A STUDY OF THE FATE OF COPPER IN SIMULATED GROUND WATER SYSTEMS

By

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A STUDY OF THE FATE OF COPPER IN SIMULATED GROUND WATER SYSTEMS

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CHAPTER I

INTRODUCTION

Heavy Metals

Heavy metals are introduced into the environment by several mechanisms. The increased presence of heavy metals can be attributed to the increased industrial development, the application of pesticides to agricultural lands, inadequate waste disposal practices, and natural leaching of the soil.

The heavy metal before entering a ground water system must exist in different phases. There will be the source, transport to and on the earths surface, movement through and interaction with the soil, and finally it enters the zone of saturation (Barnes and Schell, 1973).

It is important to determine the source, whether man-made or natural, and to study the movement or retention of the metal as it passes through the soil by percolation to the ground water system. The heavy metal is subject to many reactions with the soil and its constituents those being, sorption, chemical complexing and chemical alteration resulting from biological activity (McNabb and Dunlap, 1975).

Heavy metals may be classified as those necessary to life and those not. Humans can be directly affected by a pollutant from consumption of a contaminated water supply, or indirectly by the consumption of organic materials which retain the pollutant from another source.

Ground water contamination is the degradation of the natural quality of the ground water. The contaminant is any physical, chemical, biological or radiogical substance or matter in water (Federal Register, 1975).

Trace inorganics, i.e., heavy metals, have been of concern to health officials for many years. Copper was looked at primarily because of the increased use of copper salts for algae control. Public health official have since focused their concern on metals significant to public health. The Environmental Protection Agency (E.P.A.) has excused copper from drinking water standards because the lack of evidence that copper is a detriment to public health. It does, however, hold a restriction that the copper shall not exceed 1.0 mg/l, primarily from the palatable point of view. Concentrations of less than 1.0 mg/l can be toxic to aquatic plants and some fish (Sawyer and McCarty, 1978).

Ground Water

The intense use of natural resources and the activities of man have produced innumerable waste materials and by-products. This large production of wastes in society have in many instances threatened the quality of the ground water environment due to the lack of disposal regulations.

Ground water has become a major source of drinking water in the United States. Approximately one half of the population (48%) rely on ground water as a water source (U.S. Environmental Protection Agency, 1977). The E.P.A. has also reported that more than one third of the nation is underlain by aquifers capable of yielding at least 75,000 gpd.

Comparing ground water to surface water for drinking, ground water is more accessible and available. It is not subject to the large fluctuations, the evaporation loss is less, and temperature of ground waters stay constant relative to surface waters. Ground water on the average has a higher mineral content than surface waters, but generally is very low in organic and suspended materials because of the filtering affect of the unsaturated zone (Johnson Division, UOP Inc., 1975).

The primary course of action toward surface water problems is to eliminate or control the source of contamination. Surface waters such as streams have a faster recovery rate because of the purification effects of air, light, and biological organisms. The opposite is the case for ground water. The source can be eliminated removing the possibility of further contamination, but it does not aid in the cleansing of the aquifer (U.S. Environmental Protection Agency, 1977). Because the movement of ground water is very slow, it may take many years for a pollutant to show up in the water system. On the other hand, because of the slow movement, it can take many years to clean-up an aquifer. Clean-up procedures such as pumping a well are neither economically or technically feasible.

Shallow aquifers are normally the most easily accessible, therefore, considered the most important for water supply purposes. Consequently, because of their shallowness, these aquifers are the most susceptible to contamination (U.S. Environmental Protection Agency, 1977).

For these reasons, it would be advisable to closely regulate effluent discharge and disposal site selection to protect the now uncontaminated ground water systems.

CHAPTER II

REVIEW OF LITERATURE

Behavior of Copper in Soil Systems

Copper will most likely enter the ground water system by percolation through the zone of aeration which consists of three subzones: the soil water zone, vadose water zone and finally the capillary fringe (Bear, 1979). Copper can also be directly injected into the zone of saturation i.e., ground water.

The metal as it passes through the soil is subject to several attentuating mechanisms. Copper can undergo processes of sorption, chemical complexing, and chemical alteration. These reactions are affected by the soils texture, colloidal content cation exchange capacity, i.e., C.E.C., pH, oxidation reduction potential, i.e., redox, and microbial population. Colloidal content will be discussed as organic or inorganic.

Adsorption

As a liquid comes in contact with the soil surface, a thin layer of ions is held to that surface by a phenomenon called adsorption. Adsorption, as a mechanism of metal uptake, can be categorized as three general types; physical, exchange, and chemical adsorption (Sawyer and McCarty, 1978).

Physical adsorption is a surface phenomenon between molecules by electrical attraction. The heavy metal is not affixed to a specific adsorption site, but is free to undergo movement over the surface (Weber, 1972). Physical adsorption is generally reversible (Sawyer and McCarty, 1978; Maes and Cremers, 1975). When the potential adsorption sites are no longer available, the process becomes one of exchange.

Exchange adsorption is the result of electrostatic attraction to sites of opposite charge. The determining factor for exchange adsorption is the charge on the ion. Negatively charged exchange sites hold cations which carry a positive charge. Cation exchange is a process by which heavy metals are attracted to exchange sites and displace hydrogen, sodium and potassium ions which initially occupy the site (U.S. Environmental Protection Agency, 1977). The cation exchange capacity (C.E.C.) is a measurement of the ability of the soils negatively charged colloids to remove added cations. C.E.C. capacity is measured in terms of milliequivalents per 100g of oven dryed soil. The greater the C.E.C. the stronger the heavy metal is adsorbed (Leeper, 1978).

Chemical adsorption or chemisorption is the chemical bonding in the crystal lattice. The adsorbed molecules are considered to be free to move on the surface, but fixed because of the strong localized bonds formed (Weber, 1972).

Adsorption on clay minerals and quartz are increased with an increase of pH. Muller (1959) observed that raising the pH, Cu was more firmly fixed and therefore less toxic. As reported by Shawney (1972), large monovalent cations are sometimes so strongly bonded they are said to be fixed. Some cations are more selectively sorbed than others. The major factor controlling selectivity is considered by Shainberg and Kemper (1966) to be a function of low hydration energy. Cations with low hydration energy become fixed in the interlayer sites due to interlayer dehydration and layer collapse (Shawney, 1972). Ca^{2+} ions on the other hand, produce expanded interlayers as a result of their high hydration energy. Consequently they are not fixed (Shawney, 1972). Completing Ca^{2+} ions for the exchange sites tend to decrease the maximum adsorption level of the soil for the Cu^{2+} (Cavallaro and McBride, 1978). In addition, their studies have shown that in the surface soils, Cu^{2+} activity was controlled by ion calcareous soils, copper is precipitated and removed as $Cu(OH)_2$.

The adsorption of Cu^{2+} ion has been found to increase with higher pH values and with increasing copper concentrations (Menzel and Jackson, 1950).

Soil Composition

The soil, is that part of the ground surface of the earth that will support the growth of vegatation. Soil is a mixture of mineral debris from the degradation of rock; organic matter from the decomposition of plant and animal tissues; gases, carbon-dioxide and water vapor; bacteria and fungi; and finally soil moisture.

The mineral constituents of the soil are the results of degradation and decomposition of rocks, by either, mechanical or chemical weathering. Products of which are mainly silica in the form of quartz. During weathering, fragments may vary in size and shape. Grains may be angular, subangular, or rounded. Minerals occur as fragments of all sizes, and can be found in sands, silts and clays.

Organic Colloids

The organic colloid content in the soil varies according to location and climate. The organic content generally ranges from 1.0 to 5.0% in surface soils and is less in subsurface soils (Leeper, 1978).

Organic soil substances are able to form various complexes with metals by ion exchange, adsorption on surfaces, and formation of chelates.

Leeper (1978) observed that the organic colloid may have five times the retention capability as compared to the inorganic. The concept that the organic fraction of the soil generally contains the bulk amount of exchangeable copper (McLaren and Crawford, 1973; McLaren and Crawford, 1974) supports Leepers (1978) findings that the organic colloid has a greater ability to retain the metal than the inorganic colloid. Hodgson et al., (1966), found that Cu levels in calcareous soils of Colorado ranged from 5 to 16 ppb in the soil solution with 98 to 99% of the Cu found in the organic complexes.

Bartelett and Norman (1938) reported that exchange mechanisms in soil organic matter generally depends on the charge and hydrated size of the exchanged ion. Hydrogen and hydroxyl are the most strongly fixed; followed by polyvalent cations; the monovalent cations are arranged according to decreasing radius. Gambrell et al. (1976A) noted that oxides and hydroxides of many divalent metals are favored by soils at high pH and redox potential.

Schnitzer and Skinner (1965) observed that in the absence of clay, fulvic acids react with divalent and trivalent ions. Chelates complexes are insoluble in water (Schnitzer and Skinner, 1965).

Organic colloids, weight for weight have a greater C.E.C. than do inorganic colloids. Not only does the organic colloid strongly hold heavy metals as reflected by its high C.E.C., it also has the ability to combine metals with its chelating groups (Leeper, 1978).

Cu^{2+} in solution is strongly held by the organic matter. It would be expected that in the presence of organic matter, soluble Cu would be adsorbed. However, organic colloids do not allow all the Cu to be removed (Himes and Barber, 1957). A deficiency of Cu has been noted in peaty soils and it was believed the organic matter was responsible for the deficiencies through its chelating power. The apparent deficiency was satisfied by the addition of small amounts of Cu. The reasoning is that Cu can circulate in an anionic form (Himes and Barber, 1957).

The anionic form of heavy metals have not been recognized until recently (Geering and Hodgsen, 1969) and the anionic form is only a minute proportion of the total that is mobile. In normal conditions when Cu moves with an organic combination, it does so as a neutral molecule or an anion. The chelated Cu is significantly less toxic than the cationic form (Steeman and Wium-Anderson, 1979).

Metal solubility can be increased to levels greater than the concentration of soluble free ions as a result of chelate formation. This provides a sink for many metals (Gambrell et al., 1976).

Several factors govern the stability of these metal chelating agents such as pH (Lindsay et al., 1967), and adsorption by soil particles (Hill-Cottingham and Loyd-Jones, 1958). The redox potential also has a significant effect on the stability of metal chelates. Reddy and Patrick (1977) found that as the redox potential decreased the percentage of Cu that remained in solution decreased. They also observed that at high redox potentials the Cu chelates appeared to be more stable but their stability decreased with time, apparently due to physical adsorption and microbial decomposition of the metal chelate. High unstability was noted at lower redox potentials which was due to chemical fixation of the Cu and not due to physical or microbial decomposition (Reddy and Patrick, 1977).

Inorganic Colloids

The subsoil can remove large portions of a heavy metal after the reaction with the surface. The subsoil is composed primarily of inorganic colloids (i.e., clays) as compared to organic matter. All soils contain negatively charged colloids. The range of inorganic colloids vary from 0% (pure sand) to over 50% for a heavy clay.

Cu is adsorbed onto negative surfaces in soils. The ability of these surfaces to remove added cations from the soil is referred to the cation exchange capacity, i.e., C.E.C. Typical values for an inorganic clay may range from 10-50 meg/100g. As mentioned previously, the greater the C.E.C. the stronger the metals are adsorbed (Leeper, 1978). Various clay minerals differ in their ability to adsorb cations. Clays are known to have a higher cation exchange capacity than a pure sand or silt. For example, montmorillonite > illite > kaolinite (Terzaghi and Peck, 1967).

