

EFFECT OF OXIDATION-REDUCTION POTENTIAL ON THE
RELEASE OF CHROMIUM, COPPER, LEAD, AND ZINC
FROM SEDIMENT FROM THE ARKANSAS RIVER

By

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TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. LITERATURE REVIEW	3
Redox Potential	3
The Redox Potential in the Aquatic Environment	4
Chromium	5
Copper	6
Lead	6
Zinc	7
Oxidation-Reduction Reactions in Soil-Water Systems	8
pH and Eh	9
Microbiological Aspects of Anaerobic Soil-Water System	10
The Effects of Aeration on Redox Potential	11
Problems Encountered in Measuring Redox Potential	12
III. MATERIALS AND METHODS	13
Research Approach and Setup	13
Experiment Procedures	14
IV. RESULTS AND DISCUSSION	16
V. CONCLUSIONS	30
VI. RECOMMENDATIONS FOR FUTURE WORK	31
BIBLIOGRAPHY	32

TABLE

Table	Page
I. Results of Analyses of Heavy Metal Quantities in The Sediment at the 23rd Street Bridge After Nitric Acid Hydrogen Peroxide Digestion	16

LIST OF FIGURES

Figure	Page
1. Soluble Chromium Versus Sediment Eh	19
2. Soluble Copper Versus Sediment Eh	21
3. Soluble Lead Versus Sediment Eh	23
4. Soluble Zinc Versus Sediment Eh	25
5. Water-Sediment Eh Versus PH	28

CHAPTER I

INTRODUCTION

During recent times, heavy metal pollution of aqueous systems has become an acknowledged and pressing problem. A large number of researchers in both the United States and Europe are currently conducting studies designed to further elucidate the role and behavior of heavy metals in the environment.

Once many metals are discharged into a surface water supply from either a point or non-point source they may participate in several reactions. They may remain soluble in the aqueous phase or be chemically precipitated with aqueous phase anions. In addition the metal ions may be adsorbed onto sediments and suspended organic and inorganic matter. They may be adsorbed by bacteria and algae or react to form metallic complexes with the many available ligands occurring in natural water systems. Complexation of the metal may serve to reduce its biotoxicity.

An understanding of the fate and behavior of heavy metals in aquatic systems is essential for the effective management of those pollutants. Changes in various environmental conditions can promote a redistribution of the metals among their various phases. Two important environmental conditions that may affect the fate of heavy metals in surface water systems are pH and the oxidation-reduction potential. pH governs the solubility of the metal whereas oxidation-reduction potential determines the form of the metal available for reaction. Redox potential is important even for those metals that do not undergo oxidation-reduction

reactions. A change in redox potential could alter the availability of naturally occurring ligands and therefore could promote or enhance metal complex formation.

The purpose of this work is to study the effects of artificially altering the redox potential of laboratory systems on the release of four heavy metals from river sediments. The sediments were obtained from the Arkansas River as it flows through Tulsa, Oklahoma. The four heavy metals studied include chromium, copper, zinc, and lead. All of these metals appear on EPA's list of priority pollutants and are of significant environmental interest.

CHAPTER II

LITERATURE REVIEW

Heavy metals create toxic conditions for an organism when the heavy metal interferes with the normal functioning of that organism. Such a condition can be mild, chronic, acute or even lethal for the organism. These elements may be referred to as "trace metals" for the toxic effects may occur at exceedingly low metal concentrations. Each heavy metal has its own environmental significance and certain industrial hazard or pathological effects. The availability of heavy metals for uptake by organisms is governed by pH and oxidation-reduction potential.

Redox Potential

Redox potential (Eh) may be defined as the electron-escaping tendency of a reversible oxidation-reduction system, and thus is an intensity factor. Zobell (1) indicated that positive Eh values are generally characteristic of ^{top?} bottom deposits which are well oxygenated including those which consist of coarse sediments or those which are poor in organic matter. Negative Eh values are characteristic of bottom deposits rich in organic matter and which consist largely of fine sediments. An abundance of readily decomposable organic matter appears to promote reducing conditions. In the presence of organic matter, bacteria and allied micro-organisms create reducing conditions.

The Redox Potential in the Aquatic Environment

In distilled water saturated with oxygen the redox potential is about 500-600 mv (relative to the calomel reference electrode). Water from a hypolimnion which is deprived of oxygen will show a lower redox potential down to about 100 mv which indicates the solution has a strong reducing capacity. Below the mud-water interface, the redox potential often falls sharply and values of -100 mv can be found (2).

Higher redox potentials favor the presence of heavy metals in their higher oxidation state, while lower oxidation states are usually found in reducing environments. For example, in an oxidizing environment, iron and manganese are oxidized to ferric and manganic ions which are quickly precipitated as $\text{Fe}(\text{OH})_3(\text{s})$ and $\text{MnO}_2(\text{s})$. As these precipitates settle toward the sediments, they remove other heavy metals, hence, the solubility of heavy metals would be decreased simultaneously. However, in some aquatic systems, such as eutrophic lakes that experience anaerobic conditions in the sediments, the ferric and manganic precipitates are reduced respectively to ferrous (Fe^{++}) and manganous (Mn^{++}) ions, which are much more soluble. This causes the heavy metals to be released into the overlying waters and to be cycled throughout the system. Once the aerobic conditions are restored, the ferrous and manganous ions are again reprecipitated as ferric hydroxide and manganic dioxide. Then the cycle described above is repeated.

