WATER QUALITY AND SEDIMENTS OF AN AREA RECEIVING ACID-MINE DRAINAGE IN NORTHEASTERN OKLAHOMA

By

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PREFACE

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CHAPTER I

INTRODUCTION

Surfacing mine water has impacted Tar Creek, located in Ottawa County, Oklahoma (OWRB, 1983). In December 1980, enactment of Comprehensive Environmental Response, Compensation, and Liability Act (Superfund) provided funding for cleanup of hazardous wastes sites. Superfund provides immediate funds for clean up of sites ranked by a national interagency committee as hazardous to human health and environmental quality. The extent of the toxic metal contamination in the water that flooded abandoned mineshafts in the Picher field and the potential threat to domestic groundwater supplies placed Tar Creek near the top of hazardous waste sites nationally.

The Picher field underlies the Tar Creek drainage area and approximately 1,028 ha are undermined by lead-zinc mines (OWRB, personal communication). Many of the mineshafts are connected throughout the mining field and presently contain approximately 96,000,000 m^3 of contaminated water. During the mining operations, inflow of water from surface runoff and groundwater into the mines necessitated pumping to keep the mines in operation. The pumped water and other metal contaminated water was released, resulting in the elimination of fishes along stretches of Spring River (Ellis, 1939). Prior to impoundment of the Grand River (Neosho River), Ellis (1939) recognized that "... the mine-field wastes, entering the Pensacola impoundment via Spring River constitute perhaps the greatest single pollution hazard to fish and other aquatic life in the completed reservoir." Similar concerns were expressed about pumping mine-water into the Neosho and Spring rivers after impoundment (Mitchell, 1942). Mining activities had all but ceased by late 1950's and the abandoned mines began to fill with water.

In November 1979, the level of water in the mine shafts formed artesian springs at several locations. These artesian waters had low pH and high dissolved metals. The primary contaminants were iron and zinc, with lead and cadmium at lower concentrations; which severly impacted Tar Creek and eliminated almost all 'normal' aquatic life. Waters from Tar Creek at several locations have shown significant mortality and teratagenic acitivity in FETAX studies attributed to the elevated quantities of metals (Dawson et al., 1985). Tar Creek empties into the Neosho River approximately 16 km upstream of Grand Lake. Large quantities of iron hydroxide precipitate on the stream bottom of Tar Creek. During high flow, most of the unconsolidated sediment and associated metals are transported into the Neosho River and ultimately into Grand Lake. The upper reaches of Grand Lake occurs at the confluence of Spring and Neosho rivers. Spring River flows southward on the eastern boundary of the Picher Mining Field and also receives an unknown quantity of mine discharge water from a site southeast of Quapaw, Oklahoma (personal observation).

Historical physicochemical data for Grand Lake, Neosho River, and Spring River are not available. Grand Lake is managed by the Grand River Dam Authority and little or no baseline water quality data have been gathered.

The occurrence and chemistry of metals in Tar Creek, Neosho River, and Grand Lake are not well understood. The low solubility of most trace metals suggests that sediments are the major repository. The potential for release of these metals from the sediments of Tar Creek, Neosho River, and Grand Lake is unknown. Additionally, toxicity of metals depends on physicochemical conditions such as hardness and pH. The primary objectives of the study were to:

1. Gather baseline water quality data on Tar Creek, Neosho and Spring rivers, and Grand Lake;
2. Determine total concentration and estimate potential availability of iron, zinc, cadmium, and lead in sediments at the Tar Creek-Neosho River confluence, Neosho River, and Grand Lake;
3. Determine if levels of metals toxic to Daphnia could be released from sediments at the Tar Creek-Neosho River confluence, Neosho River, and Grand Lake;
4. Determine LC50 for available metals if concentrations in test water resulted in mortality.

The null hypotheses tested were:

H_o: There is no increase of iron, lead, zinc, and cadmium in the water column of the Neosho River and Grand Lake.

H_o: There is no significant acid-mine contamination of sediments in the Neosho River and Grand Lake.

H_o: Concentration of biologically available metals from the sediments of Tar Creek-Neosho River confluence, Neosho River, and Grand Lake are not sufficient to result in toxicity to Daphnia.

CHAPTER II

REVIEW OF LITERATURE

Chemistry of Metal Release and Acid Formation

Acid mine seeps and runoff from tailings into Tar Creek have contaminated sediments in lower Neosho River and upper end of Grand Lake with high concentrations of metals from the abandoned lead-zinc mining operations. The extremely high concentrations of metals is due to the oxidation and dissolution of sulfide minerals, e.g. pyrite, galena, marcasite, and sphalerite. Iron and zinc sulfides are the primary minerals that produce the acidity and resulting metals load in the surfacing mine water due to their abundant occurrence (OWRB, 1983).

Sulfides are generally formed in anoxic environments and thus are stable only at reducing conditions. Sulfide orebodies a hundred meters deep can undergo oxidation at even extremely low oxygen concentrations via groundwater (Hawley and Shikaze, 1971). Oxygen at 10^{-60} atmospheres or more is sufficient for pyrite oxidation (Barnes and Romberger, 1968).

The oxidation pathway for iron sulfide (pyrite, marcasite) is typical of the sulfide minerals that result in the release of protons (acidity) and promote solublization of heavy metals. The mining of lead and zinc ores results in exposure of iron sulfide (FeS_2) deposites to oxygen. The FeS_2 reacts with water and oxygen, oxidizing the sulfide to sulfate to form ferrous sulfate ($Fe(II)SO_4$) and sulfuric acid (Figure 1). Ferrous sulfate can then react with oxygen to yield ferric sulfate ($Fe_2(III)(SO_4)_3$). Alternatively, the ferrous sulfate may react with another ferrous sulfate and sulfuric acid to yield ferric sulfate, eliminating the oxygen requirement for this reaction (Stumm and Morgan, 1970). The mine water surfaces and becomes oxygenated (i.e., redox potential becomes more positive) and the $Fe_2(III)(SO_4)_3$ will combine with water to give the amorphous iron hydroxide precipitates ($Fe(OH)_x$) and sulfuric acid. The large quantities of iron hydroxides in Tar Creek are characteristically an orange flocculent precipitate on sediments.

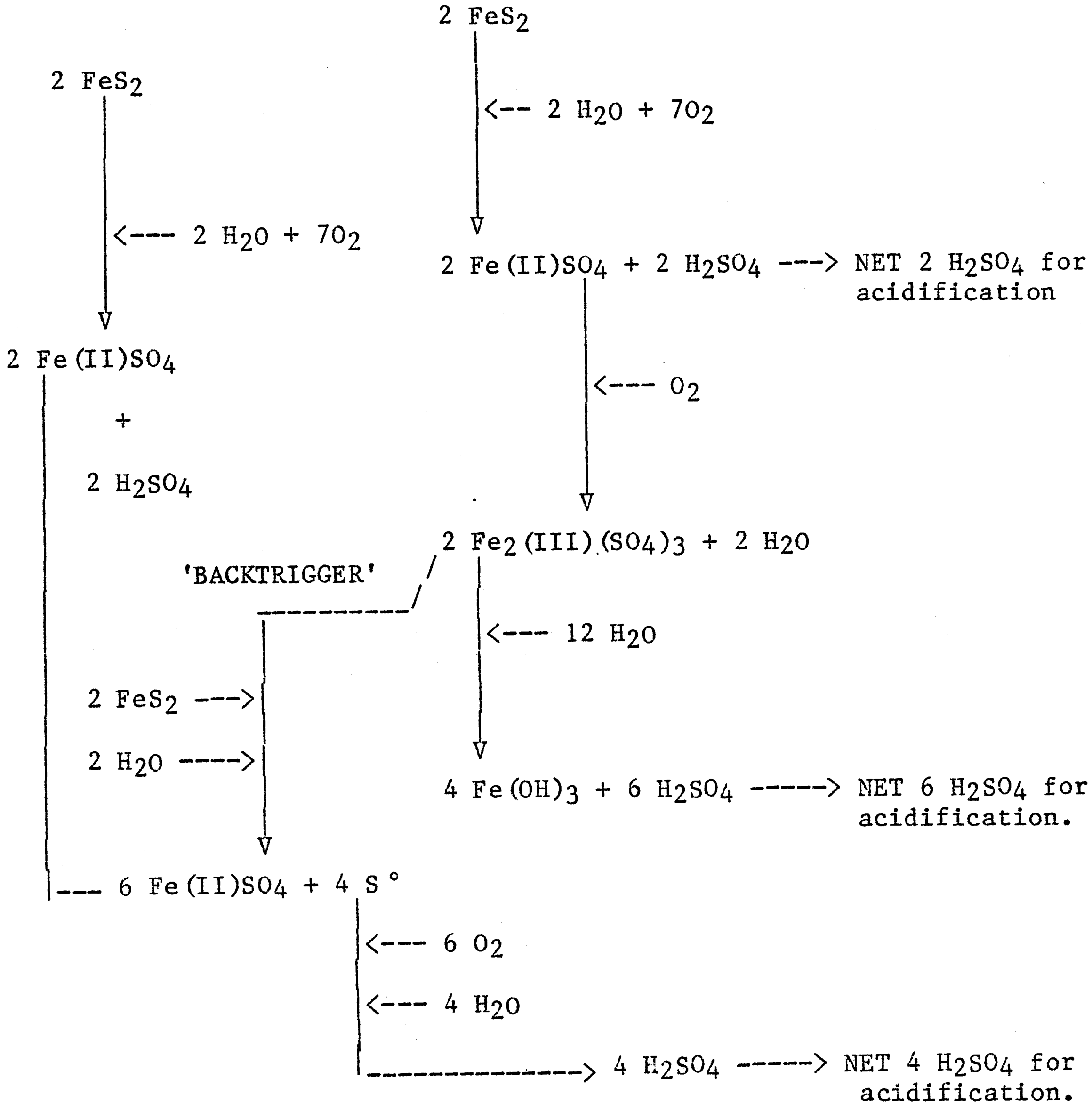
Ferric sulfate in mine waters with low oxygen concentrations may react directly with the ferrous sulfide (FeS_2) ores yeilding ferrous sulfates and eliminating the oxygen requirement. This 'backtrigger' reaction permits the remaining iron sulfides (e.g. pyrite and marcasite) to be oxidized, releasing toxic metals and producing sulfuric acid even in the absence of oxygen (Garrels and Thompson, 1960; Hawley and Shikaze, 1971; Stumm and Morgan, 1970).

The acidity (protons) produced by the sulfide oxidation in the mine shafts and rock fractures elicits changes in the surrounding bedrock. The sulfide ores were formed within the carbonate rocks in the tri-state area and acid (H^+) reacts readily with carbonates. The reaction produces free calcium and magnesium ions and bicarbonate, carbonic acid and carbon dioxide depending on the pH (Loewenthal and Marias, 1976, Drever, 1982). The reaction is,

$$(Ca,Mg)CO_3 + H^+ \text{---->} Ca^{2+},Mg^{2+} + HCO_3^- \qquad (1)$$

$$HCO_3^- + H^+ \text{---->} H_2CO_3 \text{---->} CO_2 + H_2O \qquad (2)$$

Figure 1. Summary of chemical reactions of iron sulfide with oxygen and water. (From Krauskopf, 1979; Stumm and Morgan, 1970; Barnes and Romberger, 1968)


2 FeS_2
<--- 2 H_2O + 7O_2
2 Fe(II)SO_4 + 2 H_2SO_4 ---> NET 2 H_2SO_4 for acidification
<--- O_2
2 Fe_2(III)(SO_4)$_3$ + 2 H_2O
<--- 12 H_2O
4 Fe$(OH)_3$ + 6 H_2SO_4 -----> NET 6 H_2SO_4 for acidification.
2 FeS_2
<--- 2 H_2O + 7O_2
2 Fe(II)SO_4
+
2 H_2SO_4
'BACKTRIGGER'
2 FeS_2 --->
2 H_2O ---->
6 Fe(II)SO_4 + 4 S°
<--- 6 O_2
<--- 4 H_2O
4 H_2SO_4 -----> NET 4 H_2SO_4 for acidification.

It is common to note high concentrations of magnesium and calcium, in addition to the ions released from the sulfide ores, in surfacing mine waters passing through carbonate bedrock. The large amount of carbonate tends to remove protons (neutralize acidity), elevating the pH and bicarbonate alkalinity. If an excess of protons (H^+) and a slightly depressed pH occurs, large amounts of carbon dioxide may accompany dissolution of the carbonate bedrock. I observed effervescence at several discharging mine water sites in the Tar Creek and Spring River drainage.

The measured pH of Tar Creek and its' tributaries have been as low as 2.75, approximately 500 times more acidic than the discharging mine water (personal observation). The primary reason for this is related to the oxidation states of iron. Surfacing mine water is low in dissolved oxygen, permitting ferrous iron (+2) to be stable (Krauskopf, 1979). Upon surfacing of the mine water, oxygenation occurs and drives the ferrous oxidation reaction, i.e., $Fe^{2+} \dashrightarrow Fe^{3+}$. Precipitation of the amorphous ferric hydroxide and formation of large amounts of acid increase as the water becomes oxygenated. The protons (H^+) combine with bicarbonate ions to form carbonic acid and release carbon dioxide when supersaturation of carbonic acid occurs. These reactions produce rapid changes in acid-base equilibria of mine water discharged into surface streams, i.e., an initially high 'apparent' alkalinity and immediately downstream a high acidity (equation 2).

Large areas in the mining district are covered by mounds of crushed rock (e.g., tailings piles), residue from ore extraction procedures. These tailings piles contribute significant quantities of heavy metals to surface runoff and therefore probably have significant sulfides

(OWRB, 1983). Sulfide oxidation reactions also occur in these tailings piles as reported in other sulfide contaminated tailings piles (Mink et al., 1972).

Microorganisms as Catalysts for Sulfide Oxidation

Bacterial oxidation of sulfides, especially iron sulfide, is commonly associated with deposits of pyrite and marcasite. In the absence of microorganisms the iron sulfide oxidation reaction is relatively slow (Figure 1). Bacteria significantly increase the initial oxidation rate of iron sulfide (FeS_2) (Barnes and Romberger, 1968). The relative contribution of bacterially-catalyzed oxidation of exposed pyritic material in the abandoned lead and zinc mines has not been documented. The bacteria responsible are the *Thiobacillus* and *Ferrobacillus* (Vishniac and Santor, 1957). *Thiobacillus thiooxidans*, *T. ferrooxidans*, and *Ferrobacillus ferrooxidans* are commonly associated with acid environments. *T. thiooxidans* readily oxidizes elemental sulfur and thiosulfate at a pH optimum of <5. Oxidation of sulfur by *T. thiooxidans* may result in acid production to the extent that negative pH's (e.g. $pH < 0$) may occur (Vishniac and Santor, 1957).

T. ferroxidans, an obligate autotroph, can use reduced sulfur compounds and ferrous iron as the electron donor. Temple and Colmer (1951) noted the dependence of *T. ferrooxidans* on rather high concentrations of ferrous ions (125 mg/l) and low pH (optimum 3.5). This bacterium has been implicated in oxidizing of pyrite and marcasite (Temple and Delchamps, 1953; Bryner and Jameson, 1958; McGoran et al., 1969; Tuttle et al., 1968).

Ferrobacillus ferrooxidans has a pH optimum of near 3.5 with the ferrous iron ion as its sole electron donor. T. ferrooxidans and F. ferrooxidans readily convert ferrous sulfate to ferric sulfate ($Fe_2(SO_4)_3$) and are difficult to distinguish (Noike et al., 1963; Silverman and Lundgren, 1959; Silverman and Lundgren, 1960). This occurs by the following reaction in the presence of sufficient oxygen:

$$2\ Fe(II)SO_4 + H_2SO_4 \longrightarrow Fe_2(III)(SO_4)_3 + 2\ H^+ \qquad (3)$$

$$Fe(II) \longrightarrow Fe(III) + e^- \qquad (4)$$

The previous reaction is slowed in low pH waters, though the bacteria can accelerate the oxidation of FeS_2 by coupling with the 'backtrigger' reaction discussed earlier. This can result in oxidizing large quantities of iron sulfide and an increase in acidity. Increasing water temperatures may promote this acceleration (Wakao and Shiota, 1982).

The Thiobacilli and Ferrobacilli using reduced sulfur compounds as electron donors find more than sufficient quantities of these compounds in acid mine waters. Carbon dioxide, abundant in acid waters contacting carbonate rocks, is used as a carbon source for these organisms.

Transport and Speciation of Iron, Zinc, Lead, and Cadmium

Transport of metals into the water column and away from the source varies among metals. Classification of the transport of iron, lead, cadmium, and zinc may be based on their physicochemical properties. No single transport phenomena is acting on a metal; the equilibrium among the chemical forms is a result of interaction of the metal with surrounding ions, the redox potential of the water, organic matter, flow of the water, and other factors.

Classification schemes for trace metal speciation are generally based on extractability of the metal (Gibbs, 1973; Slowey and Hood, 1971; Slowey et al., 1967) or charge and size of the metal species (Hart and Davies, 1981; Florence and Bately, 1975; Florence and Bately, 1976). Gibbs (1973) found that it was possible to distinguish among several forms of iron transport in rivers. Using a series of chemical extractions, he concluded that the most to least dominant forms of iron were crystalline and/or precipitated (coating) > bound by organics > solution (ionic and complexed) > adsorbed.

Florence and Bately (1977, 1980) and Florence (1982) refined earlier work and based on many types of analyses proposed categories for chemical forms of metals: 1) particulate forms, those retained by a 0.45 micron filter; 2) simple hydrated species (Zn^{2+}); 3) simple metal-inorganic complexes ($CdCl_4^{2-}$, $PbSO_4$, $ZnCO_3$); 4) simple metal-organic complexes (Zn-citrate); 5) stable metal-inorganic complexes ($PbSiO_3$); 6) stable metal-organic complexes (Zn-cysteinate); 7) metal adsorbed on inorganic colloids (Zn^{2+}-clay); 8) metal adsorbed on organic colloids (Zn^{2+}-organic detritus). This classification while based on species also incorporates approximate sizes involved. de Mora and Harrison (1983) report a five component classification scheme with three broad categories: soluble, colloidal, and particulate. Although the two classifications merely differ in the grouping of categories, the latter includes use of a continuous scale for species diameter.

