

EFFECT OF pH ON THE RELEASE OF CHROMIUM,
CADMIUM, COPPER, LEAD, AND ZINC FROM
SEDIMENTS FROM THE ARKANSAS RIVER

By

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CHAPTER I

INTRODUCTION

Much attention has been focused on the problem of heavy metal pollution in the environment in recent years. Many of the heavy metal compounds which are emitted to the environment from industrial activities become the pollutants of soil and water. Since the outbreak of Minamata disease in Japan caused by mercury (1), concern over heavy metal contamination covers a wide range of metals including cadmium, chromium, copper, lead, and zinc.

Toxicity of these metals to humans as well as to microorganisms depends on pH and high metal concentrations in the environment. Most of these metals have been proven to be widely dispersed and can persist in the aqueous environment for some period of time (2).

The discharge of municipal wastewaters into rivers also increases prospects of polluting the flowing water and sediment with metals. There are many processes that would contribute to the distribution of heavy metals when the river is polluted (3). Metals may be accumulated in stream sediments and only be released when the deposits are disturbed during periods of high flows.

Most of the metal compounds occur in natural forms such as sulfides, oxides, carbonates, and silicates. It has been shown that many metal ions in soils may react to form compounds which are bound in soils or held against extraction (4).

pH and oxidation-reduction potential are important factors in metal uptake and release because they affect all the chemical processes which induce the exchange between the sediments and water. The pH values may vary considerably in the aqueous environment; therefore, the effect of pH on the distribution of the heavy metal ion complexes would be significant. The purpose of this investigation was to determine the effects of pH on the distribution of cadmium, chromium, copper, lead, and zinc in sediments which were obtained from the Arkansas River in Tulsa, Oklahoma.

CHAPTER II

LITERATURE REVIEW

add / The physical and chemical properties of heavy metals in the aqueous environment are a function of solubility, cation exchange capacity, and complexation reactions. However, } pH may be one of the most important factors in determining heavy metal distribution in the environment. According to Malo (5), sediments, both suspended and bottom, constitute a potential source for many dissolved chemical species. Metals in the surface coatings of sediments, both in suspension and in bottom deposits, may be brought into solution by changes such as the intrusion of water of different quality or changes in pH.

Chromium

Two common valence forms of chromium in soil are the trivalent form and the hexavalent form. In natural water, chromium exists in the form of the divalent chromate ion, CrO_4^{2-} ; and when it converts to the trivalent ion, it is completely hydrolyzed and precipitates as hydroxide.

add // Bartlett et al. (6) reported that organo-chromium complexes are soluble and stable when the soil pH is raised to the value of 5.5 at which chromium normally precipitates. They further found that many soils would oxidize trivalent chromium to hexavalent chromium which would then exist in soils as a soluble anion.

The ability of soluble chromium to convert rapidly to insoluble forms of chromium has been seen in soils having widely varying pH values (7). Chromium in the trivalent oxidation state often forms a large number of soluble complexes. The chromic ion, Cr^{3+} , also reacts with the hydroxide ion under basic conditions to precipitate the insoluble hydrous oxide. However, the hydrous oxide compound is amphoteric and can dissolve in an excess amount of strong base.

Phase diagrams describing the chemistry of chromium in aqueous solution were developed a long time ago. Although $\text{Cr}(\text{OH})_3$ is expected to precipitate in solutions with a pH greater than 6.0, it can convert to the less soluble and more stable oxide complex or a mixed oxide-hydroxide species (8, 9, 10). The chromates which are slightly soluble may also dissolve in solution under acidic conditions because of the change of the chromate ion to the dichromate ion.

Bartlett et al. (9) found that chromium-organic complexes which are soluble are formed under acidic conditions in areas where organic matter accumulates. In addition, more than half of them remained stable even after the pH was raised to neutrality by calcium carbonate. The small amount of soluble chromium in the neutral solution indicated that the equilibrium had shifted to the less soluble chromium oxide. The solubility of chromium would also be reduced under the alkaline soil-water system. It was found that with the presence of aluminum in the solution, chromium was precipitated at a pH in the range of 4.0 to 5.0, became insoluble near pH 6.0, and then solubility increased again above pH 8.0 (10).

In a study of kaolinitic montmorillonitic clay, Griffin et al. (11) found that soluble chromium decreased when the pH of the suspensions

decreased. They explained that this happened because of HCrO_4^- adsorption by pH-dependent anion exchange sites on clay colloids.

According to Mertz (4), chromium has the capability of existing in four states under normal pH and oxidation-reduction potential conditions found in soils, two trivalent, Cr^{3+} and CrO_2^- , and two hexavalent, CrO_7^{2-} and CrO_4^{2-} . Bartlett et al. (12) concluded that the solubility of chromium decreased as solution pH was raised above 4.0. They also noticed that the compound was completely precipitated at pH 5.5.

Copper

The solubility of copper in soils is determined by different mechanisms which are dependent on the chemical properties of the soil. Many researchers suggest that copper binds to silicate and carbonate clays through ion exchange and fixation processes (13, 14). It is also thought that copper binding by soils decreased when the soil pH was decreased. This suggests that there are more soluble copper compounds present in the acidic condition than in the neutral condition. Baes et al. (13, 15) found that many of the copper hydroxide ions remained in the suspension and were strongly dependent on the pH of the solution.

McBride et al. (16) studied the solubility of copper organic complexes in different pH solutions. They found that these soluble copper complexes were present in the solution over a wide range of pH values. The pH of the solution in which interactions between the copper ions and organic matter occur is an important factor in releasing copper compounds to the solution because hydrogen ions would compete with copper ions for binding sites on the functional groups of soils (17). It was seen that

as the pH of the solution was decreased, resulting in an increase of free binding sites, the solubility of copper complexes increased.

The adsorption of copper in neutral soils is also affected by the amount of salts in the solution (18). In a study of copper solubility under different pH and oxidation-reduction potentials, Sims et al. (19) noticed that solubilized copper did not remain water-soluble at low pH and oxidation-reduction potential. Copper compounds which were solubilized would be associated with exchange and organic sites in soils. They also reported that the largest percentage of soluble copper was present in the solution when the redox potential was at +500 mV.