The type of colloidal clays also may have a bearing in its adsorption capability. Approximately 90 to 98% of colloidal clay is made up of four main constituents: silica, iron, alumina, and combined water (Shawarbi, 1952).

Two structures that are common to all crystalline clay minerals are silicon tetrahedron and aluminum octahedron. Occasionally, magnesium or iron can substitute for aluminum causing the structure to carry additional charges (Means and Parcher, 1963). Many times on the surface of a structure, iron and aluminum sorption reactions take place.

Clay minerals can be broken down into very thin sheets. This sheeted structure, carries a negative electrical charge on the flat surface of the crystals.

These crystals may be tied together with cations of sodium, calcium or other elements between the negative surface (Means and Parcher, 1963). These cations are exchangeable with other cations without changing the structure of the mineral. Therefore, these exchangeable cations can become an important factor governing the mobility of heavy metals.

Frayed edges of clays resulting from the weathering of micas enhanced selective sorption as suggested by Jackson (1963) and Rich (1963).

The high charge density and the location of the charge within the structure may be factors in determining selectivity. Jackson, believes selectivity of potassium over calcium is due to the expanded portions of the particles referred to as, "wedge" zones (Jackson, 1963). In these zones, mobility depends on the size of the hydrated cation. The lower hydration of the potassium ion compared to the calcium ion, makes the potassium ion effectively smaller; thus the potassium penetrates the wedge zone more effectively. As the exchange sites become saturated with the cations, sorption occurs on nonselective sites in addition to the selective sites (Shawney, 1972).

The size of the hydrated radius also influences adsorption. The smaller the radius, the greater the attraction. Likewise, the larger the exchange sites, the greater the adsorption.

Steger (1973) observed a majority of exchange sites are lattice hydroxyl groups found on edges of clay. He also found that the remaining sites were occupied by organic matter which was adsorbed by the clay.

Copper can become imbedded in octahedral sites on montmorillonites. The Cu^{2+} ion remains hydrated until there is enough thermal energy available to dehydrate the Cu^{2+} ions ligand water which then allows them to migrate into the hexagonal holes of the lattice (McBride and Mortland, 1974). McBride and Murry (1976) suggest that exchange sites can exist on the surface of silicate. These sites strongly prefer divalent to monovalent ions.

Soil Texture

Soil texture is another characteristic that must be taken under consideration when examining retention of heavy metals by soils. Finely textured soils usually have a greater C.E.C. Generally speaking, the more finely textured soils have a greater tendency to immobilize heavy metals (Phillips et al., 1976).

Soil pH and Oxidation-Reduction Potential

The retention and/or mobility of copper can be affected by soil pH. Misia and Trivari (1962) observed that an acid soil adsorbed much less Cu^{2+} than a neutral soil. Cavallaro and McBride (1978) reported that neutral soils or soils containing calcium carbonates have a greater ability to remove Cu^{2+} from a solution than does a low pH soil. Norvell and Lindsey (1972) noted low solubilities in alkaline soils which corresponded to an increase stability of the metal ion. Solubility is dependent on the acidity or alkalinity of the soil. Increases of soil pH from 5 to 7 generally caused the copper to become less soluble and less exchangeable.

Low pH values due to oxidation tend to make the metal more soluble (Patrick et al., 1977; Gambrell et al., 1976B). Page and Pratt (1975) observed that under anaerobic conditions the solubility of Cu was generally lower than under aerobic conditions.

Increasing pH values cause an increase of cation exchange capacity. Lewis and Broadbent (1961) reported that there is limiting pH value, above which adsorption ceases regardless of the amount of exchangers present.

Immobilization and mobilization of metals are influenced by both, pH and redox potential (Gambrell et al., 1976A). These can also influence metals bioavailability.

Biological Activity

The subsurface environment contains sufficient quantities of organic matter to sustain microbial growth. Microbial growth becomes limited when the level of tolerance of two basic physical properties are exceeded, these being hydrostatic pressure and temperature (McNabb and Dunlap, 1975). Contaminants can also limit growth or destroy microorganisms if tolerance levels of toxicity are exceeded.

The significance of a microbial population in the subsurface is its ability to decompose a metal-chelate complex thus affecting the chelating stability.

The pH and redox potential can affect the biological activity by influencing the metals bioavailability. Sulfate bacteria can grow in an environment in which the lower limit of the redox potential is -450mv at pH 9.5, and at an upper limit of +850mv for iron bacteria (McNabb and Dunlap, 1975).

McNabb and Dunlap (1975) have indicated by their reviews that sulfur reducers, specifically that cultures of Desulfovibrio desulfuricans dominate the subsurface environment.

Under anaerobic conditions, sufficient SO_4^{2-}, adequate growth periods and with appropriate nutrients Desulfovibrio desulfuricans will produce S^{2-} which will precipitate Cu^{2+} (Pugsley et al., 1970).

The retention of heavy metals by soils can become a complicated phenomenon. In analyzing the retention, all mechanisms previously mentioned should be considered, not only individually, but as any combination.

CHAPTER III

MATERIALS AND METHODS

Experimental Apparatus

Models used during the duration of this experiment consisted of a three inch diameter plexi-glass tube standing approximately thirty-six inches in height as shown in Figure 1.

Columns were filled with soil to a depth of twenty-four inches. Columns differed in the type of soil used as the percolation media.

Three withdrawal ports were positioned on each soil column. One port was located at the base of the column. Two other side ports were spaced at one foot intervals from the bottom.

Air diffusers were used as a means of drawing water from the column. The diffusers prevented soil from being pulled into a sample bottom or clogging tubing when a vacuum was applied. Columns were gravel packed at the bottom to prevent clogging by the finer sediments carried through the column by percolation.

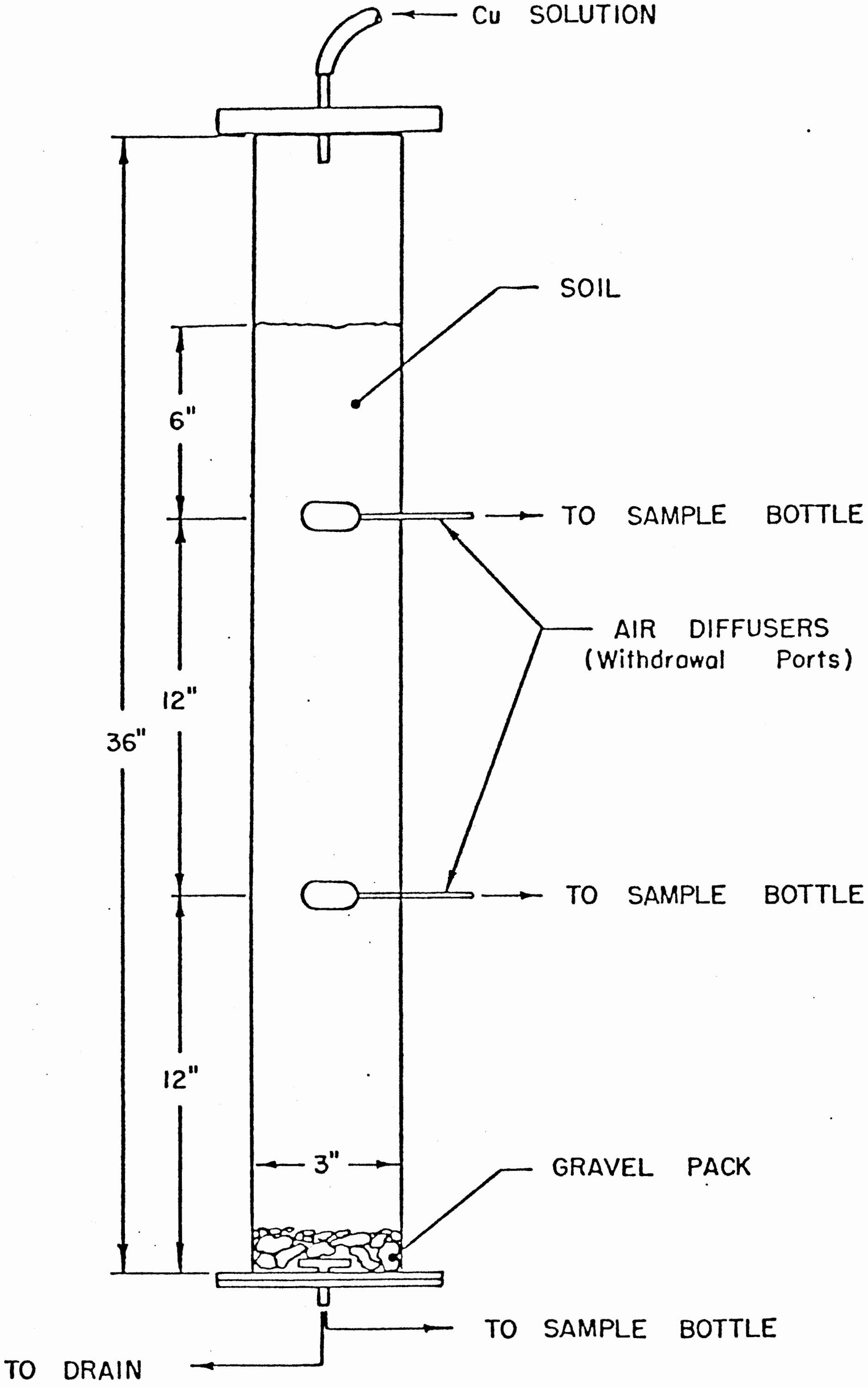

Figure 1. Model of Soil Column

The withdrawal ports enabled the removal of water sampler at different soil depths, which aided in the evaluation of copper retention as a function of depth.

A series of four columns were used during the course of this experiment. The soil columns varied in soil content and/or applied flowrate (See Table I).

Stock copper solution was stored in a five gallon glass container. Water containing the copper solution was pumped at a constant flowrate to the top of the column. From this point, the solution was allowed to percolate through the soil column into a drain (See Figure 2).