Rygwelski (1984) described two separate mechanisms of adsorption. Physical adsorption is a nonspecific adsorption, highly reversible with relatively weak attractions. Chemisorption is rather dependent on the solid, many times irreversible and with a much stronger attraction than physical adsorption. Iron hydroxide, indicted in trace metal adsorption, is typically referred to as a colloid; however, it is properly a colloid and crystalline suspension (Skoog and West, 1969). A complex is the association of an ion with another resulting in either a charged or uncharged, stable or labile species. Labile complexes generally have small stability constants, while stable complexes possess larger stability constants. Stability constants exist for many compounds and are the reciprocal of the dissociation constant (Drever, 1982).

Transport can now be approached from the aspect of speciation (form) of the metal; the complexity of the classification scheme would be dictated by desired levels of resolution. Transport in an aquatic system begins at the primary sink, e.g., minerals contacting water, where free and complexed ions are released into solution. Based on the calculated redox potential of the environment, particulate and colloidal species would be minimal (Stumm and Morgan, 1970). However, the presence of acidophilic bacteria might result in various organic complexes. As the mine water contacted the surface, oxidation and formation of iron hydroxides occur. These inorganic colloids form amorphous materials with large surface areas which adsorb (scavenge) trace metals from the water column (Bradley and Lewin, 1982). Lead transport is not likely to be in soluble forms; more likely its in the stable or particulate form (Benes et al., 1985) and organic particulate species (Salim, 1983), though lead carbonate may appear (Florence and Batley, 1980).

Zinc and cadmium will have lower stabilities when metal-organic complexing is occurring and generally form more soluble species than lead (Guy and Chakrabarti, 1976; Florence and Bately, 1977). As pH decreases, trace metals adsorbed onto the amorphous iron hydroxides may be released and complex with anions and organics. Generally, as the flow rate of a stream increases, metals (e.g. lead) are more commonly associated with particulates and labile species, indicating desorption or ion exchange from the colloidal iron hydroxide (Benes et al., 1985). In either case, pH is regulating the stability of the form.

Upon being transported into a lower velocity stream (e.g. Neosho River) the iron will continue as an amorphous colloid and as a coating on particulates. The lead occurs as organic-metal complexes and/or adsorbed onto particulates, either through scavenging by the iron colloids and coatings, scavanging by clay or uptake by plankton. An increase in salinity can also increase the concentration of dissolved lead (Duinker and Kramer, 1977).

Cadmium is predicted to exist as a free Cd^{2+} ion or as a carbonate complex in freshwaters (Florence and Bately, 1980); however, Gardiner (1974a, 1974b) reported that naturally occuring organic compounds and various suspended sediments can readily adsorb free Cd^{2+}.

Zinc, more mobile than the other elements mentioned, is transported as ionic zinc and inorganic complexes. Guy and Chakrabarti (1976) found that in acidic pH's, the organically bound zinc (humic acid) was extremely labile (100%) while at neutral pH's less then 50% was in the labile form.

The reduced velocity of the water will result in sedimentation of the larger particulates (a transient-secondary sink) until a higher velocity resuspends some of the material. Ultimately, the metals are either lost by river sedimentation or transported to a more permanent or metastable sink (e.g. Grand Lake).

Speciation studies have also used thermodynamic modeling of solutions. The WATEQF model was developed for modeling chemical speciation and equilibria of major elements (Truesdell and Jones, 1973). Ball et al. (1979) incorporated trace metal speciation and equilibria modeling with major and trace metals into WATEQ2. Sposito (1983) has reviewed the ion-association models GEOCHEM, MINEQL, PHREEQE, and MICROQL. MEXAMS is a model developed to predict speciation and environmental fate of compounds (USEPA, 1984). Most thermodynamic models do not yet account for dissolved organic compounds, a distinct disadvantage.

Sediments and Iron, Zinc, Lead, and Cadmium

Metal distribution and activity in sediments is intimately linked to the species deposited and subsequent transformation. In lakes of sufficient depth, sedimentation removes the majority of the particulate and dense colloidal forms of metals. Shallower lakes may have deposition but wind, inflow, and other factors may result in resuspension. Species of metals in the sediments may be categorized as previously outlined; however, most studies have reported results in the more generalized format.

Extraction procedures for sediment evaluation of metals has received much attention (Agemian and Chau, 1976, Nembrini et al., 1982, Malo, 1977, Brannon et al., 1976, USEPA, 1979). Although the numerous extraction procedures used permit generalizations to be made for metal contaminated sediments, specific comparisons are impractical.

The most common extraction procedures define particulate metals as those that can be released only by strong acids, e.g. hydrofluoric, nitric-hydrochloric (Agemian and Chau, 1976). Organic substrata for metals include simple and stable complexes as well as colloidal or biotic particulates, all susceptable to digestion with hydrogen peroxide (Evans and Parliament, 1984). Stable metal-inorganic complexes, simple complexes, and hydrated species may be removed by a number of extractants, e.g. dilute HCl, $MgCl_2$ solutions, hydroxylamine HCl-acetic acid, citrate solutions, and many more (Nembrini et al., 1982; Malo, 1977). Placement into these categories admits significant overlap in some cases.

Iron

Iron occurs in the Fe^{3+} oxidation state in oxygenated waters. The oxidation of Fe^{2+} to Fe^{3+} forms an amorphous ferric hydroxide which precipitates out of solution. The reduction-oxidation potential (Eh) of the water and sediments influence species, flux, and quanity of iron released from the sediments. A decrease in pH and/or a decrease in redox (Eh) will mobilize Fe^{2+} from sediments which is commonly noted in stratified lakes (Lue and Chen, 1977, Schindler et al., 1980, Wetzel, 1983). An increase in Fe^{2+} often results in precipitation of pyritic materials onto the sediments. Within the sediments, particulate and amorphous hydroxides may be the dominant forms (Sakata, 1984). The amorphous hydroxide form may be especially common in areas where acid mine drainage exists. Iron-organic fractions are much less abundant than the labile and stable complex species.

The presence of iron is not recognized as a toxic agent; however, the amorphous hydroxide influences transport of other toxic metals since it readily scavenges trace metals from solution, e.g. lead, zinc, and cadmium.

Zinc

Zinc, as well as lead and cadmium occurs in sediments in the Zn^{2+} oxidation state. Zinc occurs commonly as a sulfide in mineral formations (Krauskopf, 1979), but infrequently as a sulfide in aquatic sediments. Unlike iron, zinc is potentially highly mobile in sediments (Calmano and Wellershaus, 1982). Sediments at neutral and alkaline conditions may readily adsorb zinc; however, decreases in pH below neutral will result in release with little readsorption when the pH is raised to neutral (Schindler et al., 1980; Nienke and Lee, 1982). This is likely due to adsorption of other elements (i.e. cation exchange) which form more stable attractions than zinc, in addition to changes in the adsorbed zinc species. Lue and Chen (1977) determined that a seawater-sediment system released zinc under oxidizing conditions probably by forming more soluble carbonates. Under reducing conditions insoluble sulfides may form resulting in a reduction of zinc concentrations.

Zinc, as with lead and cadmium, may primarily occur as an adsorbed species on iron hydroxides and manganese oxides. Organic contribution appears to be of secondary importance (DePinto et al., 1984). Similar to aquatic sediments, soils also have a pH dependant zinc binding activity. Adsorption-desorption processes are of major importance at pH's less than 7, while precipitation-dissolution processes are important at pH's greater than 7 (Brummer and Herms, 1983; Tiller et al., 1984a, 1984b; Brummer et al., 1983).

At high zinc concentrations (>300 ppm), the labile and stable complexes are more predominant than particulate and organic forms. (Kitano et.al., 1981). In other sediments Kitano and Sakata (1980) determined the distribution was about equal between the particulate and organic species. Sakata (1984) found that the majority of the zinc in a sediment was within the crystalline silicate lattice.

Lead

Lead occurs in the Pb^{2+} oxidation state in galena (PbS), water, and sediments. Lead is an immobile element and is adsorbed strongly to iron hydroxides and manganese oxides in sediments and soils (Calmano and Wellershaus, 1982; DePinto et al., 1984; Tiller et al., 1984a, 1984b). In soil solutions, a decrease in pH elevates lead concentrations (Tills and Alloway, 1983a, 1983b). Lue and Chen (1977) also found a release of lead under oxidizing conditions apparently through the formation of more soluble carbonates and hydroxides while under reducing conditions a sulfide or adsorbed species was present. Little agreement exists on contribution of the organic-lead interactions. Iskander and Keeney (1974) found no consistant relationship between lead content and organic carbon. Brummer and Herms (1983) determined that lead was the least immobilized by organics, as compared to zinc and cadmium in soils. Evans and Parliament (1984) and DePinto et al. (1984) found the organic fraction to be an important lead component. In general, it appears that lead occurs primarily as an adsorbed species.

Cadmium

Cadmium, like lead, is a toxic element to aquatic organisms. Unlike lead, cadmium is potentially a highly mobile element in sediments (Calmano and Wellershause, 1982). Cadmium occurs as the Cd^{2+} oxidation state, often found as an accessory mineral sulfide in ore deposits. As with lead and zinc, cadmium binding in sediments and soils strongly depends on pH and Eh of the systems (Tiller et al., 1984a, 1984b; Krauskopf, 1979). Release of cadmium from sediments occurs as Eh and/or pH of the water-sediment interface decreases (Lue and Chen, 1977; Brummer and Herms, 1983). This high mobility of cadmium suggests that much is weakly adsorbed or occurring as complexes. DePinto et al. (1984) reported that iron hydroxides and manganese oxides were the primary sinks for cadmium, while organics are of secondary importance. Iskander and Keeney (1974) found no consistant relationship between organic carbon and cadmium concentrations. However, Gardiner (1974) found that the highest proportion of cadmium was associated with organics (e.g. humic acids) in river muds. In soils, organics will immobilize cadmium more strongly than zinc and lead (Brummer and Herms, 1983).

Summary of Sediment-Trace Metal Interaction

Iron is most likely to occur as a particulate species or an insoluble amorphous hydroxide. Lead, and to a lesser degree zinc and cadmium, are readily scavanged by these iron species. The low solubility of lead indicates low mobility, while zinc and cadmium are relatively mobile elements. Sediment type, pH, and Eh are the major factors controlling metal species and release from the sediments. Lue and Chen (1977) stated that under the same redox conditions, the migration trend is controlled mainly by the redox condition and the flux is controlled chiefly by sediment type.

Toxicity and Bioavailability

Bioavailability of toxic metals is indirectly estimated by measuring a response in organisms or by physicochemical fractionation. The bioavailability of a metal not only depends on speciation or partitioning between water and sediments, but also on the organisms' physiology. Uptake by organisms from the surrounding water or in food involves complex interactions such as uptake across membranes, metabolism, and elimination. Toxicity and bioconcentration are a result of an organisms inability to sequester and/or eliminate deleterious metals.

Methodology to measure the metal concentration and estimate bioavailability has been diverse. Anodic stripping voltammetry is used to measure the fraction of metal which is reducible at the electrode surface. This may include free and labile forms; however, other biologically unavailable forms may be included during the stripping procedure (Luoma, 1983, Neubecker and Allen, 1983). Ion specific electrodes detect the free ion which is considered to be the toxic species to aquatic organisms. The disadvantage of ion specific electrodes is that the detection limit for trace metals is inadequate to be used in most natural waters (Luoma, 1983; Hart, 1983).

Complexation capacity (binding capacity) is the concentration of unbound ligand in the water sample (Neubecker and Allen, 1983). Complexation capacity has been used as a measure of potential for toxic effects of metals. Humic and fulvic acids are important complexing organics for metals (Neubecker and Allen, 1983). Other organic compounds may be present with specificity for individual metals (Ramamoorthy and Kushner, 1975). Giesy et al. (1978) and Alberts et al. (1984) have noted that lead binding capacity is primarily due to organic matter while cadmium binding is predominantly inorganic ligand-binding. Complexation capacity has the disadvantage in that free metal ion concentration initially present may not be accounted for (Luoma, 1983).

Kaiser (1980) modeled toxicity based on similar electron configurations. The validity for this approach may only be acceptable when free ions predominate or are the toxic species present. The correlation of toxicity with atomic properties (e.g. electronegativity, ionic radius) has differentiated elemental classes of similar toxicity (Stokes, 1983). The use of atomic similarity correlation with toxicity has not been widely pursued.

The importance of iron and zinc in organisms is well documented (Epstein, 1972; Florence and Bately, 1980). Iron is required for proteins and porphyrin molecules and zinc is necessary for enzymes active in RNA and DNA synthesis (Rodwell et al. 1977; Salisbury and Ross, 1978). Lead and cadmium have not been documented to be necessary micronutrients. Luoma (1983) classified several cellular uptake mechanisms for metals. Essential metals (e.g. zinc) are complexed and actively transported into cells (homeostatic regulation). Other nonessential metals may be similar enough to essential cations that entry is via carrier facilitated uptake (e.g. Ca-Sr, K-Rb). Metals that complex with essential nutrients and nonspecific complexing may lead to uptake (e.g. cadmium, lead). Less common is lipid soluble partitioning in which a metal is in the form of a nonpolar metalloorganic compound and passively diffuses across the membrane (e.g. methylmercury). Metals are often eliminated or inactivated by a class of metal binding proteins, the metallothioneins (Talbot and Mages, 1978). Rapid elimination of cadmium has been observed upon termination of exposure (Giesy et al., 1981).

Uptake of metals may be controlled by physicochemical conditions. Miller and Mackay (1980) found that $pH < 4.7$ was antagonistic to copper availability in trout; however, at pH levels > 5.4 the interaction was synergistic. Zinc and sulfide were antagonistic in Selenastrum and cadmium and selenium antagonistic in Chlorella, both green algae (Hendricks, 1978; Wong et al., 1978). Bartlett et al. (1974) reported that cadmium, copper, and zinc were synergistic to carbon uptake in phytoplankton with zinc antagonistic to cadmium and copper uptake.

Subcellular effects may occur at metal concentrations below acutely toxic levels. Ten to 100 ug/l cadmium was reported to severly damage mitochondria and chloroplasts (Soyer and Prevot, 1981). Hessler (1974) also reported that sublethal concentration of lead interfered with cell division. Lead chloride as low as 0.1 ug/l suppressed photosynthesis and respiration by 25 to 50% in a marine diatom (Woolery and Lewin 1976).

Wolter et al. (1984) concluded metabolism was involved in cadmium accumulation in phytoplankton. Bioconcentration was high via active transport, at low cadmium concentration, while passive diffusion was the primary mechanism at elevated cadmium concentration. A decrease in species diversity of algae occurred under conditions of metal contamination resulting in metal tolerant algae such as Chlorella (Zn, Pb) and *Anacystis* (Zn, Pb, Cd) (Stokes, 1983; Austin et al., 1985). Adding organic acid to the water furthur reduced toxicity of trace metals to *Chlorella* (Helliwell et al., 1983).

Aquatic invertebrates have been used extensively as indicators of water pollution. *Mytilus* lives in the sediment-water interface, a distinct advantage in bioconcentration experiments (Luoma and Bryan, 1979). Marquenie et al. (1983) determined that bivalves bioconcentrated cadmium with respect to sediment. Lead enrichment in bivalve shell of 9,000 times in comparison to water concentrations has been reported (Sturesson, 1976). Snails were exposed to lead concentrations of 36 and 48 ug/l with a resultant 50 and 100% decrease in biomass production, respectively (Borgmann et al., 1978). Bioconcentration of cadmium and lead of 600 to 30,000 times and 1,000 to 9,000 times, respectively, was reported in stoneflies (*Pteronarys*), caddisflies (*Hydropsyche*), and snails (*Physa*) (Spehar et al., 1978).

Daphnia or waterflea have been used to test many types of pollutants (LeBlanc, 1980). Advantages are ease of culture, reproducibility of test results, and good sensitivity. Studies with *Daphnia* have primarily examined pollutants within the water column; however, sediment-water bioassays with *Daphnia* have been reported (Schuytema et al., 1984; Malueg et al., 1983). In fact, *Daphnia* was found to be the most sensitive of the test organisms used in EPA sediment-water comparison studies (USEPA, 1981). Schuytema et al. (1984) used recirculating test chambers and water-sediment slurries in *Daphnia* bioassays to assess toxicity of cadmium. The control water had an LC50 of 39 ug/l cadmium, while the sediment-water bioassay LC50 was 91 ug/l cadmium. The significantly higher LC50 for sediment water bioassays was attributed to organic carbon and cadmium complexation. The concentration of cadmium adsorbed onto the sediment had little effect on mortality to Daphnia.

The recreational, economical, and ecological value of fish has resulted in research on toxicity of a variety of contaminants. A wide range of LC50 values have been reported for many different fish species and toxicants. McCarty et al. (1978) reported an LC50 for cadmium to goldfish in softwater (20 mg/l as $CaCO_3$) and hardwater (140 mg/l as $CaCO_3$) of 2.13 and 46.8 mg/l, respectively. The decrease in toxicity with increasing hardness is common to many fish species and other aquatic organisms (Davies et al, 1976, Solbe, 1974). Larvae of seven fish species were found to be more sensitive than embryos (Eaton et al., 1978). The acutely lethal effect of metals to aquatic organisms has been shown to decrease with increasing levels of organic matter (Carlsson and Lidin, 1978); however, Giesy et al. (1977) found that organic matter reduced cadmium toxicity to zooplankton but not fish.

The effect of toxic metals on humans is less well documented for aquatic systems. Kobayashia (1971) found a relationship between itai-itai (ouch-ouch) disease and the concentration of lead, cadmium, and zinc in water discharged from lead and zinc mines and transported into water used for rice irrigation. Consumption of the rice resulted in severe osteomalacia, extreme brittleness of bones. Calcium replacement by cadmium was the reported causal agent.