It has been shown that soluble cupric hydroxide which is amphoteric would precipitate under alkaline conditions. This compound can dissolve in a strongly basic solution to form the soluble cuprate ions. Cavallaro et al. (20) compared the effects of acid and calcareous soils on the adsorption of copper. They found that soluble organic-complexes of copper were adsorbed by functional groups of soil organics in the surface soils and that low pH soils are less effective in removing copper from the solution than are neutral soils containing calcium carbonates. These results indicated that calcium ions removed copper ions from the solution of neutral soils.

Cadmium

Two of the major soil conditions that affect the solubility of cadmium are the pH values and oxidation-reduction potential of the soil solution (21). Hydrolysis of cadmium at different pH values has been seen as one of the most important factors in determining the solubility of this

metal. Cadmium is considered to belong to the group of oxyphilic and sulfophilic compounds (22).

Since reactions in aqueous media represent a large proportion of those reactions occurring in the environment, knowledge of cadmium ion species distribution as a result of hydrolysis becomes significant. Hahne et al. (22) investigated the effect of hydrolysis of cadmium ions over a wide pH range. The results indicated that the hydroxy complexes may contribute to the mobilization of cadmium ions in the aqueous environment. It was also shown that cadmium combines as divalent ions in solutions having a pH of 6.0. $\text{Cd}(\text{OH})^+$ starts forming at the neutral pH of 7.0 and formation increases to a maximum level at a pH ranging from 8.2 to 9.0. $\text{Cd}(\text{OH})_2$ is formed at pH 9.0 and peaks at pH of 11.0. Cadmium forms a soluble $\text{Cd}(\text{OH})_4^{2-}$ complex under strongly alkaline conditions.

Oxidation-reduction potential of sediments also affects the release of soluble cadmium in the solution (23). Reddy et al. (21) found that water-soluble cadmium increased as the pH of the sediment was decreased and the redox potential was increased. The concentration of cadmium decreased when the solution had a low oxidation-reduction potential and high pH. The increase of cadmium uptake in plants under low suspension pH conditions studied by Gotoh et al., (24) indicated that an increase of hydrogen ions promoted the release of soluble cadmium from the sediment into the water.

Anderson et al. (25), investigating the solubility and mobility of cadmium in the soil-water system, showed that the removal of cadmium from the soil increases and allows more cadmium to enter the solution when the pH of the system is lowered. They also found that there is a great mobility in acid soils in which organic matter proved to play an important

role. Street et al. (26), on the other hand, found that an increase of pH from 5.7 to 7.8 reduced the concentration of soluble cadmium significantly. Miller et al. (27) also indicated similar results from their laboratory investigations. Solubility measurements of cadmium in the acidified soils showed an increase in the concentration of the soluble cadmium. In soils having a pH of 7.25, the solubility of cadmium is limited by cadmium carbonates (23).

The cadmium ion activity in soils having a pH of less than 7.5 was studied by Santillan-Medrano et al. (28). They reported that the activity of cadmium ions in the solution depended on the pH of soils. Results indicated that when the pH of the solution was decreased, the activity and solubility of these cadmium ions increased. Maruyama et al. (29), in a study of metal removal by physical and chemical treatment processes, found that cadmium would form an insoluble hydroxide and soluble complexes with ammonia at a high pH of 10.0 or above.

Lead

There are many processes which affect the solubility of lead in a sediment-water system. The processes which are influenced by the chemical properties of lead include (1) precipitation as insoluble sulfides under strongly reduced conditions, (2) formation of metal oxides and hydroxides of low solubility, and (3) complex formation with soluble and insoluble organic matter under all conditions of pH and oxidation-reduction potential (30, 31).

In a study by Reddy et al. (21), water-soluble lead decreased with an increase in pH and redox potential. Many reactions contributed to the decreased levels of water-soluble lead as the pH was increased from

5.0 to 8.0, including the precipitation of soluble lead carbonate and lead hydroxide in the solution. There were also indications that lead in the sediment-water system is combined with hydrous oxides (31).

Griffin et al. (32) calculated the solubility products of lead and showed that lead carbonate would not precipitate at pH 4.0 until the lead concentration exceeded 2000 ppm. The increase in soluble lead in the solutions having low pH values was seen in this laboratory experiment. They explained that the solubility increased because of an increase in competitions for adsorption sites by hydrogen ions. They also found that a sudden decrease in pH released large amounts of lead into the aqueous phase in places where lead carbonates accumulated.

Gambrell et al. (31) studied the release of sediment-bound metals to the water under different equilibrium pH and oxidation-reduction conditions. They found that increasing the redox potential from -150 mV to +50 mV resulted in a considerable increase of chelate extractable lead at pH 5.0 and 6.0. It was suggested that the lead binding capacity of the sediment was reduced as the sediment-water system became oxidized.

Lagerwerff et al. (33) investigated the exchange reactions of lead with calcium and sodium ions in the soil. It was found that the solubility of lead increased with a decrease in both pH and the concentration of sodium chloride. Work by Santillan-Medrano et al. (28) studying the solubility of lead as influenced by pH shows that under experimental conditions, lead hydroxide regulates lead activity when the solution pH is less than 6.6. As the pH increases, the formation of lead orthophosphate, lead hydroxy-pyromorphite, and tetraplumbite phosphate becomes a possibility.

Significance of pH on hydrolysis of lead was studied by Hahne et al. (22). Divalent lead ions and predominant monovalent lead hydroxide ions

occurred at a pH ranging from 6.0 to 7.0. At pH above 9.0, the distribution of lead was determined by the solubility of lead hydroxide. Hem (34), in another report, suggested that lead solubilities in many natural sediment-water systems were regulated by lead carbonate.