The interaction between heavy metal ions and inorganic and organic substances is important because it establishes the ultimate chemical form of heavy metals in the sediments, and in addition it determines the rate and extent of metal distribution in the sediments. It also affects the toxicity of the metal with respect to organisms such as bacteria.

For example, if a toxic heavy metal is strongly complexed within an organic molecule, the overall toxicity of the metal ion toward the organisms in the sediments can be substantially reduced.

It is very important to understand the chemical, physical and biological reactions of heavy metals that take place at the sediment-water interface. It is notable that heavy metals adsorbed by the solid phase of sediments are usually in the reducing zone of the aquatic system and undergo reduction reactions. These heavy metal ions would become more soluble with the aid of gases from the decomposition of organic materials and diffuse upward to reach the aerobic zone. Upon reaching the aerobic zone, those heavy metals would again reprecipitate as oxidized states immediately. Thus, heavy metals are mobilized upward and then oxidized and precipitated downward as a cycle in a closed aquatic systems.

Chromium

Chromium has oxidation states ranging from Cr^{-2} to Cr^{+6} and most commonly occurs as Cr^0 , Cr^{+2} , Cr^{+3} and Cr^{+6} (3). Divalent chromium is relatively unstable and can be oxidized to the trivalent form. Thus, only two forms-- Cr^{+3} and Cr^{+6} -- are found in nature. The reduction potential of hexavalent to trivalent chromium is strong. The Cr^{+6} , almost always linked to oxygen, is a strong oxidizing agent. The hexavalent form of chromium appears to be relatively stable in water, probably because of the low concentrations of reducing materials. The trivalent form is associated with particulate matter, which suggests that organic particles may reduce and bind the element, leaving the hexavalent form in solution (3).

Chromates and dichromates are easily reduced to trivalent

chromium in acid solution and in the presence of organic matter. The trivalent state is the most stable oxidation state. It has a strong tendency to form complexes whose ligand rates of exchange are low.

Copper

Copper is one of the transition elements with four possible oxidation states: Cu^0 , Cu^{+1} , Cu^{+2} and Cu^{+3} (4). In aqueous solution the only stable oxidation state is Cu^{+2} , for Cu^{+1} will disproportionate to Cu^0 and Cu^{+2} as follows:



Insoluble aqueous complexes of Cu^{+1} are quiet stable in aqueous media. The relative stabilities of Cu^{+1} and Cu^{+2} species in solution depend on the nature of ligands present and vary with the composition of the solution. In aqueous solution, only a low concentration of Cu^{+1} soluble species can exist (4).

Cu^{+3} is a strong oxidant and can be obtained only under highly oxidizing conditions. Such conditions can be achieved by heating in the presence of oxygen.

In the sedimentary cycle, copper is concentrated in the clay mineral fractions. Reducing conditions are common in many organic rich environments.

Lead

Lead exists in three oxidation states 0, +2, and +4 but lead exists in aqueous solution almost entirely as Pb(II) species (5). The equilibrium $\text{Pb}^{+4} + 2\text{e}^- \text{ -----} \rightarrow \text{Pb}^{+2}$ has a E^0 value of over .21 and thus Pb(IV) species like PbO_2 exist only under extremely oxidizing conditions.

Pb^{+2} dominates in acidic conditions. The divalent inorganic lead

compounds are very stable. In a simple model of freshwater system of pH between 6 and 8, the lead will be entirely complexed as the carbonate species $\text{Pb}(\text{CO}_3)_2^{-2}$ and PbCO_3 at more acid pH values.

Zinc

The behavior of zinc as a function of redox potential has not fully been resolved (6). Some investigators have concluded that zinc is more soluble under reducing conditions because of the iron and manganese hydrous oxides, which tend to sorb or coprecipitate zinc under oxidizing conditions (7). An alternative view is that the low solubility of zinc in the presence of sulfides, which are produced under reducing conditions, make trace metals more soluble under oxidizing condition (8).

O'Connor and Renn (9), who studied the soluble-adsorbed zinc equilibria in river water concluded that the adsorption equilibrium was more strongly related to pH than to the Freundlich isotherm. Young (6) indicated that zinc always has an oxidation state of +2 in aqueous system and is not directly affected by changes in Eh. However, the valences and reactivity of ligands reacting with zinc are affected by Eh.

Huang et al. (10) showed the equilibrium solubility and stable solid species of zinc at pH 5 is a function of pE ($\text{pE} = -\log \text{Eh}$). Precipitation of zinc compounds appears to be important only in reduction states. Holmes et al. (8) concluded that formation of zinc sulfide controls the mobility of Zn in an estuarine system. Seasonal fluctuations in dissolved zinc levels are also attributed to variations in redox potential. In the summer, when reducing conditions prevail in the hypolimnion due to the combined effects of lower O_2 solubility and greater biological oxygen demand, zinc is incorporated into the sediments by formation of ZnS. In winter, Eh increases and zinc is

released to the water.

Oxidation-reduction Reactions in Soil-water Systems

Some factors that are correlated to redox reactions in an aquatic soil system are water saturation, organic matter, temperature, oxygen content, and pH value. Actually, reduction may take place if the following conditions are met simultaneously: presence of organic matter, absence of an oxygen supply, presence of anaerobic microorganisms and an environment suitable for their growth.

The presence of organic matter in an aquatic system will affect the redox potential. Burrow and Cordon(11) studied the development of redox potential in relation to the decomposition of various types of organic matter in soil. They found that the type of decomposable organic matter present in the soil is a highly important factor in the determination of the degree of reducing intensity. The redox potential will not change greatly from those samples with no organic matter.