Soils

Locations

Soils were selected on the basis of their representation of the general soil types in Payne County, Oklahoma. Two samples (i.e., Soils I and II) were taken from the Cimarron River at the Cimarron River bridge one mile south of Perkins off United States 177, Payne County, Oklahoma. The difference in Soils I and II were in the date of removal from their natural location, August 1979 and June 1980, respectively. The other (i.e., Soil III) soil was taken from the Brush Creek drainage basin near Stillwater, Oklahoma. All soils were removed from their

TABLE I

COLUMN PARAMETERS

	Column I	Column II	Column III	Column IV	Column V
Soil Classification	Sand	Sand	Sand	Sand	Silty-Sand
Discharge (ml/min)	0.2	2.0	2.0	2.0	2.0
Duration (hr/day)	2.0	24.0	24.0	24.0	24.0
Copper Concentration (mg/l)	200.0	200.0	200.0	200.0	200.0

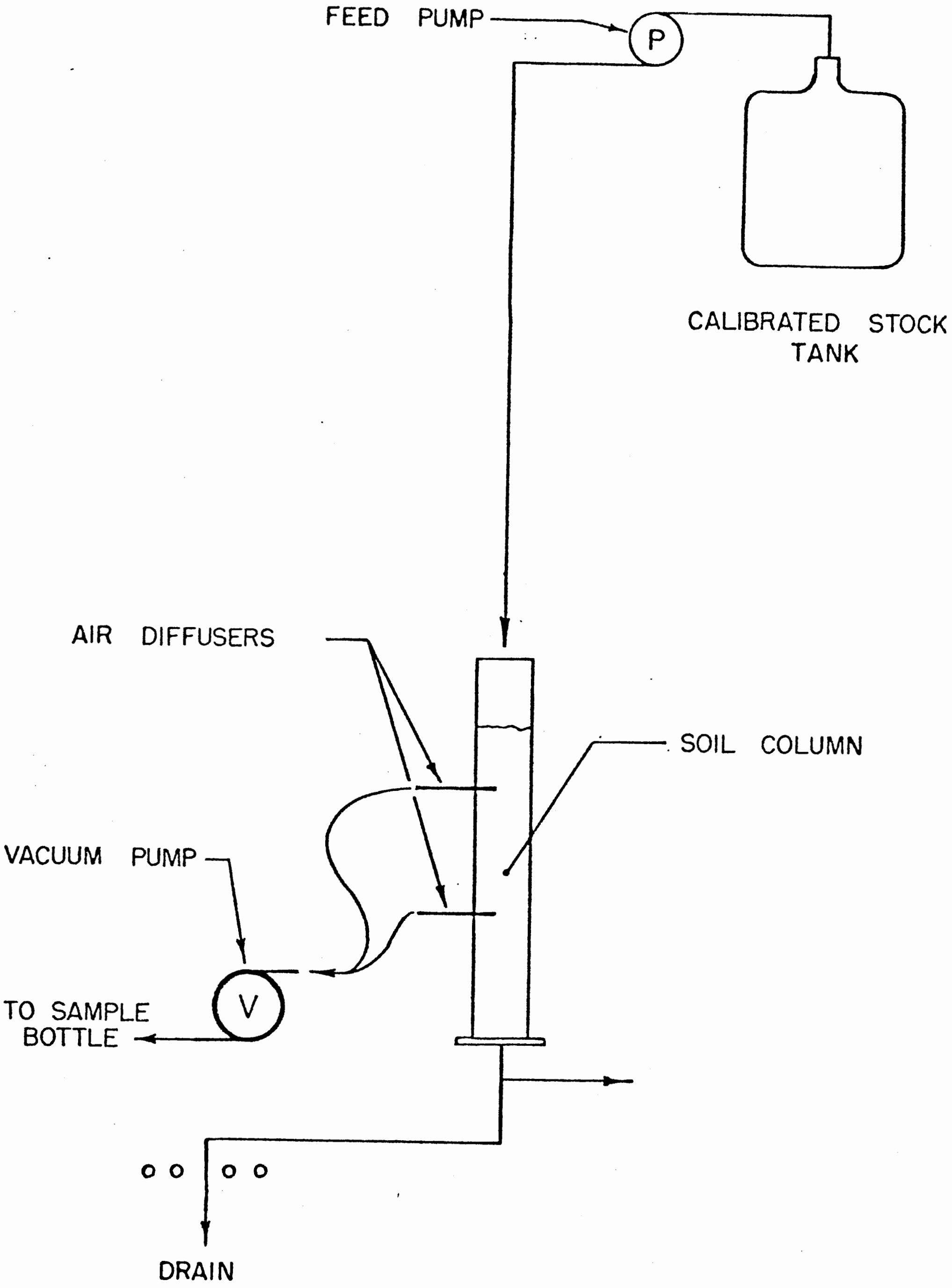

Figure 2. Laboratory Apparatus

respective sites at a depth of approximately two feet beneath the surface.

Soil Classification

Grain size distribution was determined by wet mechanical analysis. The percentage of sand, silt and clay size particles in the sample were determined. Soils I and II were classified as a sand, and III as a red silty-sand (See Table II).

TABLE II

THE PERCENT OF SAND, SILT, CLAY AND ORGANIC MATTER IN THE SOILS

Soil	Sand	Silt	Clay	Organic Matter
I - Cimarron River	100%	0%	0%	0.093
II - Cimarron River	--	--	--	0.051
III - Brush Creek Basin	90%	10%	0%	0.210

Once in the laboratory, the soils were dried. After drying, the soil to be placed in each column was weighed.

The soils once in the columns, were saturated with distilled water and vibrated.

Table I indicates the types of soils used in each column.

Organics

The organic content of a soil is an important factor governing metal retention, as previously discussed. The organic portion of a soil was determined by the method suggested by Standard Methods (1975) for volatile residue. The intent for determining the organic content was simply to establish, which soil had the larger percent of organic matter (See Table II).

Flowrate

Milton-Roy pumps were used to apply water containing a copper sulfate solution. Hydraulic loadings were adjusted so as, not to exceed the permeability of the soils.

Discharges of 0.2 ml/min and 2.0 ml/min for durations of 2 hrs/day and 24 hrs/day respectively, were discharged to the top of the appropriate columns. See Table I for a further explanation of column loadings.

Copper Solution

Water containing a copper concentration of 200 mg/l was discharged to the surface of each column.

Copper Solution Preparation

The water-copper solution was prepared by dissolving 3.929 grams of reagent grade cupric sulfate (crystals) in five liters of distilled water.

Frequency of Withdrawal

Water samples were withdrawn initially on a daily basis and then once every two or three days when the experimental period increased beyond a month. The allowable range of the spectrophotometer was no greater than 3.0 mg/l, therefore, samples needed to be diluted prior to analysis. The size of samples taken were governed by the estimated copper concentration in the ground water solution and the type of test to be performed (i.e., concentration or pH). Generally, sample sizes varied from 5 ml to 25 ml.

Analytical Techniques

All methods of analysis of experimental data are given below.

Soil Classification

The hydrometer method of wet analysis was performed at the Oklahoma State University Soils Testing Laboratories. See Appendix A for results of the test.

Organic Content of Soil

Procedure followed that which is suggested in Standard Methods (1975).

Ground Water pH

Ground Water (i.e., water which has percolated through the soil column) pH levels were determined by the use of Orion Research, digital pH meter/Model 701.

Ground Water Conductivity

The conductivity of ground water was analyzed using the Hach Chemical Company, Portable Conductivity Meter/ Model 16300.

Copper Concentration

The Hach dr/2 Spectrophotometer by Hach Chemical Company, was used for determination of copper concentrations.

CHAPTER IV

RESULTS

Soil Properties

Results in soil analysis are presented in Table II. The data in Table I indicates that Soil I, retrieved from the Cimarron River consisted of 100% sand. It was assumed the classification of Soil II to be the same as I (see Figure 3)。 Brush Creek soil, i.e., Soil III, contains 90% sand and 10% silt (See Figure 4). Classification of Soil I and II is sand and Soil III is referred to as silty-sand. It can be seen that all soils contain low amounts of organic matter, however, the silty-sand has slightly more organics than the sand.

From the Appendix A, Table III is observed that 72.9% of the silty-sand is smaller than 0.15 mm in diameter. While 3.2% of the sand has a particle size of less than 0.15 mm (Appendix A - Table IV).

Soluble Copper Concentrations in Soil Systems

The following section reflects data obtained by the removal of ground water from the soil columns. Care was taken in trying to minimize probable error. However, experimental error could arise when diluting a sample by a factor of 100.

All figures reflect measurements made of soluble copper in ground water (i.e., water that has undergone contact with the soil). Dashed lines have been used on all figures to approximate the pattern followed either by copper concentration or pH changes. These graphs will be referred to as, breakthrough curves.

Figures 5 through 7 represent the soluble copper remaining in the ground water of Column II at depths of 6, 18, and 30 inches. Figure 8 is a combination of these. Its purpose is to yield a better overall understanding of adsorption relative to depth. Data points were left off Figure 8 to relieve confusion caused by the congestion of data. Figures 5 through 8 show an increase of soluble copper in the ground water as time increases. Figure 8 illustrates that as depth increases, the amount of copper in the water decreases at all three depths along the column. As time increases, the curves at depths 18 and 30 inches appear to approach the copper concentration at 6 inches.

It is apparent from Figure 9 that soil types do have a bearing on heavy metal adsorption. Figure 9 indicates the difference in adsorption rates with equivalent hydraulic loading and application of copper concentration.

