PATHWAYS AND INTERACTIONS OF COPPER WITH AQUATIC SEDIMENTS

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ABSTRACT

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By

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The reactions of Cu^{++} with bottom sediments and sediment pore waters were studied to delineate the pathways of copper within sediments. Organic rich sediment from Burke Lake, Michigan, was utilized in controlled laboratory experiments to develop a schematic model for Cu^{++}-organic sediment reactions. The model was tested on sediments and water from Houghton Lake, Michigan, a copper contaminated lake. The reactions of Cu^{++} and for comparison Co^{++} with the colloidal organics in sediment pore water were investigated, without disturbance of the system, by means of a computer-centered spectrophotometer-spectrofluorimeter combination instrument. The changes in fluorescence, absorbance and light scatter emissions of the organics due to their reaction with Cu^{++} and Co^{++} show that these metal ions react with the pore water organics. Cupric ion reacts strongly with the organics in a non-linear step function. The Cu^{++}-organic reaction is also pH dependent, reversible and the complex formed is stable under dilute conditions. The Cu^{++}-organic reaction is likely a chelation. Cobaltic ion reacts more weakly and is probably surface adsorbed. Cupric ions are more efficient than Co^{++} in the flocculation of pore water organics. A low specific gravity organic-metal precipitate results which, under turbulent conditions, in an aquatic system, could cause copper mobilization and distribution in the sediment. The uptake of Cu^{++} by bottom sediments is rapid until saturation, as predicted by ligand complex theory, but continued diffusion dependent reaction occurs at a slow rate ranging from 0.28 to 0.18/day. The Cu^{++}-sediment reaction has high stability constants ranging from a log (Q) of 2 to 8 depending on conditions. The reaction reaches an adsorption endpoint at about 8070 Cu/gm of Burke Lake sediment. After initial Cu^{++}-sediment reaction as much as 65% of the Cu^{++} is exchangeable as organically complexed Cu^{++} and surface adsorbed Cu^{++} while 35% is in a non-exchangeable form. Then, with burial the Cu can accumulate upward in the sediment as a result of an upward migration by diffusion, on bubble surfaces, or with sediment pore water. A schematic model quantitatively and qualitatively presents the trends of these laboratory results. A test of the schematic model in a natural aquatic system, Houghton Lake, shows that Cu^{++} is (1) highly associated with low specific gravity organic floccules and other particulate

matter in the water, (2) quantitatively removed from solution by sediment reaction, (3) associated with bottom sediment organic matter and (4) the most highly concentrated in the upper centimeters of sediment.

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INTRODUCTION

Heavy metals have been proven toxic to man and aquatic organisms in small but excess quantities (Federal Water Pollution Control Administration, 1970). Many of these, such as the cations copper, mercury, cadmium, zinc, chromium, selenium, and iron and the anionic radicals borate and arsenate have been found in concentrations above background levels in the aquatic environment (Upchurch, 1973). These findings have led to studies of metal distribution (Kennedy *et al.*, 1971; Walters *et al.*, 1972) and correlations between increased levels of metal toxicants and disruption of the food chain (D'Itri, 1972; Massaro and Giblin, 1972; Thommes *et al.*, 1972). Thus, the pathways of heavy metals through the aquatic and subaquatic environment (sediment) are of current concern. This study will present by means of a schematic model the quantitative and qualitative interaction of copper with sediment and sediment water.

Heavy metals occur naturally in solution in minute quantities, except near ore deposits, and are usually in the form of complexes or simple cations as aquo complexes. The metal ions may be complexed by anions such as carbonates, chlorides, sulfates, phosphates, and nitrates

(Garrels and Christ, 1965). The minute concentrations of the heavy metals in aquatic environments cannot be reconciled by these inorganic complexes alone. Organic anions, adsorbates, and complexing agents interfere with inorganic complexes and establish more stable, heavy metal-organic equilibria (Oden, 1922; Krauskopf, 1956; Kitano *et al.*, 1970; Faust and Hunter, 1971).