The decomposition of organic matter starts in an optimal temperature range after the dry sediment is waterlogged. Under some circumstances bacteria rapidly proliferate, and the oxygen is depleted. The reduction of nitrate commences with the disappearance of oxygen and a concurrent initiation in the reduction of manganese and iron oxides also. This is followed by reduction of sulphates and phosphates.

Several efforts have been made to establish a relationship between soil oxygen content and redox potential. Scott and Evans (12) attempted to measure oxygen content and redox potential in saturated soil but no close relationship was measured. Armstrong (13) found a fairly close relationship between redox potential and oxygen diffusion rate through-

out the soil profile, with the Eh decreasing to +100 to +200 mv as the oxygen diffusion rate decreased to about $0.4 \text{ g } 10^{-8}/\text{cm}^2/\text{min}$.

Turner and Patrick (14) found that the decreasing oxygen content had little effect on redox potential until an oxygen content of below 4 percent was reached. Below 4 percent oxygen, a marked change in redox potential occurred with an average Eh at zero oxygen of 332 ± 5 millivolts.

If oxygen is available, oxygen may function as an electron acceptor and if oxygen is not available, other reducible compounds may function as electron acceptors. Under soil conditions, NO_3^- , Mn(IV) Mn(III), Fe(III) and S(VI) are important reducible compounds, but reduction of these compounds by organic matter is very slow.

From Quispel's experiments (15), he drew a conclusion that in an FeS containing soil, the redox potential is mainly determined by the mutual relation between the capacity of oxygen and the capacity of sulfide ions. In the reducing organic containing soil, the reducing organic substances and bacteria may be equally important. When no reducing substances are present and the soil is well aerated, the potential is mainly determined by oxygen.

pH and Eh

Redox potential in many ways is analogous to pH (16). It measures the ability of an environment to supply electrons to an oxidizing agent, or to supply protons (hydrogen ions) to a base or to take up protons from an acid.

In a complex solution like seawater or fresh water and a soil, the redox potential is determined by a number of reactions, just as pH is determined by the combined effects of the carbon dioxide system, the

boric acid system and various organic acids. The particular reactions are difficult to identify, and are less important than the overall ability of the environment to maintain the Eh and pH constant when small amounts of foreign material are added.

Pearsall (17) found that while the various potential values (Eh) were determined at different pH levels, an arbitrary correction is employed which expresses the potential at a constant pH value as pH 5.00, termed E_5 , for purposes of comparison of various samples. For every unit of pH above 5.00, the potential is increased by 58 mv.

Microbiological Aspects of Anaerobic Soil-water System

Many researchers have worked on incubation of water logged soils (18), (19), (20). It is essentially an anaerobic system at the aquatic soil interface. Due to submergence of soil, reduced conditions and anaerobic environments are created and these bring about different physical, chemical and biological changes in the soil.

On waterlogging, the arable soil changes from an oxidizing to a reducing condition. One possible reason is the oxygen consumption and the accumulation of reduced materials by decomposing soil organic matter under limited oxygen supply from the surface water.

Takai (21) concluded the following from his study which investigated the reaction process in paddy soils:

1. In the early stage of the incubation process, Eh drops rapidly and ferric iron is reduced vigorously.
2. Nitrate disappears at the beginning of incubation, and ammonia is liberated along with the progress of reduction.
3. An active sulfide formation takes place after a periods of

incubation time.

4. The dominate bacterial type are followed as the orders of aerobe, anaerobe and sulfate reducing bacteria.

He also noticed that:

1. Dissolved oxygen is consumed within one day.
2. Hydrogen occured.
3. Carbon dioxide increased rapidly at the beginning and then decreased continuously.

4. Methane occured as the carbon dioxide decreased, that may relate to the methane bacteria reduces carbon dioxide to methane anaerobically.

The Effects of Aeration on Redox Potential

Pearsall and Mortimer (22) observed the effects of aeration on redox potential. They found that a sudden rise in potential occured on addition of air. In the absence of air the potential will later fall. They also tested these bottles by bubbling with nitrogen to remove all trace of oxygen. The potential fell 110 mv in 1 hour.

In 1941, Mortimer and Pearsall (23) observed the change in redox potential and the concentrations of dissolved substances in artificial mud-water systems subjected to varying degrees of aeration. They used three difference treatments. In one the artificially aerated tank was subjected to continual aeration. A second aerated tank was allowed to stand with the water surface exposed to the air. The third tank, an anaerobic one, was covered and sealed with paraffin. They found the greatest change in the anaerobic tank. At 70 days, the mud surface had darkened in colour and the dissolved oxygen in the water had disappeared. Nitrate had become completely reduced in the water and the ammonia concentration had begun to rise.

Bloomfield (24) investigated the influence of anaerobic and aerobic conditions on the solubilities of Zn, Ni, Cu, Pb, Cd, and Cr in sludge. He found that aerobic incubation caused the pH to fall, whereas, under anaerobic conditions, the sludge became more alkaline. He found that under anaerobic conditions the amount of Cu dissolved in water decreased, yet the amount of Cd and Pb had a net increase in the water solubility. Bloomfield also aerated the sludge after a previous anaerobic incubation. He found that subsequent aeration increased the amount of water soluble Cu, Zn and Cr, but the corresponding effect on Ni, Pb and Cd was small.

Problems Encountered in Measuring Redox Potential

Morris (25) and Bohn (26) indicated that the true redox equilibrium can not be observed in any natural aquatic system, because most redox reactions are extremely slow for lack of suitable biochemical catalyst and partly because of the continuously input of photosynthetic energy source that disturbs the trend toward equilibrium conditions.

