nitrogen concentrations with an average of 5.3 mg/l; Tierra Blanca Creek data are comparable with these "worst case" situations, and TKN is only one part of total nitrogen [75]. For additional contrast, less than 25% of the water concentrations in sites in various ecoregions in Colorado were higher than 1.5 mg/l, the lowest value recorded in this study [91]. Although no concentration found exceeded 20 mg/l, (the Texas Water Commission is alerted for possible concern when a TKN value greater than 20 mg/l is entered onto their computer system), elevated levels above 5 mg/l indicate significant nitrogen loading is occurring in Tierra Blanca Creek.

At the time field work for the current study was done, the creek consisted of a series of separated pools rather than a free-flowing creek, so localized runoff may have influenced the results. U.S. Geological Survey data for 1987 in the Prairie Dog Town Fork of the Red River had no nitrogen (ammonia+organic N) concentration greater than 1.2 mg/l. This value was calculated by adding the reported values of ammonia + organic nitrogen, because a total kjeldahl nitrogen (TKN) value was not reported by the Geological Survey.

Sediment Data Results:

Range: The highest TKN value in sediment was found at site SW, in the bottom sludge taken from a feedlot wastewater treatment/retention lagoon. The sediment in this holding pond contained 24,000 mg/Kg TKN. In-stream sediment TKN concentrations were much lower, ranging from 713 mg/Kg in sediment from Garcia Lake (site PL), and 1100 mg/Kg in sediment from the upper Tierra Blanca Creek (site TRB), to 5950-8720 mg/Kg in sediment from the stream below the cattle feedlot site TRIS.

Gradient Monitoring Levels: In Garcia Lake (site PL), and the upper Tierra Blanca Creek (site TRB), sediment TKN was 713 and 1100 mg/Kg, respectively. The extremely elevated TKN value (7720 mg/Kg) below the feedlot (site TRIS) may have contributed to the elevated TKN (2500 mg/Kg) which occurred at all sampling sites downstream.

Discussion: The concentrations at site TRIS, a site suspected of being impacted by a cattle feedlot, were more than twice the concentrations of any other values found along the creek. Concentrations of TKN at all locations downstream from the feedlot remained elevated at 2500 mg/Kg.

By contrast, the upstream values do not differ greatly from the TKN of an average (fertilized, agriculture area) topsoil 1000 mg/Kg in the region. However, a TKN value greater than 2400 mg/Kg (as in the downstream and feedlot sites), would be considered high, and comparable to values found in a field which had received fertilizer applications (Dr. Harold V. Eck, soil scientist, USDA, Bushland, TX, personal communication).

Although apparently no fish and wildlife criteria have been proposed for TKN concentrations in sediments, nitrogenous inputs may alter an ecosystem by stimulating productivity, increasing oxygen demand, or increasing concentrations of nitrate, nitrite and ammonia.

For additional comparison, some of the sediment concentrations of TKN found in this study were elevated when contrasted with the following values:

<u>Freshwater TKN Sediment Levels Considered To Be Highly Elevated</u>:

Texas: The statewide 90th percentile value for this compound was 2,816 mg/kg dry weight [43]. The feedlot pond values greatly exceeded this, and the sites downstream of the feedlots in the creek approached this value. Concentrations above 2070.0 mg/kg and 3896.4 mg/kg are higher than 50% and 85% of lake samples statewide, respectively [124].

<u>EPA Region 6 proposed guidelines for determining acceptability of Dredged Sediment Disposal</u>

The screening level guideline proposed by EPA in 1973 for TKN in sediments was 1,000 mg/kg [44].

<u>Orthophosphate phosphorus (O-PO_4-P, $PO4^{3-}$-P, or Orthophosphorus)</u>

Orthophosphates are reactive, "available" phosphorus compounds [92]. Orthophosphorus is the most important form of phosphorus in terms of immediate availability to algae [92]. It is the main component of dissolved phosphorus [92]. In fact, orthophosphorus is a term which some use interchangeably with soluble reactive phosphorus (SRP), since orthophosphorus is a soluble inorganic component [92]. However, some investigators measure both dissolved (filtered) and total (non-filtered) orthophosphorus [42].

Orthophosphates are present in sewage and fertilizer inputs to surface waters [23] and are the most easily utilizable form of phosphorus for algae growth [93]. In general, orthophosphates are the only form directly bioavailable for organism uptake and usage. Phosphate is very reactive and combines with many cations, especially under oxidizing conditions. Water samples should be free of suspended matter or filtered to provide accurate results, as availability of phosphate is reduced by adsorption to colloids and particulates. Soluble inorganic orthophosphates have been shown to be the single factor best correlating with increases in productivity associated with eutrophication.

Unlike many metals and other pollutants, orthophosphates were not consistently and efficiently removed by a wetland receiving highway runoff [42].

<u>Water Data Results</u>:

Note: There is an anomaly or possible interference in some of the water data for phosphorus compounds; orthophosphate phosphorus concentrations were higher in some water samples than total phosphate phosphorus concentrations (Fig. 3). Both methods used an ascorbic acid process. Arsenates are known to interfere with the ascorbic acid/molybdate reagent used in the analysis to

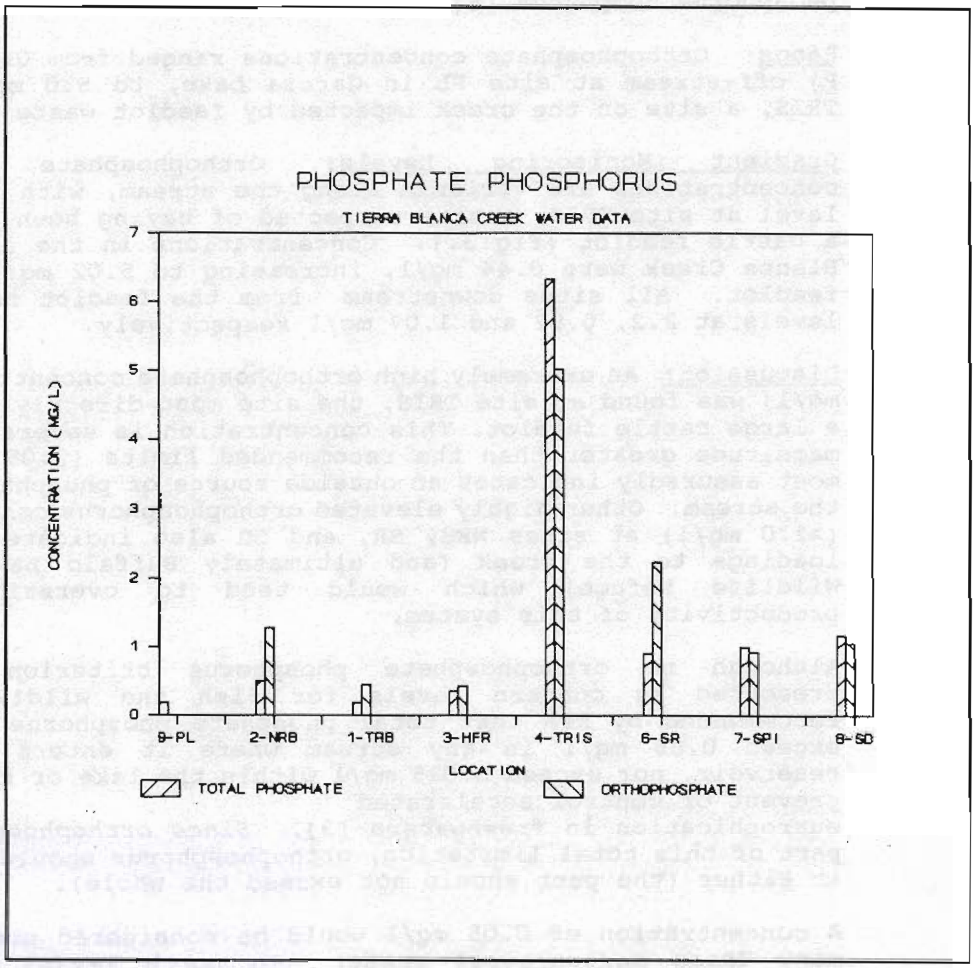

Fig. 3. Phosphate Phosphorus

produce a blue color similar to that formed with phosphate. Although arsenic was not measured in water or sediment samples during this study, high arsenic levels have been found in widespread sediment samples of playa lakes in the Texas High Plains.

Despite reanalyzing the samples and looking for other possible explanations, the laboratory could not find a good explanation of why ortho would show up higher than total phosphorus, but noted that this particular type of anomaly usually shows up with very high phosphorus levels (Bill Cyrus, Trinity River Authority Water Quality Laboratory, Grand Prairie, Texas, personal communication). The data obtained is presented with the caveat that no explanation has yet been found to explain the reason for the anomalies (ortho being higher than total phosphate phosphorus at some sites). Nevertheless, it is apparent that phosphorus was quite high in many of these samples; the important TRIS site sample and several other samples did not have the anomaly, and total phosphate phosphorus sediment samples, which were done by a separate lab, also revealed high phosphorus concentrations. It is also widely known that cattle feedlots are potent sources of phosphorus compounds [5].

Range: Orthophosphate concentrations ranged from 0.01 mg/l (as P) off-stream at site PL in Garcia Lake, to 5.0 mg/l at site TRIS, a site on the creek impacted by feedlot waste (Fig. 3).

Gradient Monitoring Levels: Orthophosphate phosphorus concentrations are variable along the stream, with the highest level at site TRIS, a site suspected of having been impacted by a cattle feedlot (Fig 3.). Concentrations in the upper Tierra Blanca Creek were 0.44 mg/l, increasing to 5.02 mg/l below the feedlot. All sites downstream from the feedlot had elevated levels at 2.2, 0.92 and 1.07 mg/l respectively.

Discussion: An extremely high orthophosphate concentration (5.02 mg/l) was found at site TRIS, the site most directly impacted by a large cattle feedlot. This concentration is several orders of magnitude greater than the recommended limits (0.05 mg/l), and most assuredly indicates an outside source of phosphate entering the stream. Other highly elevated orthophosphorus concentrations (>1.0 mg/l) at sites NRB, SR, and SD also indicate phosphorus loadings to the creek (and ultimately Buffalo Lake National Wildlife Refuge) which would tend to overstimulate the productivity of this system.

Although no orthophosphate phosphorus criterion has been presented as concern levels for fish and wildlife, it is recommended by EPA that total phosphate phosphorus should not exceed 0.05 mg/l in any stream where it enters a lake or reservoir, nor exceed 0.025 mg/l within the lake or reservoir to prevent or control accelerated eutrophication in freshwaters [3]. Since orthophosphorus is a part of this total limitation, orthophosphorus should not exceed it either (the part should not exceed the whole).

A concentration of 0.05 mg/l would be considered pretty low in many Texas agricultural areas. In north Texas, some small streams do have orthophosphate levels lower than the EPA criteria, although they are sometimes considered too phosphorus limited to have a rich aquatic fauna and flora [93]. Orthophosphate levels greater than recommended total phosphate concentrations are indicative of serious phosphorus input.

In this study, only one site, PL (Garcia Lake), had a concentration (0.01 mg/l) less than the EPA recommended limit. All sites located on the stream channel had orthophosphate concentrations which greatly exceed EPA total phosphate recommendations.

The seriousness of the elevations of orthophosphate can also be seen by comparing the results with the following other comparative data:

U.S.Geological Survey data for Prairie Dog Town Fork of the Red River showed no dissolved orthophosphate phosphorus concentration greater than 0.02 mg/l in 1987.

Guam has set their freshwater water quality standard to protect high quality, mixed use (including propagation of aquatic life) surface waters at 0.05 mg/l orthophosphate, the same level others have used to limit phosphate phosphorus [56]. Illinois, for example, limits total phosphate phosphorus at these same concentrations [56]. Several other states limit "phosphorus" in the 0.025 to 1 mg/l range, but EPA's summary of the state standards does not always make it clear which specific form of phosphorus is being regulated at those levels [56].

Oxychlordane

This long lasting organochlorine compound was detected in low concentrations (≥ 0.01 mg/kg wet weight) in several tissue samples, including:

1) one fat-only sample from yellow mud turtles from station PL (the concentration was 0.01 mg/kg wet weight).
2) three whole body composite samples of fathead minnows from station PL (the concentration in each sample was 0.01 mg/kg wet weight).
3) three whole-body samples of crayfish for site SR (the concentrations in the three samples were 0.01, 0.02 and 0.03 mg/kg wet weight).

Oxygen (Dissolved):

Dissolved oxygen concentration is one of the most critical of all water quality parameters to aquatic life. Dissolved oxygen levels in water must be maintained to provide sufficient available oxygen for aquatic life. Factors that can affect the solubility of oxygen in water include temperature and salinity, but many other factors influence dissolved oxygen concentrations, such as the amount of plant photosynthesis, the amount of decomposing organic material (see discussion on biochemical oxygen demand), and physical characteristics (wind, wave action, basin topography, etc.).

Water Data Results and Discussion:

The range of dissolved oxygen was 0.8 to 7.1 mg/l. Garcia Lake in the Upper Tierra Blanca watershed is a playa lake separate from Tierra Blanca Creek. Dissolved oxygen concentration in a pit at this site (PL) was 7.1 mg/l, a level sufficient for supporting aquatic life. The presence of available oxygen at this site may influence the concentrations of other chemical parameters. For example, sufficient oxygen was available to allow nitrification to occur at this site where nitrate concentration was highest.

Dissolved oxygen along Tierra Blanca Creek itself was much lower (0.8-5.2 mg/l). Most levels were below levels which would comfortably support a normal variety of aquatic life.

In Texas, approximately 90 % of undisturbed, small perennial streams have a maintenance 24-hour criterion (dissolved oxygen mean) greater or equal to 4 mg/l DO (Steve Twidwell, Texas Water Commission, personal communication). Some degree of dissolved oxygen depression in drying pools of intermittent streams can result from natural causes. The Texas Water Quality Standards for intermittent streams have been made less stringent in recent years, now requiring a 24-hour mean DO concentration of 2.0 mg/l and an absolute minimum dissolved oxygen at any time of 1.5 mg/l. However, the already stressed organisms in drying pools of intermittent creeks are especially susceptible to additional stress from pollution sources.