State and Federal Water Quality Standards

The toxicity of contaminants in aquatic systems and potential human toxicity has necessitated water quality standards to be established. Water quality standards have been developed at both state and federal levels. The current Oklahoma water quality standards are based on EPA criteria, published toxicity data, and designated beneficial uses, e.g., recreation, fishing, of the water resource. Tar Creek, Spring and Neosho rivers, and Grand Lake are all classified under Stream Segment 121600, with the same standards (Table I) (Oklahoma Water Resources Board, 1982). USEPA water quality criteria and Oklahoma water quality standards are currently under revision (Table I) (Environment Reporter, 1984, Pat Powell, personal communication).

TABLE I

SUMMARY OF 1982 OKLAHOMA WATER QUALITY STANDARDS AND 1980 EPA WATER QUALITY CRITERIA FOR FRESHWATER LIFE

Parameter	Oklahoma[1] Criteria ug/l	EPA Criteria[2] ug/l 24-h average	EPA Criteria[2] ug/l maximum
Arsenic	40	---	440
Cadmium	10	$e^{(1.05[\ln(\text{hardness})]-8.53)}$	$e^{(1.05[\ln(\text{hardness})]-3.73)}$
Chromium (VI)	50	0.29	21
Copper	20	5.6	$e^{(0.94[\ln(\text{hardness})]-1.23)}$
Lead	120	$e^{(2.35[\ln(\text{hardness})]-9.48)}$	$e^{(1.22[\ln(\text{hardness})]-0.47)}$
Zinc	462	47	$e^{(0.83[\ln(\text{hardness})]+1.95)}$

---

[1] Pb, Cd, and Zn currently under revision.

[2] Proposed revisions (Environment Reporter, 1984):

Cadmium
maximum = $e^{(1.16[\ln(\text{hardness})]-3.841)}$

Chromium (VI)
30-day average = 7.2 ug/l
maximum = 11 ug/l

Lead
30-day average = $e^{(1.34[\ln(\text{hardness})]-5.245)}$
maximum = $e^{(1.34[\ln(\text{hardness})]-3.014)}$

CHAPTER III

DESCRIPTION OF THE STUDY AREA

Grand Lake, is located in Ottawa and Delaware counties of northeastern Oklahoma. Major emphasis for field sample collection was on the upper end of Grand Lake and the two major tributaries, Neosho and Spring rivers. The major source of contamination is from acid-mine seeps which discharge into Tar Creek. The confluence of Tar Creek with Neosho River is approximately 16 km upstream from the upper end of Grand Lake.

Grand Lake (Lake O' the Cherokees) was constructed in 1940 for flood control, hydroelectric power, and recreation. Grand Lake has a shoreline of 1004 km; volume of 1.84 km^3; drainage area of 26,672 km^2 and a shoreline development ratio of 20.7. The mean depth is 10.9 m with a maximum of 50 m (Oklahoma Water Resources Board, 1984; U.S. Geological Survey, 1982).

Neosho River drains 15,219 km^2 and an average discharge of 3.09 km^3 per year. Spring River has a drainage area of 6,501 km^2 and an average discharge of 1.70 km^3 per year (U.S. Geological Survey, 1982).

Tar Creek, a minor tributary to the Neosho River, has a drainage area of 134.7 km^2 and a discharge for 1982 water year ranging from 0.007 m^3/s to 85.7 m^3/s (U.S. Geological Survey, 1982). The headwaters of Tar Creek are located in southern Cherokee County, Kansas, and at one point stream disappears into a mine collapse (subsidence).

All sites used for collection of water samples during this study were located on Tar Creek, Spring and Neosho rivers, and Grand Lake (Table II, Figure 2). Sites 28 and 29 were mine discharges that enter Tar Creek directly, these sites corresponding to Oklahoma Water Resource Board sampling stations #14 and 4, respectively (OWRB, 1983). Sites were generally chosen for their proximity to mine water discharges or surface waters receiving acidic mine wastes.

Geologic Setting for the Picher Mine Field

The Picher mining field district bedrock is composed of alternating units of chert and limestone with minor sandstone layers. The entire sequence is overlain by shale. Both Mississippian and Pennsylvanian rocks outcrop in the study area. The Pennsylvanian rocks have a thickness from 55 to 91 m. Stratigraphically, below the Pennsylvanian are strata of Mississippian age, specifically the Boone Formation with a thickness from 106 to 122 m in the Picher mining district. The Boone Formation is the rock unit of most interest to miners because of the deposits of zinc and lead sulfide ores (McKnight and Fischer, 1970).

Pennsylvanian shales and less carbonaceous sandstone overlay the ore-bearing Mississippian rocks. The Pennsylvanian system, though not productive as an ore-bearing zone, supplied coal to local residents in the early 1900's (Jim Davis, personal communication). A generalized section of the rock units has been compiled from numerous sources by McKnight and Fischer (1970). Briefly, the lowermost unit within the Pennsylvanian is a carbonaceous sandstone (Hartshorne Formation) which is overlain by a black fissile shale-siltstone. McAlester Shale and Warner Sandstone which contain thin coal beds overlie this unit. The

TABLE II

SAMPLING SITES AND CORRESPONDING LEGAL DESCRIPTION

Site 1 - R23E T24N S5. 0.55 km west (upstream) from the Will Rogers Turnpike bridge on the Neosho River.

Site 2 - R23E T28N S5. Neosho River, 0.2 km west of I-44.

Site 4 - R24E T28N S30. Spring River, 0.55 km north of Highway 10.

Site 5 - R24E T27N S30. 1.2 km downstream of the Neosho and Spring rivers confluence.

Site 6 - R24E T25N S15. 0.8 km west of Cowskin Bridge (Highway 10).

Site 7 - R24E T25N S12. Confluence of Elk River and Grand Lake.

Site 10 - R24E T27N S30. Highway 60 bridge on the Neosho River.

Site 12 - R24E T25N S14. 1.8 km upstream from Cowskin Bridge (Highway 10) on Elk River.

Site 13 - R22E T25N S26. Highway 85A Horse Creek Bridge.

Site 14 - R24E T25N S15. Cowskin Bridge (Highway 10).

Site 15 - Grand Lake Dam. East end of dam.

Site 16 - R24E T24N S17. Honey Creek Bridge (Highway 10).

Site 17 - R23E T28N S31. Approximately 0.3 km downstream from Highway 125 bridge on Neosho River.

Site 18 - R23E T28N S31. Highway 125 bridge over Noesho in Miami OK.

Site 19 - R23E T27N S26. Mudeater Bend Bridge over Neosho River.

Site 20 - R24E T27N S19. Highway 60 Bridge and Spring River.

Site 22 - R24E T28N S5. Devil's Promenado Bridge over Spring River.

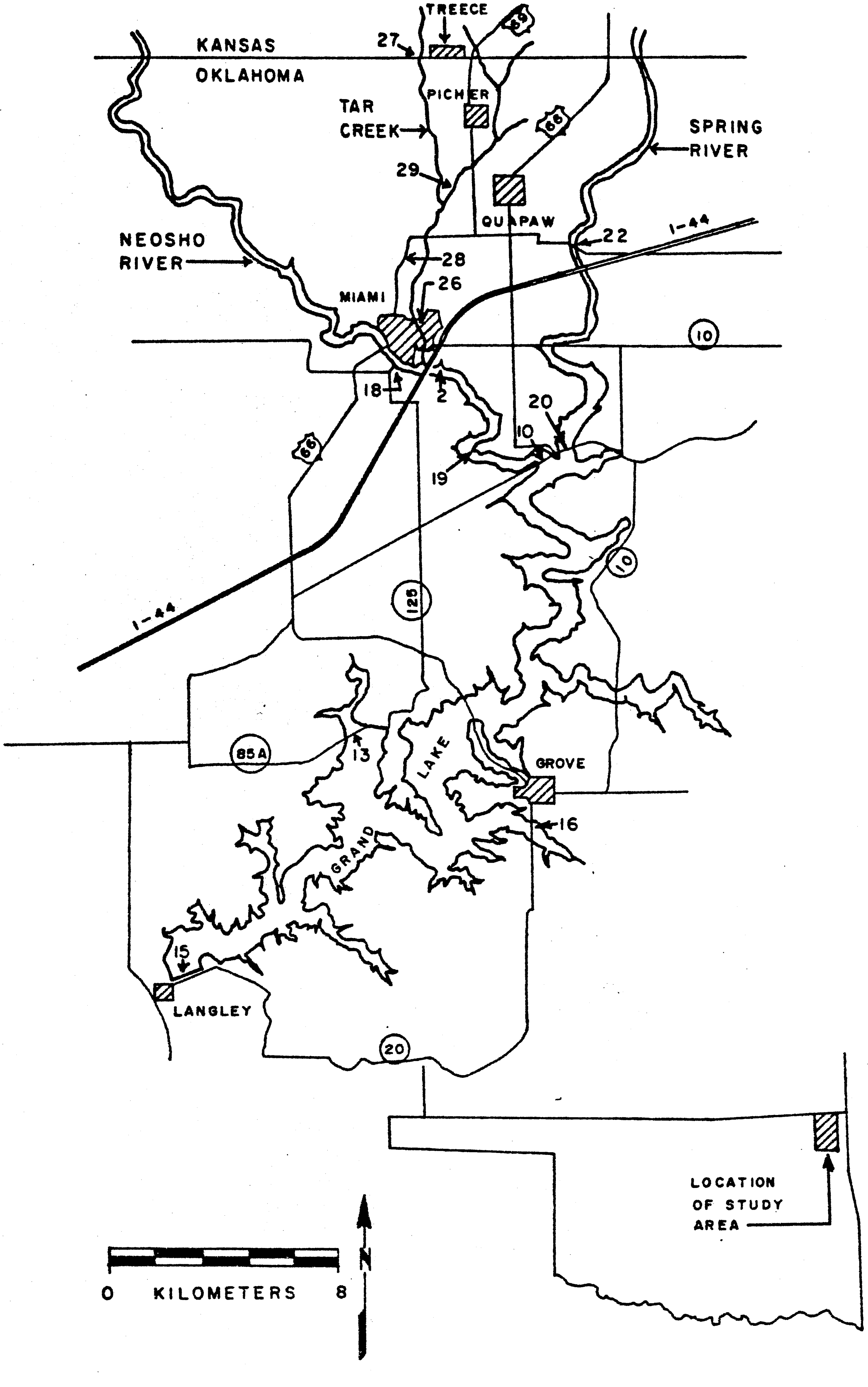
Site 26 - R23E T28N S30. Tar Creek and Channel Street Bridge (OWRB #20).

Site 27 - R23E T29N S18. Tar Creek and Treece OK. (OWRB #7)

Site 28 - R23E T28N S7. Farmers Horse Pasture, Commerce OK. (OWRB #14).

Site 29 - R23E T29N S29. Near confluence of Tar and Lytle Creeks. (OWRB Site #4)

Figure 2. Location of sampling sites for Tar Creek, Neosho River, Spring River, and Grand Lake


TREECE
KANSAS
OKLAHOMA
27
69
TAR CREEK
PICHER
66
SPRING RIVER
29
QUAPAW
22
I-44
NEOSHO RIVER
28
26
MIAMI
10
18
2
20
10
19
66
10
125
I-44
85A
13
LAKE
GROVE
16
GRAND
15
LANGLEY
20
LOCATION OF STUDY AREA
0 KILOMETERS 8
N

surface rock is primarily Savannah Shale which contains minor amounts of sandstone and limestone.

The Mississippian System (Boone Formation) is composed of interbedded chert and limestone units, the latter being the strata in which ore mineralization occurred. The principal ore-producing zones are located in the Joplin and Baxter Springs members as limestone replacement minerals with less coming from the Grand Falls Chert and Moccasin Bend members. Ore beds within these members are primarily tabular in nature, thought to be a result of migration of hydrothermal solutions from deep magma sources that rose and flowed laterally into areas where limestone solution had occurred (McKnight and Fischer, 1970).

The ore is composed primarily of sphalerite (ZnS), galena (PbS), dolomite ($CaMg(CO_3)_2$), and jasperiod (SiO_2) with abundant marcasite (FeS_2). Pyrite (FeS_2), luzonite (Cu_3AsS_4), chalcopyrite ($CuFeS_2$), and enargite (Cu_3AsS_4) are common accessory minerals. McKnight and Fischer (1970) report that the zinc to lead ratio in the ore is 4.1:1.

CHAPTER IV

MATERIALS AND METHODS

Collection of Water Samples

Water samples and general water quality parameters were taken at each site. A YSI Model 33 conductivity meter, YSI Model 54 dissolved oxygen/temperature meter, and an Orion Model 211 field pH meter were used to measure specific conductance, dissolved oxygen and temperature, and pH, respectively. Alkalinity was determined by electrometric titration or color change titrimetric methods (D 1067 Method B) for surface waters containing no substances (e.g. Fe^{2+}) likely to cause interference (ASTM, 1978). Samples containing acid mine wastes were treated with hydrogen peroxide (D 1067 Method E) to promote oxidation of reduced metals prior to titration (ASTM, 1978).

Water samples were collected periodically for analysis of heavy metals and other ions. Water samples for total heavy metal analyses were collected from mid-depth or at several depths with a 3.2 liter VanDorn (Wildco Model 1130TT) acrylic water sampler. A 100 ml aliquot was measured into acid-washed 125 ml polyethylene bottles and preserved with 3 ml concentrated nitric acid (Baker Instra-Analyzed). The samples were transported on ice to the lab. Sample preparation and quality control were maintained as stated in Methods for Chemical Analysis of Water and Wastes (USEPA, 1979). Sample analyses were performed with a Perkin-Elmer Model 5000 atomic absorption spectrophotometer equipped with a HGA-500 Graphite Furnace and autosampler using operating conditions recommended by the Perkin-Elmer Corporation (Perkin-Elmer, 1982). The concentrations of calcium, magnesium, iron, lead, zinc, cadmium, chromium, manganese, selenium, mercury, arsenic, copper, and nickel were determined on water samples.

Selected water samples were analyzed for soluble, non-filterable metals. Water collection was performed as with total metals; however, 1 liter of water was measured into dark polyethylene bottles and not acidified. The samples were transported on ice to the lab and filtered through a 0.45 um membrane filter (Millipore). A 100 ml aliquot of the filtrate was acidified to a pH < 2 and analyzed by atomic absorption. Duplicate samples and USEPA quality control samples were analyzed to measure precision and accuracy, respectively.

Collection of Sediment Samples

Sediment cores and grab samples were collected from the mouth of Tar Creek, Neosho River, and Grand Lake. Core samples were collected using a 5 X 70 cm ballcheck single tube core sampler (Wildco Model R232 A10), PVC core tubes, and core catchers to prevent mixing when the core was withdrawn. Each core was examined to insure the extracted core was intact. Core tubes were withdrawn, endcapped, packed in ice, and frozen until analyzed.

Additional grab samples were obtained from the upper 15 cm of sediment using a standard Ekman dredge, packed on ice, and transported to the lab where they were frozen until analyzed. All sediment sampling was made from a barge type boat. The boat was equipped with a Lowrance

Model LRG-1510B depth chart recorder to determine depth and aid in locating sampling sites.

Sediment Preparation

The frozen sediment core samples were extruded from core tubes and cut into 5 cm sections. Each section was dried at 50 °C and homogenized. A 1 g aliquot was digested by refluxing (95 ° C) in concentrated nitric acid. Hydrogen peroxide (30%) was added to promote oxidation of organic matter (USEPA, 1983). After digestion the samples were diluted with double-distilled deionized water prepared by passing deionized water through a water softening column to reduce major cations and an activated charcoal column, a 0.2 um filter, and a glass still. The distilled water was then passed through a research grade mixed-bed resin to furthur reduce trace cation concentrations. The digested slurry was centrifuged (1474 x g) for 10 min using Sorvall Model RC2-B centrifuge equipped with a SS-34 rotor. The supernatant was filtered with Whatman # 42 filter paper and analyzed by atomic absorption. All results were reported in mg/kg of dry weight sediment.

Sediment grab samples were passed through a # 30 seive to insure homogeniety of the sediment. The sediments were dried at 50 ° C and 1 g was digested and analyzed for metal ions by atomic absorption.

Organic carbon was analyzed in each of the sediments and core sections using a ferrous ammomium sulfate titration of excess dichromate (Gaudette et al., 1974). A sample of sediment was dried and ground and 0.25 g subsamples were placed into a 500 ml Erlenmeyer flask. Ten milliliters potassium dichromate (1N) was added and the flask swirled for 1 min. Twenty milliters of concentrated sulfuric acid was added and the solution gently mixed for 1 min. The mixture was allowed to stand for 30 min and brought to 200 ml by adding double-distilled deionized water, 10 ml 85% phosphoric acid, 0.2 g sodium flouride, and 0.5 ml diphenylamine indicator. The solution was back titrated with 0.5 N ferrous ammonium sulfate (FAS) solution from a blue-black color to the green endpoint. Percent organic carbon was determined by the equation:

$$\% \text{ Organic Carbon} = 10(1-T/S)[1.0N(0.003)(100/W)],$$

where T was ml FAS used in sample titration, S the ml FAS used for blank, and W the weight of the sediment sample.

Sediment Leachate Procedure

Sediment leachates were obtained from the sediment grab samples at various pH's in reconstituted water. Reconstituted water (RCW) was prepared by adding 120 mg/l $CaSO_4 \cdot 2H_2O$, 120 mg/l $MgSO_4$, 192 mg/l $NaHCO_3$, and 8.0 mg/l KCl to double-distilled deionized water (USEPA, 1978). The resultant hardness ranged 160-180 mg/l as $CaCO_3$, alkalinity 110-120 mg/l as $CaCO_3$, and pH 7.6-7.8 S.U. The leachate procedure was performed at pH's of 3,4,5,6,7,8, and 9. Tar Creek, Neosho River, and Grand Lake sediments were added to the RCW and the pH adjusted with acetic acid or sodium hydroxide. Five grams of sediment were placed into 125 ml polyethylene bottles and 100 ml of the pH adjusted RCW added to the sediment. This suspension was extracted for 48 h on a rotary residue extractor (USEPA, 1982). The pH was readjusted at 1 h, 6 h, and 24 h and checked at 47 h to insure maintainence of the desired pH during extraction. At 48 h the samples were centrifuged (1475 x g for 10 min) and filtered with Whatman # 42 filter paper. Nonfilterable metal concentrations were determined by atomic absorption and reported in mg/l.