Quispel (15) found that the measurement of the redox potential of soil should be made in an undisturbed condition. Since the inserting of the electrodes in itself produces a disturbance of the soil equilibrium, one should wait until equilibrium has become reestablished before measuring the redox potential.

CHAPTER III

MATERIALS AND METHODS

The sample sediments used in this study were collected from the Arkansas River below the 23rd Street Bridge, Tulsa, Oklahoma. After they were brought to the laboratory, the sediments were completely air-dried in thin layers in acid-washed plastic pans at room temperature. Then, the sediments were thoroughly mixed and were stored in the refrigerator until they were used. These sediments were brought to room temperature before being used.

The sediments were mainly composed of sand deposits in the river. A former report showed that the quality of the river water is unsuitable for municipal purposes because of the excessive concentrations of total dissolved solids and chlorides (27).

Research Approach and Setup

The experiment was set up to measure the amount of chromium, copper, lead, and zinc found in the sediments and the water soluble concentration of each metal at different redox values (Eh). All containers and glassware used in this experiment were acid-washed with a solution of concentrated nitric acid and then were rinsed thoroughly with distilled deionized water before using.

Experiment Procedures

In the first part of this experiment, the amount of each metal in the sediments was measured by the method described by Krishnamurty et al. (30) that basically involves nitric acid and hydrogen peroxide digestion. 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.

To determine the effects of oxidation-reduction potential on the release of soluble metals from the Arkansas River sediments, ten grams of dried sediments were placed in 200-ml Erlenmeyer flasks with 150-ml of distilled deionized water. Oxygen or nitrogen was then bubbled into duplicate flasks for 30, 60, and 120 minute time intervals. After bubbling, the flasks were immediately sealed with parafilm and put on a shaker table for shaking and incubation for 7 to 15 days. During this time the redox potential dropped due to microbial activity. After removal from the shaker table, the redox potential was determined by directly inserting a redox probe through the parafilm. Once

the Eh value had been obtained, the sample was immediately filtered and the filtrate was analyzed directly using a Perkin-Elmer Model HGA-400 graphite furnace.

For the experimental units, mixing was accomplished by an Eberbach Box-type mechanical shaker. Redox potentials (Eh) were measured using an Orion Research, Digital pH and mv Meter, and the platinum electrode probe, Fisher, Model 94-06 was calibrated by several methods. The first method for electrode calibration uses a solution of M/300 $K_3Fe(CN)_6$ and M/300 $K_4Fe(CN)_6$ in M/10 KCl, which has an Eh value of +0.430 volt at 25°C (1). The second method is that of Michaelis (29) using a solution that contains 4,000 grams of NaOH and 12.006 grams of acetic acid per liter of distilled water. A stream of hydrogen is then bubbled through the solution until it is saturated. Such a solution has an Eh value of -0.273 volt at 25°C.

CHAPTER IV

RESULTS AND DISCUSSION

The results from the analyses for the amounts of copper, lead, chromium and zinc contained in the sediment samples are shown in Table I.

TABLE I

RESULTS OF ANALYSES OF HEAVY METAL QUANTITIES
IN THE SEDIMENTS OF THE ARKANSAS RIVER AT
THE 23RD STREET BRIDGE, TULSA, OKLAHOMA

Element	Concentration (microgram/gram)
Cr	30.0
Cu	11.0
Pb	12.0
Zn	70.0

The quantity of total chromium in the Arkansas River sediment was found to be 30 microgram/gram of dried sediment. The distribution of soluble chromium at different Eh values ranged from 0.03 micrograms/gram to 0.08 micrograms/gram of dried sediment. When the Eh was increase

from +150 mv to +400 mv , the amount of soluble chromium in the water increased. The relationship of soluble chromium versus Eh value in the sediment solution is shown in Figure 1.

This result compares favorable with that obtained in Bloomfield's (24) work in which the water soluble chromium was also found to increase as aeration continued. However, with respect to the anaerobic reaction, Bloomfield found that the longer the anaerobic incubation, the more water soluble chromium was released. This trend is not observed in this experiment, however, the lowest redox potential attained for this work was -250 mv.

Figure 2 shows the effects of Eh on the solubility of copper. It is obvious that the higher the redox potential the lower the water solubility of copper. This relationship has also been shown by Sims (20). He found that water-soluble Cu was related inversely to Eh value, and indicated the inverse relationship was caused by the formation of different metal-organic complex. Bloomfield found the same results in that the longer the aerobic incubation, the less water soluble copper.

From Figure 3, the solubility of lead also changed significantly as the Eh value changed. The higher Eh, the lower solubility of lead. Bloomfield (24) also found that the water soluble lead decreased within the first month period of aeration. Reddy and Patrick's (7) work has the same result that water-soluble lead decreased with an increase in Eh and pH. They also indicated that precipitation of Pb as $Pb(OH)_2$ and $PbCO_3$ may be the main factor governing Pb concentration in soil systems.