The EPA national "Gold Book"" 7-day mean minimum concentration of 4.0 mg/l is established as warmwater criterion for most life stages other than critical early life stages, with absolutely no anthropogenic depression in dissolved oxygen below the potentially lethal 1-day minimum concentration of 3.0 mg/l [3]. Dissolved oxygen concentrations less than 4.0 mg/l are potentially lethal to aquatic life. Dissolved oxygen was below 4.0 in five of the seven study sites, and below State Standards at two sites, along the Tierra Blanca Creek system. Severe depletion of dissolved oxygen is evident in this system, as only two of the sites had dissolved oxygen concentrations above the established warmwater criterion of 4.0 mg/l.

In the upper Tierra Blanca watershed, site PL had a dissolved oxygen concentration of 7.1 mg/l; in Tierra Blanca Creek at Smith Ranch site SR the dissolved oxygen concentration was 5.2 mg/l. Exclusive of these two sites, dissolved oxygen ranged from 0.8 mg/l - 3.8 mg/l. The lowest dissolved oxygen concentrations measured along Tierra Blanca Creek were 0.8 and 0.9 mg/l, below a cattle feedlot (TRIS) and in an unnamed tributary (NRB), respectively.

In contrast to the low oxygen levels found in Tierra Blanca Creek, dissolved oxygen in the Prairie Dog Town Fork of the Red River (another small stream in the Texas Panhandle) ranged from 5.9 to 11.6 mg/l during U.S. Geological Survey 1987 sampling, levels which are all above criteria and are sufficient to support aquatic life. These data suggest Tierra Blanca Creek has a problem with depressed levels of dissolved oxygen. Oxygen demands placed upon this system are greater than the system can supply. Many species of fish and other aquatic organisms which might otherwise inhabit this creek would not have sufficient oxygen for survival.

pH

In simple terms, pH is a measure of the acidity of a sample. In more technical terms, the pH of natural waters is a measure of the acid-base equilibrium, the hydrogen ion activity, and is primarily regulated by the carbonate system. The unit "pH" is used to designate the logarithm (base 10) of the reciprocal of the hydrogen ion concentration, expressed by the equation: $pH = -\log_{10}[H^+]$ [32].

The pH of waters is both biologically and chemically important as organisms can survive only within a suitable pH range, and many chemical processes are pH dependent.

In addition to creating a more acidic environment in which some metals are more mobile and toxic, low pH is positively correlated with increased accumulation of mercury by fish [94]. Low levels of monomeric aluminum can be toxic to some fish species at pH levels below 7.3 [95,86]. Additional factors relating to pH are discussed in the sections on aluminum and fish kills.

The toxicity of many other compounds, as well as the solubility of metal compounds, is also pH dependant. The toxicity of the metals and other compounds which can be influenced by pH is discussed separately in the individual sections on each contaminant.

RESULTS:

Range: The range of pH in Tierra Blanca Creek was 7.6-8.4. This range of pH might be expected from natural processes such as photosynthesis and decomposition, and is well within limits protective of aquatic life. The greatest pH value measured along Tierra Blanca Creek was 8.4 at Stuart Dike, the location farthest downstream and an impoundment of receiving water from Tierra Blanca Creek.

Gradient Monitoring Levels: There was no observable upstream/downstream pattern to the variation of pH. The United States Geological Survey recorded a pH range of 7.8 to 8.2 during the 1985-1986 sampling year in the Prairie Dog Town Fork of the Red River [54].

Discussion: For comparison, the 50th percentile of 290 (not especially clean) NASQWAN and NWQSS river sites in the U.S. in a USGS survey was a pH value of 7.8; the 25th percentile was 7.3, and the 75th percentile was 8.1, with values trending upward more often than downward [55]. These riverine sites in the USGS study were mostly in (or downstream of) agricultural and urban areas [55].

EPA's latest water quality criteria for pH of freshwater for aquatic life is 6.5-9.0 [3]. All pH values recorded in this study were within this range. Since all pH levels recorded in this study were within water quality criteria range, none of the pH levels were above concern levels for pH alone.

Pheophytin-a:

See discussion under Chlorophyll-a section and a complete list of values in appendix 2.

Phosphate Phosphorus (Total Phosphate Phosphorus, T-PO_4-P):

Total phosphate phosphorus is a term which typically refers to the total phosphorus portion of phosphates, expressed as P. Total phosphate 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 [23,92]. Therefore, in some samples values of total phosphorus (TP) and total phosphate phosphorus may be very similar.

Most monitoring and state limitations are now in terms of total phosphate phosphorus (Jack Pfaff, EPA, personal communication). However, this generalization has exceptions. Although elemental phosphorus is toxic and bioaccumulates, phosphorus as phosphate is required for plant growth and is essential for life [3]. Phosphorus in the form of phosphate (PO_4) is bioavailable to organisms for growth and utilization [92]. Phosphate has proven to be the single most important nutrient correlating with eutrophication in water bodies [92].

In technical terms, total phosphate phosphorus is usually a measure of phosphates after rigorous persulfate digestion with heat and acid. Perchloric and nitric acids are also sometimes used in the digestion, but in all cases, the goal is to oxidize all organic phosphorus to release phosphorus as orthophosphorus [23]. A large proportion of phosphates are bound in organic phosphates and cellular constituents, or adsorbed to particulates. Organic and bound forms of phosphate are included in total phosphate phosphorus analysis, therefore, theoretically, total phosphate phosphorus concentration should be greater than orthophosphate concentration.

Waterfowl in high densities can add to the phosphorus in a lake [92]. The impact of elevated phosphorus levels on fish and wildlife can be indirect, as eutrophication eventually disrupts the natural oxygen balance of aquatic systems [92].

In addition to uptake by phytoplankton, aquatic macrophytes such as Potamogeton can be important in phosphorus uptake [92]. Invertebrates also take up phosphorus, but are not as important in this regard as various plants [92]. However, unlike many metals and other pollutants, phosphate phosphorus is not consistently and efficiently removed by detention ponds and wetlands

[42].

Water and sediment data is summarized separately as follows:

Water Data Results for Phosphate Phosphorus:

Note: There is an anomaly or possible interference in some of the water data for phosphorus compounds (see orthophosphate section for detailed discussion). The phosphate phosphorus data is presented with the same caveat used in the orthophosphate section: other than the possible interference of arsenates, no explanation has yet been found to explain the reason for the anomalies (ortho being higher than total phosphate phosphorus at some sites). However, it is apparent that phosphorus was quite high in many of the samples collected for this study; the important TRIS site sample and several other samples did not have the anomaly, and total phosphate phosphorus sediment samples, which were done by a separate lab, also revealed high phosphorus concentrations.

Range: Total phosphate phosphorus concentrations ranged from 0.18 (site PL) to 6.40 mg/l (Site TRIS) in this study (see figure 3 in the orthophosphate section, which contains data for both orthophosphate and phosphate phosphorus).

Gradient Monitoring Level: Total phosphate phosphorus concentrations upstream from site TRIS, the large cattle feedlot, are distinctly lower than they are in the stream below the feedlot. The upstream range of concentrations was 0.19-0.51 mg/l. Downstream of site TRIS, the concentrations ranged from 0.91 - 6.3 mg/l.

Discussion: Historically, phosphorus (as P) concentrations were often high in Buffalo Lake before it was drained [119]. A level of 0.1 mg/l of phosphorus is considered a eutrophic level which will produce algal blooms and nuisance weed growths [119]. The average of all past values in Buffalo Lake was 1.02 mg/l, and in August of 1984 (presumably creek inflow waters since the main lake had been drained) a concentration of 2.6 mg/l was recorded [119]. Most of the phosphorus probably originated in feedlots. However, one estimate was that up to 10,000 pounds per year of phosphorus may have been contributed by migratory waterfowl [119].

However, waterfowl use has not been a big factor since the lake was drained. The current results show a shift to higher concentrations of total phosphate phosphorus downstream of site TRIS. This would tend to support the idea that inflows of animal waste were still impacting downstream sites at the time the collections were made. Very high phosphorus loads are known to come from animal feedlots, usually much higher than from various types of nonpoint source runoff [5]. An extremely high average total phosphate phosphorus concentration (6.3 mg/l) was found at site TRIS, the site most directly impacted by a large cattle feedlot. All of the downstream concentrations are extremely high levels (appendix 2). In fact, in this creek (which is surrounded by general agriculture and bordered by many feedlots) even the upstream phosphorous values in this study were above 0.07-0.1 mg/l levels considered to be "hypereutrophic" by most authors [91,96]. The following comparative data for water concentrations of phosphate phosphorus and total phosphorus helps illustrate the degree to which Tierra Blanca Creek concentrations are considered elevated:

Although no total phosphate phosphorus criterion has been finalized by EPA to prevent or control accelerated eutrophication, EPA's national water quality criteria recommended that total phosphate phosphorus should not exceed 0.050 mg/l in any stream where it enters a lake or reservoir, nor exceed 0.025 mg/l within a lake or reservoir [3]. Stream concentrations this low do occur naturally in some areas. For example, in Ohio, streams in the southeastern part of the state typically have total phosphorus levels below 0.05 mg/l, whereas streams in areas of heavy agricultural and urban land use typically have higher phosphorus concentrations [91]. The SCS Water Quality Guide also states that background or natural (non-polluted) waters usually contain phosphorus (parameters) in concentrations below 0.05 mg/l [2].

Utah and a few other states use the water quality standard that phosphate phosphorus should not exceed 0.05 mg/l in any stream where it enters a lake or reservoir, nor exceed 0.025 mg/l within the lake or reservoir, for water uses which include protection of aquatic life [56, Bruce Waddell, FWS, personal communication]. Illinois limits total phosphate phosphorus at 0.05 mg/l in lakes and streams which feed lakes [56]. Nevada has a freshwater water quality standard to protect high quality, mixed use (including propagation of aquatic life) surface waters at 0.15 mg/l for phosphates [56]. Several other states also limit "phosphorus" in the 0.025 to 1 mg/l range, but EPA's summary of the state standards does not always make it clear which specific form of phosphorus is being regulated at the various listed levels [56]. It should also be noted that limitations of phosphate phosphorus and other particular forms of phosphorus should not be exceeded by any regulatory measure of "total phosphorus", since in no case should it be higher than any total phosphorus measure.

Standards for phosphorus are usually established according to the degree of protection a state wishes to afford a particular water [13]. The State of California has established a mean annual concentration of soluble phosphorus for Lake Tahoe (a very oligotrophic lake) at 0.007 mg/l, while mean annual concentrations for soluble phosphorus in other state waters in California are as high as 0.100 mg/l [57]. The maximum allowable mean annual concentration for soluble phosphorus in the delivery water to Everglades National Park is 0.020 mg/l [13].

NOTE: although these concentrations are reported as TP, they are still somewhat comparable to total phosphate phosphorus, as above: According to Wetzel, phosphorus levels in non-polluted natural waters generally range from 0.01 mg/l to 0.05 mg/l but variation is high [96]. In the upper (epilimnetic) layers of freshwater lakes, total phosphorus concentrations above 0.1 mg/l are hypereutrophic, those between 0.03 and 0.1 mg/l are eutrophic, those between 0.01 mg/l and 0.03 mg/l are meso-eutrophic, those between 0.005 mg/l and 0.01 m/l are oligo-mesotrophic, and those less than 0.005 mg/l are ultra-oligotrophic [96].

USGS Data from 1974-1981: The 50th percentile of 381 (not especially clean) NASQWAN and NWQSS river sites in the U.S. for total phosphorus as P was 0.13 mg/l; the 25th percentile was 0.06 mg/l, and the 75th percentile was 0.29 mg/l, with concentrations trending upward in some parts of the country, probably due to nonpoint sources and downward in other parts, probably due to reductions in output from point sources [55]. These riverine sites in the USGS study were mostly in (or downstream of) agricultural and urban areas [55].

Groundwater concentrations of phosphorus are typically low (average 20 µg/l) since phosphorus adheres to soil particles [92]. Nevertheless, the phosphorus content of most soils is low, between 0.01 and 0.2 % by weight [2].

Data from disturbed tributaries of Lake Ray Roberts (just north of Dallas/Fort Worth) impacted by dam-building disturbances, cropland, general agriculture, and one significant sewage treatment plant can be summarized as follows:

<u>Range:</u> Most total phosphorus water values in this disturbed system fell in the 0.2 to 0.6 mg/l range, with lower values during higher flow (dilution) and in areas not impacted by a sewage plant. The lowest value (0.07 mg/l) was from a relatively upstream and undisturbed site and the highest value (2.22 mg/l) was from just below a sewage outfall during worst case (low flow) summer conditions [93].

<u>Sediment Data Results for Total Phosphate Phosphorus</u>:

<u>Range</u>: Average dry weight total phosphate phosphorus concentrations in sediments ranged from 303 mg/Kg at site TRB to 15,000 mg/Kg at site SW, a wastewater lagoon at a feedlot.

<u>Gradient Monitoring Levels</u>: There is an apparent increase in total phosphate phosphorus progressing from upstream to downstream. However, each site seems to exhibit phosphate concentrations independent of other sites. This is probably due more to localized activity in the nearby watershed at each site rather than accumulation along the stream gradient.

A study by the U.S. Corps of Engineers indicated the mean total phosphate concentration of 40 different lake sediments was 360 mg/Kg [97]. This level is not much different than the concentrations found at upstream locations site TRB (303 mg/kg), and site NRB (486 mg/Kg). Concentration nearly doubles at the Hereford site HFR (830 mg/Kg) then increases to 2500 mg/Kg at site TRIS.

Discussion: Although no official fish and wildlife concern levels are currently published for total phosphate phosphorus concentrations in sediments, the high water and sediment concentrations of phosphates existing at several sites along Tierra Blanca Creek far exceed the levels which would be required to provide adequate protection for water quality in the creek and in Buffalo Lake National Wildlife Refuge. Nutrient resuspension during storm runoff events and annual turnovers in downstream reservoirs, such as those in Buffalo Lake National Wildlife Refuge, can make excess nutrients available, stimulating productivity and other undesirable eutrophic conditions such as insufficient dissolved oxygen.

Concentrations above 635.75 mg/kg and 1349.8 mg/kg are higher than 50% and 85% of lake samples statewide, respectively [124]. It is significant that the highest total phosphate phosphorus concentration was found in sediments of a feedlot wastewater lagoon. Phosphates were also high in the sediments from site HS (below feedlots and a sugar processing plant, 3,160 mg/Kg) and at the site suspected of being impacted by a cattle feedlot (Site TRIS, 2,500 mg/Kg). In Texas the statewide 90th percentile value for this compound was 1,571 mg/kg dry weight [43].