Sediment extractions were also performed for use in *Daphnia* chronic (life cycle) bioassays. Fifty grams of sediment per liter of pH adjusted RCW was extracted. A RCW pH of 6 was chosen based on observed 'natural' values. Two liters of each sediment suspension was placed in 1 l dark polyethylene bottles. Control treatments were pH adjusted RCW. Extraction was for 48 h at room temperature (25 °C) using the rotary residue extractor. Sediment suspensions were centrifuged at 1475 x g for 10 min in acid washed polyethylene 250 ml bottles and filtered with Whatman # 42 filter paper. A 100 ml aliquot was taken and atomic absorption analysis performed. The remaining leachate was used in the *Daphnia* bioassay procedure.

Bioassay Procedure

Daphnia magna 96-hour bioassays were performed on sediment-RCW mixtures with neonates (< 24 h) supplied from cultures maintained by Water Quality Research Lab, Oklahoma State University. Five grams of sediment from Grand Lake was mixed with 100 ml RCW for 24 h on a rotary shaker. The suspension was allowed to settle for 24 h. Five *D. magna* neonates were placed into each of 12 treatment and control test chambers and fed alfalfa/trout chow daily (USEPA, 1978). Five chironomid larvae were introduced at 24 h into three sediment-RCW and three RCW test chambers. Mortality was recorded daily.

D. magna 9-day toxicity bioassays were performed on Grand Lake sediments. The sediment-RCW was as above; however, one neonate was place in each of 10 replicates RCW (control) and 15 replicates of sediment-RCW. Five chironomid larvae were introduced at 24 h in each of five control and five sediment-RCW test chambers. Mortality and neonate production were recorded.

Ceriodaphnia sp. 5-day bioassays were performed on sediment-RCW mixtures with neonates <24 h old. The sediment-RCW preparation was described previously. Five *Ceriodaphnia* were placed in each of three RCW and three sediment-RCW treatment chambers. *Ceriodaphnia* were fed with a slurry of Bakers yeast, and mortality was recorded daily.

D. magna 10-day bioassays were performed on sediment leachates with neonates (< 24 h). The treatment and control RCW water was completely renewed daily. Bioassays were carried out in a constant temperature room maintained at 24 ° C and a 16:8 light:dark cycle. The *D. magna* were fed trout chow/alfalfa prior to tests and daily after first 48 h of exposure until terminating the assay. Ten ml of pH adjusted RCW or leachate water was added to a 18 ml glass tube (surface:volume = 1.9). Each treatment consisted of 10 replicates with two *Daphnia* per tube. At the end of each 24 hr period the neonates were removed, the treatment solution renewed, and the neonates returned to the tube. This minimized furthur absorption of metals to the tube wall. The pH was monitored daily for changes that might result in pH toxicity. Mortality and neonate production were recorded daily and new neonates hatched were removed. Dissolved oxygen was measured in the stock treatment solutions to insure adequate oxygen concentrations.

Daphnia 48- and 96-hr LC50 Determination

Toxicity of Tar Creek and Neosho River leachate waters necessitated LC50 determinations (USEPA, 1978). Ten *D. magna* neonates <24 h old were used in each of two replicates per dilution; each replicate was 100 ml. Dilutions of leachate water were prepared to give final concentrations of 90, 55, 30, 15, and 8% by volume. The D. magna were incubated with a 16:8 h light:dark cycle at 24 ° C. At 48 h the Daphnia were fed trout chow/alfalfa and daily thereafter. The mortality was recorded at the end of each 24 h period and the 48-and 96-h LC50 calculated by the Litchfield and Wilcoxon method.

Statistical Analyses

Statistical analysis was performed on the data with Oklahoma State University's IBM 3081 computer with Statistical Analysis System (SAS). One-way analysis of variance (ANOVA), general linear modeling (GLM), regression, protected LSD (LSD.05), and correlation procedures were used.

CHAPTER V

RESULTS

Physicochemical Conditions

Neosho River

Depth, water temperature, dissolved oxygen, and specific conductivity were measured (Appendix Table VI). Depth at Site 1 decreased from 6 m on 15 July to 1 m on 1 August, while mean water temperature increased from 28 to 31 ° C, respectively. Dissolved oxygen concentration generally exceeded 5.7 mg/l. Mean specific conductivity increased from 365 uS/cm on 15 July to 434 uS/cm on 1 August. At Site 2, depth also decreased between the two sampling dates. Dissolved oxygen exceeded 5 mg/l and conductivity values were similar to Site 1. At Site 10, water depth was greater than 7 m while specific conductivity and dissolved oxygen values were similar to Site 2.

The pH for two rainfalls measured in August 1983 averaged 3.6 at a site 0.5 km from the Neosho and Spring rivers confluence. Following rainfalls on 22 October and 6 March, pH, alkalinity, calcium, and magnesium concentrations decreased significantly (Appendix Tables VI and VII). The similar trend for pH, alkalinity, calcium, and magnesium values was confirmed by calculation of pairwise correlations (Appendix Table VIII). Regression equations were calculated with pH or alkalinity as the regressor for significant correlations (Appendix Table IX). Manganese, iron, and zinc concentrations were highest following the rainfalls and negatively correlated with alkalinity, pH, calcium, and magnesium (Appendix Tables X and VIII). Lead concentration averaged 0.006 mg/l and cadmium was below detection limits (<0.005 mg/l) in all samples (Appendix Table X).

Spring River

Depth, water temperature, dissolved oxygen, and specific conductivity were measured at Site 4 on two dates (Appendix Table XI). Depth decreased from 3 m on 17 July to 2 m on 27 July, while mean water temperature increased from 26 to 30 ° C. Dissolved oxygen exceeded 5.3 mg/l on both dates and specific conductivity increased from 365 to 400 uS/cm. The pH, alkalinity, and calcium concentration decreased following two rainfalls (Appendix Tables XII and XIII). Trends for pH, alkalinity, calcium, iron, and zinc were similar to the Neosho River (Appendix Table VIII). Regression equations with alkalinity and pH as the regressor were calculated for the significant correlations (Appendix Table IX). Physicochemical water quality parameters in Spring River were similar to Neosho River; however, lead concentration was significantly greater in Spring River (OSL < 0.05).

Grand Lake

Depth, water temperature, dissolved oxygen, and specific conductivity were measured at sites 5, 6, 7, and 12 (Appendix Table XIV). The dissolved oxygen, water temperature, and specific conductivity values for Grand Lake were generally similar to those observed for Spring and Neosho rivers. Thermal stratification was observed only at Site 6 on 20 July; however, dissolved oxygen and specific conductivity stratification were detected at all sites. Dissolved oxygen at sites 6 and 7 was strongly stratified at > 2 m on 20 July and a second gradient existed at > 4 m. In general, dissolved oxygen was stratified at all sites with a minimum value 0.8 mg/l. Alkalinity and pH values were similar to Neosho and Spring rivers, though the range in alkalinity was less for Grand Lake (Appendix Table XV). The mean calcium and magnesium concentrations were 37.9 and 6.8 mg/l, respectively (Appendix Table XVI). Significant correlations existed for calcium with magnesium and zinc, while magnesium correlated with zinc (Appendix Table VIII). Grand Lake had a significantly higher magnesium concentration than Spring River (OSL < 0.005). Manganese concentration was <0.25 mg/l and was significantly correlated with lead, zinc, and cadmium (Appendix Table VIII). Iron and zinc ranged from <0.04 to 2.2 mg/l and <0.05 to 0.78 mg/l, respectively. Mean lead concentration was 0.020 mg/l, while cadmium was generally below detection limits.

Tar Creek

Water temperature at Tar Creek sites was similar to Neosho River; however, specific conductivity was much higher (Appendix Table XVII). Dissolved oxygen was > 5.0 mg/l at sites 26 and 27 and < 3.0 mg/l at the mine discharge sites 28 and 29. Maximum pH was 7.3 at Site 27 and a minimum of 3.3 at Site 26 (Appendix Table XVII). Alkalinity was > 500 mg/l at Site 28 and decreased to < 1 mg/l at Site 26. Tar Creek had significantly higher concentrations of calcium, magnesium, manganese, iron, cadmium , and zinc than Neosho River, Spring River, or Grand Lake (Appendix Table XVIII). The mean iron and zinc concentrations were 250 and 78.9 mg/l, respectively. Lead concentration was generally below detection limit (<0.005 mg/l), while the mean cadmium concentration was 0.033 mg/l. Cadmium was significantly correlated with magnesium, iron, and zinc (Appendix Table VIII).

Heavy Metals in Sediment Cores

Sediment cores taken from Grand Lake were analyzed for the concentration of iron, lead, zinc, cadmium, chromium, and percent organic carbon (Appendix Table XIX). Little vertical variation existed in the concentration of iron, chromium, and organic carbon. Values averaged 30,429 mg/kg for iron, 3.15 mg/kg for chromium, and 2.11% organic carbon. Significant inverse correlations existed for lead, zinc, and cadmium with depth (Figures 3, 4, and 5). Values ranged from 90.5 to 130.9 mg/kg for lead, 129 to 1,045 mg/kg for zinc, and 0.7 to 6.2 mg/kg for cadmium. Lead was highly correlated with zinc and cadmium ($r = 0.90$, OSL < 0.001 and $r = 0.87$, OSL < 0.001, respectively).

Sediment Extraction

Sediment from Grand Lake, Neosho River, and mouth of Tar Creek were digested and analyzed for total iron, lead, zinc, cadmium, chromium, and percent organic carbon (Table III). Minimum values of iron and zinc were measured in Grand Lake, while maximum values existed in the mouth of Tar Creek. Iron concentration ranged from 47,922 -98,324 mg/kg and zinc from 1,176 -3,535 mg/kg. Lead and cadmium concentration were minimal in Neosho River and maximal in Grand Lake. Values for lead ranged from 63.8 -132.2 mg/kg and cadmium values from 3.7 -9.9 mg/kg. Minimum concentrations of chromium and organic carbon were measured in

Figure 3. Regression of total lead (mg/kg) verses depth (cm) in a sediment core from Grand Lake

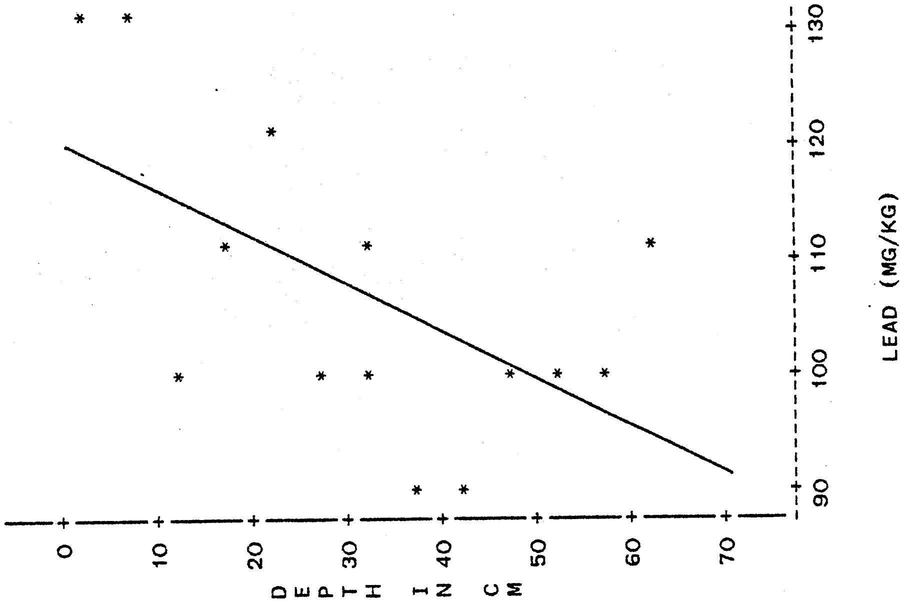

0
10
20
30
40
50
60
70
DEPTH IN CM
90
100
110
120
130
LEAD (MG/KG)

Figure 4. Regression of total zinc (mg/kg) verses depth (cm) in a sediment core from Grand Lake

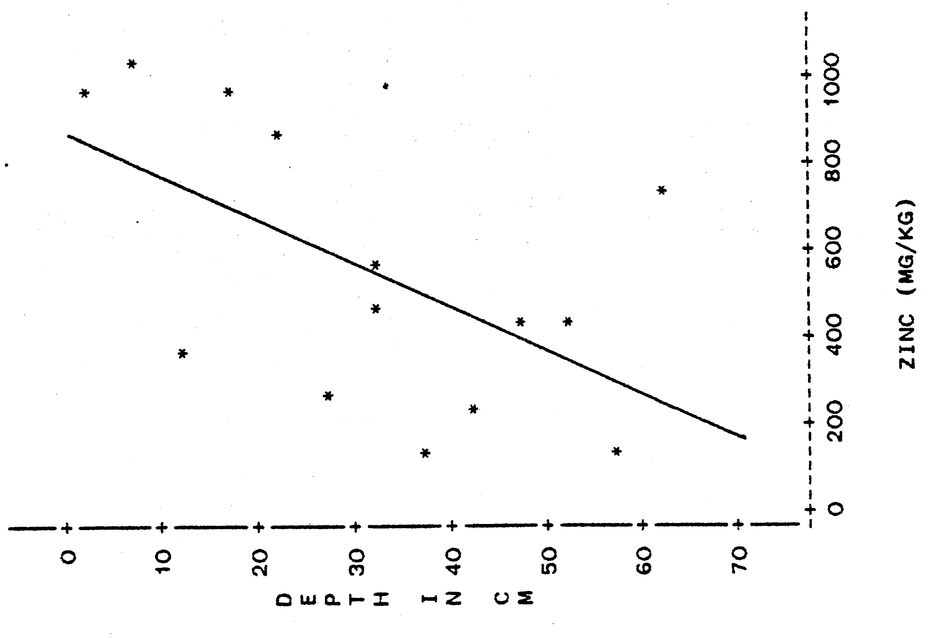

DEPTH IN CM
0
10
20
30
40
50
60
70
ZINC (MG/KG)
0
200
400
600
800
1000

Figure 5. Regression of total cadmium (mg/kg) verses depth (cm) in a sediment core from Grand Lake

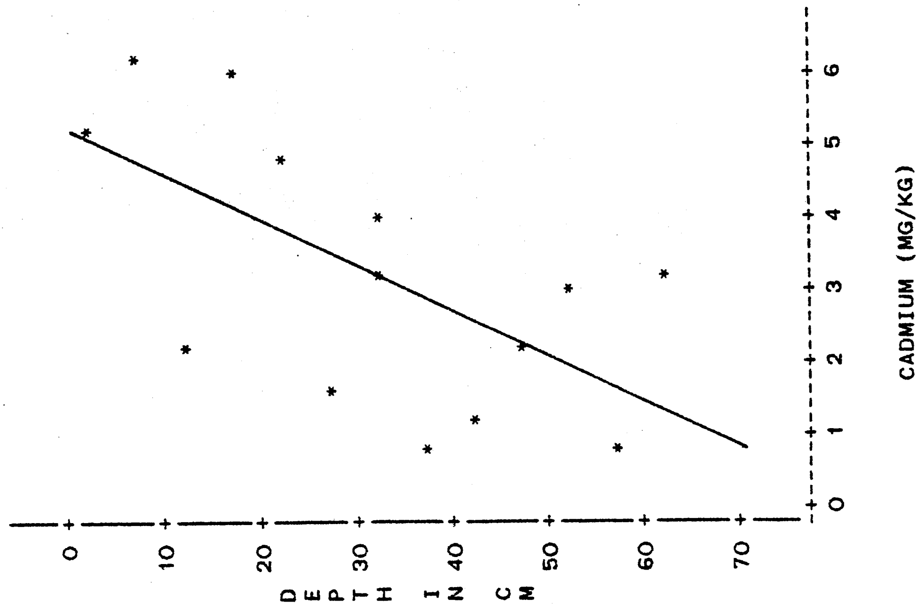

DEPTH IN CM
0
10
20
30
40
50
60
70
CADMIUM (MG/KG)
0
1
2
3
4
5
6

TABLE III

TOTAL METALS AND ORGANIC CARBON IN SEDIMENTS FROM TAR CREEK-NEOSHO RIVER CONFLUENCE, NEOSHO RIVER, AND GRAND LAKE USED IN EXTRACTION EXPERIMENT

Sample Identification	mg/kg					Organic Carbon (percent)
	Iron	Lead	Zinc	Cadmium	Chromium	
Mouth of Tar Creek	98,324	84.0	3,535	7.4	10.4	1.64
Neosho River	88,116	63.8	2,600	3.7	6.7	1.36
Grand Lake	47,922	132.2	1,176	9.9	9.0	1.47

Neosho River, while maximam values occurred in mouth of Tar Creek. Chromium concentration ranged from 6.7 -10.4 mg/kg and organic carbon from 1.36 -1.64%.

An aliquot of the sediment sample was extracted with reconstituted water and filtered to obtain a measure of dissolution of trace metals at pH levels ranging from 3 to 9 (Appendix Table XX). Total dissolved iron extracted from Tar Creek sediments was significantly higher than Neosho River or Grand Lake sediments ($p = 0.05$). The pH 3 extract solublized significantly more dissolved iron from Grand Lake and Neosho River sediments than other pH levels ($p=0.05$) (Figure 6). Dissolved iron concentration was significantly higher at pH 3 and 9 in Tar Creek extracts than at other pH levels ($p=0.05$).

Total dissolved lead extracted was significantly higher in Grand Lake sediments than other sediments due to the quantity extracted at pH 3 ($p=0.05$) (Figure 7). At pH levels >3 the dissolved lead was not significantly different for the sediment extracts.

Total dissolved zinc concentration extracted was significantly higher for Tar Creek sediments than Grand Lake ($p=0.05$). The quantity of dissolved zinc extracted significantly decreased with decreasing pH acidity ($p=0.05$) (Figure 8).