Zinc

The pH of the sediment is a dominant factor in the solubility of zinc because the concentrations of soluble zinc are controlled by this parameter (35). Shaw et al. (36) found that decreasing pH in many soils was associated with increasing extractable zinc. In calcareous soils which have high pH values, the solubility of zinc decreases as soil pH increases (37). In some mineral soils, an increase of soil pH from 6.0 to 7.0 would decrease the extractable zinc (38).

Zinc forms a slightly soluble hydroxide under the alkaline condition in the presence of the hydroxide ion. The predominant species of zinc below pH 7.7 is zinc ions and above this pH, the predominant species is zinc hydroxide. In strongly basic solutions with the presence of excess hydroxide, the precipitate would redissolve as the soluble zincate ion (39, 40).

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Chemical precipitation of zinc as hydroxide is determined by the high concentrations of various cations present (41). Shukla et al. (42), studying the solubility of zinc in different pH solutions, found that zinc was retained in forms having low solubility throughout the pH range of 6.8 to 3.2. When the pH of the soil solution is decreased from 3.25 to 0.70, the concentration of soluble zinc is 5 to 15 times that extracted between a pH range of 6.8 to 3.25. The results also showed that in the neutral soil pH condition, a small quantity of zinc existed in water-

soluble forms. The experiment indicated that the hydrolysis of zinc played an important role in zinc solubility in the soil. Hahn et al. (22) found that at pH ranging from 6.0 to 7.0, zinc which undergoes hydrolysis would be present in the divalent ionic form in solution. Divalent ions of zinc at pH 6.0 are completely soluble.

Diffusion of zinc in soils as a function of soil pH was investigated by Melton et al. (43). It was found that zinc was soluble in acid soils. As the soil pH was increased by the addition of lime, zinc was precipitated as zinc hydroxide or zinc carbonate. Gambrell et al. (31), in a study of solubility of zinc in sediment suspensions as affected by pH and oxidation-reduction potential, found that suspension pH had a large effect on the dissolved and exchangeable levels of zinc. Dissolved and exchangeable zinc were greatest at pH 5.0 and decreased to low levels at pH 8.0. All of the dissolved zinc was present in the free cationic form. Under strongly reduced conditions which were at -150 mV, levels of the exchangeable zinc were lower than under oxidized conditions at pH of both 5.0 and 6.0. Complex formation with insoluble organic matter also contributed to a decrease in soluble zinc under reduced conditions.

The effect of soil pH on zinc solubility in solutions was studied by Giordano et al. (44). They have found that small pH changes below pH of 6.0 can induce large changes in the concentrations of zinc in the soil solution. The concentration of soluble zinc decreased when the pH was increased above 6.1.

CHAPTER III

MATERIALS AND METHODS

The sediments used in this study were taken from the Arkansas River in Tulsa, Oklahoma. All of the sediment samples from the river were collected at the 23rd Street Bridge. The sediment was brought to the laboratory and was air-dried in thin layers in acid-washed plastic pans at room temperature. After complete drying the sediments were thoroughly mixed and were stored in the refrigerator until they were used. These sediments were allowed to reach room temperature again before being used.

The existing deposits in the river are mainly sands and the bank deposits are sandy silts and silty sands with some sandy clay lenses over a layer of medium to coarse sands (45). The results of the analysis of water quality showed that the water is unsuitable for municipal purposes because of the excessive concentrations of total dissolved solids and chlorides (45).

Research Approach and Setup

The experiment was set up to measure the amount of soluble cadmium, chromium, copper, lead, and zinc found in the sediments at different pH values. A determination of total concentrations of cadmium, chromium, copper, lead, and zinc in the dry sediments was also carried out.

All glassware and containers which came into contact with the sediment or water samples were acid-washed with a solution of concentrated

nitric acid, and they were rinsed thoroughly with distilled deionized water.

The initial pH of the sediment was found by wetting the dry sediment with distilled deionized water and allowing 10 minutes for equilibration. The pH was determined with a Beckman pH meter model N. Distilled deionized water was prepared by passing distilled water through a Gelman Sciences Water 1 Deionizer.

For the experimental units, mixing was accomplished by the aid of an Eberbach box-type mechanical shaker. Twelve 250 ml Erlenmeyer flasks were used and were each filled with 10 grams of dried sediment. Fifty milliliters of deionized water with pH values ranging from 1.0 to 12.0 (pH of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12) were added to the 12 250 ml flasks. Hydrochloric acid and ammonium hydroxide solution were used to decrease or increase the pH of the distilled deionized water in order to reach these exact pH values. All of the flasks were covered with cotton to minimize evaporation in these units. The mixtures of sediments and water were mechanically shaken for three days. All experiments were done in duplicate.

Experimental Procedures

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The concentrations of soluble cadmium, chromium, copper, lead, and zinc were measured after three days of continuous shaking. Thirty ml of each of the 24 water samples were taken after they were allowed to settle for one hour and were filtered through a 0.45 micron Millipore membrane filter. Samples were then analyzed for soluble metal using a Perkin-Elmer atomic absorption spectrophotometer Model 5000 equipped with background corrector and a graphite furnace, Model HGA-400.

A dried sediment sample was also analyzed for cadmium, copper, lead, and zinc by the method described by Krishnamurty et al. (46). First, the sediment sample was dried completely in an oven at 110°C. Approximately 0.5 gram of it was then slurried with 0.5 ml of distilled deionized water. Ten ml of concentrated reagent-grade HNO_3 were added to the slurry in a 150-ml beaker covered with a watch glass. After a 2-hour acid digestion at about 100°C on a hot plate and cooling for 15 minutes, 3 ml of 30 percent H_2O_2 were added dropwise to the extraction mixture. Heating was continued for another hour with intermittent stirring by gentle swirling of the beaker. The cooled digestate was filtered through a funnel into a glass tube. The filtered digestate was diluted with distilled deionized water to 50 ml in a volumetric flask and analyzed directly using the Perkin-Elmer Model HGA-400 graphite furnace.

CHAPTER IV

RESULTS

The distribution of heavy metals between the sediment and solution as a function of pH was studied in laboratory units with natural river sediments covered with distilled deionized water having different pH values. Samples were analyzed to determine the soluble chromium, cadmium, copper, lead, and zinc in the overlying water.