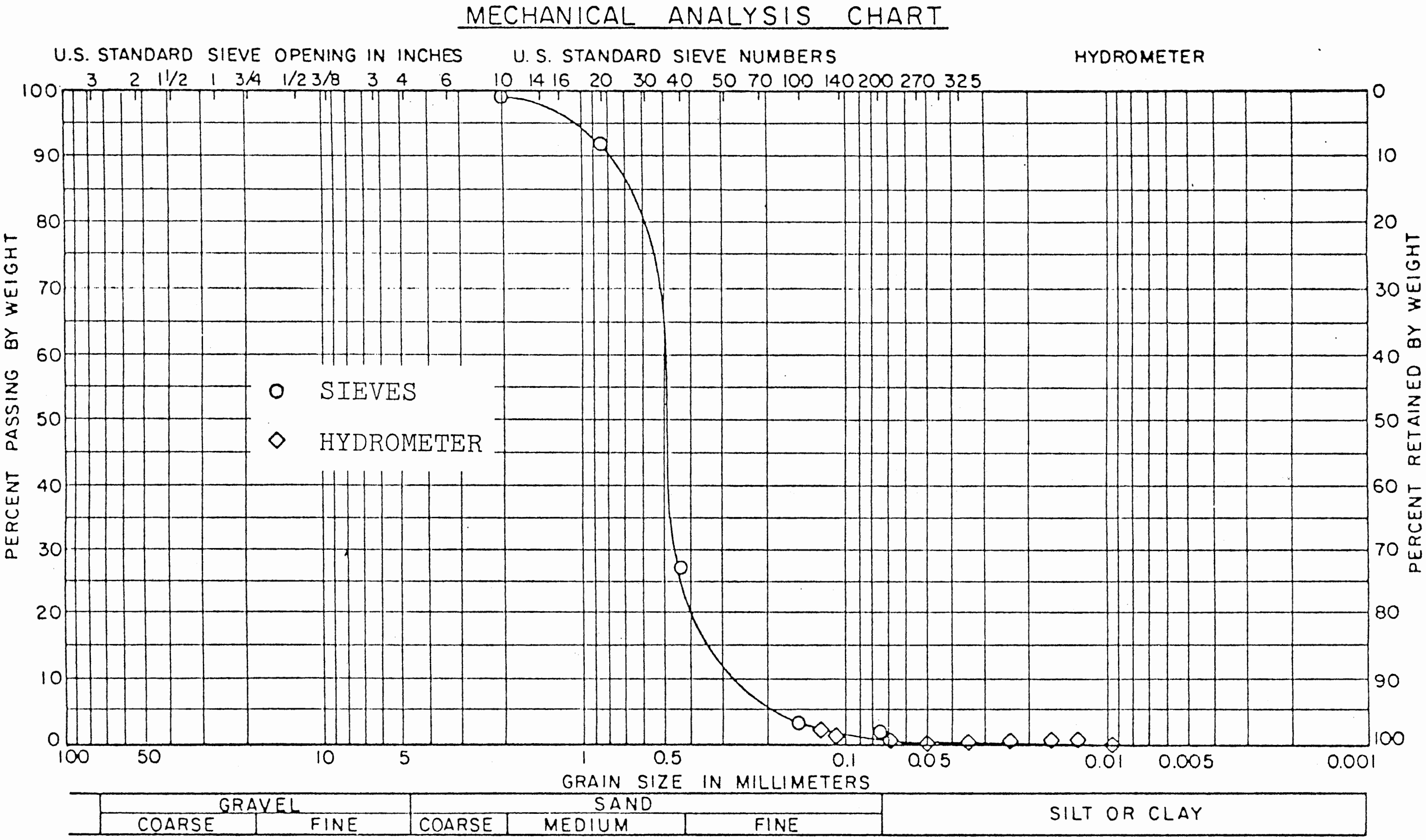

Figure 3. Soil II - 100% Sand

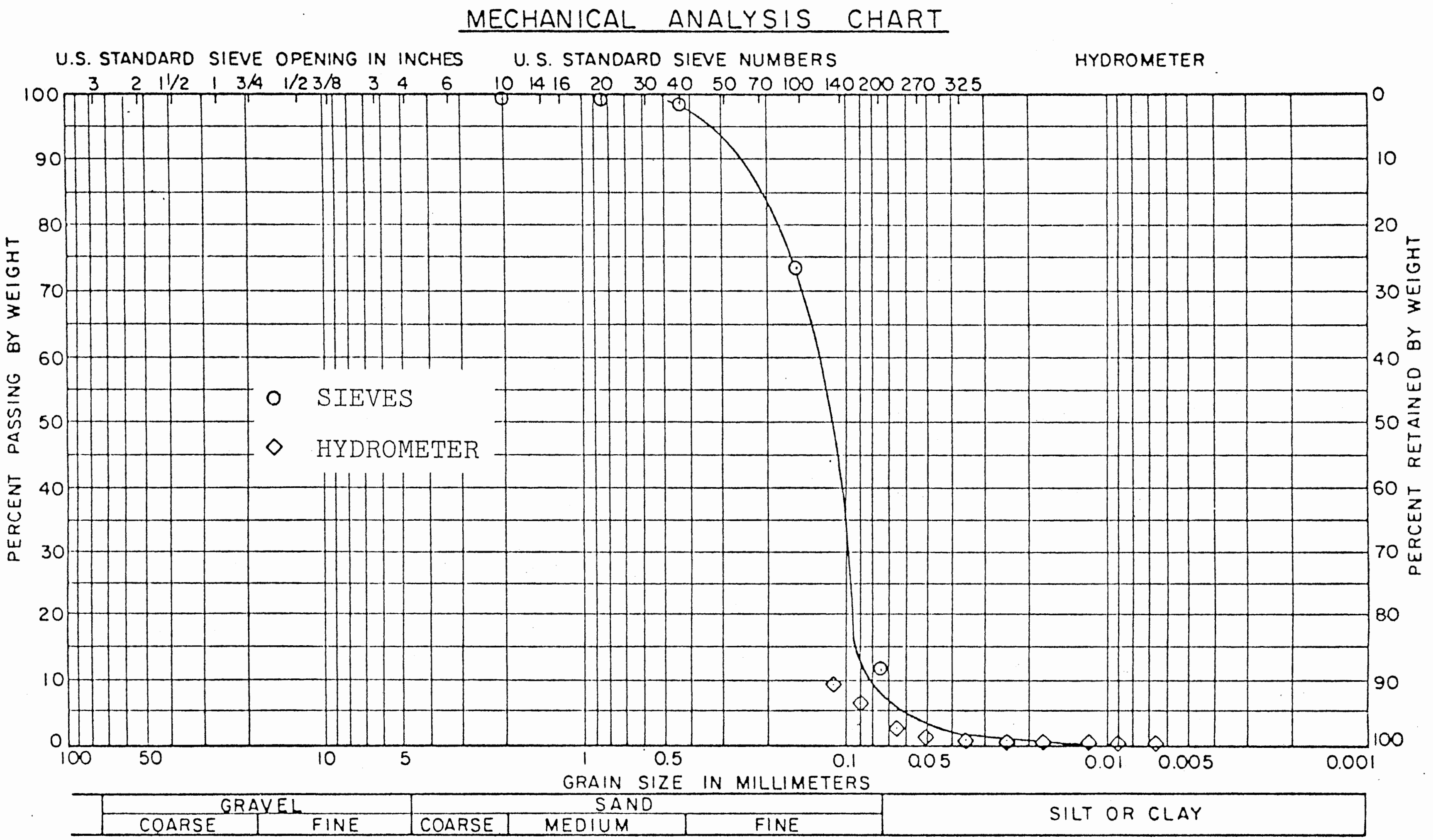

Figure 4. Soil III - 90% Sand/10% Silt

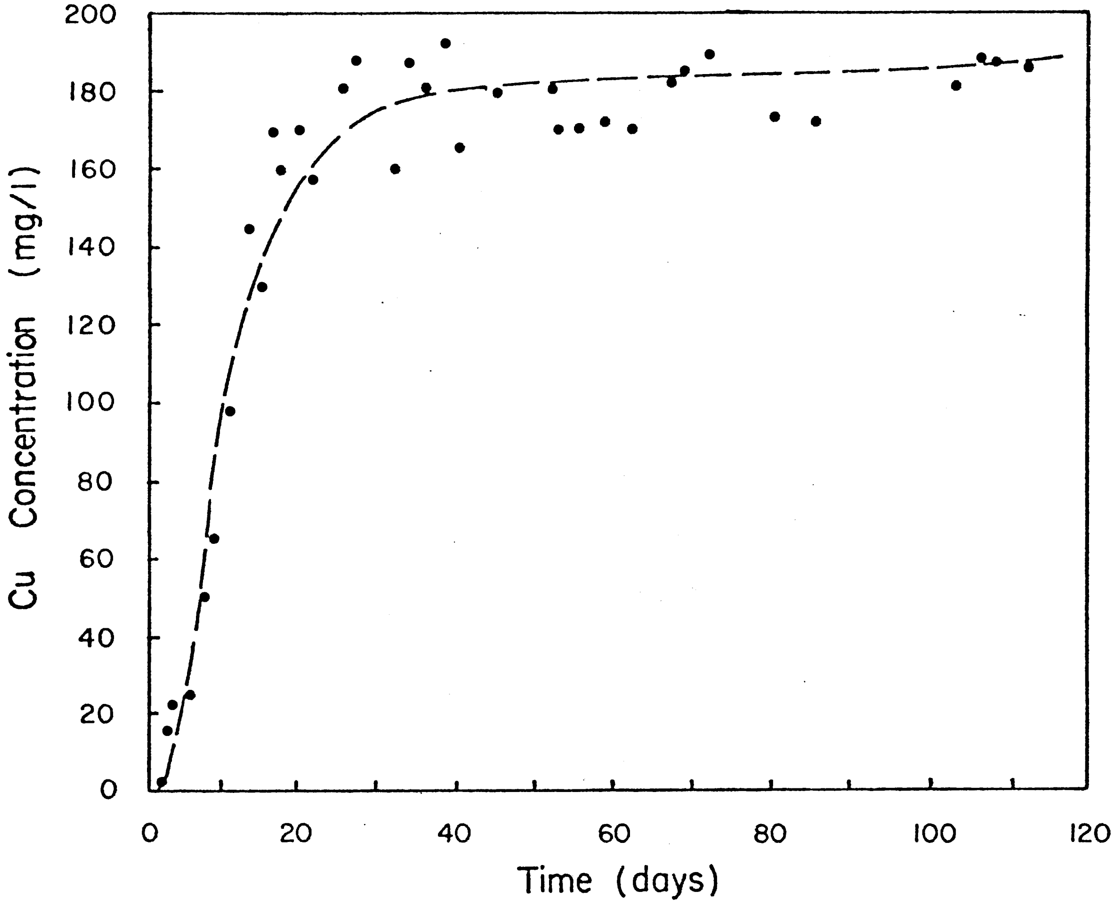

Figure 5. Breakthrough Curve of Soluble Copper in Ground Water 6" Below Soil Surface - Column II

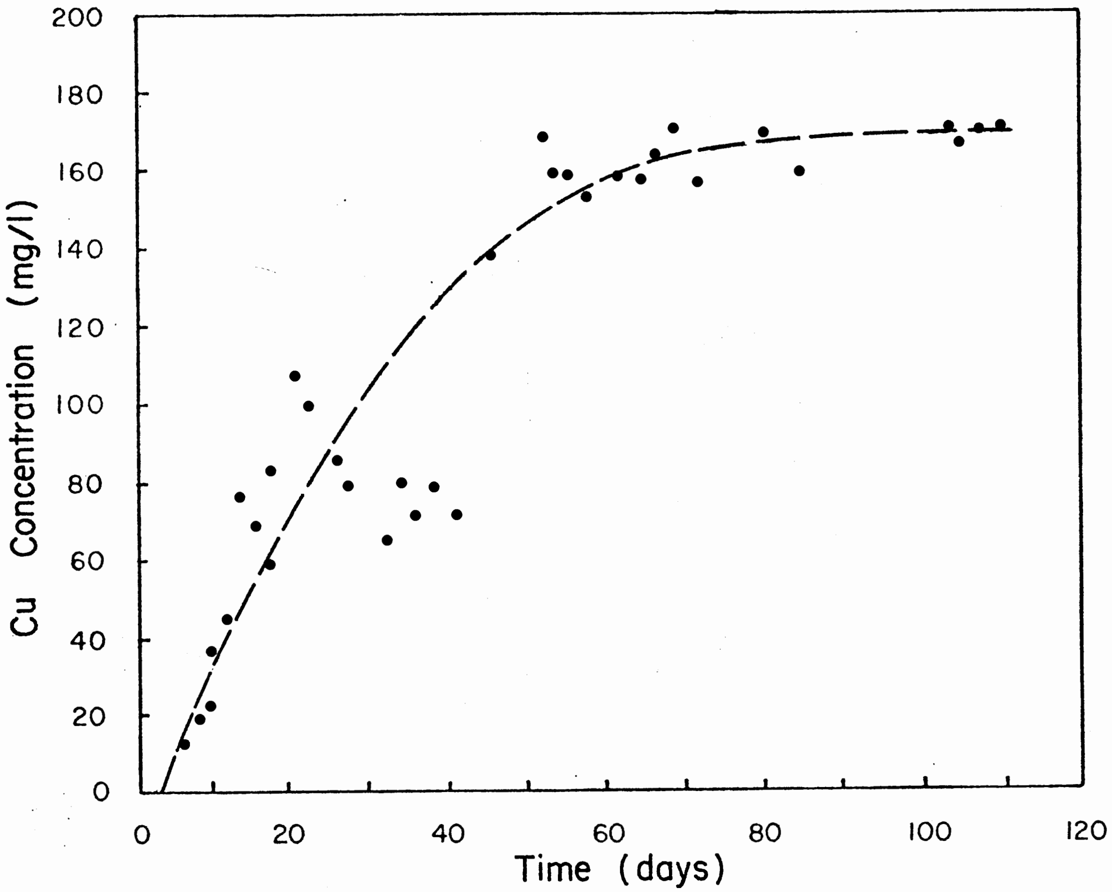

Figure 6. Breakthrough Curve of Soluble Copper in Ground Water 18" Below Soil Surface - Column II