The effects of sediment Eh on the quantity of soluble zinc is shown in Figure 4. The lowest amount of soluble zinc for this study was found in the range of Eh values of 200 to 300 mv. Beyond that range, soluble

Figure 1. Soluble Chromium Versus Sediment Solution Eh

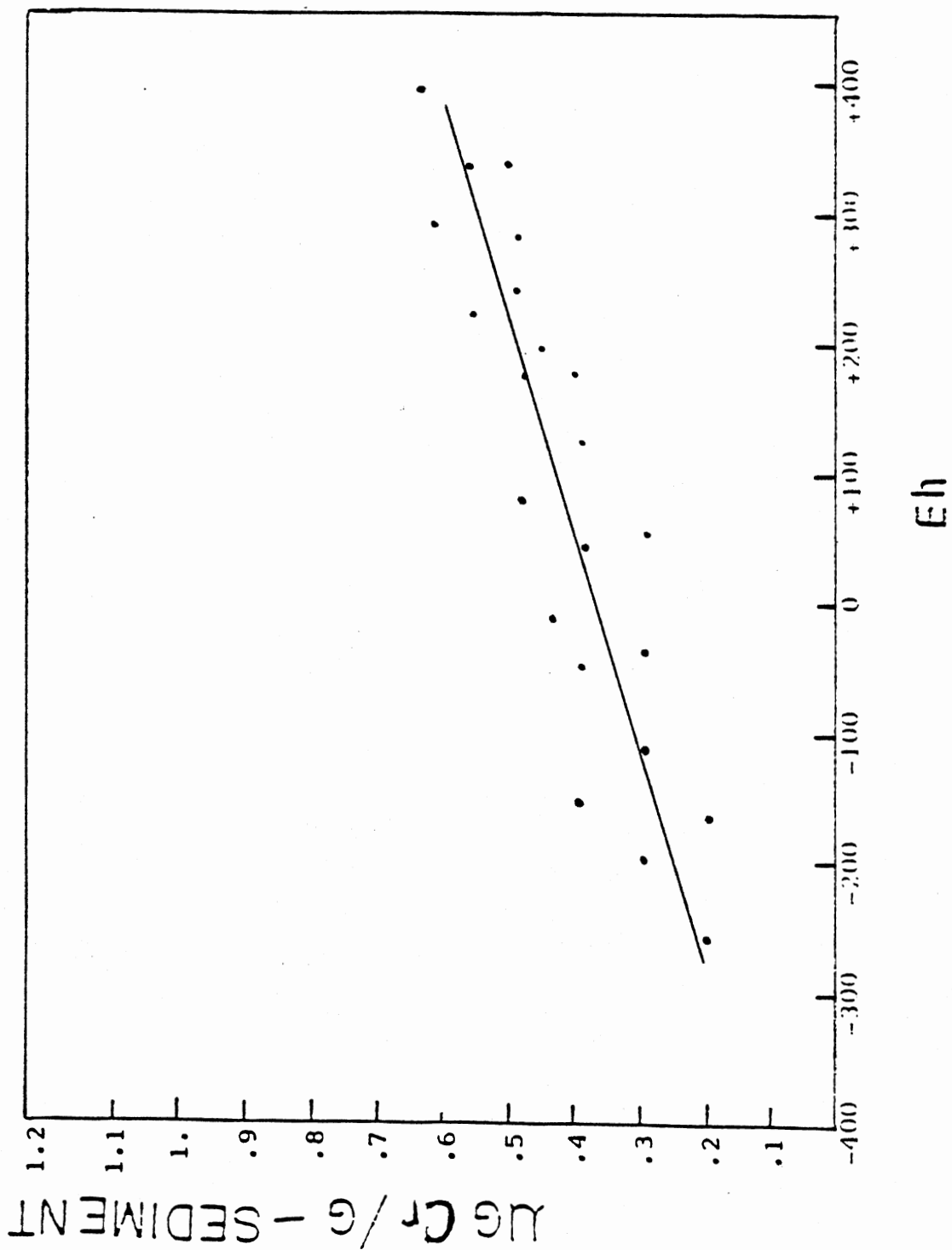


Figure 2. Soluble Copper Versus Sediment Solution Eh