Total dissolved cadmium concentration in Grand Lake extracts was significantly higher than Neosho River or Tar Creek extracts ($p=0.05$) As pH decreased the quantity of dissolved cadmium increased (Figure 9). At a pH of 6 or above cadmium extracted was below detection limits for all sediments (<0.005).

Total dissolved chromium concentration showed no significant increase at any pH ($p=0.05$) (Figure 10).

Figure 6. Extracted, dissolved iron (mg/l) for pH values ranging from 3 to 9. Grand Lake (*), Neosho River (+), and Tar Creek (O) sediment extracts are indicated

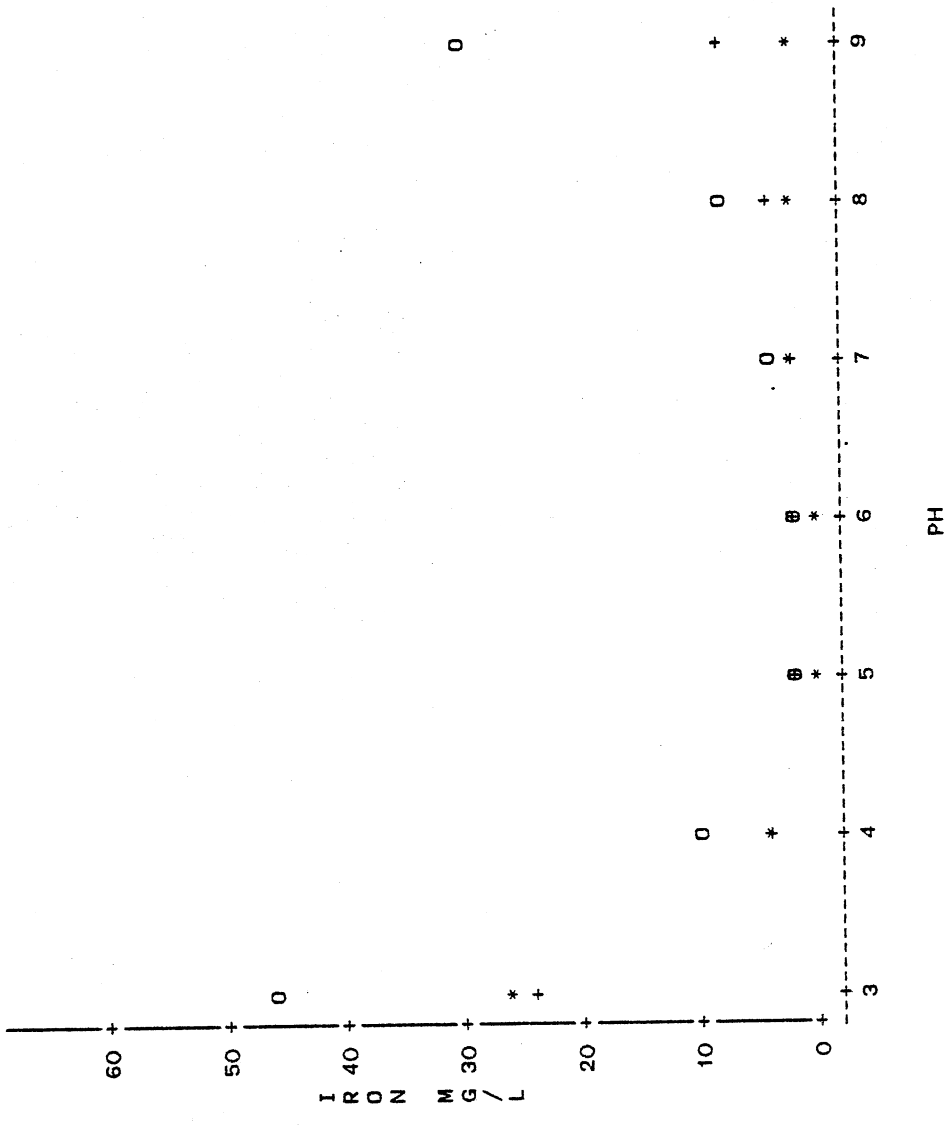

IRON MG/L
0
10
20
30
40
50
60
PH
3
4
5
6
7
8
9

Figure 7. Extracted, dissolved lead (mg/l) for pH values ranging from 3 to 9. Grand Lake (*), Neosho River (+), and Tar Creek (O) sediment extracts are indicated

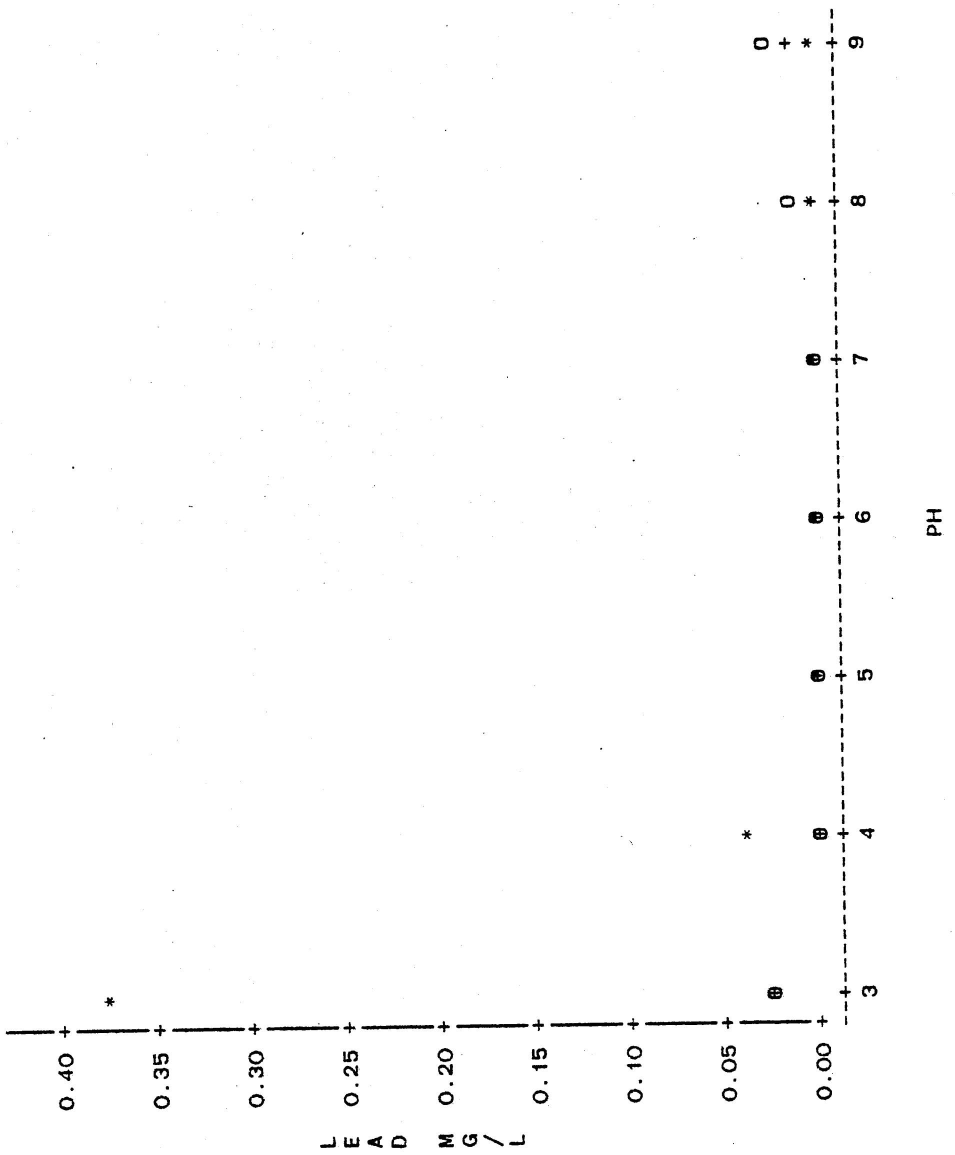

LEAD MG/L
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3
4
5
6
7
8
9
PH

Figure 8. Extracted, dissolved zinc (mg/l) for pH values ranging from 3 to 9. Grand Lake (*), Neosho River (+), and Tar Creek (0) sediment extracts are indicated

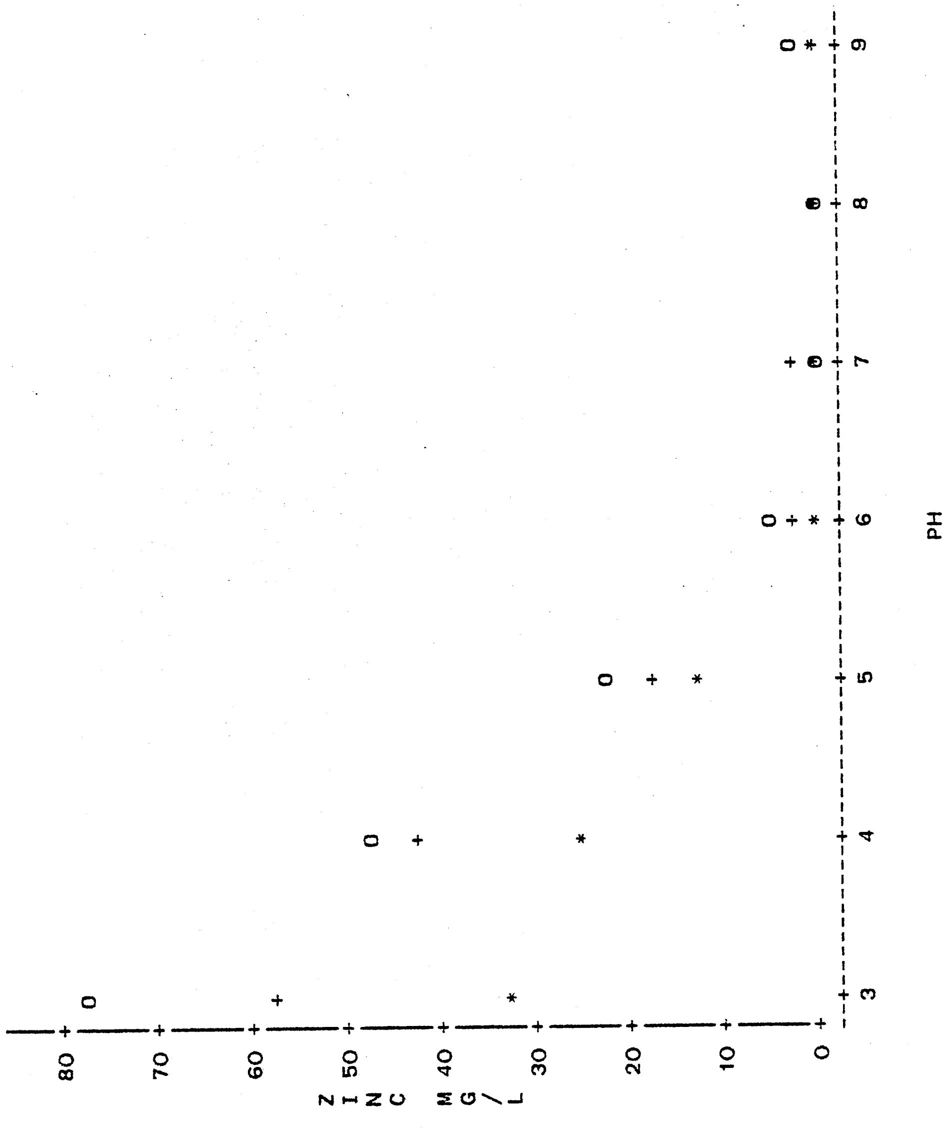

80
70
60
50
40
30
20
10
0
ZINC MG/L
3
4
5
6
7
8
9
PH

Figure 9. Extracted, dissolved cadmium (mg/l) for pH values ranging from 3 to 9. Grand Lake (*), Neosho River (+), and Tar Creek (0) sediment extracts are indicated

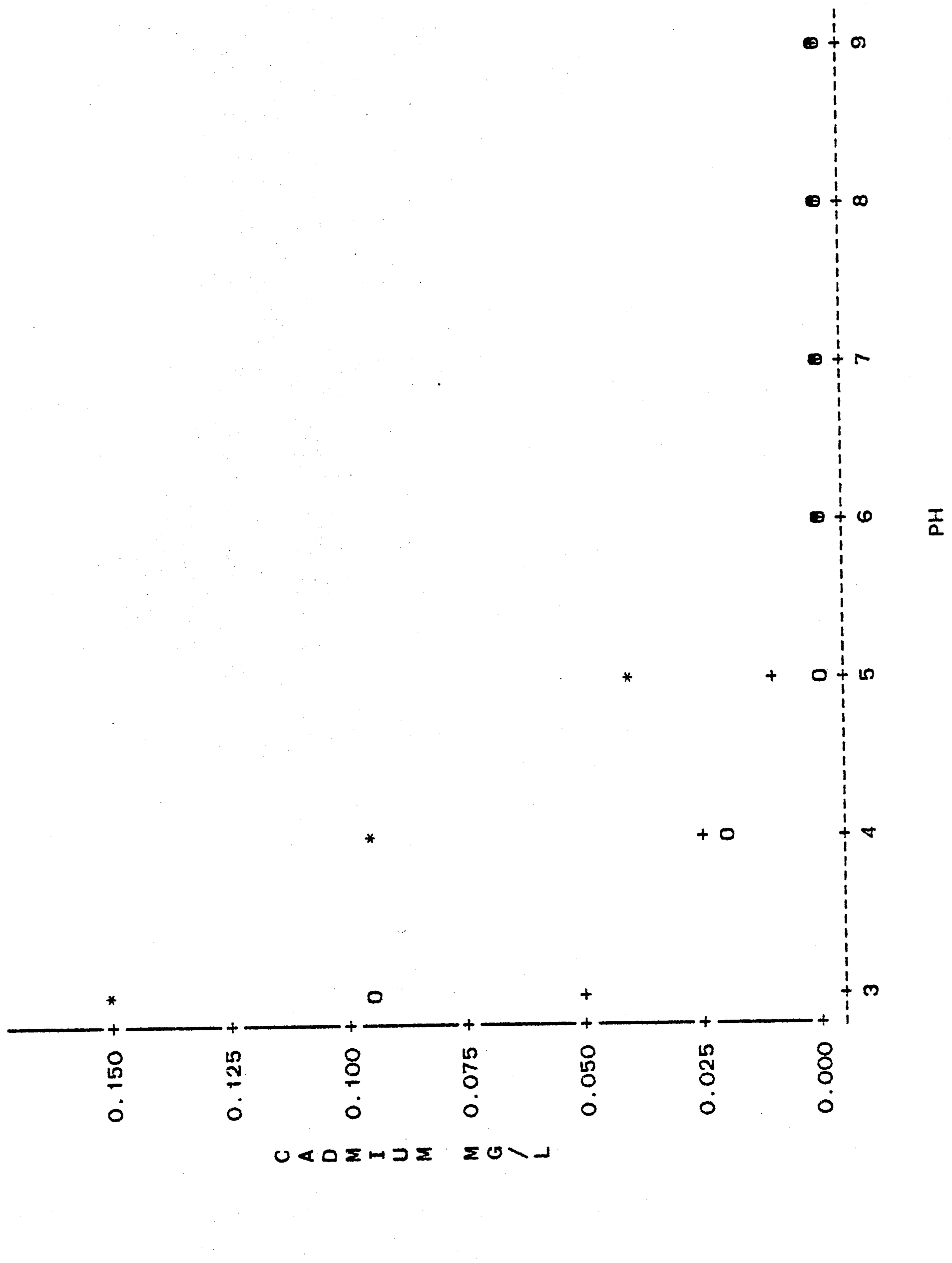
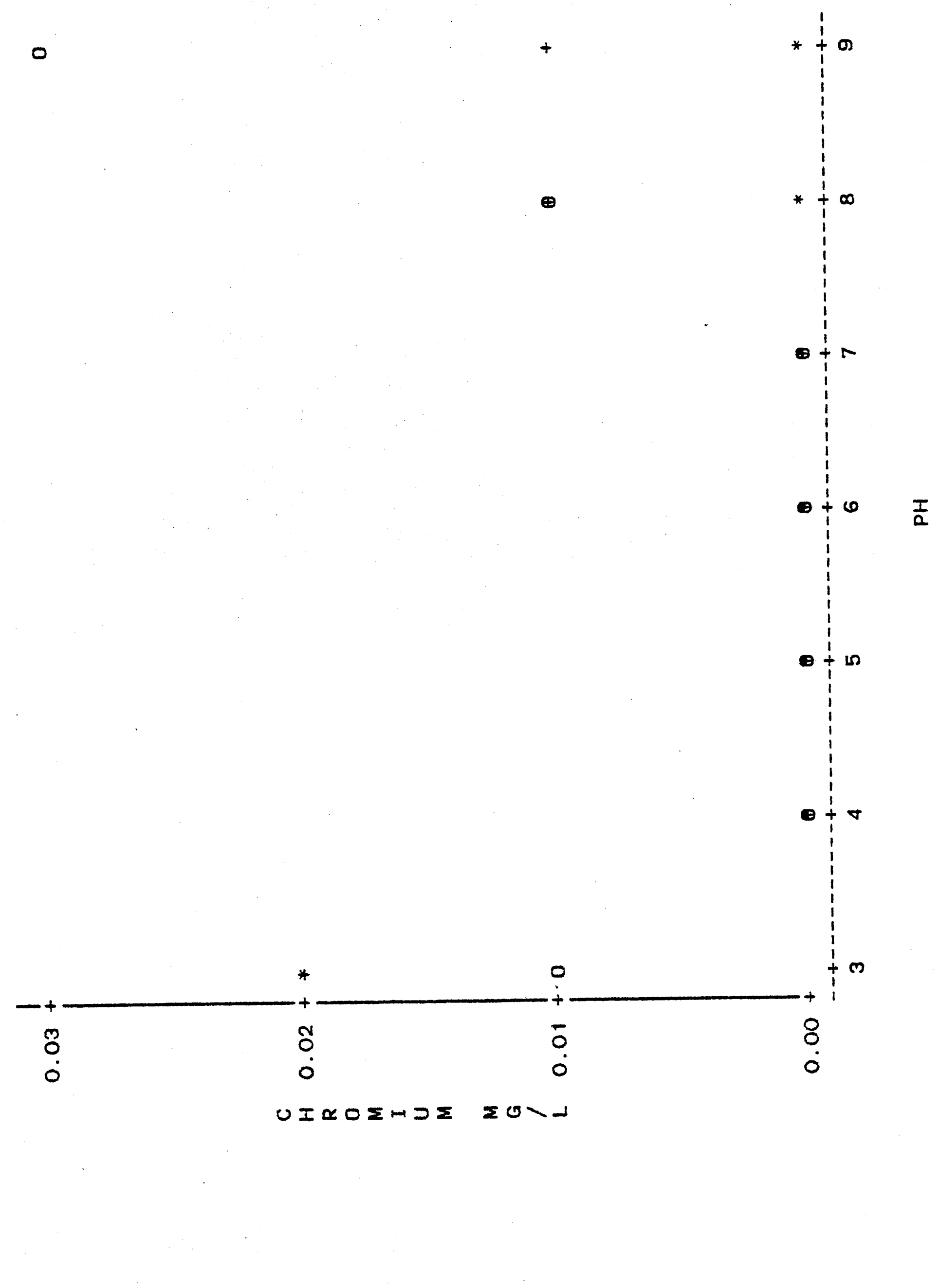

CADMIUM MG/L
0.150
0.125
0.100
0.075
0.050
0.025
0.000
3
4
5
6
7
8
9
PH

Figure 10. Extracted, dissolved chromium (mg/l) for pH values ranging from 3 to 9. Grand Lake (*), Neosho River (+), and Tar Creek (O) sediment extracts are indicated


CHROMIUM MG/L
0.03
0.02
0.01
0.00
PH
3
4
5
6
7
8
9

Sediment-Water Toxicity

Bioassay tests were performed to assess possible acutely lethal effects of Grand Lake sediment on _Daphnia_ in the presence and absence of chironomid larvae. Grand Lake sediments were mixed with reconstituted water (RCW) 48 h prior to introducing the test organisms. An aliquot of the suspension was filtered, digested, and analyzed for dissolved iron, lead, zinc, and cadmium. Reconstituted water (control) had a dissolved iron concentration of 0.381 mg/l, zinc 0.01 mg/l, lead 0.006 mg/l, and cadmium concentration below detection limits (<0.005).