Salinity/Chloride/Sulfate

Salinity is a measure of the dissolved salts in a volume of water [74]. The principal inorganic anions in waters are chloride, sulfate, carbonates, and nitrates, and the principal cations are sodium, potassium, calcium, and magnesium. In some studies, salinity is not measured directly. Instead, chloride, sulfate, calcium, and magnesium are measured separately.

Since the term salinity is used most often in conjunction with ionic mixtures similar to seawater, the Texas Water Commission instructs their field staff to report conductivity, chloride, or TDS rather than salinity in (inland) waters having salinities of less than 3% (Dave Buzan, Texas Water Commission, personal communication).

In freshwater, salinity is generally related to conductivity (see Table provided below) and total dissolved solids. This is because all of the measurements are related to ions in solution. Greater salinity would correspond with higher conductivity and greater total dissolved solids. This is important to fish and other aquatic life because substances in solution exert osmotic pressure on aquatic organisms [32]. When osmotic pressure becomes too high it can draw water out of vital body organs and cause cellular damage or death. Most aquatic life can adapt to minor or slow changes, but wide or sudden variations (such as a sudden intrusion of oil field brine into a freshwater ecosystem) can be too severe for adaptation and result in elimination of species from impacted areas [32,58,59].

Water Data Results:

Range: Tables and equations are available to convert freshwater conductivity measurements [98] and seawater conductivity measurements [99] to salinity. Using a table (see Appendix 3) supplied by LaMotte Chemical Products Company to convert the conductivity results (177-667 μmhos, based on a temperature of around 21 degrees centigrade, produces a salinity equivalent close to zero. Chlorides ranged from 2.5 to 36.3 mg/l.

Gradient Monitoring Levels: Sulfate showed an increasing tendency along the stream, ranging from 7 mg/l at the uppermost site to 45 mg/l at Smith Ranch. With the exception of sulfates and nitrates, the maximum concentration of all the major cations and anions occurred below site TRIS, the cattle feedlot.

Discussion: The greatest conductivity/salinity reading along Tierra Blanca Creek was taken just below a cattle feedlot (667 μmhos at Site TRIS). Conductivity is related to the types and amounts of ions in solution, and the high level at site TRIS corresponded with elevated levels of individual ions at this same site, a site suspected of being impacted by a cattle feedlot.

However, there are no national water quality criteria for salinity for the protection of freshwater species of fish and wildlife [3], and salinity levels were low. Levels of chloride and sulfate ions in Tierra Blanca Creek are well below recommended limits (that dissolved solids should not cause an osmotic pressure to exceed that of a 15,000 mg/l NaCl solution for most freshwater fishes) [3].

Chlorides were especially low (2.5 mg/l) at the upper sites, but sites impacted by feedlot runoff showed ten-fold increase in chlorides (36.3 and 22.0 mg/l).

Although these levels are still relatively low when compared with the U.S. Geological Survey data for the Prairie Dog Town Fork of the Red River, the Prairie Dog Town Fork data is not as relevant as the different levels (especially at sites impacted by feedlots) along Tierra Blanca Creek; the Prairie Dog Town Fork flows through exposed layers of halite and gypsum. Naturally occurring salts from these minerals are the probable source of chloride concentrations greater than 1800 mg/l and sulfate concentrations greater than 1500 mg/l in the Prairie Dog Town Fork of the Red River, notably one of the most saline rivers in the state.

Selenium

Selenium has many teratogenic and toxic impacts upon fish and wildlife at high concentrations [100]. Selenium is listed by the Environmental Protection Agency as one of 129 priority pollutants [25].

Waterfowl feeding on zooplankton or on algae may be more sensitive to selenium contamination than those feeding on seeds [101]. Mallards, cinnamon teal, and pintails, which consume large amounts of seeds, are therefore less at risk than gadwalls and northern shovelers, which consume primarily algae and zooplankton [101]. Using the same criteria, green winged teal and widgeon would be at intermediate risk [101].

Humans require minute quantities of selenium to maintain tissue elasticity and prevent premature aging, muscle pain, and heart disease [61]. The range between insufficient selenium in the diet of animals and too much is narrow, and the effects of either problem can be serious [102].

Results: Tissue Concentrations:

Range: Only tissue samples were analyzed for selenium. Selenium was detected in all 16 tissue samples having sufficient volume for analysis. The concentrations ranged from 0.15 mg/kg wet weight in whole body samples of crayfish at site SR to 1.46 mg/kg wet weight in liver samples of Yellow Mud Turtles from site SPI.

Discussion: Selenium whole-body levels above 0.5 mg/kg are considered harmful to fish and predators [38]. With the exception of the liver samples (which were not whole body samples), none of the samples had selenium concentrations higher than 0.475 mg/kg wet weight.

There is limited data available for interpreting the meaning of the tissue concentration results. Wet-weight legal limits for concentrations of selenium in fish and fishery products include a legal limit of 0.05 mg/kg (Chile) [70,71]. Three countries have limits less than or equal to 2.0 mg/kg, but the U.S. apparently has no limit [70,71].

The California Department of Health Services recommended a maximum allowable residue level of 1.0 mg/kg wet weight for muscle (fillet) tissue of edible fish [101]. It was from this that the water concentration concern level of 0.8 ppm was derived (through back calculation from the tissue concern level) [101].

An estimate of a no effect selenium concentration in fish was a whole-body concentration of 1.1 mg/kg wet weight [101]. This was the no effect level for the fish itself, not predators which might be eating many fish of the same species. A predator protection level based on this data would therefore have to be well below 1.1 mg/kg wet weight.

The geometric mean of whole-body (wet weight) concentrations of fish in a 1980-1981 national survey was 0.47 mg/kg [73]. A more recent (1976-1984) NCBP survey report gave the national geometric mean level for selenium in whole-body fish as 0.42 mg/kg, the maximum level as 2.3 mg/kg, and the 85th percentile level as 0.73 mg/kg wet weight [39]. In the present study, the only whole-body fish tissue sample comparable with these figures was a black bullhead whole body sample from site SPI, which had a selenium concentration of 0.318 mg/kg wet weight.

Overall, none of the tissue samples in this study had especially elevated selenium concentrations.

Solids

Solids are present in water in various forms which can be subdivided into different categories. The distribution and type of solids in water is helpful to know because there are different types of problems associated with the various solid types, and information is gained from understanding the composition of solids. Each type of measure of solids is discussed separately below, under the following headings: Solids (TDS), Solids, (TS), Solids (TSS), and Volatile Solids (VS):

Solids (TDS, Total Dissolved Solids)

Total dissolved solids is a freshwater measure of those solids that are present in solution, often minerals or salts [3]. Fish, aquatic organisms, and wildlife must be able to tolerate a range of dissolved solids. However, extremes or wide variations in dissolved solids occurring with time or distance may cause osmotic stresses to the organism.

Total dissolved solids is related to conductivity and to salinity, because they all have to do with ions in solution. Greater total dissolved solids would generally correspond to greater conductivity and higher salinity. This is important to fish and other aquatic life because substances in solution exert osmotic pressure on aquatic organisms [32]. When osmotic pressure becomes too high it can draw water out of vital body organs and cause cellular damage or death. Most aquatic life can adapt to minor or slow changes, but wide or sudden variations (such as a sudden intrusion of oil field brine into a freshwater ecosystem) can be too severe for adaptation and result in elimination of species from impacted areas

[32,58,59].

In Texas, total dissolved solids are sometimes calculated by halving conductivity measurements (Dave Buzan, Texas Water Commission, personal communication). However, in the current study, water samples were done separately using a gravimetric procedure rather than a calculation method based on conductivity (Bill Cyrus, Trinity River Authority Water Quality Laboratory, Grand Prairie, Texas, personal communication)

Water Data Results:

Range: Study range of dissolved solids was 165 mg/l at the uppermost site, Garcia Lake, to 496 mg/l in an unnamed tributary to Tierra Blanca Creek.

Gradient Monitoring Levels: The greatest TDS values were 496 and 446 mg/l measured in the unnamed tributary site NRB, and below a large cattle feedlot site TRIS, respectively. Otherwise, total dissolved solids along Tierra Blanca Creek was different at each site but showed no clear upstream/downstream patterns.

Discussion: Texas has no TDS water quality standard for the purpose of protection of fish and wildlife. Various other states have set the following water quality standards for TDS for waters having aquatic life propagation as a use or as one of the uses [56]:

500 mg/l (NY, NJ, and NV)
750 mg/l (IA, MI)
1000 mg/l (Illinois)
1500 mg/l (AK, OH)

For freshwater fish, the tolerance levels for different concentrations of dissolved solids are not definitely known but have been found to range from 5,000 to 10,000 mg/l, according to species and prior acclimatization [13]. Some species of fish are adapted to living in more saline waters; however, a few species of freshwater fish have existed in natural waters with salt concentrations of 15,000 to 20,000 mg/l [13]. Fish have the capacity to slowly adapt to higher salinities than those to which they are accustomed, but the sudden introduction of high salinities, such as from oil field brines, can be deadly [13].

Most fish and aquatic life must be able to tolerate a range of TDS in order to survive. Recommended limits for most freshwater fishes is 15,000 mg/l or concentrations producing the osmotic pressure equal to that of a 15,000 mg/l NaCl solution [3].

One study reports that 95% of inland waters in the U.S. supporting varied fish fauna have dissolved solid concentrations below 400 mg/l [32]. There were some TDS levels above 400 mg/l in Tierra Blanca Creek. However, when compared with values in other prairie creeks, the levels do not appear to be high enough to cause undue concern for fish and wildlife. Most TDS values found in this study, at least those below 400 mg/l, are well within acceptable tolerance for freshwater species of fish.

Solids, (TS, Total Solids)

Total solids is the dry weight of all solids present in a given volume of water sample that has been evaporated to dryness at 103-105 C and is reported in units of mg/l. Although total solids were not measured directly in this study, a close estimation can be made by adding the total dissolved solids (TDS) and the total suspended solids (TSS). Very high total solids loads are known to come from animal feedlots, usually much higher than from various types of nonpoint source runoff [5]. However, in concert with common practice, the results for solids are discussed elsewhere in this report in detail under individual sections for Total Dissolved Solids (TDS), Total Suspended Solids (TSS), and Volatile Solids (VS).

Solids (TSS, Total Suspended Solids)

Suspended solids are those small particles suspended in water which can be filtered out of solution and remain trapped on a preweighed filter paper [23]. Suspended solids reduce water clarity, can prevent sunlight penetration through the water column, and can be abrasive to equipment. Suspended solids can be impacted by land use in the watershed and storm events. Suspended solids may affect aquatic life adversely in several ways such as preventing successful development of eggs or larvae, acting directly on the organism to reduce growth or resistance to disease, modifying natural movements, migrations or environment, or by reducing the abundance of available food.

Apart from possible toxic effects attributable to substances leached out by water, suspended solids may kill fish and shellfish by causing abrasive injuries, clogging the gills and respiratory passages of various aquatic species, smothering eggs, and destroying spawning beds [13]. Suspended solids can also be harmful when they screen out light or trap bacteria and detritus on the bottom, resulting in oxygen depletion [32].

Suspended solids problems are not limited to rural habitats. The present increase in urbanization due to the population explosion presents additional soil-erosion problems; sediment loads in nearby streams may increase as much as 500 to 1,000 times over that recorded in nearby undeveloped stretches of stream [103]. Soil erosion not only despoils the earth for farming and other uses, but also increases the suspended-solids load of the waterways and wetlands. This increase interferes with the ecological habitat by posing siltation problems.

TSS should not be confused with the USGS measure "suspended sediment" which is an unfiltered (just dry and measure) parameter. There also appears to be some variation between various agencies and methods as to the extent to which total suspended solids includes materials which resist separation by conventional means (sedimentation). The Texas Water Commission method (used in the current study) includes solids which could easily be settled via sedimentation in their definition of suspended solids (Dave Buzan, Texas Water Commission, personal communication.)

EPA published an aquatic life ""Gold Book"" water quality criterion (water concentration concern level) for suspended, settleable solids and turbidity in 1986 [3]. The criterion was that settleable and suspended solids should not reduce the depth of the compensation point for photosynthetic activity by more than 10% from seasonally established norm for freshwater fish and other aquatic life [3]. Rainfall events significantly alter TSS (and many other parameters) in streams.

Water Data Results:

Range: The range of suspended solids in this study was 2 mg/l at Stuart Dike site SD to 151 mg/l in the unnamed tributary site NRB.

Gradient Monitoring Levels: Suspended solids were slightly higher in the upper Tierra Blanca Creek (116 mg/l), in the unnamed tributary (151 mg/l) and in downtown Hereford (122 mg/l) than at the downstream sites. TSS below the feedlot (87 mg/l), Smith Ranch (77 mg/l), and Stuart Pond inflow (28 mg/l) show decreasing tendency with the least TSS at Stuart Dike (site SD, 2 mg/l) as would be expected where an impoundment produces a settling basin effect.

Discussion: Freshwater in Texas that is considered to be very transparent, mostly spring-fed streams, deep-long reservoirs, and rivers flowing in areas with thin soils, little erosion, and rock substrates, generally have TSS values of less than 5 mg/l (Dave Buzan, Texas Water Commission, personal communication. A few of the values found in the current study were below the 5 mg/l level, and most of the other TSS levels found in Tierra Blanca creek were not especially high compared to levels found in the Prairie Dog Town Fork of the Red River during similar flow conditions (5-27 mg/l) or to levels found in disturbed tributaries of Lake Ray Roberts [93].

Overall, the results for suspended solids did not indicate any unusual problems. As would be expected, the lowest levels were at the sites where most settling had occurred.

Solids (VS, Volatile Solids)

Characterization of solids as volatile solid fractions (of each of the groups of solids discussed above) can be achieved by determining the amount of solids remaining before and after ashing in a furnace at a temperature of 550 C. Generally, organic (carbon containing) components will combust, and the weight lost on ignition (difference in weight) is the volatile solid component, the remaining solids being fixed solids. Thereby one can analyze for "Total Volatile Solids (TVS)" and "Volatile Suspended Solids (VSS)". The ratio of total solids to volatile solids may be used to estimate the proportion of solids which are organic. Characteristic feedlot waste has a TS/VS ratio of 2:1 [118].