The results of final sediment pH values under the continuous mixing condition are shown in Table I. The initial pH of the collected sediment was found to be 7.95.

The results that were obtained from the analysis of river sediment sample at the 23rd Street Bridge for the metal in question are shown in Table II.

The quantity of total chromium in the natural sediment was found to be 20 $\mu\text{g/g}$ of dried sediment. The distribution of soluble chromium in the solution and its pH for the mixing units is shown in Figure 1. Under the acidic condition at a pH of 1.20, soluble chromium was measured to be 1.10 $\mu\text{g/g}$ of sediment. When the pH was increased from 1.20 to 7.70, the amounts of soluble chromium in the water decreased significantly; and under neutral pH conditions, the amounts of soluble chromium were very low in the solution. From the pH of 7.70 to 8.36, soluble chromium increased only slightly. The amount of soluble chromium began a gradual

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*20 ug/g
20 ug/g*

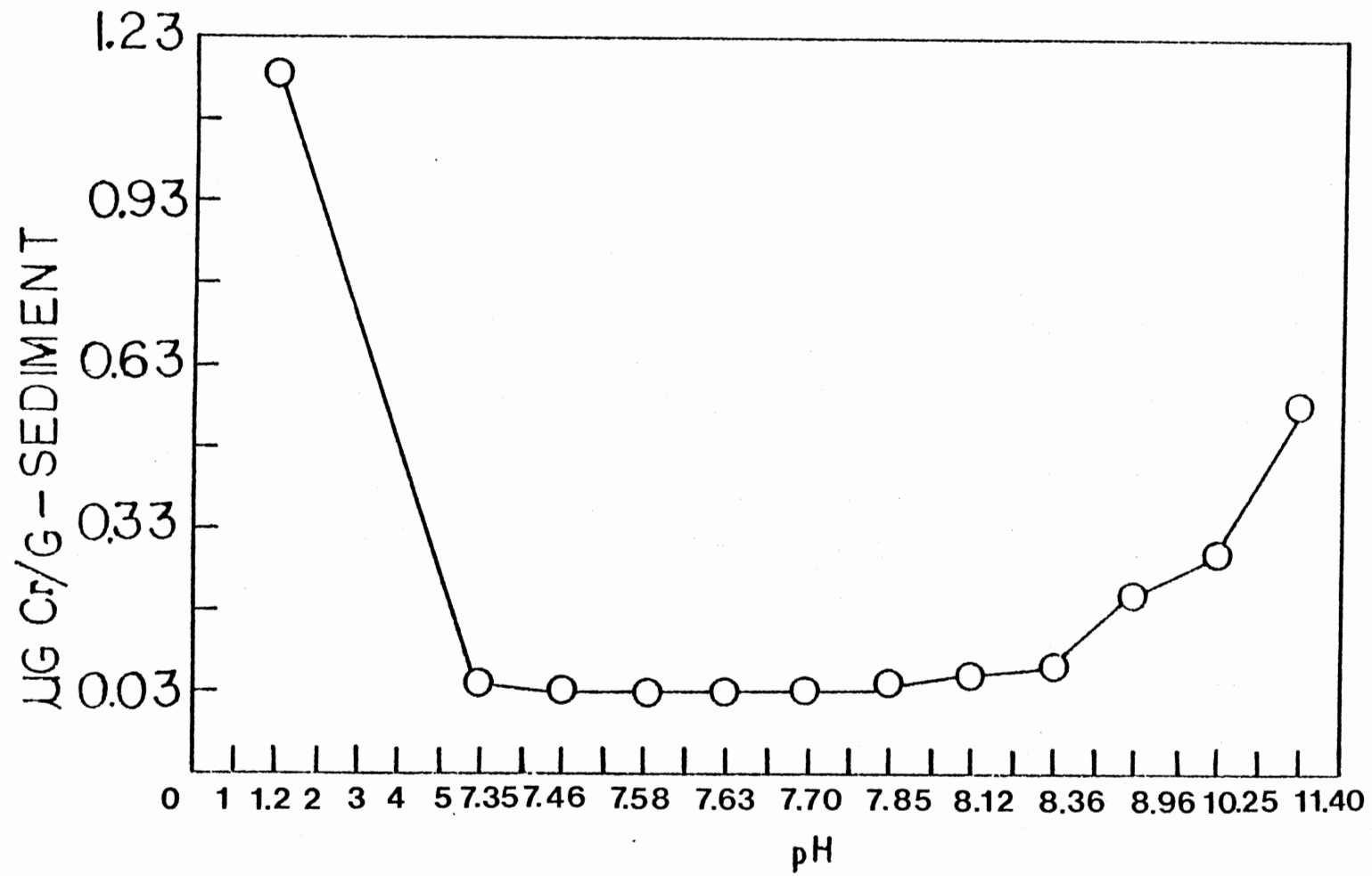
TABLE I
 EXPERIMENTAL OVERLYING WATER pH VALUES
 AND FINAL SEDIMENT pH

Experimental Over- lying Water pH	Initial Sediment pH	Final Sedi- ment pH
1	7.95	1.20
2	7.95	7.35
3	7.95	7.46
4	7.95	7.58
5	7.95	7.63
6	7.95	7.70
7	7.95	7.85
8	7.95	8.12
9	7.95	8.36
10	7.95	8.96
11	7.95	10.25
12	7.95	11.40

TABLE II
 RESULTS OF ANALYSES OF HEAVY METAL QUANTITIES
 IN THE SEDIMENT AT THE 23RD STREET BRIDGE
 AFTER NITRIC ACID-HYDROGEN
 PEROXIDE DIGESTION

Element	Total Metal Con- centration $\mu\text{g/g}$
Cr	30.0
Cd	0.9
Cu	11.0
Pb	12.0
Zn	70.0

Figure 1. Soluble Chromium Versus Sediment pH



increase from pH of 8.35 and continued until it reached the value of 0.560 $\mu\text{g/g}$ sediment at a pH of 11.40.