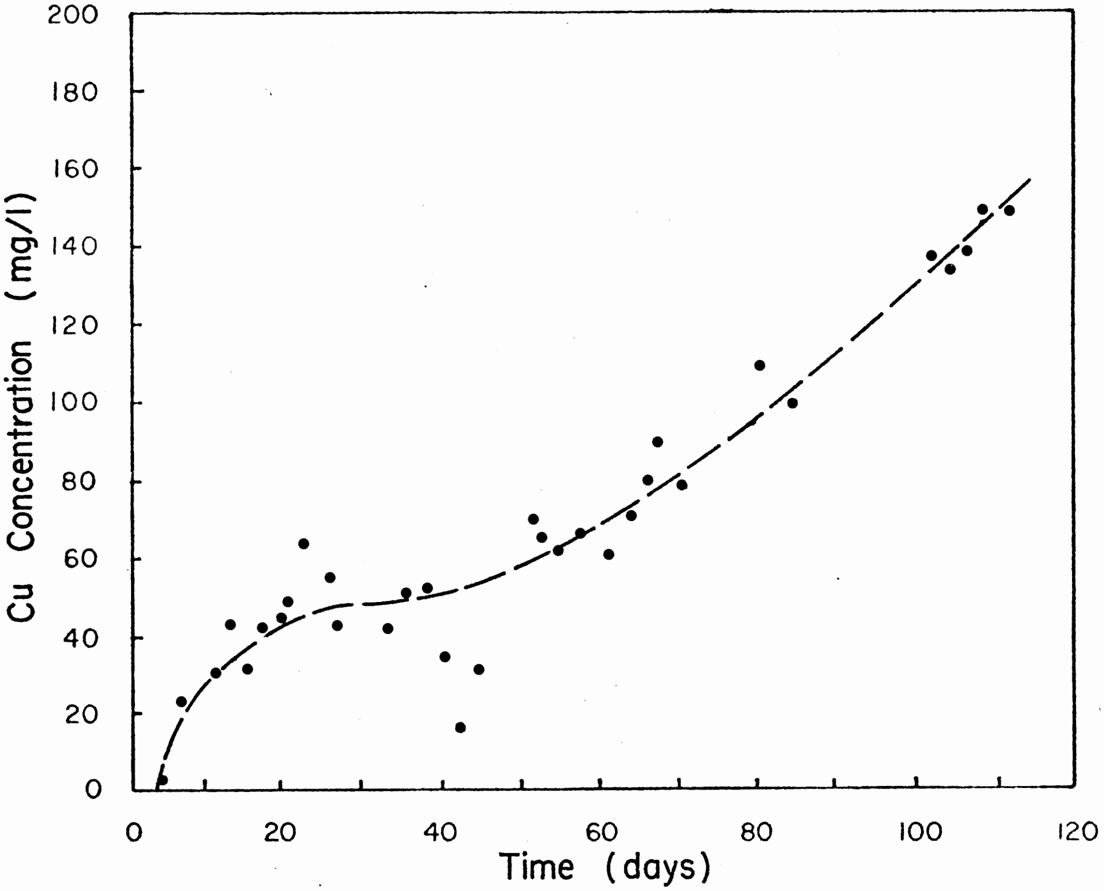

Figure 7. Breakthrough Curve of Soluble Copper in Ground Water 30" Below Soil Surface - Column II

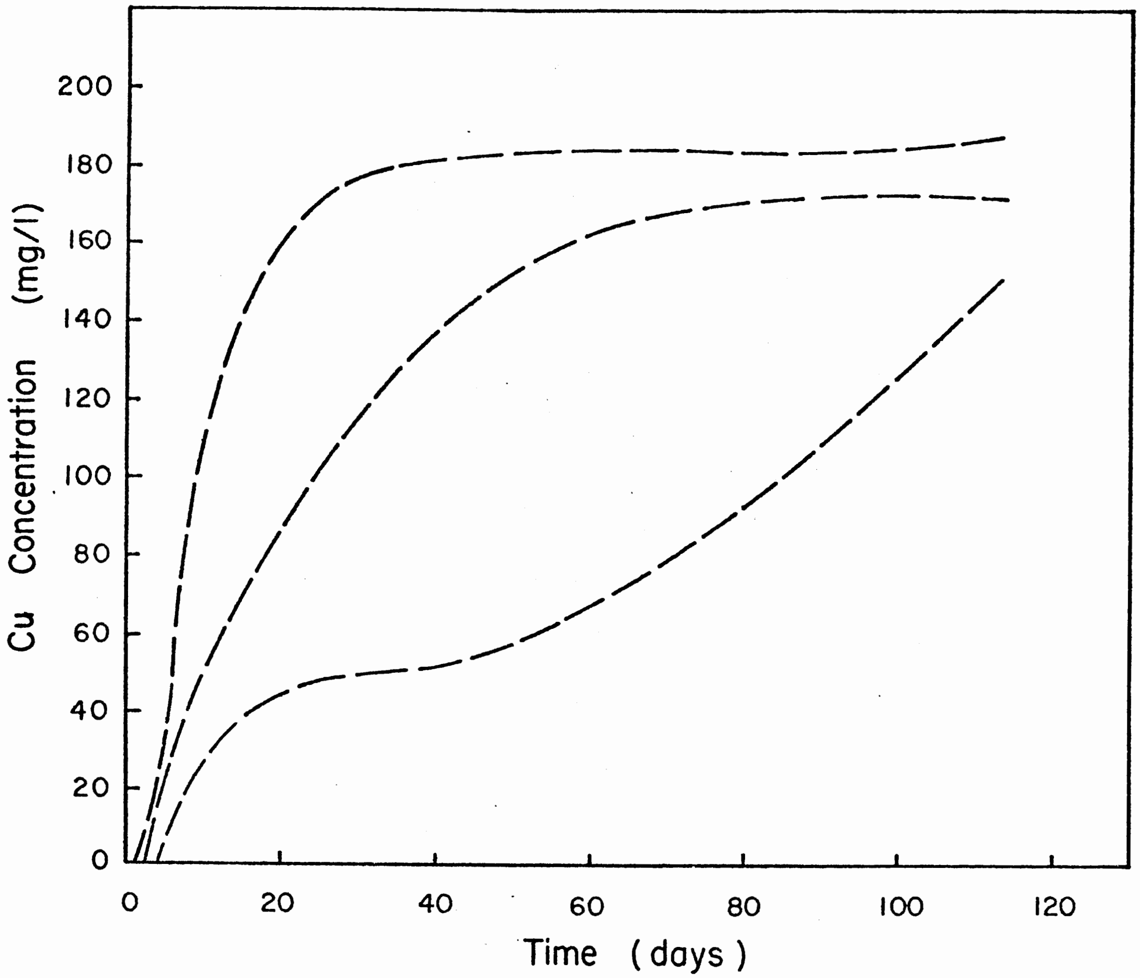

Figure 8. Breakthrough Curve of Soluble Copper in Ground Water 6", 18", and 30" Below Soil Surface - Column II

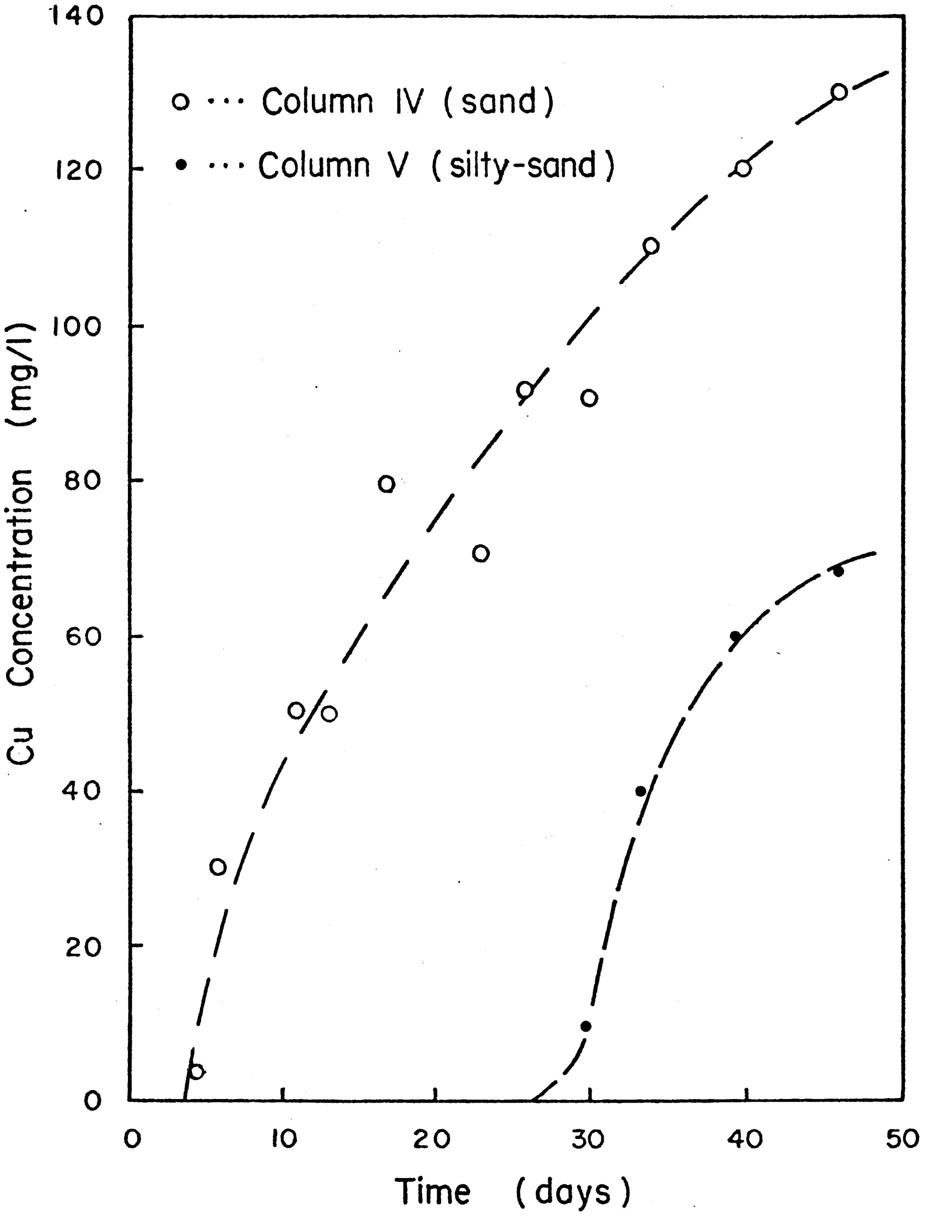

Figure 9. Breakthrough Curve of Soluble Copper in Ground Water 30" Below Soil Surface - Column IV and V

Figure 9 is a comparative graph of Columns IV and V. The breakthrough curve of the silty-sand indicates a lower concentration of soluble copper in the ground water at 30 inches as compared to the sand. There was no noteable copper concentration in Column V (i.e., silty-sand) for the first 30 days of the experiment, afterwards breakthrough occurred. Once copper penetrated the column, the copper concentration increased at a rate of 0.67 mg/day, compared to 1.10 mg/day for Column IV (i.e., sand).

The silty-sand has a higher organic content than does the sand. Data indicates the organic content of the silty-sand is 0.21%. Column IV, the Cimarron River sand has a level of organic matter of 0.051%.

The soil with the higher organic content adsorbed the larger amount of Cu^{2+}, represented by the lower amount of soluble copper in the ground water.

Figure 10, is a mass diagram of the accumulated values of copper retained in the column versus the amount of copper applied to the column. Column IV has an efficiency of removal at approximately 93% and Column V of 98%. Measurements of soluble copper in the effluent were recorded for a forty day period.