Water Data Results:

Range: Range of volatile suspended solids (VSS) in this study was 1 mg/l at Stuart Dike to 47 mg/l below the TriState feedlot.

Discussion and Gradient Monitoring: Sites below site TRIS, the TriState Feedlot in Hereford, had TS/VS ratios between 1.8:1 and 4.6:1. These lower ratios are probably a result because of the animal waste, although a phytoplankton bloom stimulated by excess organic waste can also depress these ratios (Dave Buzan, Texas Water Commission, personal communication). Sites above this feedlot had TS/VS ratios of 7.6:1 and 17.4:1. A distinct shift in the ratio is evident downstream of the feedlot. This provides one of several indications that feedlot wastes were leaking into the creek at or near the feedlot.

Strontium (Sr)

Strontium is a soft, silvery metal with physical and chemical properties similar to those of calcium [104]. It is a fairly common alkaline earth metal [117]. In localities where it is elevated, strontium is an important freshwater quality ion which contributes to water "hardness" [3]. In humans, the major hazard of exposure to strontium is from general environmental pollution from radioactive fallout of strontium 90 [18].

Many radioactive isotopes of strontium are produced in nuclear reactors [104]. Strontium 90 is a radioactive nuclide which is considered to be one of the more undesirable fission products [117]. Highly elevated amounts of radioactive isotopes of strontium are usually the result of nuclear activity. Strontium 90, with a half-life of 28 years, is formed in nuclear explosions; because it accumulates in the bones, it is considered the most dangerous component of radioactive fallout [104].

Body burden issues are not well understood. Some studies indicate that 70 to 90 percent of cattle's strontium 90 intake came from native grass hay and that farm to farm differences in the strontium-90 concentrations in the hay feed correspond to differences in the concentration of strontium 90 in the milk [105].

Uptake of Strontium 90 and other radioisotopes by ducks maintained on radioactive leaching ponds for 43-145 days in southeastern Idaho was significant [132]. The calculated total dose rate to the ducks from both super(90)Sr and the transuranic nuclides was 0.69 mGy d super(-1), of which 99% was to the bone [132].

Although pure strontium does not appear to be very toxic, many strontium compounds are hazardous to fish and wildlife [106]. Strontium chromate is carcinogenic and several strontium compounds are very reactive or explosive [106].

Oral administration of different concentrations of strontium chloride to laboratory bred mice in vivo induced chromosomal aberrations in bone marrow cell metaphase preparations [131]. The degree of clastogenicity was directly proportional to concentration used at 6, 12, and 24 h of treatment [131].

<u>Results and Discussion:</u>

Only sediment samples were analyzed for strontium. All samples had dry weight concentrations between 54 mg/kg (Site PL) and 626 mg/kg (Site DLB). Only upstream sites PL, NRB, and TRB had strontium levels below 66 mg/kg dry weight strontium. All the other sites (which had more likelihood of influence from cattle feedlots) had strontium levels higher than 130 mg/kg dry weight. Comparative data related to tissue concentrations versus the well being of fish and wildlife have proven to be hard to find.

Strontium concentrations in three sediment samples from the upstream Tierra Blanca Creek site (NRB) and three sediment samples from the playa lake (PL) off-stream site were at or below 56 mg/kg dry weight. By contrast, three samples from the Tierra Blanca Creek site (TRIS) suspected of being polluted by a large feedlot had higher strontium concentrations (from 209-226 mg/kg dry weight) and the waste water pond in the feedlot had highly elevated strontium concentrations (300-310 mg/kg).

Strontium occurs in most plants, a potential source in cattle feed. A Mann-Whitney statistical test showed strontium concentrations from the six upstream samples to be significantly lower than the concentrations in the six samples known or suspected of being influenced by feedlot wastes (significant at 0.0051).

Dry weight concentrations of strontium in four cattle feedlot-impacted playa lakes (in the Texas Panhandle) the senior author has analyzed in a separate study, ranged from 149-189 mg/kg. In the same study, four (non-feedlot) ephemeral row-crop agriculture playas had strontium concentrations of 38.9 to 68.6 mg/kg. A Mann-Whitney statistical test showed strontium concentrations from the four row-crop agriculture samples to be significantly lower than the concentrations in the four samples known to be impacted by feedlot wastes (significant at 0.0304).

Cattle are good concentrators of strontium from plants (this is the source of concern about strontium 90 in milk) [105], and strontium is excreted in urine and feces [18].

Sulfate

See Appendix 2 for a list of the sulfate values in water and the salinity section for a discussion of the values.

Temperature

The climate in this semi-arid region varies seasonally and diurnally with wide ranges occurring naturally due to low humidity and daily fluctuations in temperature. Temperature affects both biological and physical processes. Generally, at lower temperatures, plant growth, nutrient uptake, and organism activity are reduced. Temperature also affects chemical reactions, microbial degradation, and physical properties such as the solubility and saturation of dissolved oxygen in water. Therefore, temperature indirectly affects various oxygen variables, such as biochemical oxygen demand (BOD), discussed separately in this report.

Range: The temperatures observed in this study were 20.6-30.5 C.

Discussion: The observed temperatures were within the expected range for this region during summer months (June,1987). The temperatures observed do not constitute a significant (separate) cause for concern for fish and wildlife, although elevated temperatures in combination with other stresses can contribute to cumulative stress.

Tetradifon (Tedion, Duphar, Sulfone, p-Chlorophenyl 2,4,5-Trichlorophenyl)

Tetradifon is a diphenyl acaricide and insecticide [107,108]. Its molecular formula is C12-H6-Cl4-O2-S and it is used on a wide variety of fruits, vegetables, cotton, and other crops [109].

In this study only one sample contained tetradifon above the 0.01 mg/kg detection limit: a fat sample from a yellow mud turtle from the playa lake site (PL) had a wet weight concentration of tetradifon of 0.02 mg/kg. This is well below known concern levels and far below concentrations allowed for residues of tetradifon in fruits and vegetables in the marketplace [18].

Vanadium (V)

Vanadium is widespread in nature; its abundance in earth's crust is 0.01% by weight [76]. Vanadium can be found in trace amounts in fossil fuels [18]. Vanadium is found in soil and is deposited in water as a result of fallout from air pollution [26] and is often found in ore along with uranium [30].

Vanadium and its compounds are toxic [110]. Vanadium is considered to be one of the 14 most noxious heavy metals, but has a much higher bioconcentration potential in mollusks than in fish [26]. Preliminary data suggests the potential for bioaccumulation or bioconcentration of vanadium is low or limited for the following biota: mammals, birds, and fish. It appears to be high to very high for mollusks, crustacea, and lower animals and moderate for higher plants, mosses, lichens, and algae [26]. Plants take up vanadium from soil, groundwater, surface water, and air pollution [26]. Animals take up vanadium from contaminated air, contaminated water, and contaminated food [26].

Results: Sediment Concentrations:

Only sediment samples were analyzed for vanadium. Vanadium concentrations in sediments did not vary much. All samples had dry weight concentrations between 8.6 mg/kg (Site DLB) and 22.0 mg/kg (Site SR). Only a few of the literature references found so far are even remotely relevant to the results for sediment concentrations:

Typical Igneous Rocks (Earth's Crust) Concentrations: **EPA 1981:** 135.0 mg/kg dry weight [26].

Dietary vanadium has been shown to suppress egg production of laying hens [33]. Dietary vanadium at levels as low as 0.5 mg/kg have been shown to alter metabolism in mallards [111]. These two items might be of interest in areas where birds are ingesting sediments during normal feeding. However, typical soil concentrations of vanadium as high as 100 mg/kg dry weight have also been reported in the literature [26].

Zinc (Zn)

Zinc is listed by the Environmental Protection Agency as one of 129 priority pollutants [25]. Zinc in low to moderate amounts is of very low toxicity in its ordinary compounds and in low concentrations is an essential element in plant and animal life [112]. In humans, some zinc in the diet is essential for normal growth and maturation, cell metabolism, development of reproductive organs, prevention of anemia, functioning of the prostate gland, healing of wounds, enzyme activity, regulation of zinc dependent enzymes, manufacture of proteins, and manufacture of nucleic acids [61,62,112].

However, there have been cases of too much zinc causing poisoning in humans as well as fish and wildlife, and excess zinc in the water column or sediments can cause considerable toxicity to aquatic organisms, especially to various invertebrate species which form part of the balanced diet of many waterfowl and shorebird species.

Since zinc was found in elevated amounts in the current study, more detail related to incidences of zinc toxicity to animals is provided:

1. Poisoning has been observed in ferrets and mink from chewing corroded cages or from food stuffs containing particles of metal, and in pigs and hens from use of zinc plated funnels. Young animals are much more susceptible to poisoning by zinc than mature animals [18].

2. Symptoms of zinc toxicity are lassitude, slower tendon reflexes, bloody enteritis, diarrhea, lowered leukocyte count, depression of cns, and paralysis of extremities. [18]

3. In mammals excess zinc can cause copper deficiencies, affect iron metabolism, and interact with the chemical dynamics of lead and drugs [62,113]. The levels of dietary zinc at which toxic effects are evident depend on the ratio of zinc to copper [62].

4. Although zinc at low levels is an essential to many animals and humans, zinc is toxic to fish at levels exceeding the minimum amount needed [33].

5. Water is not a significant dietary source of zinc [30], but fish, especially those living or foraging in sediments contaminated by zinc, may accumulate it directly from the sediments [35].

6. Some plants and animals living in zinc-polluted environments have evidently become more tolerant of this metal than populations of the same species from cleaner areas [62].

7. Skeletal anomalies were observed with increased frequency among the offspring of mice injected with 1.5 - 2 times the usual human therapeutic dose of zinc during pregnancy [114].

8. Abnormal fur and immunosuppression occurred among the offspring of pregnant mink fed a diet containing about 50 times the usual amount of zinc [114].

9. The frequency of congenital anomalies was no greater than expected among the offspring of pregnant rats fed a diet containing 2.5 - 31 times the usual amount of zinc [114].

10. Elevated concentrations of zinc in water are particularly toxic to many species of algae, crustaceans, and salmonids [62].

11. Elevated water concentrations of zinc have especially strong impacts on macroinvertebrates such as mollusks, crustaceans, odonates, and ephemeropterans [115].

Synergism and other interactions of zinc include:

1. Zinc in water acts synergistically with copper and ammonia to produce an increased toxic effect on fish [22,65].

2. A study in an Arkansas river system showed that macroinvertebrate concentrations were negatively correlated with zinc concentrations but not with concentrations of iron or copper [115].

3. Preliminary exposure to acetic acid vapors tended to prepare the host for development of zinc metal fume fever by permitting contact between leukocytes and zinc oxide particles, resulting in release of endogenous pyrogens to metal fume fever. [18]

Bioconcentration factors for zinc include:

1. The bioconcentration factor in edible portions of _Crassostrea virginia_ (adult oyster) is 16,700. [18, Shuster CN, Pringlo BH; Proc Nat Shellfish Assoc. 59: 91 (1969) as cited in USEPA; Ambient Water Quality Criteria Doc: Zinc p.C-5 (1980) EPA 400/5-80-079].

2. The bioconcentration factor in edible portions of _Mya arenaria_ (soft-shell clam) is 85. [18, Pringle BH et al; J Sanitary Engineer Div 94 (SA3): 455 (1968) as cited in USEPA; Ambient Water Quality Criteria Doc: Zinc p.C-5 (1980) EPA 400/5-80-079].

3. The bioconcentration factor in edible portions of _Mytilus edulis_ (mussel) is 500. [18, Pentreath RJ; J Exp Mar Biol Ecol 12: 1 (1973)].

4. Earthworms concentrate this metallic element relative to soil concentrations, which is one potential hazard of birds feeding on sewage sludge amended soils [69].

Results: Sediment Concentrations:

Results from this study revealed that zinc concentrations in three sediment samples from the upstream Tierra Blanca Creek site (NRB) and three sediment samples from the playa lake (PL) off-stream site were at or below 29 mg/kg dry weight. By contrast, three samples from the Tierra Blanca Creek site (TRIS) suspected of being polluted by a large feedlot had higher zinc concentrations (from 128-139 mg/kg dry weight) and the waste water pond (Site SW) in the feedlot had highly elevated zinc concentrations (491-538 mg/kg). These results may be compared to the following high/low and concern levels:

Freshwater Sediment Concentrations of Zinc (Dry Weight) not Considered Elevated:

Great Lakes Harbors, EPA 1977: Sediments having sediment concentrations lower than 90.0 mg/kg were classified as "non polluted [46]."

International Joint Commission, 1988: The International Joint Commission considered <120 mg/kg as a background sediment level [46]. The control site in one Great Lakes study had a sediment concentration of 45 mg/kg [46].

Leland and Kuwabara, 1985: In non-polluted areas, baseline sediment concentrations as low as <10 mg/kg have been recorded [45].

Zinc Freshwater Sediment Concentrations Considered Elevated:

Texas: The statewide 90th percentile value was 120 mg/kg dry weight [43]. Concentrations above 63.0 mg/kg and 105.0 mg/kg are higher than 50% and 85% of Texas lake samples statewide, respectively [124].

Great Lakes Harbors, EPA 1977: Sediments having concentrations higher than 200 mg/kg dry weight were classified as "heavily polluted [46]."

Illinois EPA, 1984: Sediments having concentrations higher than 100.0 mg/kg dry weight were classified as "elevated" [46].

Highway Runoff, 1989: Detention pond sediments receiving runoff from highways averaged 250 mg/kg dry weight of zinc; the cypress wetlands the detention pond effluent was routed to, by contrast, had a median value of 14 mg/kg zinc, indicating most was removed by the detention pond [42].

Various Concern Levels for Concentrations of Zinc in Sediment/Soil (Dry Weight):

EPA Region 6, 1973: The concentration proposed by EPA Region 6 as a guideline for determining acceptability of dredged sediment disposal was 75 mg/kg [44].

Ontario, 1978: The concentration proposed by the Ontario Ministry of the Environment as a threshold for evaluations of dredging projects was 100 mg/kg [46].

International Joint Commission, 1988: The IJC suggested sediment concentrations not exceed background levels of 120 mg/kg [46].