About ten percent of these organic complexing agents are small-chained hydrocarbons and identifiable as amino acids, urea, phenols, alcohols, esters, amino sugars, lipids, fatty acids and proteins (Degens, 1970). The other ninety percent of the organic compounds are referred to as humic substances or humic "acids". All of these natural organic compounds are distributed widely over the earth's surface in soils, lakes, rivers, and in the ocean.

Humic substances are classified by solubility and the two classes most often referred to are; humic acid which is soluble in base, insoluble in acid, and fulvic acid which is soluble in both acid and base (Kononova, 1966). The humic substances have very high molecular weights ranging from 2000 to 300,000 (Schnitzer, 1966; Eglington, and Murphy, 1970). The molecules consist of long carbon chains; complex aromatic structures (Christman and Minear, 1971); and oxygen, nitrogen, sulfur and phosphorus functional groups (Saxby, 1969), such as the aromatic amino ($-N:$) and carboxylate ($-COO^-$) groups (Martell, 1971).

In surface sediment the humic substances have an average C:O:N:H ratio by weight of 51:45:1:3 (Schnitzer, 1971). In deeper sediments the percentage of carbon and hydrogen increases while oxygen and especially nitrogen become depleted due to biological activity (Hood, 1970). Humic substances and less complex organic compounds such as amino acids, proteins, carbohydrates and lipids, often occur in combination as polymers or are joined by means of oxygen and nitrogen functional groups in a six membered ring called a clathrate compound (Degens, 1970). These large organic molecules often display colloidal properties in solution (Oden, 1922) such that changes in ionic strength, presence of heavy-metal cations or changes in pH can cause precipitation of a low specific gravity floc (Breger, 1970).

All of these various organic substances often directly influence the chemistry of dissolved substances in water, especially heavy-metal cations. Malcolm _et al._ (1970) theorized that fulvic acid is an important scavenger of heavy-metal ions such as cobalt and iron, and that the acid should be a major factor in the physico-chemical transformations of these ions in the natural environment. Heavy metals can be complexed by both natural organic compounds such as humic substances (Kraynov _et al._, 1966; Schnitzer and Skinner, 1966; Ellis and Knesek, 1971; Christman and Minear, 1971), and by synthetic, organic compounds (NTA, EDTA) (Knesek, unpublished; Childs, 1971). Schnitzer (1971) studied the chemical structure, reactions and reactivities of soil humic substances and found that they form complexes with metal ions that are both water soluble and insoluble. In solution these metals become bound to or complexed by natural, organic compounds through low energy bonds (adsorption), high energy bonds (chelation), and very high energy, carbon-metal covalent bonds.

Much research has been done to establish the parameters for complex stability of natural organic compounds found in soils (Kononova, 1966; Schnitzer, 1971). Few studies (Krauskopf, 1956; Schindler, et al., 1972; Chau, V.K., personal communication, 1973) have characterized organic heavy metal interactions in bottom sediments, interstitial waters and surface waters. As a result, little is known about the consequences of metal interactions on man and his environment.

Prior to investigations by Birge and Juday (1934), it was assumed that lakes, streams and rivers were inorganic solutions as long as they were not contaminated by organic refuse or industrial waste (Ruttner, 1962). The organic matter in these waters was considered to consist of organisms and organic detritus and the plants of the associated aquatic communities were supported by assimilation of inorganic nutrients. Birge and Juday (1928) showed that lake waters contain small amounts of particulate organic matter and considerably larger amounts of dissolved organic matter. Soil scientists, limnologists and geochemists (Birge and Juday, 1928; Krauskopf, 1956; Hutchinson, 1957; Scheffer and Ulrich, 1960; Ruttner, 1962; Shapiro, 1964; Kononova, 1966; Hobson and Colombo, 1967; Eglington and Murphy, 1969; Breger, 1970; Bremmer *et al.*, 1970; Schnitzer, 1971) have found that this dissolved organic matter is important in the chemistry of waters, soils and sediments.