Behavior of pH in Soil Systems

Ground water pH was monitored for Columns IV and V. As indicated by Figure 11, the pH of the effluent had

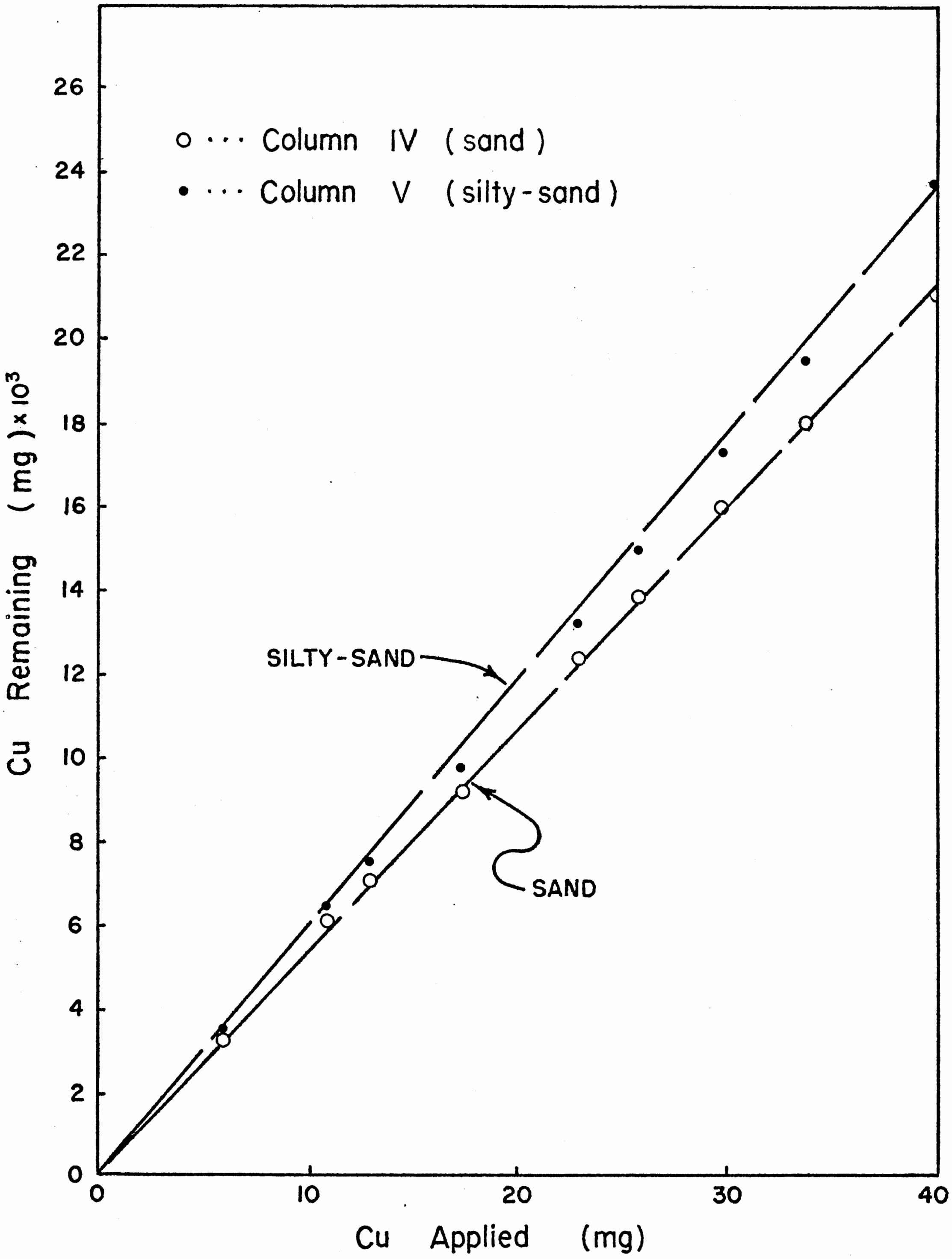

Figure 10. Mass Diagram of Columns IV and V

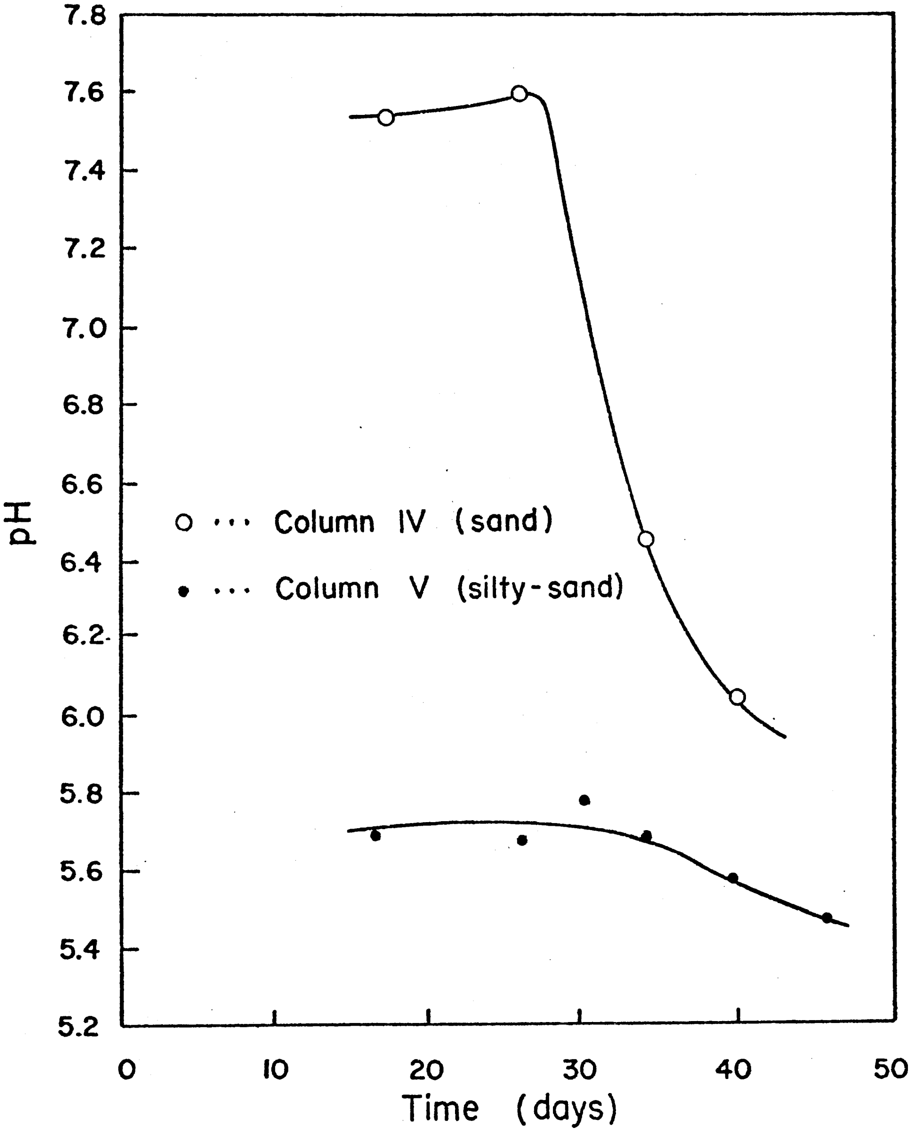

Figure 11. pH Levels in Ground Water 30" Below Soil Surface - Columns IV and V

dropped, when they were compared at time zero to those at forty days. Initial pH readings at day zero were 7.55 and 5.70, and final pH's of 6.05 and 5.50, for Columns IV and V respectively. Time permitting, pH values would have been expected to continue to drop approaching the stock solution pH at 5.0.

Aiding in the evaluation of data, pH and copper concentration graphs were constructed for Columns IV and V. Figure 12 and 13 illustrate the relationships of pH and soluble copper in ground water along the abscissa, and time on the ordinate. Both Figure 12 and 13 indicate a decline in pH as the soluble copper concentrations in the aqueous solution increases.

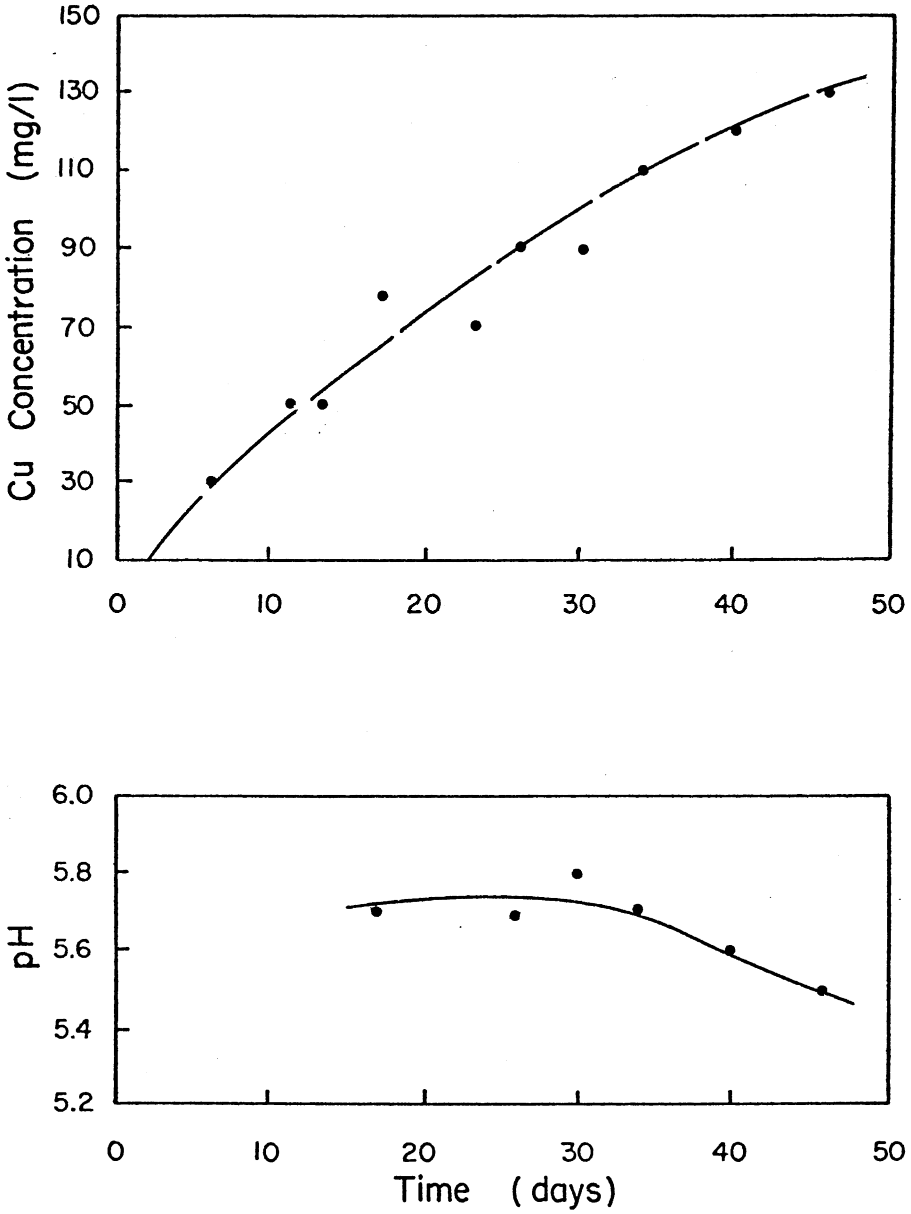

Figure 12. Breakthrough Curve of Soluble Copper and pH Levels in Column IV, 30" Below Soil Surface