NOAA 1990 Concern Levels for Coastal and Estuarine Environments: After studying its own data from the National Status and Trends Program as well as many literature references concerning different approaches to determining sediment criteria, NOAA suggested that the potential for biological effects of this contaminant sorbed to sediments was highest in sediments where its concentration exceeded 270 mg/kg dry weight and was lowest in sediments where its concentration was less than 120 mg/kg dry weight [47].

The 1987 soil (clean up) criteria given by the New Jersey Department of Environmental Protection for zinc is 350 mg/kg dry weight [31,68].

Discussion of Sediment Results for Zinc: Most of the benchmarks (listed above) from the literature would seem to indicate that zinc was elevated at the TRIS site (where feedlot contamination is suspected) and in the feedlot waste water pond. The levels at Site TRIS (128-139 mg/kg dry weight) are within the range of concentrations found at some hazardous waste sites and the levels at Site SW (491-538 mg/kg dry weight) are above the New Jersey soil cleanup level (New Jersey Cleanup Responsibility Act) [31].

Zinc occurs in many feed additives, one potential source in cattle feedlot impacted areas. A Mann-Whitney statistical test showed zinc concentrations from the six upstream sediment samples to be significantly lower than the concentrations in the six samples known or suspected of being influenced by feedlot wastes (significance level 0.0051).

For additional contrast to the results of this study, dry weight sediment concentrations of zinc in four cattle feedlot-impacted playa lakes (in the Texas Panhandle) the senior author has examined for a separate study ranged from 75.3-226 mg/kg whereas four (non-feedlot) ephemeral row-crop agriculture playas had zinc concentrations of 47.3 to 69.8 mg/kg. A Mann-Whitney statistical test showed zinc concentrations from the four row-crop agriculture samples to be significantly lower than the concentrations in the four samples from playa lakes known to be impacted by feedlot wastes (significant at 0.0304).

Results: Tissue Concentrations:

Range: Zinc was detected in all 17 tissue samples. The concentrations ranged from 7.4 mg/kg wet weight in whole body samples of tiger salamanders from site PL to 51.8 mg/kg wet weight in a coot liver sample from site SD.

Discussion of Tissue Concentrations: Zinc tends to be present in significant amounts (up to 25 mg/kg wet weight normally) in fish and animal meat products [18]. None of the tissue samples had especially elevated zinc concentrations. With the exception of the coot liver samples, all had concentrations lower than 25 mg/kg wet weight zinc. The coot liver samples from site SD ranged from 41.8 to 51.8 mg/kg wet weight. The coot livers contained the most zinc, but liver samples would be expected to contain more zinc than whole-body samples [18].

There is limited data available for interpreting the meaning of the tissue concentration results. No predator protection levels were found in the literature for zinc, and most toxicity from moderate amounts of zinc seems to be aquatic toxicity rather than dietary toxicity. Some additional comparison data is provided as follows:

> Wet-weight legal limits for concentrations of zinc in fish and fishery products include a legal limit of 30-50 mg/kg (Poland) [70,71]. Seven countries have limits less than or equal to 100 mg/kg, but the U.S. apparently has no limit [70,71].
>
> Zinc does not tend to bioaccumulate in fish as much as some other contaminants. In a recent study of contaminants in the Trinity River, zinc was one of the 3 of 67 contaminants which was not consistently higher in fish and wildlife tissues downstream of Dallas than at the reference/control site (site 1) upstream of Fort Worth. Zinc's role as a dietary requirement may be a factor [19]. Some aquatic organisms can apparently regulate the uptake of zinc, and the bioavailability of zinc is related to sediment type [35]. A nationwide study of zinc in bivalves showed less variation in zinc concentrations from various locations than from various species [116].
>
> A recent (1976-1984) NCBP survey report gave the nationwide geometric mean concentration of zinc in composite samples of whole fish as 21.7 mg/kg wet weight [39]. The same study gave the maximum nationwide (whole-body, fish) concentration as 118.4 and the 85th percentile wet weight concentration of zinc as 34.2 mg/kg. In the present study, the only whole body fish tissue sample comparable with these figures was a black bullhead whole body sample from site SPI, which had 19.7 mg/kg wet weight of zinc.
>
> The average normal levels of zinc in cattle are: liver, 135 ppm; kidneys, 80 ppm; feces, 200 ppm, (all dry matter) and serum 0.14 ppm [18]. In animals suffering from zinc poisoning corresponding values are: liver, 2000 ppm; kidneys, 670 ppm; feces, 3740 ppm; and serum, 0.515 Ppm [18]. Zinc is a component of many cattle feed supplements [125].

Summary/Conclusions

Elevated levels of zinc and copper were found in the bottom sediments of feedlot waste water ponds and in (some) parts of the creek suspected of being impacted by feedlots. Other pollution parameters, such as strontium, were also highly elevated in sediment samples from areas known or suspected of being influenced by feedlot wastes.

Some of the zinc concentrations documented in this study are similar to levels one encounters at hazardous waste sites and are above the New Jersey soil cleanup level (New Jersey Cleanup Responsibility Act)[31]. Note: Just as there are requirements for handling of hazardous waste in this country, other countries have developed specific requirements for handling feedlot manure as a potentially hazardous waste.

At sites thought to be impacted by feedlot wastes, water analyses revealed elevated concentrations of ammonia, calcium, chemical oxygen demand (COD), chlorophyll A, coliform bacteria, chloride, conductivity, magnesium, total kjeldahl nitrogen (TKN), sulfate, and volatile suspended solids (VSS). High concentrations of most of these same parameters, including ammonia, chemical oxygen demand (COD), coliform bacteria, chloride, conductivity, total kjeldahl nitrogen (TKN), and suspended solids, have previously been documented in the literature as characteristic of cattle feedlot runoff [136]. The shift towards a lower total solids to volatile solids ratio downstream of feedlot impacted site TRIS is seen as an additional indication that feedlot wastes were leaking into the creek.

Although not a main focus of the study, qualitative observations of the biota in the creek made during seining revealed an absence of a healthy diversity of aquatic life in areas of the creek most frequently holding water. High ammonia concentrations and elevated concentrations of some metals may help explain the lack of diversity. Zinc, a contaminant which is elevated in creek and feedlot-contaminated samples, is more acutely toxic to fish at higher temperatures than at lower temperatures [67], and high temperatures prevail in this sluggish, shallow creek in the summer. Although metals are a concern, one of the most obvious and serious concerns in this drainage is extremely low dissolved oxygen concentrations, concentrations below State and Federal water quality criteria. High biochemical oxygen demand loads due to nitrogen rich organic material add to the critically depressed dissolved oxygen levels. In intermittent creek pools which are slowly drying up, there are natural stresses on oxygen levels, and the additional stresses from oxygen-demanding pollutants can drive oxygen levels very low. Downstream in Buffalo Lake, feedlot runoff has (in the past) caused fish kills, yet diminished water available to the system tends to make storm runoff the major source of inflow water.

The segment of Tierra Blanca creek studied is not classified separately in State water quality standards; at the time of this study, such reaches were assumed to be in the limited aquatic life use subcategory. Dissolved oxygen values below 1.0 mg/l in midday were measured in the Tierra Blanca Creek samples. According to the latest Texas Water Quality standards, intermittent streams not otherwise classified should maintain an absolute minimum dissolved oxygen concentration of 1.5 mg/l, and a 24 hour mean of 2.0 mg/l. These oxygen standards for intermittent streams appear to be one of the few requirements in Texas Water Quality Standards that have been made less stringent in the last few years. Nevertheless, a 24 hour sampling regime done at the time of the current study would have undoubtedly revealed many separate instances where the state's current dissolved oxygen criteria were violated.

The depressed oxygen levels and greatly elevated concentrations of various cattle-related pollutants at several sites are thought to be primarily the result of feedlot leakage rather than the result of human sewage or non-point source runoff from pasture land or general agriculture. Rainfall runoff from a cattle feedlot typically has concentrations of oxygen demand, solids, and nutrients which are an order of magnitude greater than typical untreated human sewage [139]. Measured both in terms of concentration and areal loading rates, animal feedlot runoff also has nutrient pollution characteristics that are many orders of magnitude greater than those of other non-point sources [53]. All-year cattle grazing/feeding on unimproved pastures does not consistently produce degradation of stream water quality from nutrient concentrations or transport [123] or from fecal coliforms (see fecal coliform section).

Observed during collections made for the current study were: 1) places where bottom sediments were thick with feedlot runoff (which included cattle feed as well as waste sludge), 2) a few places where hillsides appeared to slope toward ditches with direct connections to the creek, thereby bypassing sedimentation ponds, 3) one feedlot with no treatment system, 4) a small feedlot in the creek bed, 5) feedlot horses being kept in the creek bed (the concentrated horse manure is another source of pollution) and, 6) smaller feedlots (less than 1000 head) with no treatment system and no approved NPDES permit. Note: all feedlots are supposed to use best management practices and not violate State and Federal standards, whether a permit is required or not (Steve Twidwell, Texas Water Commission, personal communication).

Even large feedlots that are regulated by permit for no discharge into the creek can discharge directly into the creek on days when the rainfall criterion has been exceeded. If the area receives substantial rainfall for several days in a row, or a brief torrential downpour as often occurs in this region, the daily limitation can effectively be bypassed.

In Tierra Blanca Creek, episodic pulses of contaminated water would have their maximum impact during low flow conditions in the hottest or coldest months of the year, when fish and wildlife are already in stress from loss of habitat due to low water, higher contaminant concentrations from lack of dilution water, low pH, temperature extremes, ammonia levels at or near toxic levels, a presence of chlorine and nitrites, low oxygen levels, and possibly body burdens of complex mixtures of contaminants.

Bird disease problems, especially avian cholera, can also be influenced by a mixture of stresses. In the case of cholera, the critical time in the Texas High Plains is during the coldest months. Organic pollution from feedlots can reduce water quality and promote disease organisms [133]. Anaerobic environments at feedlot ponds can also enhance conditions conducive to botulism [1].

One potential source of unusual stress for bottom-feeding aquatic birds in parts of the study area is the concentration of several metals in bottom sediments. In spite of the occurrence of high levels of certain metals and some other pollution parameters in the sediments, birds use feedlot waste water ponds and Buffalo Lake National Wildlife Refuge surface waters downstream from the feedlots. At times, feedlot-impacted waters are used heavily by birds, especially when less polluted waters are frozen. The potential effects upon bottom-feeding birds such as shorebirds and waterfowl of ingesting unusually large amounts of various metals while feeding in feedlot (or sewage plant) impacted waters is a concern which has not yet been fully investigated.

In Tierra Blanca Creek below the large cattle feedlots, cumulative aquatic stresses have tended to be recurrent, which probably accounts for the poor condition of the creek and the lack of aquatic life which would be present in a cleaner creek. In this setting, additional episodic effects such as pulses of feedlot-contaminated water (with even higher concentrations of ammonia, nitrites, chemical oxygen demand, biological oxygen demand, re-suspension of bottom sediments during flow increases, or any combination of the above), would contribute significant additional stress.

Data from Site DLB (Appendix 2) confirms previous reports [119] that considerable amounts of nitrogen and phosphorus still remain trapped in the dry lake bed of Buffalo Lake. The Bureau of Reclamation estimated that flooding the lake again would result in movement of enough of these past deposits of nitrogen and phosphorus into the water column to result in unacceptably high concentrations of nitrogen (2.4 mg/l) and phosphorus (5.8 mg/l) [119]. Some efforts have been made to remove excess nutrients in the dry lake bed through farming. However, excess amounts of nutrients, as well as somewhat elevated amounts of aluminum, magnesium, and strontium, continue to be trapped in the soil of the dry lake bed. Much effort would be required to thoroughly remove all the pollution problems of the past from the dry lake bed, and an intense effort to do so would make no sense until the continuing sources of the pollutants are alleviated.

Texas Surface Water Quality Standards Section 307.5(b)(3) states that high quality waters within or adjacent to National Wildlife Refuges are considered Outstanding National Resource Waters. The quality of such waters is to be maintained and protected. Although some of the nutrient pollution problems at Buffalo Lake stem from pre-regulation times, it does not take much leakage, overflow, or illegal pumping into Tierra Blanca Creek to make a large impact on such a small creek. Signs of such problems were observed during field work portions of this study. Data generated in this study is not sufficient to quantify the exact amount of leakage of feedlot wastes into the creek over time. However, significant problems were found. Indications are that the most serious water quality problems were probably caused by feedlots.

Although most of the feedlot waste water controls appear to be helping prevent water pollution in the creek most of the time, this statement could also have been made in 1969 when spills out of only a few of the retention ponds were implicated in fish kills in Buffalo Lake. There are currently many very large feedlots immediately adjacent to many different parts of the creek. Even if the dikes and other pollution controls prevented 99% of the feedlot runoff (from various types of rainfall events) from reaching the creek, the other 1% could still cause water quality problems. As in the 1969 event, leakage or runoff from only part of one big cattle feedlot could still result in significant water quality impacts on the creek and downstream waters in Buffalo Lake National Wildlife Refuge.

RECOMMENDATIONS

Additional studies and working group discussions are recommended to determine the steps that need to be taken to insure good water quality in Tierra Blanca Creek. Participation in these studies and working groups could include experts from the cattle feedlot industry, academia, extension specialists, and government agencies. Some of the questions which need to be addressed in more detail include the following:

Is it sufficient to build simple dirt berms immediately adjacent to creeks? Would the requirements imposed in other states and other countries solve the problems?

Should there be more distance separating the feedlots from the creek? One study showed vegetative strips were helpful in removing runoff pollution [121]:

> A rainfall simulator was used to evaluate the effectiveness of vegetative filter strips for the removal of sediment and phosphorus from feedlot runoff. Simulated rainfall was applied to nine experimental field plots with a 5.5-m by 18.3-m bare source area (simulated feedlot) and either a 0, 4.6-m or 9.1-m filter located at the lower end of each plot. The 9.1-m and 4.6-m vegetative filter strips with shallow uniform flow removed 91 percent and 81 percent of the incoming suspended solids, and 69 percent and 58 percent of the incoming phosphorus, respectively [121].

Do feedlot ponds and dikes need to be lined? It has been argued at least once that playas are better receptacles for feedlot wastes than are excavated basins (or just putting up dikes), since playas have natural clay liners which tend to minimize seepage of contaminants downward into groundwater [133]. However, flooding of feedlot playas often puts contaminated water out beyond the clay bottom.