An application of known parameters and an evaluation of the role played by organic complexes in trace metal equilibria in natural waters and sediments is lacking. Figure 1 shows the possible forms (phases) and pathways of a heavy metal in a water and sediment system. In this study a selected, organic-rich sedimentary environment was chosen and its sediment used as a heavy metal reactant within the laboratory. Copper was chosen as a typical heavy metal reactant, with Co and sometimes Hg used in comparison. Some of the mechanisms of organic compound-heavy metal reactions are delineated by utilizing the fluorescent, absorbent, and light scatter properties of natural organics. The stabilities of the metal-organic complexes are investigated and the kinetics of some of the reactions of Cu and Co with sedimentary components are discussed. The laboratory data and resulting hypothesis show trends that are tested by observations in a natural environment that has been Cu contaminated. Finally, a schematic model is proposed to show the general stoiciometry and direction of Cu pathways between given phases in the sediment. The results discussed are not to be interpreted as well defined numbers for all Cu^{++}-sediment reactions but should show reaction trends under a variety of similar conditions.

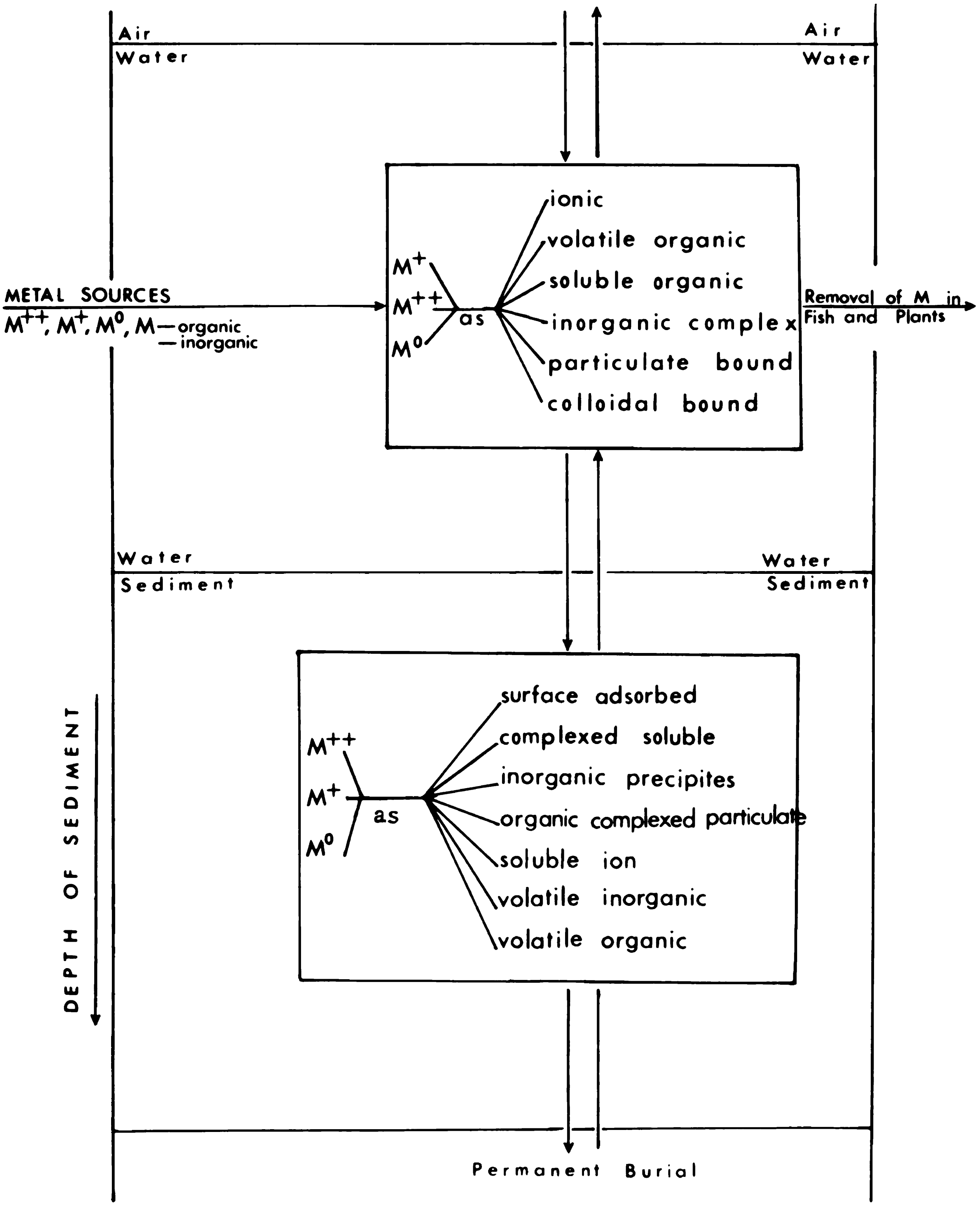


Figure 1. Generalized model of heavy metal phases and pathways in a natural fresh water environment.

DESCRIPTION OF HOUGHTON LAKE AND BURKE LAKE

Burke Lake sediment and Houghton Lake water and sediment are the systems studied. Burke Lake sediment is used as a source for controlled laboratory experiments because it is free of an excess of heavy metals and also is highly reactive. Organic rich Houghton Lake sediments are used to test the model based on the Burke Lake sediments. Specific chemical and physical descriptions of the studied sediment from the two lakes are given in Table 1.