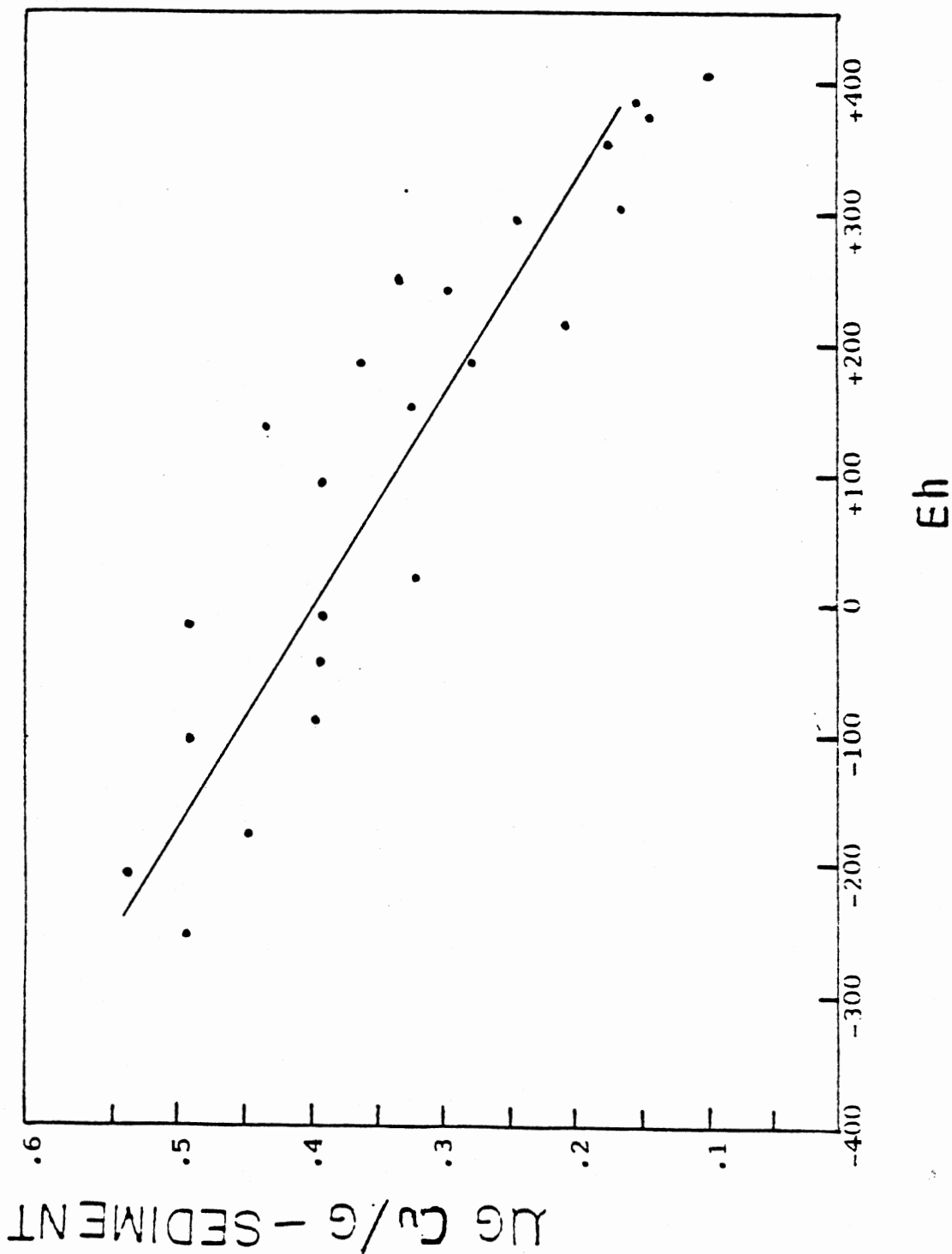


Figure 3. Soluble Lead Versus Sediment Solution Eh

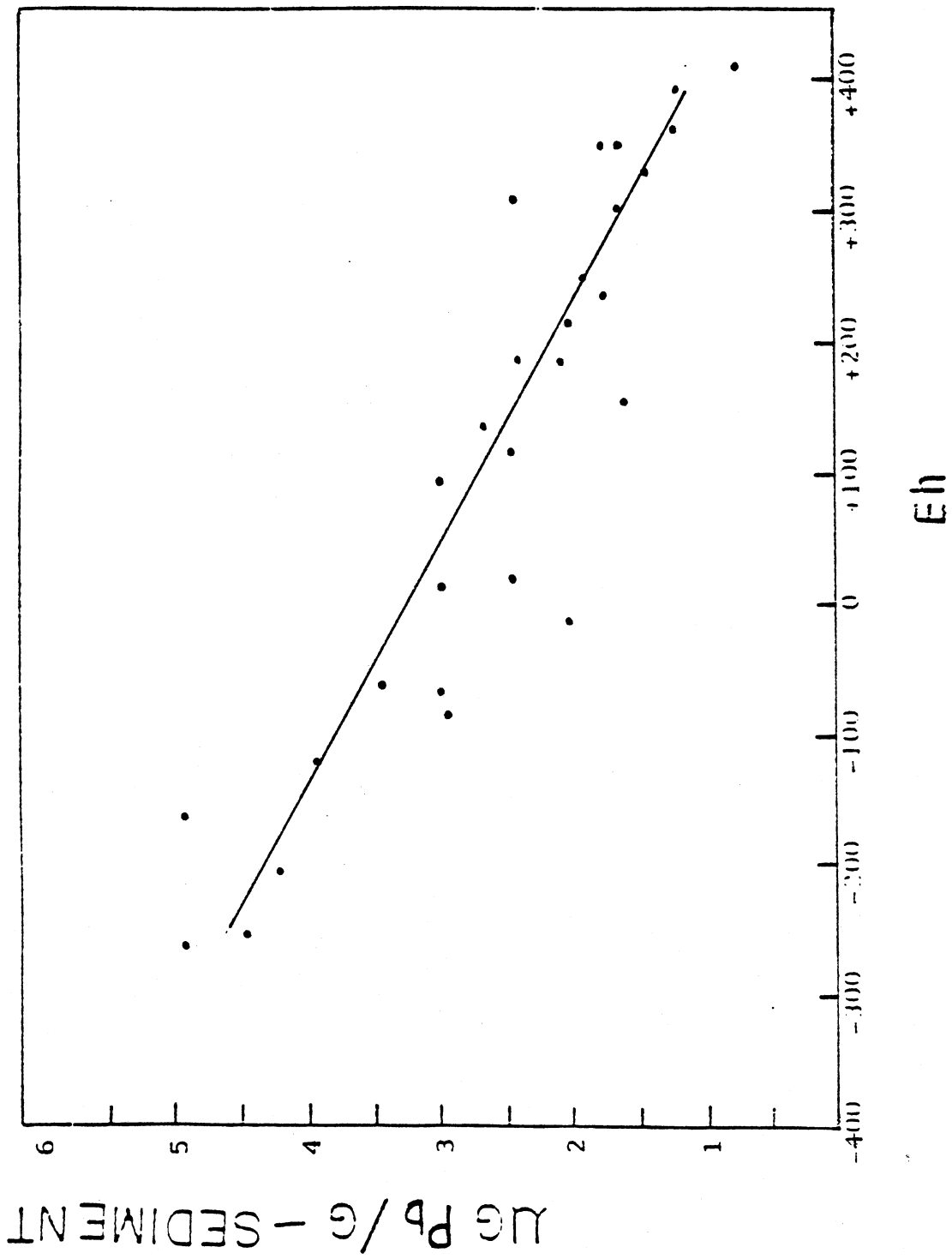
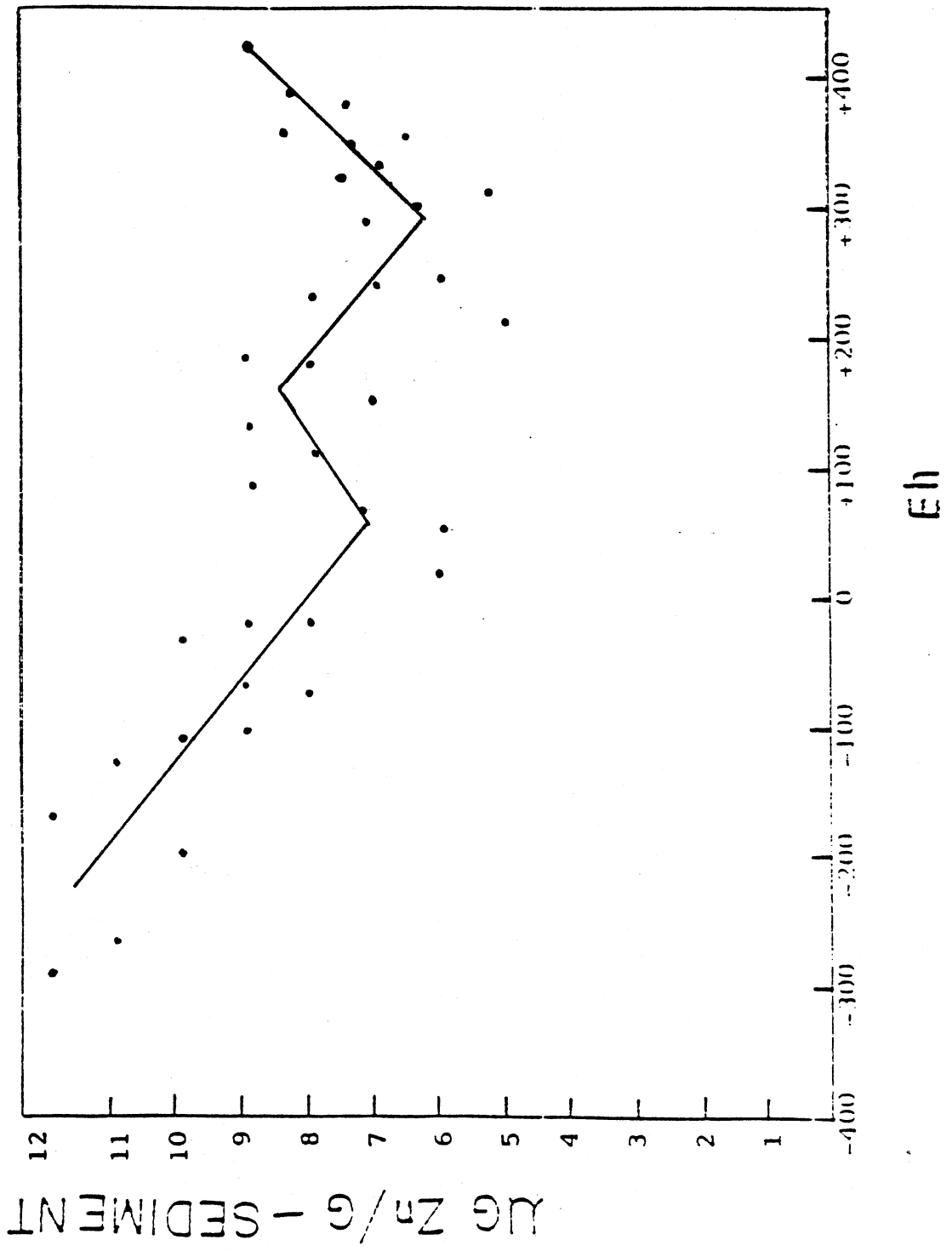