The RCW plus Grand Lake sediments had the following concentrations (mg/l): iron 0.71, lead 0.014, zinc 0.05, and cadmium <0.005.

The mean pH was 7.6 ($\pm$ 0.2), dissolved oxygen exceeded 4 mg/l, and hardness ranged 146 to 170 mg/l as $CaCO_3$ during toxicity experiments in control (RCW) and treatment water.

Neither RCW nor RCW plus Grand Lake sediments, in the absence of chironomid larvae, showed toxicity at 96 h. Adding chironomid larvae did not increase mortality of _Daphnia_ in the test chambers and visual inspection indicated no mortality of the larvae.

Daphnia neonates were placed in RCW and RCW plus Grand Lake sediments and monitored until neonates were produced. Reconstituted water alone showed significantly lower neonate production than RCW plus Grand Lake sediments ($p=0.05$). No significant mortality occurred in either RCW or RCW plus Grand Lake sediments ($p=0.05$). Chironomid larvae had no significant effect on mortality or production of neonates in _Daphnia_ ($p=0.05$).

Ceriodaphnia were placed in RCW and RCW plus Grand Lake sediments for 5 days. Neither RCW nor RCW plus sediment produced mortality.

Sediment Extractions and Daphnia Toxicity

Reconstituted water adjusted to a pH 6 was used to extract sediments from Tar Creek-Neosho River confluence, Neosho River, and Grand Lake. After extraction the pH was adjusted to 7.0 prior to use in Daphnia toxicity tests. Hardness, alkalinity, calcium, magnesium, iron, zinc, lead, cadmium, and chromium were measured for each sediment extract (Table IV). Minimum value for hardness was 133 mg/l as $CaCO_3$ in control RCW to a maximum 388 mg/l as $CaCO_3$ in Grand Lake extract. Alkalinity and magnesium concentrations were lowest in Tar Creek extracts at 80 mg/l as $CaCO_3$ and 13.41 mg/l while Grand Lake extracts were highest with 320 mg/l as $CaCO_3$ and 17.25 mg/l. RCW had the minimal values of calcium, iron, and zinc, while Grand Lake extracts had the maximal calcium concentration and Tar Creek the maximal iron and zinc concentrations. Lead, cadmium, and chromium concentrations were at or below detection limit (<0.005) in all sediment extracts.

Daphnia 96-h toxicity tests were performed on RCW (control), and extracts from Tar Creek, Neosho River, and Grand Lake. Reconstituted water and Grand Lake extracts showed no significant mortality to Daphnia at 96 h ($p=0.05$). Toxicity in Tar Creek extracts was apparent at 24 h, with 100% mortality at 72 h. Mortality in Neosho River extracts was also evident at 24 h and by 48 h the mortality was 100%.

Daphnia LC50 Determination

The high mortality observed in the previous experiment with Tar Creek and Neosho River sediment extracts necessitated determining LC50 measurements. Daphnia 48-and 96-h toxicity test was performed with Tar Creek and Neosho River sediment extracts. Reconstituted water was added

TABLE IV

WATER ANALYSIS FOR SEDIMENT EXTRACTS USED IN TOXICITY DETERMINATIONS WITH DAPHNIA

Water Quality Parameter	Extract			
	Reconstituted Water	Tar Creek	Neosho River	Grand Lake
pH*	7.0	7.0	7.0	7.0
Hardness	133	160	202	388
Alkalinity	124	80	128	320
Calcium (mg/l)	22.74	29.95	35.19	101.60
Magnesium (mg/l)	16.51	13.41	15.78	17.26
Iron (mg/l)	0.07	1.73	0.47	0.29
Zinc (mg/l)	0.09	4.16	2.56	0.66
Lead (mg/l)	<0.005	<0.005	<0.005	<0.005
Cadmium (mg/l)	<0.005	<0.005	<0.005	<0.005
Chromium (mg/l)	0.01	<0.01	<0.01	<0.01

* - Extraction was performed at pH 6 and samples were adjusted to pH 7 for use in toxicity experiments.

to give extract concentrations of 8, 15, 30, 55, and 90%. A considerable difference existed in the percent mortality of Daphnia exposed to dilutions of 8 and 15% and those exposed to higher dilutions (Table V). The maximum mortality at the lower dilutions was 28% at 96 h. At 30, 55, and 90% dilutions, the percent mortality ranged from 72-83% at 48 h and from 95-100% at 96 h. Probit analysis (Litchfield-Wilcoxin) was performed with a calculated 48-h LC50 of 26.4% (slope = 2.19287) extract and a 96-h LC50 of 23.5% extract (slope = 1.51905) (P=0.05).

Similar results were obtained for Daphnia exposed to Tar Creek extracts except for greater mortality of organisms at the 15% dilution (Table V). Probit analysis was performed with a calculated 48-h LC50 of 25.6% extract (slope = 1.74458) and a 96-h LC50 of 7.5% (slope = 1.69679) (p=0.05).

TABLE V

48- AND 96-HOUR ACUTE TOXICITY DETERMINATION FOR NEOSHO RIVER AND TAR CREEK SEDIMENT EXTRACTS TO DAPHNIA

Extract Identification	Percent Dilution	Percent Mortality Hours 24	48	72	96
Neosho River	8	0	11	22	22
	15	0	22	22	28
	30	33	72	78	95
	55	28	83	89	100
	90	12	78	89	95
Mouth of Tar Creek	8	0	17	39	39
	15	12	28	56	78
	30	17	83	89	100
	55	6	39	83	100
	90	17	89	100	100
Reconstituted Water	0	0	0	0	0

CHAPTER VI

DISCUSSION

Water Quality

Water quality in Tar Creek is controlled by the acid-mine water seeps and, to a lesser extent, leaching of the tailings piles. The observed pH values, similar to those reported for other acid-mine water seeps, were controlled primarily by the oxidation of Fe^{2+} (Figure 1) (Mink et al. 1972). The pH of Neosho River, Spring River, and Grand Lake were within Oklahoma water quality standards. The pH of two rainfalls during August 1983 had a mean pH of 3.6 indicating the area was receiving atmospheric inputs of acidity. Following rainfall during October 1983 and March 1984, alkalinity, pH, and calcium values in the Neosho and Spring rivers decreased resulting from dilution of the waters by runoff and acidic precipitation. Grand Lake had less fluctuation in alkalinity than Neosho or Spring rivers, probably due to the relatively large lake volume.

Iron concentration increased for October 1983 and March 1984 in the Neosho and Spring rivers. The source of the iron was probably iron hydroxide precipitated during oxidation of acid mine waters and transported after resuspension occurred.

Zinc concentration increased in Neosho and Spring rivers during rainfall and was likely due to the elevated flow rate carrying suspended material originating from Tar Creek and other acid-mine water contaminated tributaries along Spring River. Oklahoma and USEPA water quality standards were exceeded for zinc on 11 August 1983 for Grand Lake and 6 March 1984 for the Neosho and Spring rivers. The estimated combined daily loading rates for zinc of >680 kg/day from sites 28 and 29 into Tar Creek were probably significant sources of zinc to the Neosho River (OWRB, 1983). Zinc was positively correlated with iron in Spring and Neosho rivers suggesting a common origin and/or an association of zinc and iron. Bradley and Lewin (1982) found that zinc concentration increased during high flow rates and high suspended solids concentration; however, the highest zinc concentrations were found in receeding waters. The zinc was believed to be associated with iron hydroxide coatings on particulates.

Lead concentration was highest on 6 March 1984 in Spring River. Spring River lead concentration exceeded Oklahoma and USEPA water quality standards on 6 March 1984 in Spring River. The negative correlation of lead and zinc indicated that the lead species were associated with different materials than the zinc species. The negative correlation reflected possible differences in transport and may be a result of sampling the receeding waters. Bradley and Lewin (1982) reported the highest lead concentrations occured at peak flow in rivers and decreased as flow decreased. Transport of lead was probably as an adsorbed species on particulates and organic matter associated with the particulates (Salim, 1983; Benes et al., 1985).

Copper concentration (180 ug/1) exceeded Oklahoma and USEPA water quality standards on 11 August 1983 at Site 7 on Grand Lake. Copper did not commonly exceed water quality standards at any site on Spring River, Neosho River, and Grand Lake.

State and federal water quality criteria for zinc were exceeded on all sampling dates in Tar Creek sites. Cadmium also exceeded state and federal water quality criteria on all sampling dates at sites 26 and 29, and on 22 October 1983 at Site 27. Copper concentration exceeded standards for sites 27 and 29. Oklahoma water quality criteria were exceeded on all sampling dates for sites 26, 28, and 29 in Tar Creek. The low pH waters increased solublization of zinc and increased transport into the Neosho River.

Heavy Metals in Sediments

Sediment cores taken in the upper end of Grand Lake showed high concentrations of iron, lead, zinc, cadmium, and chromium. Chromium was used as a control metal since deposits were not reported in the mineralized zone of the Boone Formation (McKnight and Fischer, 1970). Walters et al. (1974) reported sediments from Lake Erie contained 8,900 to 31,000 mg/kg iron, 9 to 250 mg/kg chromium, 0 to 10 mg/kg cadmium, and 8 to 900 mg/kg zinc. The high concentration of these metals resulted from input to Lake Erie. Grand Lake sediments had similar iron and chromium, lower cadmium, and much higher zinc concentrations than maximum concentrations in Lake Erie sediments. Lake Erie sediment cores were similar in depth to the Grand Lake cores; however, the concentration of metals in Lake Erie decreased to levels reflective of nonpolluted sediments below 25 cm in most cores. Iskandar and Keeney (1974) reported sediment cores from eutrophic Wisconsin lakes (e.g. Mendota and Monona lakes) contained 12 to 195 mg/kg zinc, <0.1 to 167.0 mg/kg lead, 0.2 to 5.5 mg/kg cadmium, and 0.3 to 49.0 mg/kg chromium. Sedimentation rates ranged from 4.2 -5.3 mm/yr and a significant decrease existed in zinc, cadmium, and lead at >25 cm reflecting precultural sediments. In contrast, Grand Lake sediment cores showed increased concentrations of zinc, lead, chromium, and cadmium at depths > 50 cm. The relatively young age of Grand Lake suggested that the elevated quantities of metals in the sediment core probably resulted from higher sedimentation rates. Landsat (August, 1973) and high-altitude (April, 1980) infrared photographs, obtained from the OSU Center for Remote Sensing, indicated high turbidities in the upper end of Grand Lake with low turbidity below the confluence at Elk River. The significant correlations between metals demonstrate a common source of metals. This was supported by the significant correlation of zinc, lead, and cadmium with depth and lack of significant correlation of chromium with any parameter.

Organic carbon was significantly correlated with iron. Kitano et al. (1981) and Kitano and Sakata (1980) reported similar trends for iron in core samples from a polluted bay and found that the iron associated with H_2O_2 digestable fraction (organic) was relatively constant. The relationship between iron and organic carbon in Grand Lake sediments was not clear; however, the lack of correlation of iron with depth probably reflects the large quantities of iron transported to sediments in even nonpolluted rivers.

The Oklahoma Water Resources Board (1982) numerical criteria goals for cadmium, chromium, and lead in sediments are 2.0, 100.0, and 50.0 mg/kg, respectively. Cadmium and lead exceeded the numerical goals for sediment at Tar Creek-Neosho River confluence, Site 19 in the Neosho River and Site 5 in Grand Lake.

Sediment Extraction

The recommendation by USEPA (1978) for use of reconstituted water (RCW) in Daphnia cultures prompted testing RCW suitability for extracting sediments prior to bioassays. Leachate and extraction procedures were developed primarily to predict readily transportable quantities of metals, presumably a reflection of potential availability to organisms.

Sediments were analyzed for total iron, lead, zinc, cadmium, chromium, and organic carbon in Tar Creek-Neosho River confluence, Neosho River (Site 19), and Grand Lake (Site 5) (Table IV). Sediment iron concentration at the Tar Creek-Neosho River confluence was much higher than reported by Oklahoma Water Resources Board (OWRB) (1983), total zinc and lead were similar, and cadmium was lower in concentration. The total concentrations of iron, lead, zinc, and cadmium were much higher in Neosho River sediments than previously reported (OWRB, 1983). The OWRB sampled immediately below the confluence of Tar Creek and Neosho River; whereas, I sampled midway between Tar Creek and upper end of Grand Lake (Site 19). The transport of iron hydroxide, adsorbed metals, and sediment from Tar Creek to Neosho River was increased by runoff after rainfall. The floculent characteristic of iron hydroxide promoted suspension increasing transport downstream. The OWRB (1983) concluded that Neosho River sediments "... appear to be relatively free of acid mine contamination"; however, I found significant acid mine contamination in Neosho River sediments.

Total metals in Grand Lake sediments from Site 5 were much higher in iron, lead, zinc, and cadmium than at a similar site sampled by OWRB

(1983). The difference in the data reported for Grand Lake and Neosho River from the OWRB study indicated that the deposition of metals was related to sampling methodology and site location. The higher concentrations of lead and cadmium in Grand Lake sediments than Neosho River sediments was attributed to increased sedimentation of particulate associated metals.

Aliquots of Grand Lake, Neosho River, and Tar Creek sediments were extracted with reconstituted water at various pH's and filterable/dissolved iron, lead, zinc, cadmium, and chromium concentration determined. Dissolved iron extracted increased as pH decreased below 5 and increased above a pH of 6. Redox (Eh) equilibria indicate that at acidic, oxidizing conditions ($Eh > 0.4$) the predominant iron species are Fe^{2+}, Fe^{3+}, $Fe(OH)_3$, $FeSO_4$, and $FeSO_4^+$ (Nordstrom et al., 1979). The higher quantity of extracted iron from Tar Creek sediments was probably related to the greater initial concentration. No significant difference was shown between extracted iron in Grand Lake and Neosho River sediments; however, the initial concentration in Neosho River sediments was approximately twice that of Grand Lake. Filterable iron at pH exceeding 7 was probably an iron hydroxide species <0.45 um in diameter.

Extracted, filterable lead appeared related to total sediment concentration and RCW pH. Grand Lake had a total lead concentration of 132.2 mg/kg and significantly more was solublilized at pH 3 than in Neosho River or Tar Creek. Extracted lead concentrations at other pH levels were not statistically significant. The relatively low pH necessary for extraction indicated that lead was strongly adsorbed to sediment.

Dissolved zinc was strongly dependent on RCW pH and total sediment concentration. The sensitivity of zinc to pH was in sharp contrast to the insensitivity of lead. Zinc is much more mobile in aquatic systems than lead, and the amount mobilized increased as concentration in the sediments increased. At pH 7 or greater, the dissolved zinc was < 1.0 mg/l in all. The pH effect for zinc indicated that zinc was adsorbed much less strongly to sediment fractions than lead.

Extracted cadmium was also sensitive to pH conditions and total sediment concentration. Grand Lake sediment had higher total cadmium concentration and higher extracted concentrations than Neosho River or Tar Creek sediments. As the pH decreased below 6, the amount extracted increased for all sediments. Cadmium has a relatively high mobility in aquatic systems and the use of pH adjusted RCW typifies this high mobility. At pH 6 or greater cadmium was not significantly mobilized from any of the sediments.

Mouvet and Bourg (1983) estimated that the surface binding constants for zinc, cadmium, and lead on sediments from the Meuse River were $10^{-3.6}$, $10^{-3.7}$, and $10^{-1.7}$, respectively. They concluded that zinc, lead, and cadmium were all controlled by adsorption processes; however, lead was more strongly bound to particulates and organic matter in the sediment while cadmium and zinc were relatively weakly bound. Figura and McDuffle (1980) found that cadmium and zinc were in very-and moderately-labile forms and lead in the slowly labile and inert forms. Mouvet and Bourg (1983) and Figura and McDuffle (1980) results support the conclusion in the present study that concentration of zinc, cadmium, and lead extracted by pH adjusted RCW was controlled by adsorption on the sediments from Grand Lake, Neosho River, and Tar Creek.