Figure 2 represents the data collected from the study of the effects of pH on the solubility of cadmium. It can be seen from this figure that the highest quantity of cadmium released occurred at a pH of 1.20. The amount remained low at neutral pH values from 7.35 to 7.63, and then increased slightly from the pH of 7.63 to the pH of 8.36. Then there was a gradual increase as the pH values were increased from 8.36 to 11.40. The highest quantity of soluble cadmium at the pH of 1.20 was 0.022 $\mu\text{g/g}$ of sediment. The quantity of total cadmium in the natural sediment was 0.900 $\mu\text{g/g}$ of dried sediment.

The results obtained from the study of the effects of sediment pH on the release of soluble copper are shown in Figure 3. The soluble copper was highest at a pH of 1.20. The amounts of soluble copper in the solution were low in the neutral pH ranging from 7.35 to 8.12. When the pH of sediment solution was increased from 8.12 to 11.40, the amounts of soluble copper increased significantly and reached 0.800 $\mu\text{g/g}$ of sediment at a pH of 11.40. The maximum amount of soluble copper present in the solution was measured to be 1.250 $\mu\text{g/g}$ of sediment at a pH of 1.20, while the amount of total copper in the natural sediment was found to be 11 $\mu\text{g/g}$ of dried sediment.

Figure 4 shows the effects of solution pH on the quantity of soluble lead. The highest amount of soluble lead was seen in the alkaline pH range. The amount of soluble lead was also relatively high at a pH of 1.20. There was less soluble lead present in the neutral pH range. The quantity of soluble lead remained constant when the pH was increased from 7.35 to 8.12. At pH values above 8.12, a sharp increase in the release