Should "smaller" feedlots (up to 1,000 head) get additional requirements and/or scrutiny? Sweden regulates feedlots containing as few as 100 head of cattle. It is recommended that consideration be given to keeping concentrations of cattle and horses out of the creek, including small cattle operations and feedlot horses.

To what extent do cattle feed and dust transported by wind contribute to pollution in creeks and wetlands located close to cattle feedlots?.

To what extent do cattle feed and suspended solids transported by precipitation runoff contribute to pollution in creeks and wetlands located close to cattle feedlots?.

Are the current design limitations [holding a 25-year, 24-hour precipitation event (4-5" of rain in those counties)] adequate to protect the creek from specific types of rainfall events which actually occur in this part of Texas? Is it really several inches of rain in a few hours or several rainy days in a row that would be most likely to cause a problem rather than 4-5" in 24 hours? Although settling ponds can reduce solids and oxygen demanding substances from cattle feedlots by one half, effluent from such ponds still contains pollutant concentrations two to three times those of untreated human sewage [139]. Therefore, leakage or overflow of cattle feedlot ponds into creeks is unacceptable.

Once it is determined that the proper design limitations have been identified, how can it be insured that the original design limitations are maintained? Are accumulated solids removed from feedlot waste ponds in the area to consistently maintain adequate freeboard, and if not, how could such maintenance be encouraged or required?

Are manure disposal requirements and guidelines adequate? Is feedlot manure spread on surrounding lands within the drainage basin in a manner which contributes unreasonable amounts of nitrogen and phosphorus to the creek as general non-point source runoff? Should manure distribution and disposal controls required by other countries, such as the Netherlands, Sweden, Denmark, and West Germany [120], be considered for better protection of Tierra Blanca Creek?

If current regulatory requirements are not changed, is there a practical maximum carrying capacity for the number of feedlot cattle per unit area in a watershed?

Would finding additional practical uses for feedlot manure help alleviate water quality problems? In addition to use as a fertilizer, manure can be used in other applications. Cattle feedlot manure has been used to culture shrimp [122]. Investigators at the Fish and Wildlife Service Cooperative Fish and Wildlife Research Center at Texas Tech University in Lubbock have been investigating aquaculture applications of feedlot manure (Nick Parker, U.S. Fish and Wildlife Service, personal communication). Manure has also been burned in some locations as a fuel for power plants.

If finding practical uses for excess manure fails, are other treatment technologies available which would help alleviate environmental problems? Fermentation and digestion methods are among the many technologies that have been used in the past [128,130]. Fecal coliforms can be killed in fermentation technologies [128].

Since at least one recent study suggested that some feed additives (such as monensin and lasalocid) may not always have the desired result [129], and since data presented in the present report suggests a lot of extra copper and zinc is winding up in the waste ponds, are there situations where rations of biologically active feed additives could be reduced? Such reductions might reduce the number and/or quantities of potential contaminants (and their breakdown products) encountered by birds and other biota inhabiting aquatic habitats near feedlots.

To control nuisance aquatic growth and accelerated eutrophication, phosphorus loading in this drainage needs to be abated. Water and sediment samples indicated very high levels of phosphorus, the probable limiting nutrient.

Drought and "relatively wet" cycles lasting several years are common in this part of the High Plains. During dry spells, migratory birds tend to use feedlot and human sewage ponds more intensely, as natural playas tend to be dry. In the last several years, water has seldom flowed down the creek into Buffalo Lake National Wildlife Refuge, and when it has, it has typically been very polluted. Downstream reservoirs and low water dams, even small ones, provide valuable waterfowl and shorebird habitat during wet years, and it would be highly desirable for migratory birds to provide additional, relatively un-polluted habitats in this important part of the central flyway where such habitats are rare.

However, no consideration should be given to constructing additional creek-fed, low water wetlands at Buffalo Lake National Wildlife Refuge until all water quality, lake bed quality, and water supply issues are more fully resolved.

Feedlot owners have been cooperative in Fish and Wildlife Service contaminant studies on the High Plains, and initial discussions between representatives of the Fish and Wildlife Service and the Texas Cattle Feeders Association revealed that the Feeders Association was willing to work with the Service and State agencies on a cooperative basis to better define and correct any water quality problems in Tierra Blanca Creek which may be partially caused by cattle feedlots. As part of this effort, it is recommended that additional monitoring be conducted at various important sites for coliforms, the ratio of total solids to volatile solids, and nutrient parameters. It is specifically recommended that nitrogen and phosphorus compound levels be monitored throughout this drainage and associated groundwater at regular and frequent intervals, especially during rain storm events. Additional monitoring over a longer period of time would help provide a more complete understanding of the types of rainfall events and continued practices which are causing the biggest problems. What types of unusual precipitation events cause feedlot wastes to run or leak into the creek in spite of the controls now in place? Once the most important problem areas and correction factors are more completely identified, later monitoring could determine whether or not corrective factors have brought improvements.

This initial survey and a separate study being conducted on nearby playa lakes identified some metals in high concentrations in feedlot pond sediments. However, the sediments in feedlot ponds have not yet been analyzed for all the potential organic compounds (and breakdown products of these compounds) of possible concern.

Much of the recent news media concern and journal attention has been on suspected carcinogens such as diethylstilbestrol (DES, banned in 1979), feed additive drugs, tranquilizers, and the natural sex hormones estradiol, progesterone, and testosterone (which are implanted in the ears of a large percentage of commercially raised feedlot cattle) [127]. Human health concerns have been raised that, unlike the synthetic DES, residues of which can be monitored and use of which was conditional on a seven-day pre-slaughter withdrawal period, residues of potentially harmful or carcinogenic natural sex hormones estradiol, progesterone, and testosterone are not detectable, since they cannot be practically differentiated from the same hormones produced by the body [127]. From the standpoint of invertebrate, plant, and bird biology, similar problems of analyzing breakdown products and ecological impacts of urinary or fecal residues of drugs, hormones and other feed additives (chlortetracycline, monensin and lasalocid antibiotics, for example) or their breakdown products in feedlot ponds and sediments are also complex. There may be ecological impacts of the breakdown products in cattle feedlot ponds, lagoons, and wetlands impacted by feedlots, although the impacts and breakdown products would not be easy to study. There are also many other biologically active compounds used in the cattle industry, including insecticides, pass-throughs, artificial flavors, and industrial wastes [125,127].

Therefore, it is recommended that additional studies be initiated to determine which of the currently-used feedlot chemicals, and which of their potentially biologically active breakdown products, are accumulating in feedlot pond water and bottom sediments of feedlot ponds. Once these chemicals are identified and quantified, additional studies should be undertaken to determine the degree (if any) that these organic chemicals, in combination with the metals, pathogens, and unbalanced, un-natural diet the birds encounter at the ponds, are affecting migratory birds. More studies also need to be specifically aimed at determining the role that feedlot pond water quality and sediment quality is (or is not) playing in outbreaks of avian cholera in the Texas High Plains.

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APPENDIX 1

SITE LOCATION DETAILS:

Sampling Site	Location
TRB	Deaf Smith County, Texas. Main (south) branch of Tierra Blanca Creek at bridge 4.7 miles SW of Westway, TX. Directions: Three miles west of Westway on blacktop road (1058), then 3.5 miles south of dirt road. Type of site: pool in small, intermittent creek; some feedlots upstream but none very close.
NRB	Deaf Smith County, Texas. Unnamed tributary (north branch?) of Tierra Blanca Creek at HWY 1058 bridge, 1.7 miles west of Westway, TX, 9.7 miles west of Hereford, TX. Type of site: pool in small, intermittent creek; some feedlots upstream but none very close.
HFR	Deaf Smith County, Texas. Tierra Blanca Creek in the center of Hereford, TX, adjacent (South) of the Hereford sewage treatment plant. Type of site: pool in small, intermittent creek; presumably influenced by urban runoff from the town of Hereford as well as upstream sources and, at times, the sewage plant. At the time collections were made, it did not appear that there had been discharges from the sewage plant in the recent past. In fact, the upper lagoons were dry. Note: just downstream of this site, feedlot cattle were in the creek.
TRIS	Deaf Smith County, Texas. Tierra Blanca Creek just east of Hereford, TX, 0.1 miles west of HWY 2943 Bridge. At the time field collections were made, this site was closely bounded on both banks by TriState Cattle Feedyard, and there were signs that there had been discharges of manure-contaminated water from the feedyard into the creek. There was also evidence that cattle feed had gotten into the creek, presumably having been blown there by the wind. Type of site: pool in small, intermittent creek; heavily influenced by adjacent cattle feedlot.
SW	Deaf Smith County, Texas. Wastewater lagoon in TriState Feedyard. Just (0.1 miles) north of the above site (TRIS) there was a dike separating Tierra Blanca Creek from the TriState feedyard and its manure-contaminated nonpoint source runoff. This dike also formed the southern boundary of a manure-water lagoon designed to trap nonpoint source runoff from the feedyard. Site SW was the wastewater lagoon itself, and as such was not part of Tierra Blanca Creek. Type of site: wastewater lagoon in a cattle feedlot.
SR	Deaf Smith County, Texas. Tierra Blanca Creek pool backed up by a low-water dam just south of Smith Ranch. The cement bridge forming this long, narrow pool is 3.8 miles east and 1 mile south of the Hereford, TX, airport. The turnoff to the road going east from the airport is just south of the southern border of the airport; on highway 60, this intersection is 5.6 miles northeast of the intersection of highway 60 and 385. Type of site: long, low-water dam pool in small, intermittent

creek; presumably influenced by the untreated runoff from a small (about 900 head) feedlot just north of the site as well as upstream sources.

SPI Randall County, Texas. Tierra Blanca Creek in the vicinity of the western boundary of Buffalo Lake National Wildlife Refuge. This site is just upstream of where the creek flows into the Stewart Dike Waterfowl Impoundment. Type of site: a small intermittent creek filled with water backed up from a National Wildlife Refuge impoundment. The downstream portion of this site represents the farthest upstream (inflow) area of an open water impoundment of Tierra Blanca Creek. It is therefore presumably influenced by all upstream sites.

SD Randall County, Texas. The middle of Stewart Dike Waterfowl Impoundment in Buffalo Lake National Wildlife Refuge. This site is just downstream of site SPI, in the middle of the impoundment rather than in the creek inflow area as was SPI. Type of site: open water impoundment of Tierra Blanca Creek, presumably influenced by all upstream sites.

PL Deaf Smith County, Texas. Stock pond pit excavated from the middle of Garcia Lake, a large dry playa lake 2 miles north and 1 mile west of Garcia Community. Garcia community is 9.8 miles east of the New Mexico border on highway 1058. Type of site: stock pond pit trampled by cattle.

HS Deaf Smith County, Texas. Tierra Blanca Creek just downstream of Holly Sugar Refinery on the west side of Hereford, TX. This site is just east of the blacktop north/south road bridge 1 mile east of the Holly Sugar facility. Type of site: pool in small, intermittent creek.

DLB Randall County, Texas. Dry lake bed in the middle of Buffalo Lake, Buffalo Lake National Wildlife Refuge. Type of site: soil in dry lake bed.

APPENDIX 2

BUFFALO LAKE NWR CONTAMINANT STUDY - TIERRA BLANCA CREEK DATA
SEDIMENT AND SOIL SAMPLE ANALYSES: MG/KG DRY WEIGHT

NOTE: Samples from site DLB were soil samples from the dry lake bed. All others listed here were sediment samples from aquatic environments.

LOC	SAMPLE #	% MOIST	TKN	NH3-N	ORG.N	NO3-N	ORG.M	TPO4-P
PL	1	34.80	716.0	44.60	671	0.68	3.34	398.0
PL	2	36.10	717.0	48.70	668	0.52	3.50	393.0
PL	3	31.00	707.0	42.60	750	0.51	3.06	398.0
PL	AVG	33.97	713.3	45.30	696	0.57	3.30	396.3
NRB	1	36.50	1790.0	70.40	1720	4.89	5.13	463.0
NRB	2	35.20	1370.0	56.20	1320	4.39	4.93	512.0
NRB	3	34.50	1720.0	65.20	1650	11.80	4.85	485.0
NRB	AVG	35.40	1626.7	63.93	1563	7.03	4.97	486.7
TRB	1	33.90	1130.0	25.60	1100	2.96	3.65	270.0
TRB	2	35.30	1140.0	37.10	1100	3.08	3.72	343.0
TRB	3	37.80	1010.0	13.50	996	2.35	3.91	295.0
TRB	AVG	35.67	1093.3	25.40	1065	2.80	3.76	302.7
HS	1	48.80	2880.0	78.70	2800	8.83	5.79	3130.0
HS	2	48.30	2400.0	71.80	2330	12.00	5.71	3120.0
HS	3	47.30	2760.0	82.70	2680	13.20	5.90	3230.0
HS	AVG	48.13	2680.0	77.73	2603	11.34	5.80	3160.0
HFR	1	32.40	2380.0	46.90	2330	23.20	5.26	835.0
HFR	2	32.50	2050.0	41.60	2010	20.80	5.61	840.0
HFR	3	32.80	2330.0	34.10	2300	15.70	5.61	820.0
HFR	AVG	32.57	2253.3	40.87	2213	19.90	5.49	831.7
TRIS	1	47.40	5950.0	213.00	5740	40.00	12.90	2580.0
TRIS	2	49.50	8720.0	175.00	8540	45.00	12.80	2330.0
TRIS	3	47.00	8490.0	257.00	8230	46.50	12.70	2600.0
TRIS	AVG	47.97	7720.0	215.00	7503	43.83	12.80	2503.3
SR	1	55.90	2610.0	152.00	2460	3.63	6.51	543.0
SR	2	52.10	2530.0	142.00	2390	2.05	6.31	578.0
SR	3	52.00	2370.0	156.00	2210	1.36	6.27	633.0
SR	AVG	53.33	2503.3	150.00	2353	2.35	6.36	584.7
SPI	1	45.30	2450.0	60.30	2390	4.90	8.41	860.0
SPI	2	45.80	2690.0	51.80	2640	6.00	9.05	868.0
SPI	3	46.40	2250.0	43.50	2210	5.18	9.08	475.0
SPI	AVG	45.83	2463.3	51.87	2413	5.36	8.85	734.3
SD	1	57.60	2610.0	249.00	2360	0.96	8.14	1110.0
SD	2	58.50	2430.0	240.00	2190	3.11	8.11	1100.0
SD	3	57.30	2430.0	220.00	2210	1.42	7.63	1130.0
SD	AVG	57.80	2490.0	236.33	2253	1.83	7.96	1113.3