Burke Lake is a small, eutrophic, kettle lake located in a wooded area of central Michigan, 13 km northeast of Lansing, Michigan (Figure 2). It is about 2,000 m^2 (2 acres) in area and 11 m deep. There are no houses, farms or industries on the lake and it is fed by ground water. The water visibility ranges from 1 m to 5 m depending on the time of year. Around its edges is an extremely organic-rich and biologically-active, black sediment more than a meter thick. The sediment contains little clay, silt, or sand.

Houghton Lake is a copper contaminated lake located in central Michigan (Figure 2). It is a glacial lake in its final stages of in filling. The surface area of the lake is 82 km^2 (32 sq. mi.) and the average depth is

3 meters (Novi, J., personal communication, 1972). The lake is highly productive. It is surrounded on three sides by swamps which contribute organic matter to the lake resulting in the high color of its water and a low average secchi disc reading of 0.5 to 1 m. A black organic-rich sediment covers most of the bottom but sand and some marl clay sediments are also present.

TABLE 1. Description of Burke Lake and Houghton Lake sediments and corresponding pore water. All heavy metal concentrations in pore water are mg/l and in sediments mg/kg dry weight. The grain size was measured on a Coulter Counter (error = 1%) after sonic disagregation.

	Burke Lake		Houghton Lake	
	pore water	sediments	pore water	sediments
organic carbon	92 mg/l	31 to 40%	72 mg/l	12 to 31%
original pH	7.6	---	7.7	---
original Cu	0.0	0.0	1.0	30 to 90
original Co	0.0	0.0	0.0	5.0
% H_2O in wet sed.	---	72 to 80	---	70 to 75
average grain size (microns)	---	4	---	5
original Eh	negative		negative	