Figure 4. Soluble Zinc Versus Sediment Solution Eh

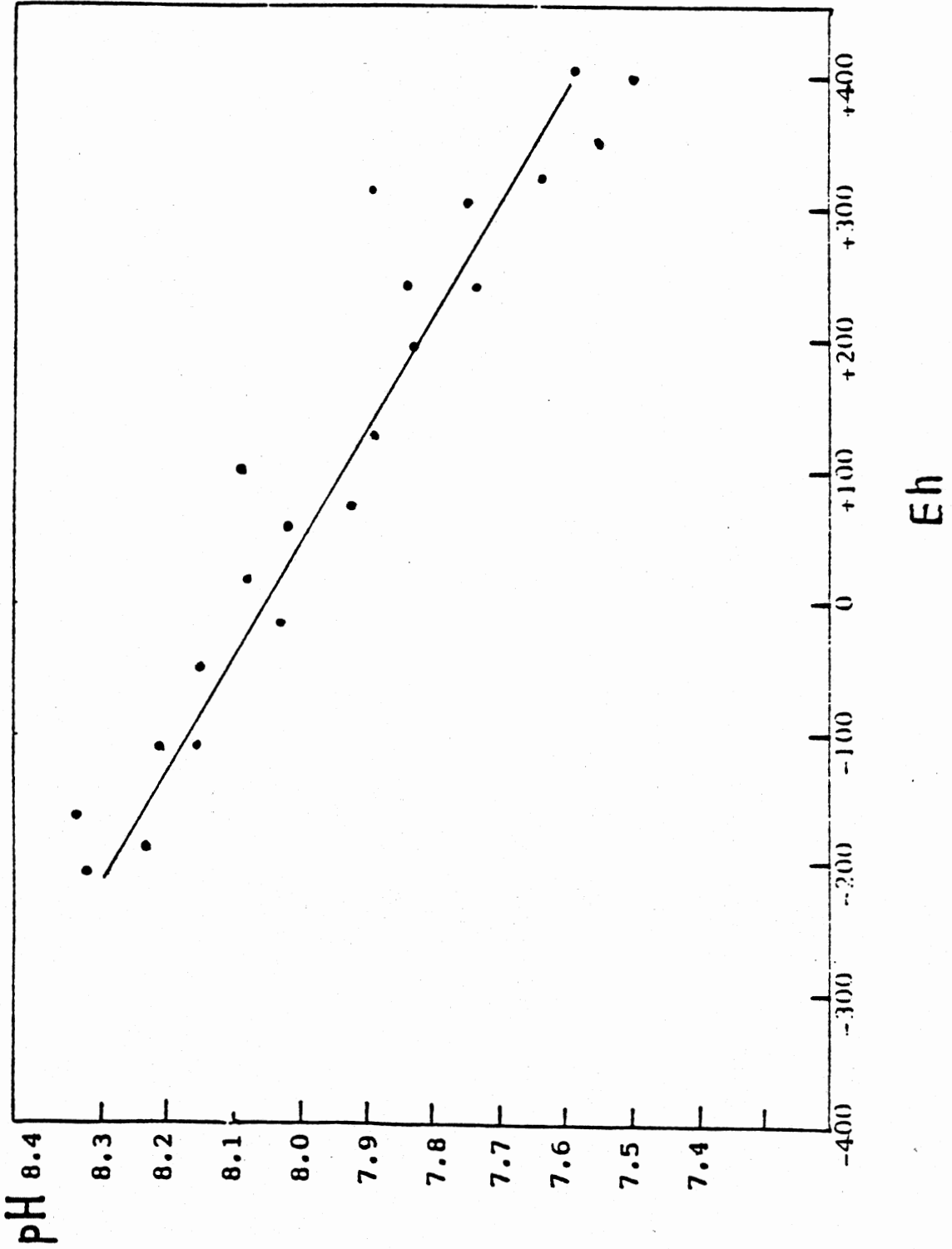


zinc increased. Bloomfield's (24) work showed that water soluble zinc increased within one month of anaerobic incubation, and decreased within the first month of aerobic incubation. Bloomfield, however, as noted before did not take Eh measurements, which makes comparison difficult. Sims (20) found that water soluble zinc decreased from 2.7% to 2.4% as the Eh value decreased from 0 to -150 mv and also decreased from 5.5% to 2.2% at Eh value between +150 mv to +300 mv. The aerobic results in this experiment are similar to what Sims reported.

A relationship does exist between pH and the oxidation-reduction potential in aquatic systems. Both the parameters are highly dependent upon the presence of organic material and the ensuing microbial and biochemical reaction. The relationship between the two parameters as defined in several experimental works is linear. According to Hesse (30) for each unit drop in pH at specific temperature there is a specific increase in the redox potential. Figure 5 plots pH versus Eh for identical solutions containing Arkansas River sediments and distilled deionized water. The linear relationship as described by Hesse is exhibited here. In addition it should be noted that according to the work by Ung (31) using sediments from the same source, the pH range of 7.5 to 8.3 is the range of minimum solubility for the metals studied.

The results of this experiment showed that the heavy metals are potentially available for release from the sediment of the Arkansas River as a result of changes in Eh. That data collected in this experiment is essentially of relative value. Using different water-sediment ratios may cause the sediment to leach more or less metals, which would provide different solubility data. In this experiment, all the samples had an identical water-sediment ratio to facilitate the investigation of

Figure 5. Water-Sediment Eh Versus PH



changes in solubility under a variety of Eh values.

The maximum release of the metals, except for lead, only represented a small fraction of the total metal content of the sediments. The maximum percentages of chromium, copper, lead and zinc released were 2.17%, 5%, 41.67% and 17.14% respectively. Maximum amounts of chromium were released under aerobic condition whereas maximum amounts of soluble copper, lead and zinc were found under anaerobic conditions. Except for lead, redox potential does not play a major role in the release of these heavy metals from Arkansas River sediments. For lead, specifically, the maximum release of the metal seen under laboratory conditions may only occur in a few areas of the river. The pool located to the north of the low water dam which is currently being constructed would be the most likely place for anaerobic condition to prevail for any substantial length of time. Natural reaeration of the river beyond the pool area would aid in keeping conditions aerobic, thereby minimizing lead release.

CHAPTER V

CONCLUSIONS

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

1. The amount of chromium, copper, lead, and zinc released in the water were influence by the changing of Eh value.
2. The amounts of all the metals released compared to the quantities bound in the sediment were small.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE WORK

The recommendations for the future work are:

1. To study the effects of Eh on metal solubility in systems containing both water and sediment from the Arkansas River. This would allow an investigation of the effects of Eh on metal solubility in the presence of ligands and other ions.
2. To study the solubility of zinc over a wider variety of Eh values.
3. To study the effects of Eh on metal solubility using additional heavy metals commonly found polluting the aqueous environment.

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