SEDIMENT AND SOIL SAMPLE ANALYSES: MG/KG DRY WEIGHT

LOC	SAMPLE #	%MOIST	TKN	NH3-N	ORG.N	NO3-N	ORG.M	TPO4-P
DLB	1	40.80	1210.0	5.79	1200	2.52	4.94	640.0
DLB	2	31.20	1490.0	1.61	1490	4.90	5.13	708.0
DLB	3	27.00	1260.0	1.67	1250	10.60	5.73	878.0
DLB	4	25.80	1660.0	1.54	1660	10.10	4.56	750.0
DLB	AVG	31.20	1405.0	2.65	1400	7.03	5.09	744.0
SW	1	68.90	22500.0	1950.00	20600	1.59	44.90	16000.0
SW	2	68.30	23400.0	1710.00	21700	0.65	42.90	15300.0
SW	3	69.60	26200.0	1820.00	24400	0.67	46.40	13500.0
SW	AVG	68.93	24033.3	1826.67	22233	0.97	44.73	14933.3

LOC	SAMPLE #	SOL.T.P	COD	Al	Ba	Be	Cr
PL	1	3.84	22500.0	8990.0	156.0	0.69	9.1
PL	2	3.37	24300.0	7340.0	152.0	0.65	7.5
PL	3	3.33	22100.0	7890.0	149.0	0.70	8.0
PL	AVG	3.51	22966.7	8073.3	152.3	0.68	8.2
NRB	1	12.50	39900.0	7320.0	134.0	0.70	7.8
NRB	2	10.60	41200.0	7910.0	136.0	0.70	8.2
NRB	3	10.40	41200.0	7560.0	140.0	0.69	8.0
NRB	AVG	11.17	40766.7	7596.7	136.7	0.70	8.0
TRB	1	5.10	21300.0	8670.0	157.0	0.74	8.6
TRB	2	2.81	22900.0	9070.0	162.0	0.81	8.8
TRB	3	2.34	25300.0	11000.0	170.0	0.84	10.0
TRB	AVG	3.42	23166.7	9580.0	163.0	0.80	9.1
HS	1	13.70	73800.0	4210.0	86.0	0.32	4.8
HS	2	19.00	70400.0	4680.0	89.0	0.37	4.9
HS	3	12.20	67300.0	4520.0	85.0	0.35	4.7
HS	AVG	14.97	70500.0	4470.0	86.7	0.35	4.8
HFR	1	7.80	55500.0	9570.0	195.0	0.75	11.0
HFR	2	7.56	53500.0	9590.0	202.0	0.73	12.0
HFR	3	8.60	57400.0	10700.0	204.0	0.79	12.0
HFR	AVG	7.99	55466.7	9953.3	200.3	0.76	11.7
TRIS	1	56.60	146000.0	8720.0	226.0	0.68	9.8
TRIS	2	508.00	148000.0	8390.0	228.0	0.68	9.5
TRIS	3	45.70	149000.0	8110.0	237.0	0.69	9.3
TRIS	AVG	203.43	147666.7	8406.7	230.3	0.68	9.5
SR	1	3.40	65000.0	13400.0	203.0	0.90	11.0
SR	2	3.19	39700.0	12200.0	197.0	0.82	10.0
SR	3	3.14	65000.0	11800.0	199.0	0.79	9.7
SR	AVG	3.24	56566.7	12466.7	199.7	0.84	10.2

SEDIMENT AND SOIL SAMPLE ANALYSES: MG/KG DRY WEIGHT

LOC	SAMPLE #	SOL.T.P	COD	Al	Ba	Be	Cr
SPI	1	13.70	97900.0	13900.0	212.0	1.20	13.0
SPI	2	21.10	78000.0	14600.0	217.0	1.20	14.0
SPI	3	18.00	85800.0	14900.0	214.0	1.20	14.0
SPI	AVG	17.60	87233.3	14466.7	214.3	1.20	13.7
SD	1	9.26	76800.0	14900.0	235.0	1.10	13.0
SD	2	6.30	82100.0	13400.0	226.0	1.10	12.0
SD	3	29.60	74700.0	13900.0	229.0	1.10	12.0
SD	AVG	15.05	77866.7	14066.7	230.0	1.10	12.3
DLB	1	3.75	30500.0	13500.0	259.0	0.89	11.0
DLB	2	6.50	35400.0	12300.0	228.0	0.81	10.0
DLB	3	7.77	39700.0	9750.0	163.0	0.81	9.6
DLB	4	10.40	37800.0	10700.0	179.0	0.85	9.8
DLB	AVG	7.11	35850.0	11562.5	207.3	0.84	10.1
SW	1	645.00	730000.0	3630.0	174.0	0.20	6.5
SW	2	559.00	730000.0	3670.0	171.0	0.19	5.9
SW	3	596.00	668000.0	3280.0	164.0	0.19	5.8
SW	AVG	600.00	709333.3	3526.7	169.7	0.19	6.1

LOC	SAMPLE #	Cu	Fe	Pb	Mg	Mn	Ni	Sr
PL	1	10.0	8820.0	10.0	2750.0	311.0	11.0	55.0
PL	2	9.3	7200.0	7.6	2490.0	306.0	9.6	56.0
PL	3	9.4	7840.0	9.2	2560.0	304.0	10.0	54.0
PL	AVG	9.6	7953.3	8.9	2600.0	307.0	10.2	55.0
NRB	1	9.9	7130.0	12.0	2560.0	330.0	9.4	53.0
NRB	2	10.0	7700.0	14.0	2700.0	337.0	10.0	53.0
NRB	3	10.0	7390.0	10.0	2700.0	346.0	9.3	56.0
NRB	AVG	10.0	7406.7	12.0	2653.3	337.7	9.6	54.0
TRB	1	10.0	8680.0	11.0	2560.0	279.0	11.0	62.0
TRB	2	10.0	8990.0	8.7	2640.0	278.0	11.0	63.0
TRB	3	11.0	11200.0	11.0	2890.0	282.0	12.0	65.0
TRB	AVG	10.3	9623.3	10.2	2696.7	279.7	11.3	63.3
HS	1	25.0	3460.0	*2.5	5470.0	220.0	3.3	383.0
HS	2	26.0	3760.0	*2.5	5610.0	229.0	3.5	374.0
HS	3	25.0	3680.0	*2.5	5340.0	220.0	2.8	380.0
HS	AVG	25.3	3633.3	*2.5	5473.3	223.0	3.2	379.0
HFR	1	19.0	8960.0	29.0	6360.0	219.0	10.0	148.0
HFR	2	19.0	9040.0	31.0	6420.0	225.0	10.0	150.0
HFR	3	20.0	9400.0	31.0	6990.0	223.0	10.0	170.0
HFR	AVG	19.3	9133.3	30.3	6590.0	222.3	10.0	156.0

SEDIMENT AND SOIL SAMPLE ANALYSES: MG/KG DRY WEIGHT

LOC	SAMPLE #	Cu	Fe	Pb	Mg	Mn	Ni	Sr
TRIS	1	25.0	7670.0	18.0	7690.0	207.0	8.4	209.0
TRIS	2	26.0	7480.0	19.0	7840.0	206.0	8.6	212.0
TRIS	3	29.0	7390.0	18.0	7920.0	223.0	8.0	226.0
TRIS	AVG	26.7	7513.3	18.3	7816.7	212.0	8.3	215.7
SR	1	12.0	11600.0	15.0	19100.0	310.0	11.0	517.0
SR	2	12.0	9300.0	15.0	18900.0	294.0	11.0	524.0
SR	3	12.0	9150.0	15.0	18900.0	287.0	10.0	538.0
SR	AVG	12.0	10016.7	15.0	18966.7	297.0	10.7	526.3
SPI	1	17.0	13200.0	19.0	5800.0	381.0	14.0	131.0
SPI	2	18.0	13800.0	22.0	5930.0	388.0	15.0	133.0
SPI	3	17.0	1400.0	19.0	5930.0	386.0	15.0	132.0
SPI	AVG	17.3	9466.7	20.0	5886.7	385.0	14.7	132.0
SD	1	17.0	13600.0	19.0	7550.0	420.0	15.0	216.0
SD	2	16.0	12400.0	15.0	6970.0	407.0	14.0	205.0
SD	3	16.0	12900.0	16.0	7460.0	420.0	14.0	217.0
SD	AVG	16.3	12966.7	16.7	7326.7	415.7	14.3	212.7
DLB	1	12.0	12200.0	13.0	17400.0	376.0	12.0	626.0
DLB	2	12.0	11600.0	15.0	16400.0	402.0	12.0	605.0
DLB	3	11.0	8830.0	13.0	7940.0	380.0	11.0	192.0
DLB	4	13.0	9450.0	16.0	9210.0	373.0	12.0	295.0
DLB	AVG	12.0	10520.0	14.3	12737.5	382.8	11.8	429.5
SW	1	90.0	3380.0	6.1	14400.0	332.0	6.5	310.0
SW	2	81.0	3160.0	5.1	14500.0	305.0	5.8	300.0
SW	3	88.0	2890.0	5.2	14300.0	324.0	5.9	302.0
SW	AVG	86.3	3143.3	5.5	14400.0	320.3	6.1	304.0

SEDIMENT AND SOIL SAMPLE ANALYSES: MG/KG DRY WEIGHT

LOC	SAMPLE #	V	Zn	LOC	SAMPLE #	V	Zn
PL	1	11.0	26.0	TRIS	1	14.0	128.0
PL	2	11.0	23.0	TRIS	2	15.0	129.0
PL	3	11.0	24.0	TRIS	3	16.0	139.0
PL	AVG	11.0	24.3	TRIS	AVG	15.0	132.0
NRB	1	9.9	28.0	SR	1	22.0	42.0
NRB	2	9.6	29.0	SR	2	21.0	40.0
NRB	3	11.0	28.0	SR	3	22.0	39.0
NRB	AVG	10.2	28.3	SR	AVG	21.7	40.3
TRB	1	15.0	25.0	SPI	1	17.0	53.0
TRB	2	15.0	26.0	SPI	2	16.0	56.0
TRB	3	16.0	29.0	SPI	3	15.0	55.0
TRB	AVG	15.3	26.7	SPI	AVG	16.0	54.7
HS	1	11.0	30.0	SD	1	15.0	53.0
HS	2	12.0	32.0	SD	2	14.0	50.0
HS	3	11.0	30.0	SD	3	15.0	49.0
HS	AVG	11.3	30.7	SD	AVG	14.7	50.7
HFR	1	15.0	82.0	DLB	1	17.0	36.0
HFR	2	15.0	85.0	DLB	2	16.0	37.0
HFR	3	15.0	95.0	DLB	3	8.6	35.0
HFR	AVG	15.0	87.3	DLB	4	14.0	40.0
				DLB	AVG	13.9	37.0
				SW	1	12.0	538.0
				SW	2	13.0	491.0
				SW	3	12.0	528.0
				SW	AVG	12.3	519.0

Note: the organic analyses showed only anecdotal elevations of organic contaminants; these are covered in the text and not repeated in these tables.

TISSUE CONCENTRATIONS IN MG/KG DRY WEIGHT

LOC	ORGANISM	TISSUE	% MOIST	Al	Be	Cd	Cr
PL	Y.M.TURT	LIVER	67.40	*0.70	*0.0215	*0.0410	*0.4650
PL	Y.M.TURT	LIVER	76.70	*1.05	*0.0310	1.7000	*0.7000
PL	TIG.SALA	WHOL.BOD	88.20	133.00	*0.0215	0.1600	2.0000
PL	TIG.SALA	WHOL.BOD	87.30	681.00	*0.0215	0.1900	2.0000
PL	TIG.SALA	WHOL.BOD	87.00	771.00	0.1300	0.1400	1.8000
SR	CRAYFISH	WHOL.BOD	73.00	298.00	0.1100	0.2700	1.8000
SR	CRAYFISH	WHOL.BOD	75.20	367.00	0.1900	0.3900	1.9000
SR	CRAYFISH	WHOL.BOD	76.00	399.00	*0.0215	0.2900	1.7000
SPI	Y.M.TURT	LIVER	68.90	*0.70	*0.0215	0.6400	*0.4650
SPI	Y.M.TURT	LIVER	70.70	*0.70	*0.0215	0.3800	*0.4650
SPI	Y.M.TURT	LIVER	68.10	*0.70	*0.0215	0.3100	*0.4650
SPI	Y.M.TURT	LIVER	66.80	*0.70	*0.0215	0.7600	*0.4650
SPI	B.BULLHE	WHOL.BOD	77.30	28.00	*0.0215	0.5800	1.1000
SPI	R.W.BLAC	WHOL.BOD[1]	70.30	59.00	*0.0215	*0.0410	1.3000
SD	COOT	LIVER	74.00	16.00	*0.0215	2.1000	*0.4650
SD	COOT	LIVER	73.00	13.00	*0.0215	0.2700	*0.4650
SD	COOT	LIVER	75.30	12.00	*0.0215	0.8000	*0.4650

[1]Redwing blackbird whole body samples were modified by removing the beak, legs, and large feathers.