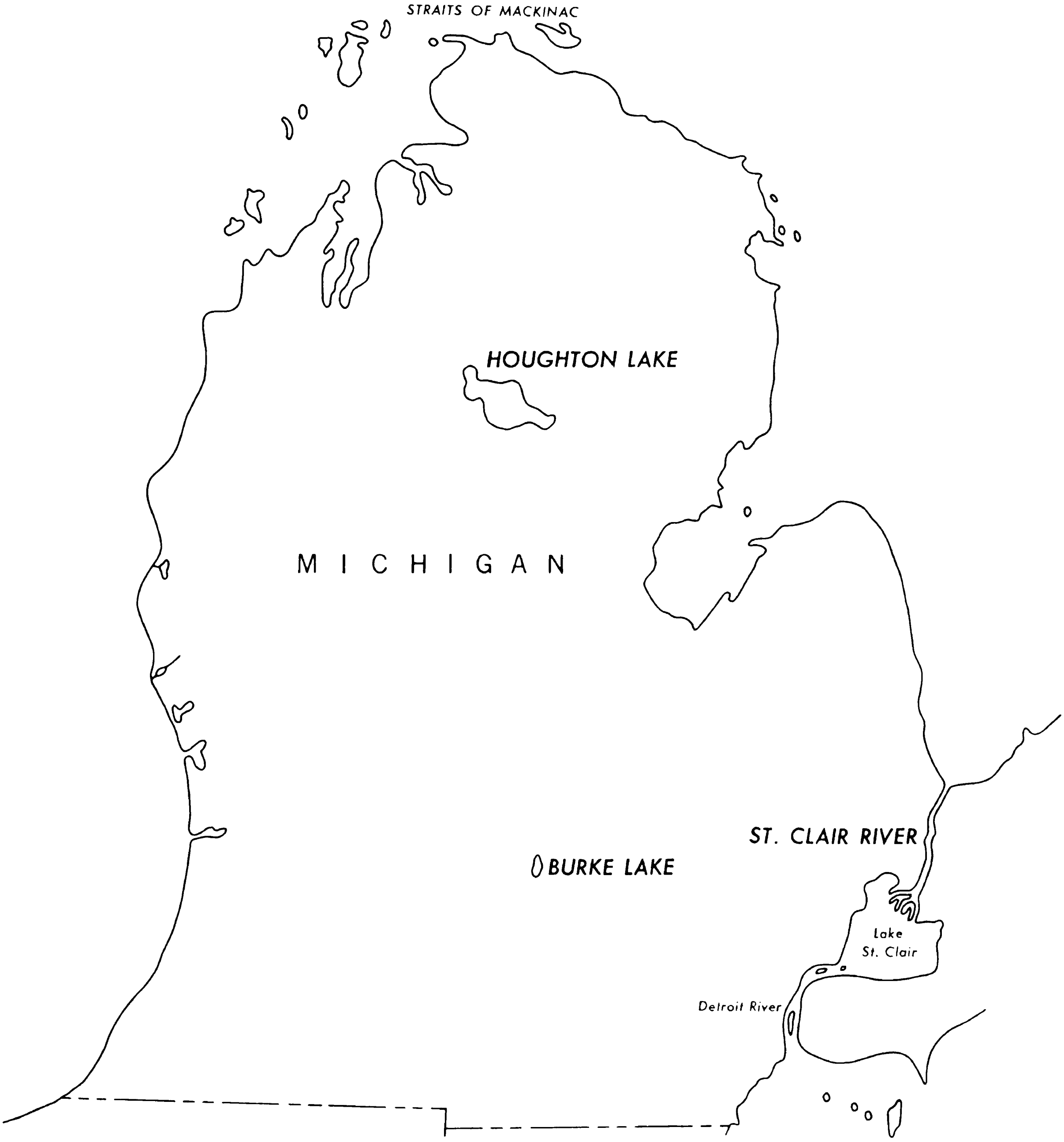


Figure 2. Map of lower Michigan showing the locations of the two sample sites. In heavy print are Burke Lake, near Lansing (increased 5:1 in scale) and Houghton Lake, in north central Michigan.

METHODS - I

Tests on Metal-Organic Pore Water Interactions

Fluorescence, Absorbance and Light Scatter of Pore Water Interactions

The fluorescing properties of natural organic compounds were utilized in studying metal-organic reactions. In general, fluorescence may be expected from organic compounds having a conjugated system, such as aromatic compounds, and not expected from aliphatic compounds (Guilbault, 1967). Thus, natural organic compounds such as tryptophan and tyrosin have functionally active amino groups which can react with a cation. The reaction will cause the amino acids to lose their fluorescing ability (Guilbault, 1967). These compounds and the proteins they are associated with are typical indicator molecules in the reactions of this study.