Figure 2. Soluble Cadmium Versus Sediment pH

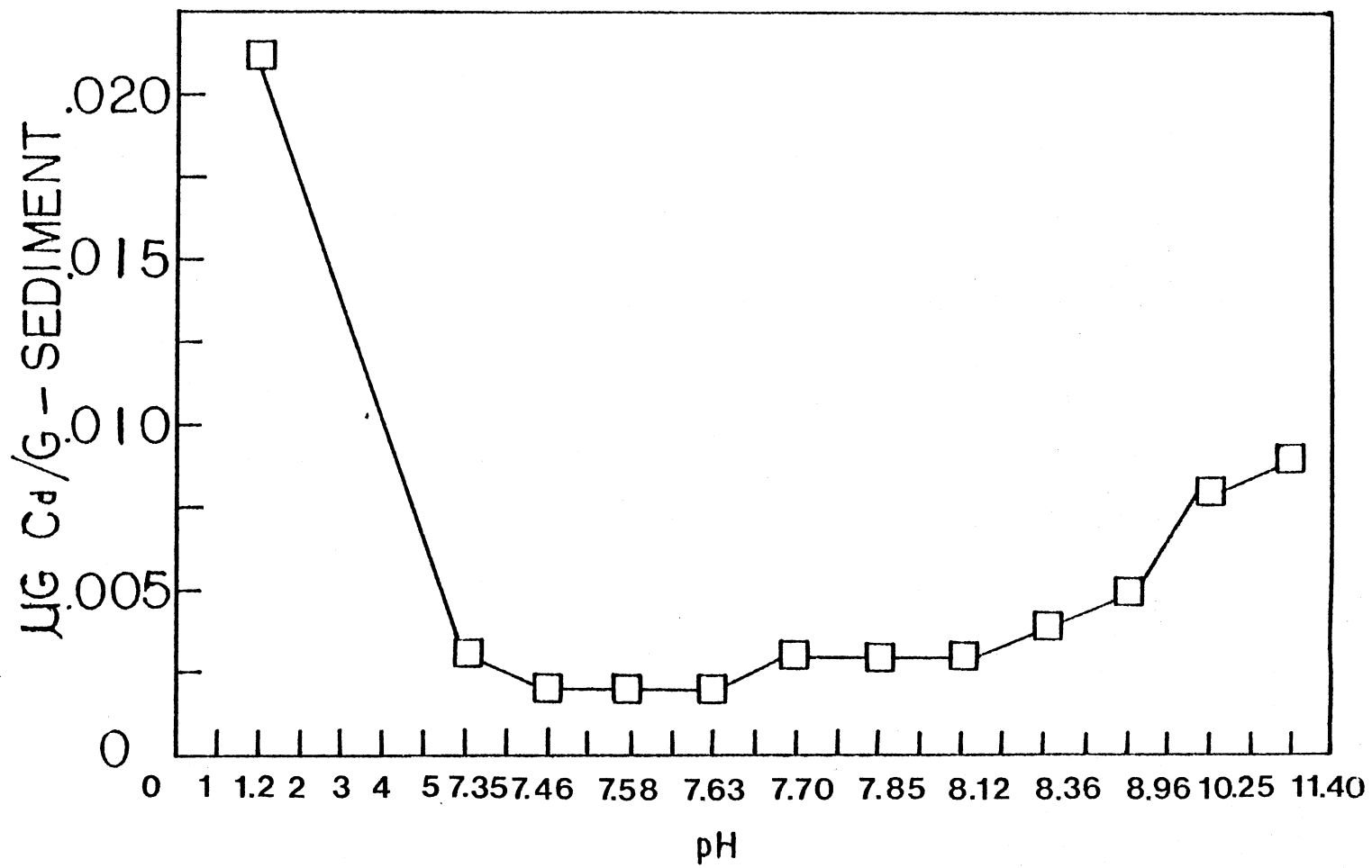


Figure 3. Soluble Copper Versus Sediment pH

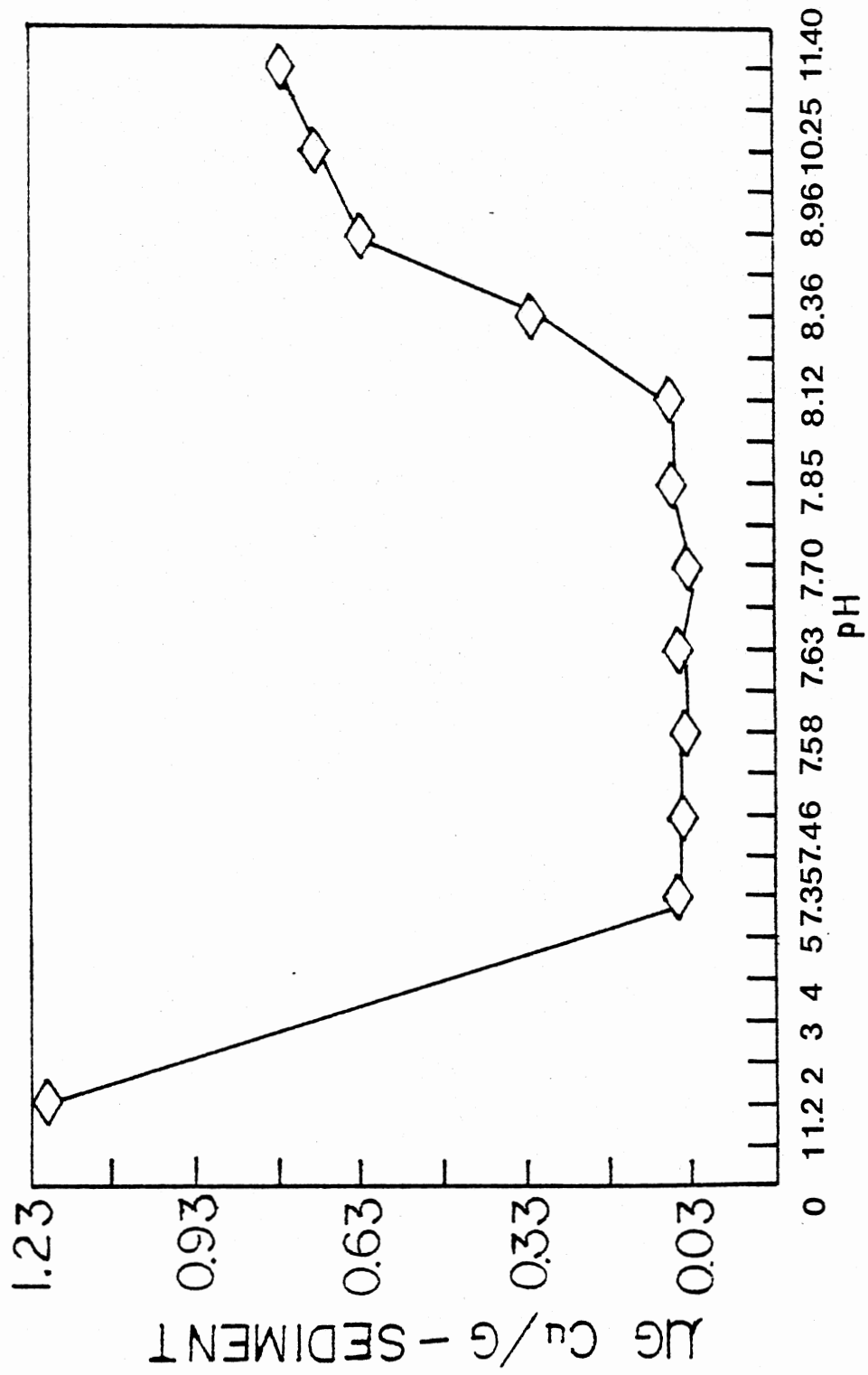
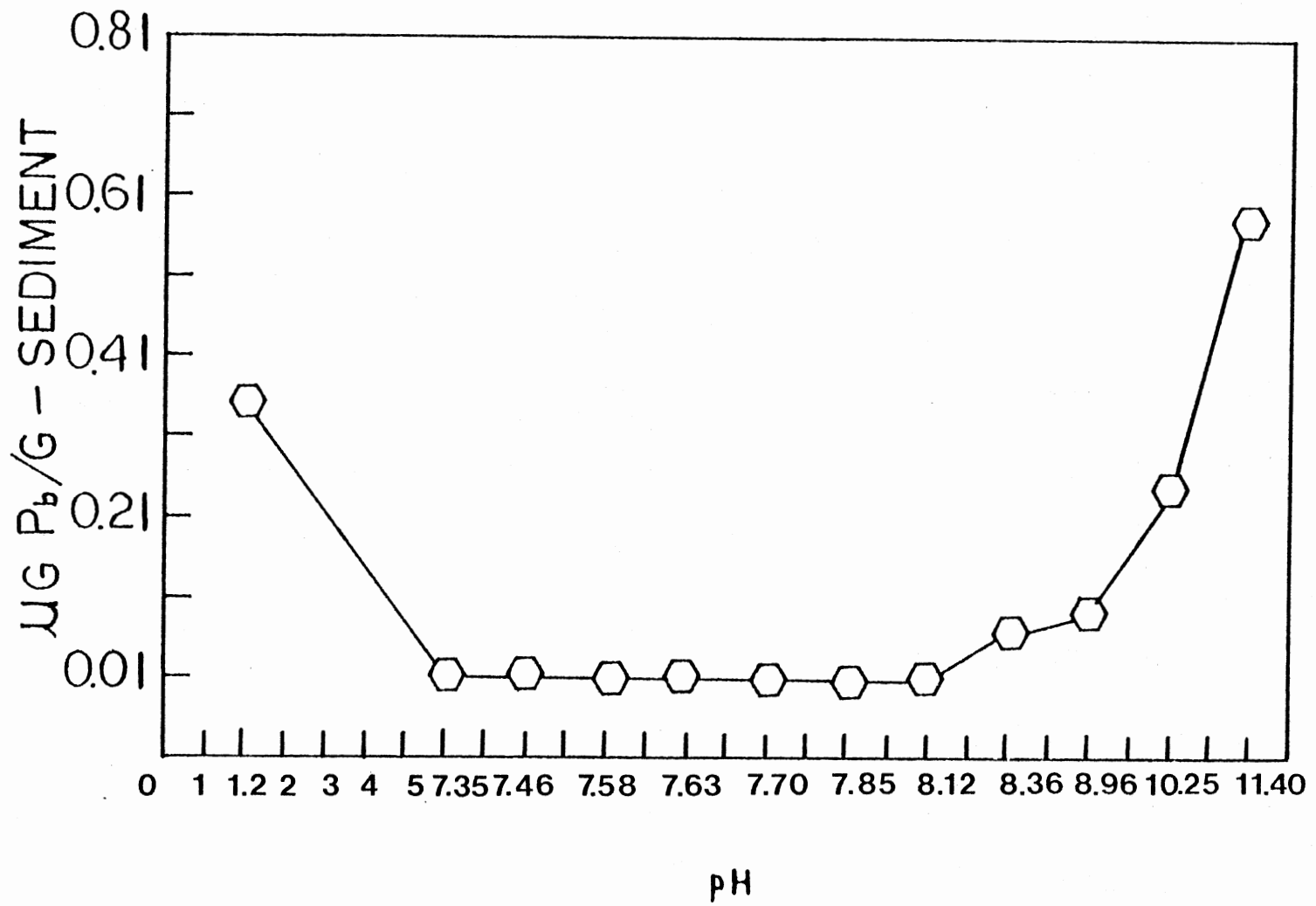