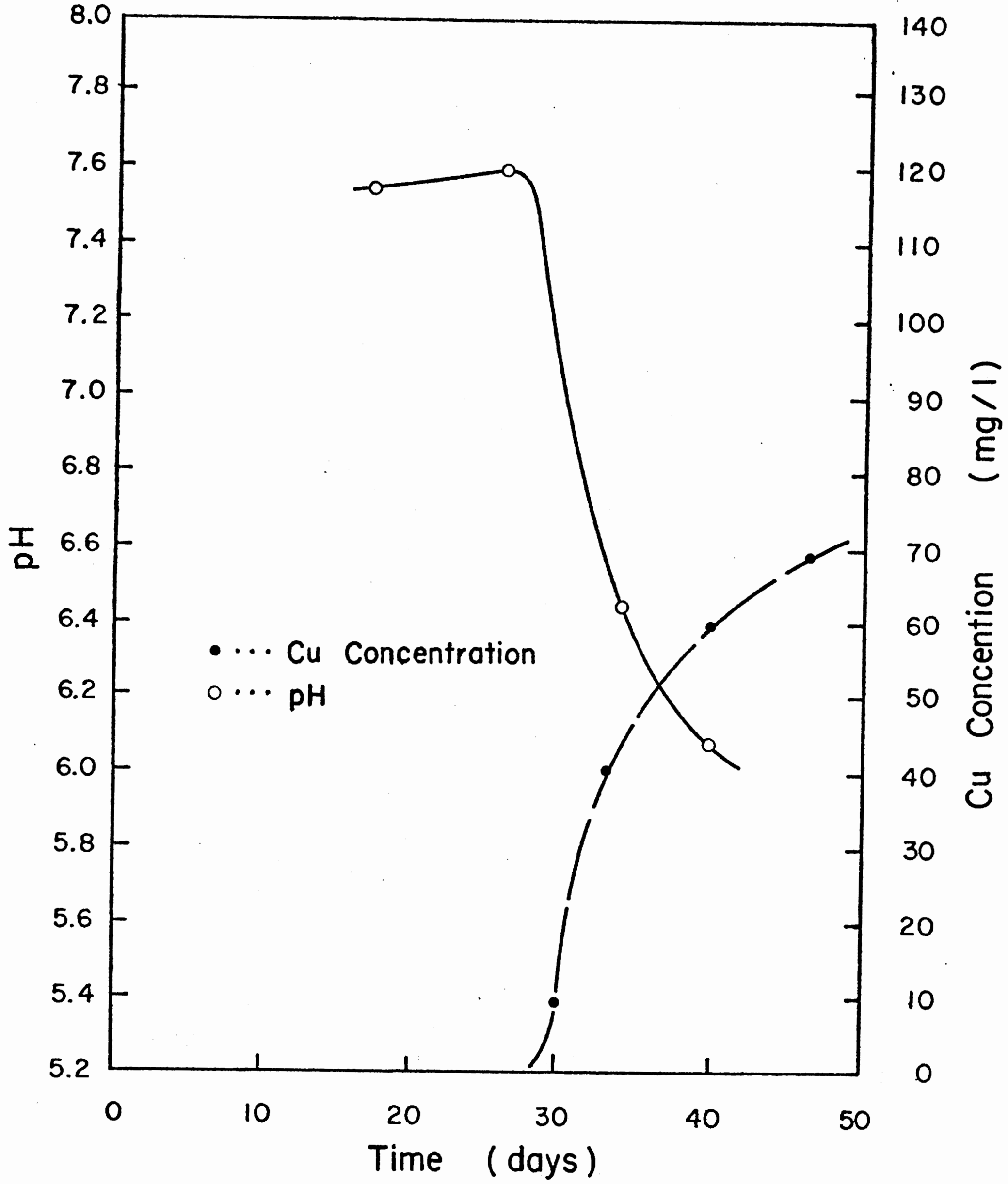

Figure 13. Breakthrough Curve of Soluble Copper and pH Levels in Column V, 30" Below Soil Surface

CHAPTER V

DISCUSSION

The data previously discussed, indicates the soils ability to retain copper. Soil characteristics such as soil type, soil texture, pH, and organic content may affect adsorption.

Figures 5 through 9 indicate the soluble copper remaining in solution. At early times, a low value of copper is present in the ground water. As time increases, the amount of soluble copper in the aqueous solution also increases. This implies that after a small period of application, the adsorption mechanisms have not completely been satisfied. However, after prolonged periods the adsorption capabilities decline as reflected by the increase of soluble copper in ground water solution.

Figures 5 through 7 illustrate breakthrough of Column II at depths of 6, 18 and 30 inches. Breakthrough occurred at 1, 3 and 5 days. A daily loading of 578 mg/l of adsorbent was applied to each column. Figure 8 is a combination of Figures 5 through 7. Figures 5 through 8 are not suggesting that the retention ability of an element of soil increases with increasing depth. It is assumed that the soils characteristics are homogeneous throughout the column. Therefore by increasing the depth of a column, the adsorption capability is not increased, but the life of the column may be increased.

As previously mentioned, the soils mechanism of retention will eventually be fulfilled whether by sorption, chemical complexing, chemical alteration or a combination of these. Idealistically, once the soils adsorption capability has reached a stabilizing level, the soil will be at a point of apparent equilibrium. The Cu^{2+} passes through a saturated portion of soil until it encounters soil that has not reached this maximum level of retention. At which time, the copper ion may undergo retention. Eventually this process would continue through the full length of the column. At this point, the column would be at apparent equilibrium. Evident by the concentration of soluble copper in the aqueous solution at 6 inches. The level of measureable soluble copper in the effluent has stabilized. As evident by Figure 5, the soluble copper in the effluent has reached a level of 180 mg/l at 6 inches. A concentration of 200 mg/l was discharged onto the surface of the column. The difference of applied loading and amount of copper remaining in solution averaged 20 mg/l. The 20 mg/l could have been tied up in an insoluble form, which would have gone undetected under the method of analysis used during the course of this experiment.

A similar situation could arise in the environment if appropriate regulations were not implemented to control allowable amounts of discharge onto the surface or into the subsurface.

Figure 9 suggests the silty-sand has an adsorption ability at a given time and concentration greater than the river sand. The breakthrough of soluble copper in the silty-sand occurred at approximately 30 days. The breakthrough in the sand was in a period of 4 days. The difference could be attributed to soil pH, soil texture, soil size, or perhaps organic content. Figure 10 is a mass diagram reflecting the efficiency of removal of the sand and the silty-sand. As evident by the steeper slope, Column V (silty-sand) has a greater removal efficiency than Column IV (sand). Heavy metal fixation is dependent of soil composition. As indicated in Table II, the organic content of the silty-sand (0.21 percent) is higher than the sands (0.051 percent and 0.093 percent). Both sands were taken from the same location but at different times of the year. The variation of organic matter could be attributed to the rise and drop of the river stage over a period of months. At times of rise and fall, the river could have added or removed various sediments, organics, and inorganics, thus changing the soil constituents of the two sands.

Leeper (1978) noted increases in the adsorption capacity, reflected by an increase of organic matter. Also, it was observed that the adsorption ability of an organic soil could be as much as five times that of an inorganic. Experimental data presented herein agrees with Leeper's (1978) research. An increase of organic matter increases the retention of copper by the soil. Breakthrough curves indicate a retention factor of the soil with a larger content by weight to have approximately two times the retention ability of the lesser (i.e., Column IV - Sand).

The average soil particle size of the silty-sand is smaller than the Cimarron River sand. This can clearly be seen in Tables III and IV. The percent soil passing the No. 100 U. S. Sieve was 72.9 percent for Soil III, as compared to 3.2 percent passing for Soil II. As stated in the review of literature, the finer textured soils generally have a greater tendency to fix heavy metal. Also, finer soils exhibit higher C.E.C., (Phillips, et al., 1976). Leeper (1978) states that high C.E.C., allows the organic colloids to more strongly hold the metal. Figure 9 coincides with these findings as seen by comparing the breakthrough curves for the silty-sand and sand. Again, the soluble copper in ground water of the silty-sand is lower than that of the sand, implying greater binding of copper.

Menzel and Jackson (1950) reported that the adsorption of Cu^{2+} ions increase with higher pH values. For this reason, pH is another important mechanism influencing adsorption. The pH level of the aqueous solution is significantly higher in comparison of Column V to Column IV. This can be seen in Figure 11, that at early times the pH values of ground water are 7.5 and 5.5 for Columns V and IV. These values do not reflect the soil pH in the columns. It could be assumed that the soil pH's would be slightly higher than 7.5 and 5.5, because of the dilution affect of the stock solution with a pH of 5.0. Column V, the silty-sand exhibited greater retention capabilities at times of 0 to 30 days than did Column IV. As pH values began to decrease, the retention of copper by the soils decreased. The opposite of this cannot be assumed. That is, if the soil pH is lower than the stock solution pH, an increase of soil pH to the stock pH may or may not reflect an increase of copper adsorption. This point cannot be justified because of insufficient data.

Since hydraulic loadings were less than the permeability of the soils, a non-flooded soil system existed. Hydraulic loading could affect anaerobic or aerobic conditions, ultimately affecting the soils redox potential. Oxidation tends to make metals more insoluble as indicated by Patrick et al. (1977). Page and Pratt (1975) noted that under anaerobic conditions, the Cu solubility was generally lower as compared to aerobic conditions. As sited in the review of literature, Gambrell et al. (1976) noted freedom of mobilization being influenced by pH and redox potential.

CHAPTER VI

CONCLUSION

These conclusions reflect the data obtained from the investigation conducted of the fate of copper in a ground water environment.

1. In general, the results indicate that the copper has a certain affinity for the soil environment.

2. Soil types strongly influence the uptake of copper. Soil characteristics that will vary among soil types will be the soil particle size, soil organic content and soil pH. All of which play an important role in copper uptake in a soil-water environment.

CHAPTER VII

SUGGESTION FOR FUTURE STUDY

The uptake of copper in a soil is not yet completely understood. Future experimental work could include:

1. Analysis of the insoluble copper forms created by copper-soil interactions. With the aid of the atomic adsorption analyzer, further insight may be given as to a more precise mode of retention.

2. Using a soil with a higher clay content. The problem with using a clay, is that percolation of a solution through a column would be very slow unless an external pressure was added to force the solution through the column. Another alternative to pressure, would be to increase the permeability by adding a sand, thus increasing the percolation rate.

3. Use a percolating media such as, a sediment from an Oklahoma aquifer (i.e., Garber-Wellington, Ogalalla).

4. Study leaching affects. Questions in this area may be answered. Does all the copper retained by the soil leach out after application of rain water to the soil surface, once the column is saturated with copper? If not, what percentage is leached out?

5. Study column characteristics under an aerobic condition.

6. Set-up a series of columns, each with the same soil; and vary the pH of the adsorbent applied to each column.

7. Break a soil down into different classifications. For example, sands, silts and clays. With the aid of atomic adsorption, analyze what portion of the soil has greater adsorption efficiency.

8. Acclimate a biological culture to a column and analyze the retention capabilities of that culture.

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APPENDIX A

SOIL CLASSIFICATION BY SIEVE AND HYDROMETER ANALYSIS

TABLE III

SIEVE ANALYSIS DATA - SOIL II (SAND)

U.S. Sieve No.	Sieve Opening	Retained Wt. Sample + Sieve	Retained Wt. Sieve	Retained Wt. Sample	Percent Retained	Sum of Percent Retained	Sum of Percent Passing
10	2.00mm	509.97	509.00	0.97	0.32%	0.32%	99.7%
20	0.850mm	622.96	598.30	24.66	8.12	8.44	91.6
40	0.425mm	585.85	390.08	195.77	64.50	72.90	27.1
100	0.150mm	420.11	347.67	72.44	23.90	96.80	3.2
200	0.075mm	343.21	339.91	3.30	1.08	97.90	2.1
Pch		363.18	362.91				
	100	903.67	897.17	6.50			
	200	900.59					

Wt. of Total Sample + Tare 461.10gm

Tare Wt. 161.10gm

Wt. of Total Sample 300.00gm

Sum of Retained Wt. 303.64gm

Loss -3.64gm

Specific Gravity G_s 2.60 (est.) 2.70 (det.)