Determination of metal species was not performed; however, dissolved-pH sensitive metal fractions in the sediments may represent the most available forms to the overlying water column.

Extracted chromium concentration suggested a sensitivity to pH 3 conditions and pH 8 or above; however, due to the low observed concentrations the extracted amounts were not significantly different. I conclude that acid-mine drainages from the Picher Field did not contribute significant amounts of chromium to the sediments of Grand Lake or Neosho River. Water quality data obtained during the study did not show elevated concentration of chromium at any sampling site. The hexavalent chromium would be detected if the acid-mine waters were a significant point source (USEPA, 1980).

Bioavailability refers to the quantity of metals available to organisms and has been correlated with bioconcentration in bivalves (Marquenie et al. 1983), EDTA extractions (Davies et al. 1981), and other biological and chemical approaches (Calmano, 1981; Luoma and Bryan; 1979; Luoma, 1983). As the acidity of RCW increases the amounts of iron, lead, cadmium, and zinc extracted increases as total metals in the sediments increase. In addition, the relative mobility: Zn, Cd > Fe > Pb in aquatic systems is similar to that extracted with RCW at pH 7 and below. Brummer et al. (1983) stated that as pH decreased in soil solutions, the solubility of zinc increased and was controlled by adsorption/desorption processes. Nienke and Lee (1982) observed similar adsorption/desorption processes in Lake Michigan sediments and zinc. Tiller et al. (1984) reported that adsorption rates of zinc and cadmium decreased rapidly as pH decreased.

Chemical extraction approaches (e.g. acetic acid, hydrochloric acid, ammonia) may overestimate bioavailability due to the pH values to which adsorbed, complexed, and chelated metals are exposed. If adsorption/desorption processes are of major importance in determining solubility of metals then contacting the sediment with solution pH conditions dissimilar from natural values will give questionable estimates of bioavailability. Extraction procedures incorporating a chelater (e.g. EDTA) must either make assumptions or verify influences of the chelater with naturally occurring complexing agents and relative binding affinities for the various constituents present. Therefore, pH-adjusted RCW (e.g. pH 6) might provide a realistic estimate of potential bioavailability of sediment metals to overlying water. Reconstituted water has the advantage that composition, hardness, pH, and other factors can be modified to model waters in most aquatic systems. A limitation might be the absence of organic acids in the RCW; however, extracting sediments with RCW would introduce naturally occurring organic acids.

Extracted Sediments and Bioassays

High concentrations of iron, lead, zinc, and cadmium in sediments from Tar Creek-Neosho River confluence, Neosho River (Site 19), and Grand Lake (Site 5) were extracted with RCW adjusted to pH 6. The observed concentration of extracted iron, lead, zinc, cadmium, and chromium were similar to previous quantities extracted at pH 6. The pH of the filtered extract was adjusted to pH 7 prior to use in *Daphnia* bioassays; however, no significant changes in trace metal content were observed probably due to the lack of particulates >0.45 um to which adsorption could occur. *D. magna* were fed at 48 h and daily thereafter to prevent starvation. Buikema et al. (1980) reported that D. *pulex* had 80% mortality after 1 day in filtered water (<0.45 um); however, no significant mortality was noted at 48 h in filtered control RCW.

A 96-hour static renewal bioassay was performed on extracts from the sediments. No significant mortality was noted in RCW or extracted Grand Lake sediments. Acute toxicity of Tar Creek and Neosho River extracts was probably due to zinc toxicity. USEPA (1980) reported zinc LC50 values for *D. magna* ranged from 0.100 to 0.655 mg/l. The dissolved zinc concentration for Tar Creek and Neosho River extracts was 4.16 and 2.56 mg/l, respectively. Lead and cadmium were below detection limits (<0.005) in the sediment extracts. I conclude that the observed mortality was a result of filterable zinc in the samples.

Grand Lake sediment extracts produced no significant toxicity. Zinc was present at 0.66 mg/l, within the upper range reported for *D. magna* LC50 values (USEPA, 1980); however, the lethal concentration of zinc, as well as lead and cadmium, shows a relationship with hardness. The LC50 for Grand Lake extracts was approximated by calculation of a regression line from USEPA (1980) reported LC50 values for zinc at several hardnesses ($r = 0.893$, $LC50 = 2.98(\text{hardness}) + 113.55$). The hardness of 388 mg/l for Grand Lake extracts results in a calculated LC50 of 1.269 mg/l zinc. Dissolved zinc in Grand Lake sediment extracts of 0.66 mg/l was much lower than the estimated LC50 at 388 mg/l hardness. The absence of acute toxicity was attributed to the lower zinc activity in Grand Lake sediment extracts, e.g., competition with calcium and magnesium adsorption and binding to cellular transport mechanisms was decreased.

LC50 Determination

Daphnia 48-and 96-h LC50 values were calculated for the extracted sediments from the Tar Creek-Neosho River confluence and Neosho River (Site 19). The calculated 48-and 96-h LC50 values for the Neosho River were 26.4 and 23.5% extract concentration corresponding to 0.676 and 0.602 mg/l dissolved zinc at 202 mg/l hardness, respectively. USEPA (1980) has reported a *Daphnia* LC50 for zinc of 0.655 mg/l at a similar hardness. Therefore, LC50 concentrations calculated for zinc in Neosho River sediments explained the observed toxicity to *Daphnia*.

The calculated 48-and 96-h LC50 for Tar Creek extracts was 25.6 and 7.5% corresponding to 1.065 and 0.312 mg/l dissolved zinc at 160 mg/l hardness, respectively. The estimated LC50 for zinc at 160 mg/l hardness from the regression equation was calculated to be 0.590 mg/l. The 48-h LC50 zinc concentration was almost twice as large as might be expected and the 96-h LC50 approximately one-half the expected concentration. The higher 48 h LC50 concentration of zinc might be attributed to adsorption to particulates < 0.45 um or formation of less toxic complexes. At 96 h the LC50 concentration of zinc was much lower than estimated by the regression equation. The low zinc concentration did not explain the observed 96 h toxicity. A possible explanation might be that the extracted iron (1.73 mg/l) contributed to the *Daphnia* 96-h mortality. Smith et al. (1979) in a review of the EPA Redbook, reported a possible iron toxicity to *Cladophora* at 450 ug/l or more and Warnick and Bell (1969) reported toxicities as low as 320 ug/l for aquatic insects. The levels of lead and cadmium (<0.005 mg/l) suggest little influence.

Bioassays

Daphnia bioassays were performed on reconstituted water (RCW) + Grand Lake sediments with RCW as the control solution in the presence and absence of chironomid larvae. The concentration of trace metals in the sediment-water solution were well below reported ranges of LC50 for dissolved lead, zinc and cadmium (USEPA, 1980a,1980b,1980c). However, total iron, lead, zinc, and cadmium for the Grand Lake sediments was high (Table III). In one-half the test chambers five chironomid larvae were introduced at 24 h to measure an increase in mortality due to increased mixing at the sediment-water interface. No mortality was noted for RCW or RCW + Grand Lake sediment and chironomid larvae. Malueg et al. (1983) using Daphnia and Hexagenia (mayfly nymph) in a sediment toxicity bioassay reported a significant increase in Daphnia toxicity when Hexagenia was present. The type of sediment contaminant(s) was not reported; however, Hexagenia increased availability of the toxicant by increasing sediment-water mixing. Visual inspection of the water column with Grand Lake sediments indicated that chironomid larvae did not produce observable increases in turbidity. Daphnia bioassays (9-day) were also performed and neonate production recorded. No significant toxicity was noted in the control or test water and chironomid larvae had no effect on mortality. In fact, Grand Lake sediment-water slurries had a neonate production higher than the control RCW. Daphnia in the RCW also appeared lighter colored than in the sediment-water mixture. This has also been observed in freshly prepared cultures of Daphnia (RCW); however, the neonate production increased and the characteristic darker coloration was apparent after several days. This may have been due to an increase in microflora which could serve as food in the culture solution.

Ceriodaphnia were incubated for 5 days in RCW and RCW + Grand Lake sediments. No toxicity was observed in either the control water (RCW) or RCW + Grand Lake sediments. The absence of mortality observed with Grand Lake sediment-water slurries to *Daphnia* and *Ceriodaphnia* indicated that five chironomid larvae were not effective in sediment resuspension in the test bottles. The hardness reported for the Grand Lake sediment extracts at pH 6 suggest that if chironomid larvae were effective in mixing the sediment the resultant hardness might have countered any acutely toxic effects.

CHAPTER VII

SUMMARY

1. Zinc exceeded Oklahoma and USEPA water quality standards in Neosho River, Spring River, and Grand Lake. The source of the zinc was attributed to acid-mine drainage.

2. Tar Creek exceeded Oklahoma and USEPA water quality standards for zinc, cadmium, and pH on all sampling dates.

3. Sediment core analysis showed that elevated concentrations of cadmium, lead, and zinc were deposited in the upper end of Grand Lake. The metals concentration at >50 cm indicated that the sediment deposition in the upper end of Grand Lake since impoundment was relatively rapid.

4. Elements whose availability is primarily controlled by adsorption were extracted by pH-adjusted reconstituted water. The pH-sensitive concentrations of metals extracted typified the mobility of zinc, cadmium, and lead reported for aquatic systems. Reconstituted water sediment extraction appears to reflect bioavailability of sediment-bound metals.

5. Grand Lake sediment-water mixtures and sediment extracts using RCW produced no mortality in *Daphnia* or *Ceriodaphnia* in the presence or absence of chironomid larvae.

6. The 48-and 96-h LC50 for Neosho River sediment extracts was

26.4 and 23.5% extract concentration, repectively. The 48-and 96-h LC50 for Tar Creek-Neosho River confluence extracts was 25.6 and 7.5% extract concentration, respectively. The toxicity was concluded to be bioavailable zinc in Neosho River sediments. Toxicity in Tar Creek extracts was due to zinc and an unidentified contaminant(s).

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APPENDIX

TABLE VI

DEPTH, TEMPERATURE, DISSOLVED OXYGEN AND SPECIFIC CONDUCTIVITY FOR NEOSHO RIVER DURING JULY-AUGUST 1983

Site & Date	Depth (m)	Temp (℃)	DO (mg/l)	Specific Conduct. (uS/cm)
Site 1	0	28.0	7.0	350
	1	27.5	7.1	350
	2	27.5	7.0	355
15 July	3	27.0	6.6	358
	4	27.0	6.4	360
	5	27.0	5.7	360
	6	27.0	5.8	380
	0	29.8	7.9	365
	1	29.3	6.5	370
20 July	2	29.3	6.5	375
	3	28.9	5.9	380
	4	28.0	5.3	
	5	27.0	1.5	
	0	30.9	5.7	431
1 August	1	30.2	5.3	431
	2	30.3	5.2	432
	3	30.2	3.9	438
Site 2				
	0	29.0	6.5	360
15 July	1	27.8	6.1	365
	2	27.8	5.9	368
	3	27.5	5.7	375
	4	27.5	5.7	380
	>4	27.5	0.8	1000
	0	31.0	8.5	380
	1	29.9	6.8	380
20 July	2	29.5	6.2	382
	3	29.0	5.6	392
	4	28.0	4.3	850
	>4	27.5	0.8	1080
	0	31.2	5.5	441
1 August	1	30.9	4.9	441
	2	30.7	4.6	447
	3	30.3	4.1	482

TABLE VI (Continued)

Site & Date	Depth (m)	Temp (℃)	DO (mg/l)	Specific Conduct. (uS/cm)
Site 10				
	0	29.0	6.6	360
	1	29.0	6.2	360
July 15	2	28.3	5.5	360
	3	28.0	5.4	360
	4	28.0	5.4	360
	5	28.0	5.1	360
	6	28.0	5.2	362
	7	28.0	5.2	365
	>7	28.0	0.6	370

TABLE VII

ALKALINITY AND PH FOR NEOSHO RIVER SITES

	Site	Date	Akalinity (mg/l as $CaCO_3$)	pH S.U.
Neosho River				
	1	7/24/83	127	8.15
	2	7/24/83	123	8.15
		8/11/83	146	7.40
	8	7/24/83	110	8.20
	9	7/24/83	117	8.05
		8/11/83	147	7.55
	10	7/23/83	109	7.50
		10/22/83	37	6.35
		3/6/84	56	6.55
		5/20/84	165	8.30
		6/23/84	134	7.80
	17	8/11/83	151	7.75
	18	10/22/83	37	6.55
		6/3/84	84	6.65
		5/20/84	167	8.00
		6/23/84	132	7.65
	19	10/22/83	39	6.55
		6/3/84	60	6.55
		5/20/84	165	8.00
		6/23/84	136	7.60

TABLE VIII

CORRELATIONS OF PHYSICOCHEMICAL PARAMETERS FOR NEOSHO RIVER, SPRING RIVER, GRAND LAKE, AND TAR CREEK

Area	Variables		r	OSL
Neosho River	pH -	alkalinity	0.84	<0.001
		calcium	0.97	<0.001
		magnesium	0.70	<0.01
		manganese	-0.69	<0.01
		iron	-0.88	<0.001
		zinc	-0.66	<0.01
	alkalinity -	calcium	0.98	<0.001
		manganese	-0.80	<0.001
		magnesium	0.72	<0.005
		iron	-0.96	<0.001
		zinc	-0.68	<0.01
	calcium -	magnesium	0.78	<0.001
		manganese	-0.72	<0.001
		iron	-0.94	<0.001
	magnesium -	iron	-0.66	<0.005
	manganese -	iron	0.90	<0.001
	iron -	zinc	0.56	<0.025
		lead	-0.60	<0.025
Spring River	pH -	alkalinity	0.91	<0.001
		calcium	0.92	<0.005
		iron	-0.83	<0.025
		zinc	-0.89	<0.005
	alkalinity -	calcium	0.99	<0.001
		zinc	-0.80	<0.025
	calcium -	iron	-0.78	<0.005
		zinc	-0.87	<0.001
	iron -	zinc	0.96	<0.001

TABLE VIII (Continued)

Area	Variables	r	OSL
Grand Lake	pH - zinc	-0.59	<0.005
	calcium - magnesium	0.55	<0.005
	zinc	0.54	<0.005
	magnesium - zinc	0.52	<0.005
	manganese - lead	0.58	<0.005
	zinc	0.61	<0.001
	cadmium	0.54	<0.005
Tar Creek	manganese - magnesium	0.77	<0.025
	iron	0.89	<0.005
	zinc	0.77	<0.05
	zinc - cadmium	0.79	<0.025

TABLE IX

SUMMARY OF REGRESSION EQUATIONS CALCULATED FOR GENERAL WATER QUALITY PARAMETERS AND SELECTED ELEMENTS FROM NEOSHO RIVER, SPRING RIVER, AND GRAND LAKE

	Variable		Calculated
Location	Dependent	Independent	Regression Equation
Neosho River	alkalinity	pH	$\text{alk} = 75.917(\text{pH}) + - 438.549$
	calcium	pH	$[\text{Ca}] = 24.193(\text{pH}) + - 138.297$
	calcium	alkalinity	$[\text{Ca}] = 0.2996(\text{alk}) + 3.4064$
	magnesium	pH	$[\text{Mg}] = 1.494(\text{pH}) + - 0.7258$
	magnesium	alkalinity	$[\text{Mg}] = 0.0190(\text{alk}) + 9.9731$
	manganese	pH	$[\text{Mn}] = - 0.4337(\text{pH}) + 3.3424$
	manganese	alkalinity	$[\text{Mn}] = - 0.00458(\text{alk}) + 0.7704$
	iron	pH	$[\text{Fe}] = - 15.9269(\text{pH}) + 123.745$
	iron	alkalinity	$[\text{Fe}] = - 0.2155(\text{alk}) + 32.3202$
	zinc	pH	$[\text{Zn}] = - 0.5448(\text{pH}) + 4.1792$
	zinc	alkalinity	$[\text{Zn}] = - 0.00672(\text{alk}) + 0.9856$
Spring River	alkalinity	pH	$\text{alk} = 53.8132(\text{pH}) + - 315.422$
	calcium	pH	$[\text{Ca}] = 23.8917(\text{pH}) + - 142.422$
	calcium	alkalinity	$[\text{Ca}] = 0.4348(\text{pH}) + - 1.6590$
	iron	pH	$[\text{Fe}] = - 7.2699(\text{pH}) + 58.575$
	zinc	pH	$[\text{Zn}] = - 0.2870(\text{pH}) + 2.3017$
	zinc	alkalinity	$[\text{Zn}] = - 0.004369(\text{alk}) + 0.5435$
Grand Lake	zinc	pH	$[\text{Zn}] = - 0.0476(\text{pH}) + 0.3886$

TABLE X

RESULTS OF ELEMENTAL ANALYSIS ON NEOSHO RIVER SITES BY DATE

Site Number Date	Total or Dis.	mg/1												
		Ca	Mg	Fe	Pb	Zn	Cu	Cr	Ni	Cd	Mn	Se	Hg	As
Site 1														
08-11-83	D	44.1	10.0	<0.04	0.017	<0.05	<0.04	<0.01	<0.1	<0.005	<0.05	<0.01	<0.002	<0.01
08-11-83	T	47.0	10.0	1.24	0.012	0.08	<0.04	<0.01	<0.1	<0.005	<0.05	0.01	<0.002	<0.01
Site 2														
08-11-83	D	41.1	8.6	<0.04	0.020	0.05	<0.04	<0.01	<0.1	<0.005	<0.05	<0.01	<0.002	<0.01
08-11-83	T	46.5	11.0	1.37	0.005	0.06	<0.04	<0.01	<0.1	<0.005	<0.05	<0.01	<0.002	<0.01
Site 10														
10-22-83	T	13.3	7.7	25.3	<0.005	0.31		0.04		<0.005	0.61			
03-06-84	T	24.8	10.4	16.80	<0.005	1.35		<0.01		<0.005	0.32			
05-20-84	T	51.7	11.0	1.10	<0.005	<0.01	<0.04	<0.01		<0.005	0.12			
06-23-84	T	50.0	11.3	1.84	0.017	<0.01	<0.01			<0.005	0.08			
Site 17														
08-11-83	T	48.2	11.4	0.04	<0.005	<0.05	<0.04	<0.01	<0.1	<0.005	0.05			
10-22-83	T	12.3	6.0	18.40	<0.005	0.10		<0.04		<0.005	0.34			
Site 18														
03-06-84	T	23.6	11.3	12.58	<0.005	0.09		<0.01		<0.005	0.33			
05-20-84	T	52.7	12.4	2.17	<0.005	<0.01	<0.04	0.01		<0.005	0.16			
06-23-84	T	44.2	10.8	8.14	0.005	<0.01		0.01		<0.005	0.27			