The specific chemical properties of the molecules in the pore water solutions were studied by means of a computer centered spectrophotometer-spectrofluorimeter combination instrument (Holland, 1971). On this instrument absorbance and fluorescence measurements are made simultaneously and light scatter measurements are made individually. The simultaneous measurement technique makes valid the interrelationships between absorption and fluorescent emission. The computer collects the data from the energy outputs resulting from absorbance, fluorescence and light scatter of the molecules, corrects the data for chemical and instrumental factors that may adversely affect the output energies, and produces a quantitative measurement that is directly proportional to the concentration of the excited molecules (Holland, 1971). This system as a whole has an accuracy of ± 0.002 absorbance units over the absorbance range of 0 to 2.0 units. This same accuracy is given for fluorescence and light scatter.

Organic-rich pore water from Burke Lake and Houghton Lake sediments were used as a source of naturally fluorescing organic compounds. The concentration of organic carbon in the pore water was 92 µgC/ml for Burke Lake and 72 µgC/ml for Houghton Lake. The pH of the pore water was 7.6 for Burke Lake and 7.7 for Houghton Lake.

The pH was adjusted in a set of samples to test for pH effects on the pore water organics. Twenty-five ml of Burke Lake pore water was pipetted into each of five 50 ml volumetric flasks. The pH of two aliquots was adjusted down to 2.1 and 5.5 with dilute HCl. The pH of two other solutions was adjusted up to 8.9 and 10.0 with 1N NaOH. All five were then diluted into volume.

The heavy metal ions Cu^{++} and Co^{++} were added to another set of flasks to study the metal-organic reactions. Twenty-five ml aliquotes of the pore water were pipetted into 50 ml volumetric flasks. To a series of the flasks, Cu^{++} was added in concentrations of 1, 2, 3, 4, 5, 10, 15, and 20 µg/ml. Cobalt ion was added in the same concentrations to another series of the flasks containing an equal quantity of pore water from the same bulk solution. No metal ions were added to one set of the flasks but the total amount of pore water in the flasks was 5, 10, 15, 20 and 25 ml diluted to 50 ml. These latter samples were the standard organic solutions. The pH of the solutions containing the metal ions was adjusted to 7.3 ± 0.1 and the samples were diluted to volume.

A last set of samples was prepared which contained Cu^{++} and Co^{++} in distilled water. These were used as background samples and therefore no results from these solutions will be presented.

Nitrogen was bubbled through each solution to purge it of oxygen. The temperature of each sample was 22°C. Then a 1 ml portion of each solution was individually excited by a source of energy through wavelengths in the ultraviolet spectrum.

Light scattering, a function of size and quantity of particles, was used on each set of solutions. Excitation was set at 330 mµ and the emission scanned from 300 mµ to 360 mµ. The computer collected the data, corrected it (Holland, 1971) and yielded an instant output in quanta of energy (Figure 3). The light scatter spectra of these solutions are shown to have a maximum intensity at 330 mμ (Figure 3).

The fluorescent and absorbant intensity of each set of solutions was then measured. The intensities of the fluorescence and absorbance emissions of each sample were measured simultaneously throughout each scan. The emission energy for each was set at 380 mμ while the excitation spectra was scanned through wavelengths ranging from 250 mμ to 360 mμ. The computer yielded absorption and corrected fluorescence curves on a single output. The error as grand variation mean for the absorbance and fluorescence experiments is 3.3% (Appendix, Table A6).

Specific Gravity of Organic Flocs

The specific gravity of the organic floc (precipitated colloid) was measured using Burke Lake pore water in order to determine its potential sedimentary behavior. Sodium hydroxide was added to a pore water solution causing flocculation of the colloidal and soluble organics. After precipitation, the water was decanted and the precipitate and remaining solution poured into two 50 ml picnometers. The picnometers were placed in a 21° constant temperature bath for 15 minutes. They were then weighed with the concentrated floc, refilled with distilled water, again placed in the 21° bath and weighed again. The organic floc was dried and weighed. In a similar experiment Cu^{++} at a concentration of 25 µg/ml was used as a flocculation agent.