Figure 4. Soluble Lead Versus Sediment pH

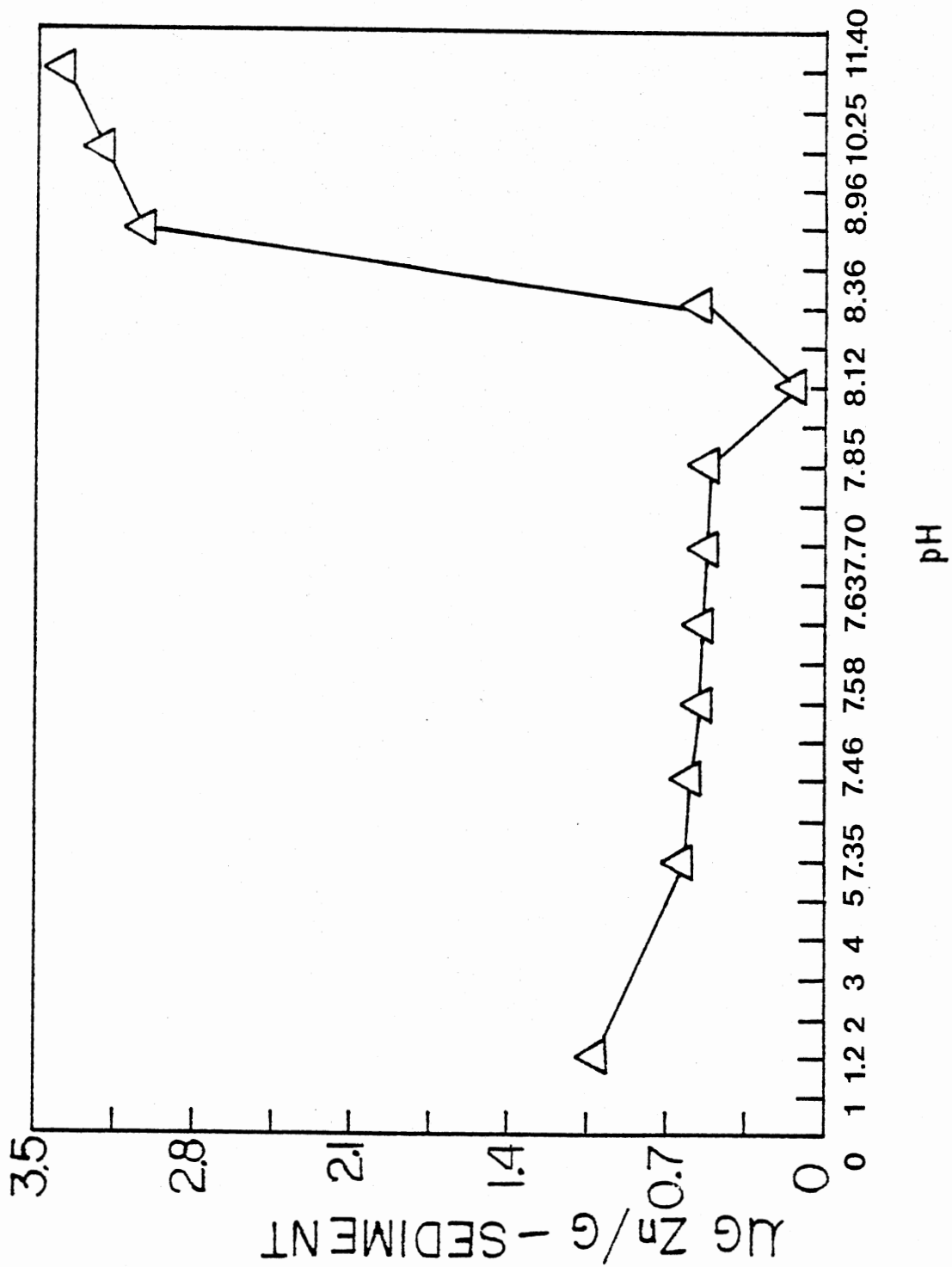


of soluble lead was seen in this figure and the highest quantity of soluble lead occurred at a pH of 11.40. At this pH the amount released to solution was found to be 0.550 $\mu\text{g/g}$ of sediment. The amount of total lead found in the natural sediment was 12 $\mu\text{g/g}$ of dried sediment.