TISSUE CONCENTRATIONS IN MG/KG DRY WEIGHT

LOC	ORGANISM	TISSUE	Cu	Fe	Ni	Pb	Zn
PL	Y.M.TURT	LIVER	4.40	314.0	1.000	*0.290	42.0
PL	Y.M.TURT	LIVER	7.50	453.0	0.840	*0.430	85.0
PL	TIG.SALA	WHOL.BOD	4.40	280.0	0.600	0.600	85.0
PL	TIG.SALA	WHOL.BOD	4.60	497.0	0.870	*0.290	73.0
PL	TIG.SALA	WHOL.BOD	4.10	554.0	0.870	*0.290	57.0
SR	CRAYFISH	WHOL.BOD	49.00	175.0	1.200	*0.290	71.0
SR	CRAYFISH	WHOL.BOD	53.00	226.0	1.500	0.990	71.0
SR	CRAYFISH	WHOL.BOD	40.00	224.0	1.300	*0.290	69.0
SPI	Y.M.TURT	LIVER	9.30	2250.0	0.370	*0.290	61.0
SPI	Y.M.TURT	LIVER	8.80	1160.0	0.470	*0.290	52.0
SPI	Y.M.TURT	LIVER	5.50	496.0	0.230	*0.290	36.0
SPI	Y.M.TURT	LIVER	6.60	435.0	0.470	*0.290	40.0
SPI	B.BULLHE	WHOL.BOD	3.10	71.0	0.470	*0.290	87.0
SPI	R.W.BLAC	WHOL.BOD	9.10	260.0	0.440	221.000	84.0
SD	COOT	LIVER	62.00	563.0	0.330	0.620	161.0
SD	COOT	LIVER	59.00	1260.0	0.300	0.290	192.0
SD	COOT	LIVER	68.00	746.0	0.570	0.620	192.0

TISSUE CONCENTRATIONS IN MG/KG DRY WEIGHT

LOC	ORGANISM	TISSUE	Se	Hg
PL	Y.M.TURT	LIVER	1.100	0.330
PL	Y.M.TURT	LIVER	ISV	ISV
PL	TIG.SALA	WHOL.BOD	1.400	0.970
PL	TIG.SALA	WHOL.BOD	0.920	0.500
PL	TIG.SALA	WHOL.BOD	0.850	0.390
SR	CRAYFISH	WHOL.BOD	0.560	0.100
SR	CRAYFISH	WHOL.BOD	1.400	0.100
SR	CRAYFISH	WHOL.BOD	1.100	0.050
SPI	Y.M.TURT	LIVER	4.700	1.800
SPI	Y.M.TURT	LIVER	3.200	1.400
SPI	Y.M.TURT	LIVER	2.100	0.920
SPI	Y.M.TURT	LIVER	1.400	0.490
SPI	B.BULLHE	WHOL.BOD	1.400	0.120
SPI	R.W.BLAC	WHOL.BOD	1.600	0.160
SD	COOT	LIVER	2.900	1.500
SD	COOT	LIVER	2.500	1.000
SD	COOT	LIVER	3.500	0.340

Note: the organic analyses showed only anecdotal elevations of organic contaminants; these are covered in the text and not repeated in these tables.

WATER SAMPLE ANALYSES

LOC	SAMPLE	TEMP (°C)	pH	DO (mg/l)	µmhos (/cm)	T.ALK (mg/l)	NH3-N (mg/l)	TKN (mg/l)	CHLORIDE (mg/l)
PL	1	20.6	7.8	7.1	269	118.0	0.200	2.00	*2.50
PL	2					121.0	0.220	2.00	*
PL	3					113.0	0.160	1.50	*
PL	AVG	–	–	–	–	117.3	0.193	1.83	* –
NRB	1	27.4	7.6	0.9	364	134.0	1.480	5.30	4.00
NRB	2					137.0	1.430	5.40	4.00
NRB	3					135.0	1.480	5.10	4.00
NRB	AVG	–	–	–	–	135.3	1.463	5.27	4.00
TRB	1	20.9	7.9	3.4	177	43.0	0.490	2.80	*2.50
TRB	2					41.0	0.440	2.50	*
TRB	3					30.0	0.470	2.70	*
TRB	AVG	–	–	–	–	38.0	0.467	2.67	* –
HFR	1	30.5	7.8	3.8	255	92.0	1.290	3.00	*2.50
HFR	2					91.0	1.280	3.10	*
HFR	3					97.0	1.250	2.90	*
HFR	AVG	–	–	–	–	93.3	1.273	3.00	* –
TRIS	1	21.8	7.6	0.8	667	261.0	0.140	8.00	37.00
TRIS	2					261.0	0.260	9.40	36.00
TRIS	3					259.0	0.130	7.70	36.00
TRIS	AVG	–	–	–	–	260.3	0.177	8.37	36.33
SR	1	20.7	7.6	5.2	430	146.0	2.150	5.60	22.00
SR	2					146.0	2.120	5.60	22.00
SR	3					145.0	2.140	5.60	22.00
SR	AVG	–	–	–	–	145.7	2.137	5.60	22.00
SPI	1		7.3		297	103.0	0.840		2.50
SD	1	22.9	8.4	3.8	377	136.0	0.510	1.30	15.00
SD	2					141.0	0.520	1.60	14.00
SD	3					144.0	0.520	1.63	15.00
SD	AVG	–	–	–	–	140.3	0.517	1.51	14.67

WATER SAMPLE ANALYSES

LOC	SAMPLE	NO3-N (mg/l)	NO2-N (mg/l)	SO4 (mg/l)	TPO4-P (mg/l)	ORTH-P (mg/l)	TOC (mg/l)	TSS (mg/l)	VSS (mg/l)
PL	1	1.380	0.010	6.0	0.180	0.010	13.30	78.0	6.0
PL	2	1.380	0.012	7.0	0.200	0.020	17.00	50.0	6.0
PL	3	1.390	0.009	9.0	0.190	0.010	12.60	84.0	4.0
PL	AVG	1.383	0.010	7.3	0.190	0.013	14.30	70.7	5.3
NRB	1	*0.010	0.020	10.0	0.570	1.440	25.40	173.0	13.0
NRB	2	*0.010	0.019	10.0	0.470	1.200	25.70	138.0	16.0
NRB	3	*0.010	0.021	11.0	0.490	1.200	25.20	144.0	29.0
NRB	AVG	*0.010	0.020	10.3	0.510	1.280	25.43	151.7	19.3
TRB	1	0.880	0.107	15.0	0.220	0.440	12.10	84.0	3.0
TRB	2	0.880	0.105	10.0	0.180	0.440	9.60	130.0	14.0
TRB	3	0.920	0.105	17.0	0.160	0.450	12.10	134.0	3.0
TRB	AVG	0.893	0.106	14.0	0.187	0.443	11.27	116.0	6.7
HFR	1	0.060	0.023	12.0	0.220	0.430	10.20	110.0	16.0
HFR	2	0.020	0.045	13.0	0.170	0.370	10.50	200.0	24.0
HFR	3	*0.010	0.019	12.0	0.670	0.510	10.40	57.0	8.0
HFR	AVG	0.030	0.029	12.3	0.353	0.437	10.37	122.3	16.0
TRIS	1	0.020	0.006	22.0	6.400	5.040	35.20	108.0	56.0
TRIS	2	0.030	0.006	19.0	6.320	5.020	33.00	82.0	50.0
TRIS	3	0.020	0.006	18.0	6.280	5.010	35.40	72.0	36.0
TRIS	AVG	0.023	0.006	19.7	6.333	5.023	34.53	87.3	47.3
SR	1	0.170	0.094	25.0	0.900	2.210	25.10	74.0	20.0
SR	2	0.170	0.091	63.0	0.950	2.070	24.60	68.0	10.0
SR	3	0.180	0.093	47.0	0.890	2.450	24.50	88.0	20.0
SR	AVG	0.173	0.093	45.0	0.913	2.243	24.73	76.7	16.7
SPI	1	0.030		22.0	1.000	0.920	13.80	68.0	28.0
SD	1	0.020	0.018	38.0	1.170	1.060	15.50	4.0	1.0
SD	2	0.030	0.017	28.0	1.170	1.080	27.80	1.0	1.0
SD	3	0.040	0.018	30.0	1.170	1.060	13.60	2.0	2.0
SD	AVG	0.030	0.018	32.0	1.170	1.067	18.97	2.3	1.3

WATER SAMPLE ANALYSES

LOC	SAMPLE	COD (mg/l)	Ca (mg/l)	TDS (mg/l)	COLI (#/100 ml)	CHLO-A (μg/l)	PHEO (μg/l)	BOD (mg/l)	Mg (mg/l)
PL	1	45.0	35.50	180.0	1100	9.90	3.80	2.0	4.00
PL	2	45.0	35.10	188.0		12.70	1.00	3.0	4.00
PL	3	42.0	35.70	128.0		10.00	3.90	2.0	4.00
PL	AVG	44.0	35.43	165.3	1100	10.87	2.90	2.3	4.00
NRB	1	90.0	30.40	516.0	500	6.50	*0.10	8.0	7.90
NRB	2	90.0	30.90	498.0		2.90	*0.10	8.0	
NRB	3	105.0	30.30	474.0		5.90	*0.10	8.0	7.80
NRB	AVG	95.0	30.53	496.0	500	5.10	*0.10	8.0	7.85
TRB	1	45.0	18.30	130.0	900	1.50	*0.10	3.0	4.40
TRB	2	48.0	16.30	156.0		*0.10	*0.10	3.0	3.70
TRB	3	48.0	17.20	134.0		1.70	*0.10	2.0	3.90
TRB	AVG	47.0	17.27	140.0	900	1.10	*0.10	2.7	4.00
HFR	1	39.0	34.60	226.0		19.00	*0.10	6.0	3.50
HFR	2	39.0	37.50	238.0		23.00	*0.10	8.0	3.90
HFR	3	39.0	37.20	208.0		7.60	*0.10	5.0	4.00
HFR	AVG	39.0	36.43	224.0		16.53	*0.10	6.3	3.80
TRIS	1	212.0	43.30	456.0		331.70	28.00	27.0	15.20
TRIS	2	171.0	43.50	450.0		310.90	49.80	31.0	15.80
TRIS	3	162.0	44.10	432.0		315.80	15.10	27.0	15.60
TRIS	AVG	181.7	43.63	446.0		319.47	30.97	28.3	15.53
SR	1	81.0	30.80	388.0	1600	34.50	*0.10	9.0	9.10
SR	2	78.0	31.00	334.0		29.00	9.00	8.0	8.90
SR	3	81.0	31.80	354.0		34.10	0.40	8.0	9.00
SR	AVG	80.0	31.20	358.7	1600	32.53	3.17	8.3	9.00
SPI	1	-	-	-	-	21.70	10.40	8.0	-
SD	1	36.0	29.90	244.0	900	1.10	*0.10	2.0	8.00
SD	2	39.0	30.00	280.0		3.10	*0.10	2.0	8.00
SD	3	39.0	29.80	304.0		3.50	*0.10	2.0	8.10
SD	AVG	38.0	29.90	276.0	900	2.57	*0.10	2.0	8.03

* Values denoted with an asterisk were actually non-detected. The value placed in the table represents one half the detection limit. This convention is often used for statistical manipulation of data which contains unknown concentrations which are lower than the detection limits (Christine Bunck, Statistician at Patuxent Wildlife Research Center, Fish and Wildlife Service, Patuxent Maryland, personal communication).

APPENDIX 3

CONVERSION TABLE FOR CHANGING CONDUCTIVITY* INTO SALINITY TEMPERATURE °C

SALINITY 0/00	0	5	10	15	20	25	30
1	1,200	1,400	1,500	1,700	2,000	2,200	2,400
2	2,200	2,500	2,900	3,300	3,700	4,100	4,500
3	3,200	3,700	4,200	4,700	5,300	5,900	6,500
4	4,100	4,700	5,400	6,100	6,900	7,600	8,400
5	5,000	5,800	6,600	7,500	8,400	9,300	10,300
6	5,900	6,800	7,900	8,800	9,900	11,000	12,100
7	6,700	7,800	8,900	10,100	11,300	12,600	13,900
8	7,600	8,800	10,100	11,400	12,800	14,200	15,700
9	8,500	9,800	11,200	12,700	14,200	15,800	17,400
10	9,300	10,800	12,300	13,900	15,600	17,300	19,100
11	10,200	11,800	13,400	15,200	17,000	18,900	20,800
12	11,000	12,800	14,500	16,400	18,400	20,400	22,500
13	11,900	13,700	15,600	17,600	19,700	21,900	24,100
14	12,600	14,600	16,700	18,900	21,100	23,400	25,800
15	13,400	15,600	17,800	20,100	22,400	24,900	27,400
16	14,200	16,400	18,800	21,200	23,800	26,400	29,100
17	15,000	17,400	19,800	22,400	25,100	27,800	30,700
18	15,800	18,300	20,900	23,600	26,400	29,300	32,300
19	16,600	19,200	21,900	24,800	27,700	30,700	33,900
20	17,400	20,100	23,000	25,900	29,000	32,200	35,500
21	18,200	21,100	24,000	27,100	30,300	33,600	37,000
22	19,000	22,000	25,100	28,300	31,600	35,000	38,600
23	19,800	22,900	26,100	29,400	32,900	36,500	40,100
24	20,600	23,800	27,100	30,600	34,200	37,900	41,700
25	21,400	24,700	28,100	31,700	35,400	39,300	43,200
26	22,100	25,500	29,100	32,800	36,700	40,700	44,800
27	22,800	26,400	30,100	33,900	37,900	42,100	46,300
28	23,600	27,300	31,100	35,100	39,200	43,500	47,800
29	24,400	28,100	32,100	36,200	40,400	44,800	49,400
30	25,200	29,000	33,100	37,300	41,700	46,200	50,900
31	26,000	30,000	34,100	38,500	43,000	47,600	52,400
32	26,800	30,900	35,100	39,600	44,200	49,000	53,900
33	27,500	31,700	36,100	40,700	45,400	50,300	55,400
34	28,300	32,600	37,100	41,800	46,700	51,700	56,800
35	29,100	33,500	38,100	42,900	47,900	53,000	58,300
36	29,700	34,200	39,000	44,000	49,100	54,400	59,800
37	30,500	35,100	40,000	45,100	50,300	55,700	61,300
38	31,200	36,000	41,000	46,200	51,500	57,100	62,800
39	32,000	36,800	41,900	47,200	52,700	58,400	64,200
40	32,700	37,700	42,900	48,300	53,900	59,700	65,700

*Conductivity values are given in micromhos/cm = μmhos/cm = μSiemans/cm = μS/cm (different ways of expressing the same thing).

The above table of salinity/conductivity conversions at various centigrade temperatures is supplied with LaMotte Conductivity Meters and copied with their permission (Steve Wildburger, LaMotte Chemical Products Company, Chestertown, Maryland, personal communication). LaMotte derived the chart from an equation of P.K. Weyl. 1964, Limnology and Oceanography, **9**:75-77 [98].

Note: a similar but less detailed conversion chart for seawater was published by Horne in his text on marine chemistry [99].