TABLE X (Continued)

Site Number Date	Total or Dis.	Ca	Mg	Fe	Pb	Zn	Cu	Cr	Ni	Cd	Mn	Se	Hg	As
		mg/1												
Site 19														
10-22-83	T	13.5	8.0	27.30	<0.005	0.31		0.05		0.017	1.10			
03-06-84	T	22.3	8.5	18.41	0.005	1.14		<0.01		<0.005	0.36			
05-20-84	T	51.8	12.0	1.38	<0.005	<0.01	<0.04	<0.01		<0.005	0.11			
06-23-84	T	45.8	10.0	2.18	<0.005	<0.01		<0.01		<0.005	0.09			

TABLE XI

DEPTH, TEMPERATURE, DISSOLVED OXYGEN AND SPECIFIC CONDUCTIVITY FOR SPRING RIVER DURING JULY-AUGUST 1983

Site & Date	Depth (m)	Temp (℃)	DO (mg/l)	Specific Conduct. (uS/cm)
Site 4				
	0	26.5	6.7	360
July 17	1	26.2	6.2	363
	2	26.0	6.2	370
	3	26.0	5.6	370
	0	30.1	5.4	393
July 27	1	30.1	5.2	400
	2	30.1	5.3	403

TABLE XII

ALKALINITY AND PH FOR SPRING RIVER SITES

	Site	Date	Akalinity (mg/l as $CaCO_3$)	pH S.U.
Spring River				
	4	7/27/83	124	7.60
		8/8/83	144	8.15
	11	7/27/83	109	7.85
	20	10/22/83	34	7.20
		3/6/84	54	6.74
		5/20/84	124	8.00
		6/23/84	113	7.95
	22	10/22/83	32	6.45
		3/6/84	52	6.55
		5/20/84	122	8.05
		6/23/84	98	7.65

TABLE XIII

RESULTS OF ELEMENTAL ANALYSIS ON SPRING RIVER SITES BY DATE

Site Number Date	Total or Dis.	mg/1 Ca	Mg	Fe	Pb	Zn	Cu	Cr	Ni	Cd	Mn	Se	Hg	As
Site 4														
08-11-83	D	55.3	5.2	<0.04	0.006	<0.05	<0.04	<0.01	<0.1	<0.005	<0.05	<0.01	<0.002	<0.01
08-11-83	D	49.2	5.1	<0.04	0.008	<0.05	<0.04	<0.01	<0.1	<0.005	<0.05	<0.01	<0.002	<0.01
08-11-83	T	53.6	5.7	0.38	0.010	0.09	<0.04	<0.01	<0.1	<0.005	0.06	<0.01	<0.002	<0.01
Site 20														
10-22-83	T	13.4	3.3	4.50	<0.005	0.27		<0.04		<0.005	0.12			
03-06-84	T	19.4	6.0	13.21	0.154	0.45		<0.01		<0.005	0.47			
05-20-84	T	48.8	4.6	0.97	<0.005	<0.01	<0.04	<0.04		<0.005	0.34			
06-23-84	T	49.5	5.0	0.87	0.010	<0.01		<0.01		<0.005	0.25			
Site 22														
10-22-83	T	14.3	3.2	5.50	<0.005	0.28		<0.04		<0.005	0.12			
03-06-84	T	18.4	5.6	15.61	0.029	0.54		<0.01		<0.005	0.58			
05-20-84	T	50.9	4.6	0.24	<0.005	0.06	<0.04	<0.01		<0.005	0.12			
06-23-84	T	45.5	6.2	1.83	0.008	<0.01		<0.01		<0.005	0.17			

TABLE XIV

DEPTH, TEMPERATURE, DISSOLVED OXYGEN AND SPECIFIC CONDUCTIVITY FOR GRAND LAKE DURING JULY-AUGUST 1983

Site & Date	Depth (m)	Temp (°C)	DO (mg/l)	Specific Conduct. (uS/cm)
Site 5				
	0	32.0	10.5	355
	1	31.0	9.4	355
July 20	2	29.5	7.6	370
	3	28.2	5.3	378
	4	28.2	5.1	398
	5	27.7	4.3	402
	6	27.3	3.0	400
	>6	27.2	3.4	421
	0	31.2	7.9	380
	1	31.0	7.2	382
July 27	2	30.6	6.6	380
	3	30.2	4.8	395
	4	29.8	3.0	398
	5	28.8	1.2	404
	0	33.0	8.3	390
	1	32.0	6.6	390
July 29	2	31.5	6.1	388
	3	31.2	5.8	385
	4	31.0	3.5	412
	5	30.1	2.0	430
	6	29.7	1.1	445
Site 6				
	0	31.5	12.6	270
	1	31.0	12.5	270
July 20	2	31.0	12.6	272
	3	31.0	12.8	278
	4	29.0	5.9	290
	5	28.5	2.0	300
	6	28.2	2.5	350

TABLE XIV (Continued)

Site & Date	Depth (m)	Temp (℃)	DO (mg/l)	Specific Conduct. (uS/cm)
<u>Site 7</u>				
	0	31.0	10.7	320
	1	30.8	10.0	325
July 20	2	30.5	10.0	327
	3	30.0	7.5	329
	4	29.0	6.4	329
	5	28.9	6.0	330
	6	27.9	1.7	325
	7	27.3	1.3	332
	8	27.2	1.0	330
	>8	27.1	0.8	465
	0	30.9	6.4	312
	1	30.7	6.3	320
July 29	2	30.5	6.0	322
	3	30.3	5.8	325
	4	30.1	5.6	325
	5	30.1	5.8	327
	6	30.0	5.1	330
	7	29.7	2.7	324
	8	29.0	1.0	338
<u>Site 12</u>				
	0	32.0	8.2	259
	1	31.0	6.3	261
July 29	2	31.0	5.4	263
	3	30.6	4.4	267
	4	30.0	2.7	278
	5	29.3	1.1	293
	6	28.5	0.9	420

TABLE XV

ALKALINITY AND PH FOR GRAND LAKE

Group	Site	Date	Akalinity (mg/l as $CaCO_3$)	pH S.U.
Grand Lake				
	5	7/23/83	115	7.35
		7/29/83	118	7.20
	7	7/29/83	99	7.50
	12	7/29/83	95	6.95
	13	8/4/83	76	7.75
		8/11/83	72	7.80
		10/22/83	99	7.50
		3/6/84	89	7.15
		5/20/84	96	8.15
		6/23/84	83	8.80
	14	8/4/83	90	6.90
		8/11/83	92	6.55
		10/22/83	109	7.25
		3/6/84	102	7.30
		5/20/84	108	7.80
		6/23/84	96	8.45
	15	8/4/83	100	7.75
		10/22/83	103	6.90
		3/6/84	92	7.15
		5/20/84		7.70
		6/23/84	96	8.45
	16	8/4/83	95	7.15
		8/11/83	89	7.70
		10/22/83	103	6.95
		3/6/84	94	7.15
		5/20/84	104	7.80
		6/23/84	92	8.25

TABLE XVI

RESULTS OF ELEMENTAL ANALYSIS ON GRAND LAKE SITES BY DATE

Site Number Date	Total or Dis.	Ca	Mg	Fe	Pb	Zn	Cu	Cr	Ni	Cd	Mn	Se	Hg	As
		mg/l												
Site 5														
08-11-83	D	45.9	10.6	<0.04	0.016	0.33	<0.04	<0.01	<0.1	<0.005	0.12	<0.01	<0.002	<0.01
08-11-83	D	31.6	5.2	<0.04	0.020	<0.05	<0.04	<0.01	<0.1	<0.005	<0.05	<0.01	<0.002	<0.01
08-11-83	D	45.0	11.6	<0.04	0.008	0.47	<0.04	<0.01	<0.1	<0.005	0.11	<0.01	<0.002	<0.01
08-11-83	T	53.5	10.6	0.42	0.018	0.68	<0.04	<0.01	<0.1	<0.005	0.15	0.01	<0.002	<0.01
08-11-83	T	40.1	6.9	<0.04	0.008	0.06	<0.04	<0.01	<0.1	<0.005	<0.05	<0.01	<0.002	<0.01
Site 7														
08-11-83	D	37.7	7.8	0.13	0.019	0.09	<0.04	<0.01	<0.1	<0.005	0.21	<0.01	<0.002	<0.01
08-11-83	T	47.2	7.7	0.97	0.010	0.23	0.18	<0.01	<0.1	0.005	0.11	<0.01	<0.002	<0.01
Site 13														
08-11-83	T	35.7	6.4	<0.04	<0.005	<0.05	<0.04	0.02	<0.1	<0.005	<0.05			
10-22-83	T	37.4	6.7	0.30	<0.005	<0.01		<0.04		<0.005	0.02			
10-22-83	T	38.6	6.9	0.30	<0.005	<0.01		<0.04		<0.005	0.02			
03-06-84	T	32.7	7.6	0.48	<0.005	0.06		<0.01		<0.005	0.05			
05-20-84	T	42.4	5.3	0.61	<0.005	<0.01	<0.04	<0.01		<0.005	<0.05			
05-20-84	T	35.2	5.2	0.73	<0.005	<0.01	<0.04	<0.01		<0.005	<0.05			
06-23-84	T	33.7	5.9	0.05	<0.005	<0.01		<0.01		<0.005	<0.05			
Site 14														
08-11-83	T	39.6	6.1	<0.04	0.005	<0.05	<0.04	<0.01	<0.1	<0.005	<0.05			
10-22-83	T	39.9	5.0	0.40	<0.005	0.08		<0.04		<0.005	0.02			
03-06-84	T	29.5	3.2	2.20	<0.005	0.08		<0.01		<0.005	0.12			
05-20-84	T	44.3	3.6	0.06	0.029	<0.01	<0.04	<0.01		<0.005	<0.05			
06-23-84	T	38.4	3.7	0.07	<0.005	<0.01		<0.01		<0.005	<0.05			

TABLE XVI (Continued)

Site Number Date	Total or Dis.	mg/l									
		Ca	Mg	Fe	Pb	Zn	Cu	Cr	Ni	Cd	Mn
Site 15											
10-22-83	T	38.9	6.8	0.20	<0.005	0.08		<0.04		<0.005	0.04
03-06-84	T	37.9	17.9	0.55	<0.005	0.09		<0.01		<0.005	0.06
05-20-84	T	37.4	5.4	0.38	<0.005	<0.01	<0.04	<0.01		<0.005	<0.05
06-23-84	T	40.4	6.8	0.16	<0.005	<0.01		<0.01		<0.005	<0.05
Site 16											
08-11-83	T	36.2	4.8	0.07	<0.005	<0.05	<0.04	<0.01	<0.1	<0.005	0.13
10-22-83	T	37.8	6.6	0.40	<0.005	0.17		<0.04		<0.005	0.05
10-22-83	T	38.8	6.8	0.50	<0.005	0.03		<0.04		<0.005	0.05
05-20-84	T	35.7	5.4	0.26	0.008	<0.01	<0.04	<0.01		<0.005	<0.05
06-23-84	T	35.9	6.6	0.09	<0.005	<0.01		<0.01		<0.005	<0.05
06-23-84	T	35.8	6.8	0.07	<0.005	<0.01		<0.01		<0.005	<0.05

TABLE XVII

TEMPERATURE, DISSOLVED OXYGEN, SPECIFIC CONDUCTIVITY, PH, AND ALKALINITY FOR TAR CREEK BY DATE

Site & Date	Temp (℃)	DO (mg/1)	Spec. Conduct. (uS/cm)	pH	Alkalinity
26					
5/20/84	25.0	10.0	2180	3.3	<1
6/24/84	26.0	7.5	2650	3.3	<1
8/9/84	NS*	NS	2200	7.2	31
9/9/84	26.0	8.7	1380	6.8	27
27					
5/20/84	24.0	8.0	1040	7.4	90
6/24/84	25.0	7.2	1250	7.0	102
8/9/84	NS	NS	2100	7.3	88
9/9/84	27.0	6.6	1680	7.3	70
28					
5/20/84	20.0	2.4	3320	6.0	550
6/24/84	18.0	1.5	3390	6.0	478
8/9/84	NS	NS	3500	6.4	454
9/9/84	19.0	1.0	3360	6.0	580
29					
5/20/84	19.0	2.9	3280	5.5	NS
6/24/84	18.0	1.5	3220	5.6	NS

* - not sampled

TABLE XVIII

RESULTS OF ELEMENTAL ANALYSIS ON TAR CREEK SITES BY DATE

Site Number Date	Total or Dis.	mg/l Ca	Mg	Fe	Pb	Zn	Cu	Cr	Cd	Mn
Site 26										
10-22-83	T	1620.0	60.0	53.90	<0.005	48.30	<0.04	<0.04	0.043	1.90
03-06-84	T	154.4	56.4	90.80	<0.005	47.37		<0.01	0.033	1.48
05-23-84	T	3040.1	793.9	10.61		62.32	<0.04			2.89
Site 27										
10-22-83	T	2480.0	8.4	2.80	0.005	5.41		<0.04	0.027	0.12
03-06-84	T	43.0	8.5	5.59	0.006	2.83		<0.01	<0.005	0.18
05-23-84	T	2615.9	124.2	0.30		5.86	0.022			0.33
Site 28										
10-22-83	T	940.0	1350.0	533.00	<0.005	73.30		<0.04	<0.005	4.62
03-06-84	T	195.6	145.7	487.19	<0.005	1.01		<0.01	<0.005	4.37
05-23-84	T	1646.3	1414.0	455.51		47.17	0.020			4.32
Site 29										
10-22-83	T	1420.0	1600.0	433.00	<0.005	217.50		<0.04	0.104	7.32
03-06-84	T	174.6	238.8	396.93	0.008	235.33		<0.01	0.055	5.16
05-23-84	T	3747.1	2569.4	338.35		178.77	0.021			5.16

TABLE XIX

HEAVY METAL ANALYSIS FOR GRAND LAKE SEDIMENT CORE

Depth	mg/kg					Organic Carbon
cm	Fe	Pb	Zn	Cr	Cd	(percent)
2.5	30502.0	130.9	979.0	9.0	5.2	1.75
7.5	26765.0	130.9	1045.0	28.0	6.2	1.25
12.5	31613.0	100.6	363.0	32.0	2.2	1.36
17.5	26967.0	110.7	965.0	29.0	6.0	1.15
22.5	31815.0	120.8	876.0	110.0	4.8	1.47
27.5	30805.0	100.6	255.0	210.0	1.6	1.42
32.5	32724.0	100.6	453.0	25.0	3.1	1.53
	30805.0	110.7	551.0	29.0	3.9	1.47
37.5	33633.0	90.5	143.0	230.0	0.7	1.47
42.5	32017.0	90.5	248.0	31.0	1.3	1.47
47.5	30704.0	100.6	426.0	17.0	2.2	1.25
52.5	23129.0	100.6	437.0	26.0	2.9	1.09
56.5	33532.0	100.6	129.0	510.0	0.7	1.53
61.5	31007.0	110.7	720.0	25.0	3.3	1.36

TABLE XX

HEAVY METAL CONCENTRATIONS IN EXTRACTS OF SEDIMENTS FROM TAR CREEK, NEOSHO RIVER, AND GRAND LAKE

		mg/l				
Sample Identification		Fe	Pb	Zn	Cr	Cd
<u>Tar Creek</u>	pH 3	46.30	0.031	77.11	0.01	0.093
	pH 4	9.50	<0.005	48.51	<0.01	0.022
	pH 5	2.02	<0.005	23.54	<0.01	<0.005
	pH 6	1.70	<0.005	4.44	<0.01	<0.005
	pH 6	2.34	<0.005	4.52	<0.01	<0.005
	pH 7	3.52	<0.005	0.93	<0.01	<0.005
	pH 8	8.80	0.009	0.92	0.01	<0.005
	pH 9	29.10	0.020	1.85	0.03	<0.005
<u>Neosho River</u>	pH 3	24.90	0.024	56.43	0.02	0.048
	pH 4	4.61	<0.005	42.46	<0.01	0.025
	pH 5	1.34	<0.005	19.47	<0.01	0.012
	pH 5	1.15	<0.005	15.18	<0.01	0.009
	pH 6	1.61	<0.005	2.37	<0.01	<0.005
	pH 7	2.35	<0.005	0.68	<0.01	<0.005
	pH 8	3.32	<0.005	0.35	0.01	<0.005
	pH 9	8.50	0.007	0.76	0.01	<0.005
<u>Grand Lake</u>	pH 3	25.90	0.380	31.79	0.02	0.151
	pH 4	4.34	0.035	22.80	<0.01	0.098
	pH 4	4.36	0.033	24.97	<0.01	0.095
	pH 5	0.81	0.006	12.10	<0.01	0.039
	pH 6	0.53	<0.005	0.70	<0.01	<0.005
	pH 7	1.21	<0.005	0.18	<0.01	<0.005
	pH 8	1.57	<0.005	0.16	<0.01	<0.005
	pH 9	1.51	<0.005	0.10	<0.01	<0.005
<u>Blank</u>	pH 3	0.12	<0.005	0.13	0.01	<0.005
	pH 6	0.08	<0.005	0.14	<0.01	<0.005
	pH 9	0.19	<0.005	0.01	<0.01	<0.005

VITA

Curt A. McCormick

Candidate for the Degree of

Master of Science

Thesis: WATER QUALITY AND SEDIMENTS OF AN AREA RECEIVING ACID-MINE DRAINAGE IN NORTHEASTERN OKLAHOMA

Major Field: Zoology/Environmental Sciences

Biographical:

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