The effects of sediment pH on the quantity of soluble zinc in the overlying water are shown in Figure 5. The quantity of soluble zinc is higher in the alkaline range than in the acidic range. An increase in the pH from 1.20 to 8.12 resulted in a decrease in the amount of soluble zinc in the system. The amount of zinc in the solution decreased to the lowest point at a pH of 8.12. There was an increase in the solubility of zinc in the solution when the pH of the system was increased in the alkaline range from 8.12 to 11.40. The highest quantity of soluble zinc was 3.4 $\mu\text{g/g}$ of sediment at a pH of 11.40. The amount of total zinc in the natural sediment was measured to be 70 $\mu\text{g/g}$ of dried sediment.

ad

Figure 5. Soluble Zinc Versus Sediment pH



CHAPTER V

DISCUSSION

There is a major difference in the chemical form in which cadmium, chromium, copper, lead, and zinc are held, solubilized, and stabilized under different equilibrium pH conditions (5). It is obvious that sediments from the Arkansas River play a role in maintaining the concentration of heavy metals in the overlying water. The results of this experiment agree with those of previous researchers with respect to pH and metal solubility.

Figure 1 relating to soluble chromium shows that there was more chromium in the water at alkaline pH values than at acidic pH values. This is supported by the finding of several authors (10) who found that water-soluble chromium increased when the pH of the sediment suspension was decreased. They proposed that chromium oxide ions were adsorbed at anion exchange sites under the neutral pH condition (10). The decrease in water-soluble chromium as the solution pH was increased could also indicate that soluble chromium was converted to less soluble forms in the neutral pH range by precipitation reactions. As can be seen from Figure 1, the water solubility of chromium was reduced significantly in the neutral pH range.

From Figure 2, it can be seen that the solubilities of cadmium are almost unchanged in the neutral pH range. However, the values of soluble cadmium were slightly higher in the acidic pH range than in the alkaline

pH range. Several authors (21) stated that the distribution and solubility of cadmium in a soil-water system is pH-dependent. A decrease in the pH can increase the solubility of cadmium in solution (21). According to the literature, cadmium could form a soluble cadmium hydroxide in a strongly basic solution (29). Other authors noticed that the formation of both cadmium carbonate and cadmium phosphate possibly occurred in the neutral pH range (23).

As seen in Figure 3, the highest concentrations of soluble copper were attained under acidic and alkaline pH conditions. It has been found by Baes et al. (15) that an acid soil releases much more copper than a neutral soil. Poor binding of copper in soil seemed to appear under acidic conditions because of competition with other cations. According to Cavallaro et al. (20), copper activity was controlled by ion exchange because the pH-copper concentration relationships showed changes in slope when the ionic strength was altered. They also found that when the pH was in the range of 7.0 to 8.0, the concentrations of soluble copper decreased to the lowest values. With respect to reduced copper solubility in the neutral pH range as can be seen in Figure 3, it is possible that carbonate mineral surfaces in soils acted as nucleation sites to precipitate copper (20).


It was shown from the plot in Figure 4 that more soluble lead was released under the alkaline pH range than under the neutral pH range. The results in this figure also showed that the solubility of lead was high in the acidic pH range. Griffin et al. (32) concluded that the increase in lead concentration at low pH values is due to an increase in competition for the adsorption site by hydrogen ions. The data from this experimental work tend to support the conclusion of several authors (28)

who stated that the solubility of lead was found to increase with a decrease in pH.

The point at which solubility of zinc is at a minimum occurred at a pH of 8.12 (Figure 5). It can be noted that more soluble zinc was released from the sediment under the alkaline pH range than under the acidic condition. It was found by Gambrell et al. (31) that zinc fixed by organic matter was released into the overlying water over the wide alkaline range of pH. According to several authors, the marked difference in the concentration of soluble zinc in different pH conditions suggested that hydroxylation played an important role in the sorption process (22). Other authors (42) stated that zinc hydroxide was an important compound which affected the solubility of zinc in basic pH solutions.

Figure 5 shows that under normal soil conditions, only a very small quantity of zinc existed in water-soluble forms. These results seem to agree with those of other researchers (44) who found that the solubility of zinc decreased in the neutral pH range. It can be partly explained by Saeed et al. (38), who stated that under neutral pH conditions, zinc in solutions may precipitate as zinc carbonate or calcium zincate which have a low solubility.

The results of this investigation showed that heavy metals are potentially available for release from the sediment of the Arkansas River to the overlying waters as the result of changes in pH. Maximum release of chromium, cadmium, and copper occurred in the strongly acidic pH range, whereas maximum release of lead and zinc were found above a pH of 8.96. The $\mu\text{g/g}$ of all the metals in solution was essentially constant and at a minimum in the pH range of 7.35 to 8.12. This pH range of minimum solubility is also within the pH range that might be expected in a natural



water system. Therefore, as long as significant pH changes did not occur in the Arkansas River, release of metals from the sediments as the result of these pH changes would not be significant. In addition, the results from this study also point out that $\mu\text{g/g}$ of metal released even under strongly acidic or basic conditions are small compared to the quantity of metal bound to the soil. At the pH values of maximum release only 5.5 percent of the bound chromium, 2.4 percent of the bound cadmium, 11.4 percent of the bound copper, 4.6 percent of the bound lead, and 4.9 percent of the bound zinc were released to the aqueous phase. This result would seem to indicate that the mechanisms of release are not heavily influenced by pH.

CHAPTER VI

CONCLUSIONS

The following conclusions can be drawn from the results of this experimental work:

1. The amounts of chromium, cadmium, copper, lead, and zinc released were at a minimum in the pH range of 7.35 to 8.12.

2. The amounts of each of the metals released increased as the pH was decreased or increased above the pH range of 7.35 to 8.12.

3. The release of chromium, cadmium, and copper was at a maximum at a strongly acidic pH (1.2).

4. The release of lead and zinc increased rapidly above a pH of 8.36.

5. The amounts of all the metals released compared to the quantities bound in the sediment were small.

6. The pH range of minimum metal release (7.35 to 8.12) was also the pH range which could be expected in a natural water system. Therefore, unless significant pH fluctuations occurred, metal release from the sediments would probably be minimal.

CHAPTER VII

RECOMMENDATIONS FOR FUTURE WORK

The recommendations for future work are:

1. Solubility of heavy metals in sediment suspensions as affected by pH and oxidation-reduction conditions.
2. Study the effect of organic compounds on the release of metals from sediments at different pH levels.

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