Diameter at 60% Passing D_{60} 0.50mm

Effective Diameter D_e - D_{10} 0.17mm

Uniformity Coefficient D_{60}/D_{10} 2.94

TABLE IV

SIEVE ANALYSIS DATA - SOIL III (SILTY-SAND)

U.S. Sieve No.	Sieve Opening	Retained Wt. Sample + Sieve	Retained Wt. Sieve	Retained Wt. Sample	Percent Retained	Sum of Percent Retained	Sum of Percent Passing
10	2mm	509.10	509.00	.10	.05%	.05%	99.95%
20	.850mm	598.70	598.30	.40	.20	.25	99.80
40	.425mm	390.12	390.08	.04	0.00	.25	99.80
100	.150mm	401.03	347.67	53.36	26.80	27.05	72.90
200	.075mm	453.67	339.91	113.76	57.10	84.15	15.90
Pan		378.48	362.91				
	100	417.53	386.13				

Wt. of Total Sample + Tare 357.94gm

Tare Wt. 157.94gm

Wt. of Total Sample 200.00gm

Sum of Retained Wt. 199.06gm

Loss 0.04gm

Specific Gravity G_s 2.70 (est.) 2.70 (det.)

Diameter at 60% Passing D_{60} 0.13mm

Effective Diameter D_e - D_{10} 0.08mm

Uniformity Coefficient D_{60}/D_{10} 1.63

TABLE V

HYDROMETER ANALYSIS DATA - SOIL II

Time	Elapsed Time	Suspension Reading r_H	Control Reading r_c	$R_H = (r_H - r_c)10^3$	D^1 (mm)	$W_D{}^2$ (%)
2:45	6 sec.	1.002	1.0005	1.5	.130	37.50
	15 sec.	1.001	1.0005	0.5	.105	12.50
	30 sec.	1.0005	1.0003	0.2	.070	5.00
	1 min.	1.0002	1.00015	0.1	.051	3.75
	2 min.	1.0001	1.000	0.1	.035	2.50
	4 min.	1.0001	1.000	0.1	.025	2.50
	8 min.	1.0001	1.000	0.1	.017	2.50
3:00	15 min.	1.0001	1.000	0.1	.013	2.50
3:15	30 min.	1.0001	1.000	0.1	.0095	2.50

Water Temperature 28°C W_s 6.5g   Tare 254.94

Spec. Gr. Solids, G_s 2.60 2.60   Wt Dry + Dish 261.44

TABLE VI

HYDROMETER ANALYSIS DATA - SOIL III

Time	Elapsed Time	Suspension Reading r_H	Control Reading r_c	$R_H = (r_H - r_c)10^3$	D^1 (mm)	$W_D{}^2$ (%)
2:15	6 sec.	1.0190	1.0005	18.5	.110	58.8
	15 sec.	1.0120	1.0005	11.5	.090	36.5
	30 sec.	1.0050	1.0005	4.5	.065	14.3
	1 min.	1.0020	1.0005	1.5	.050	4.8
	2 min.	1.0015	1.0005	1.0	.035	3.2
	4 min.	1.0010	1.0005	0.5	.024	1.6
	8 min.	1.0012	1.0005	0.7	.017	2.2
	15 min.	1.0012	1.0005	0.7	.012	2.2
2:45	30 min.	1.0009	1.0003	0.6	.009	1.9
3:15	1 hr.	1.0004	1.000	0.4	.0065	1.3

Water Temperature 29° W_s 49.16g Tare 386.13

Spec. Gr. Solids, G_s 2.70 Est. 2.70 Det. Wt. Dry + Dish 435.29

APPENDIX B

DATA EXPLANATION OF COLUMNS I AND III

Figure 14 illustrates the soluble copper in the aqueous solution withdrawn from a sand in Column I. A hydraulic loading of 0.2 ml/min for 2 hrs/day was applied to this column. Copper levels were extremely low compared to Columns II through V. The soluble copper concentration in the aqueous solution of Column I never exceeded 2.1 mg/l as compared to 160 mg/l reflected in Column II.

Perhaps, years would have had to expire before any noteable amount of copper remaining in solution could have been identified. Obviously, the adsorption rate of the soil exceeded the hydraulic loading of copper solution, as compared to Columns II through V. A discharge of 0.2 ml/min for a duration of 2 hrs/day was selected, hoping to stimulate an industrial discharge onto ground surface or rainfall. Because of the time factor, no discharge-time relationship at a concentration of 200 mg/l of copper could be approximated.

The sands in Columns I and II were mixed to make-up the contents of Column III. Figure 15 reflects pH and copper concentrations of the soil aqueous solution. The initial reading of soluble copper in the ground water was 140 mg/l in Column III. The last reading from Column II was approximately 160 mg/l of soluble copper and the last of Column I, near 1.8 mg/l. It is estimated on the basis of the initial copper concentration that the majority of column III contained sand from Column II. The trend line followed a path similar to the trend line of Column II. This line appears to be an extension of the Column II trend line, increasing to some maximum level of soluble copper in the aqueous solution.

Because of the uncontrolled mixing, no conclusions were drawn from this data. However, this data was used in the comparison of similar trend lines.

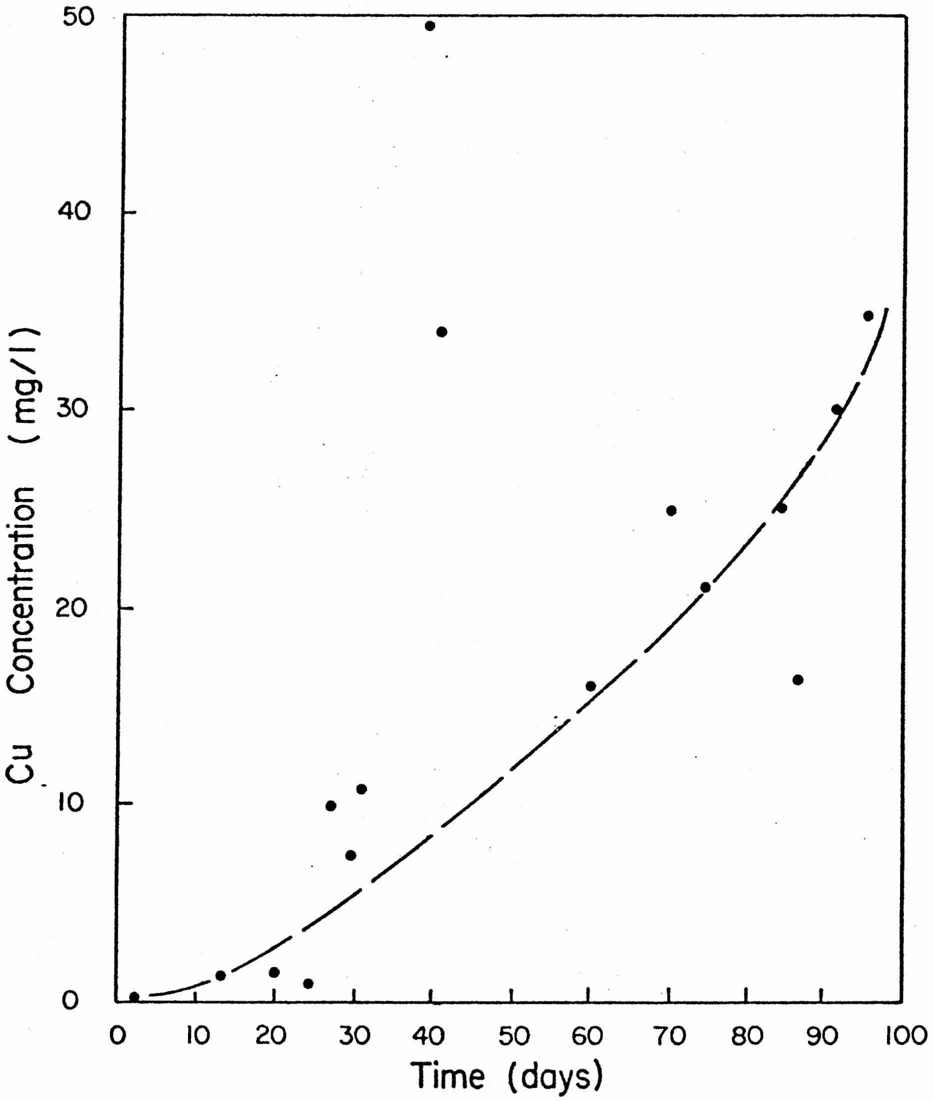

Figure 14. Breakthrough Curve of Soluble Copper in Ground Water 30" Below Soil Surface - Column I (Periodic Discharge)

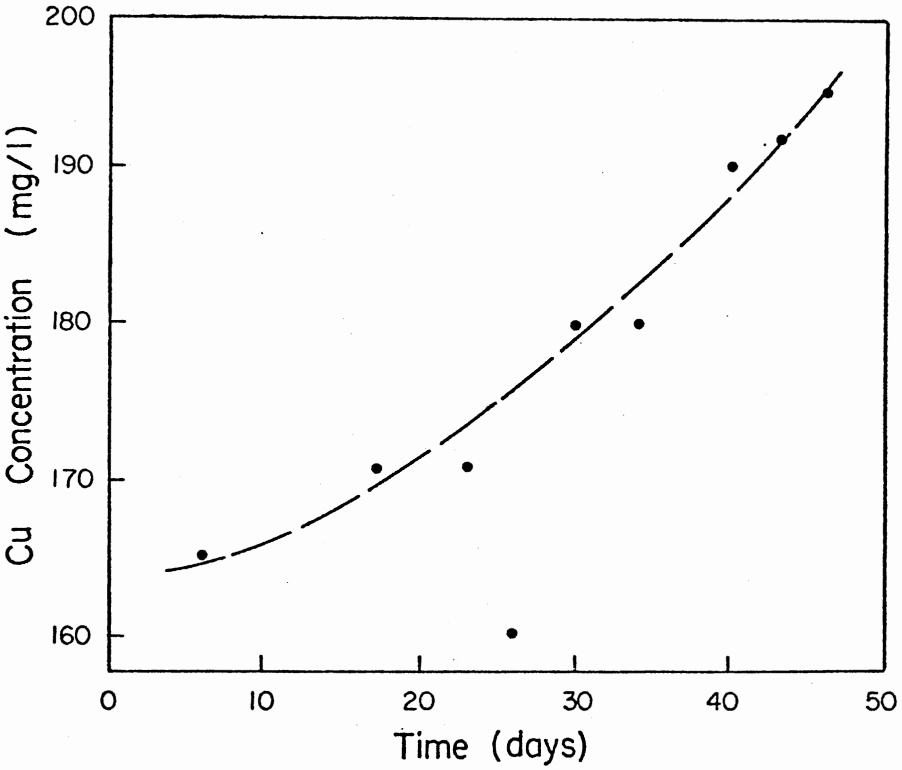

Figure 15. Breakthrough Curve of Soluble Copper in Ground Water 30" Below Soil Surface - Column III

VITA

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