Order of Reactivity of Hg^{++}, Cu^{++}, and Co^{++} with Organic Compounds

The significance and intensity of the Cu^{++}-organic reaction was better understood by a competition experiment using a supposedly strong reactor (Hg^{++}) and a weaker reactor (Co^{++}). Twenty-five ml of Burke Lake pore water was pipetted into each of six, 50 ml, volumetric flasks. The three metals Hg^{++}, Cu^{++}, and Co^{++} were individually added in equal quantities such that each flask contained an increased concentration of each metal, their concentrations ranging from 1 µg/ml to 20 µg/ml. Each flask contained a set concentration of 46 µg/ml organic carbon. The solutions were adjusted to a pH of 7.1 and brought to volume. After two hours the samples were Millipore filtered. The small pore size of the filter (0.45µ) facilitated removal of all the particulate and most of the colloidal organic compounds. This method should have removed almost all of the nonionic heavy metals (Riley, 1938; Chau, Y.K., personal communication, 1973). The filtrate was analyzed by atomic absorption spectrophotometry for metal species remaining in solution. In a similar run, Cu^{++} alone was added to the flasks and

the same procedure of filtration and analysis was done. The error in this experiment is developed in Appendix, Table A3.

Test of Chelation of Heavy Metals by Organics

Cupric ion was added to a Burke Lake pore water solution and the pH adjusted. The pH was adjusted in four of five test solutions such that two solutions had a pH above and two solutions had a pH below 7.3 ± 0.2, the pH of the original solution. Each solution had a copper concentration of 4 µg Cu^{++}/ml. Two hours later, half of each solution was Millipore filtered (0.45 µ) to extract particulate and high molecular weight organics. A clear filtrate resulted from the yellow-colored solution. The copper remaining in solution was considered unreacted, free Cu^{++} and its concentration was found by atomic absorption analysis. The quantity of Cu^{++} adsorbed by the organics filtered from solution was calculated by difference. Then, the remaining solutions containing the Cu^{++}-pore water mixture, were readjusted back to a pH of 7.3 ± 0.4. Each solution was again Millipore filtered and the Cu remaining in solution measured. The precision of this experiment is developed in Appendix, Table A4.

METHODS - II

Tests on Sediment-Metal Interactions

Rates of Reaction

The rates of copper and cobalt uptake were investigated using Burke Lake sediment as a reactant. The reaction temperature was ambient (22°C to 24°C), sediment pH was 7.4 ± 0.2, mean grain size was 4 u, percent carbon was 35 and sediment water content was 73 percent. Cupric ion was added in quantities of 0.5, 2, 5, 10, 25, 50, 75, and 100 mg to a series of solutions containing 25 ml of wet sediment. The solutions were all diluted to 125 ml. To a similar series of sediment solutions, Co^{++} was added in quantities equal to the Cu^{++} additions. After two hours and every day for 11 days, the concentration of heavy metal in the solution overlying the sediment was measured by atomic absorption analysis. Then, each sediment was dried and weighed. The precision of the methods used and the fit of the resulting data to a linear curve is developed and discussed in Appendix, Tables A9 and A10.

Quantitative Aspects of Uptake

To find the extent of the organic-heavy metal reaction in the general model (Figure 1) in terms of log Q,

Cu^{++}, and as a comparison, Co^{++}, were allowed to react with Burke Lake sediment and pore water. Cupric ion, ranging in concentration from 1 to 20 µg/ml, was pipetted in increasing quantities into a series of 50 ml volumetric flasks containing 25 ml of Burke Lake pore water. The pH of the solutions was adjusted to 7.3 ± 0.1. The pore water solution was analyzed for organic carbon according to the methods of Van Hall, et al., (1963). The pore water contained 46 µg/ml of organic carbon. After two hours and a probable reaction steady state for metal-pore water reactions, each solution was Millipore filtered (0.45 µ) and the copper remaining in solution measured by atomic absorption analysis.

Burke Lake sediment was also used as an adsorbant. Cupric ion was added in duplicate in concentrations of 2.172, 10.86, 27.15, 54.30, and 5.430 mg to a series of flasks containing 25 ml of wet sediment. Each was brought to a total volume of 100 ml. After an initial shaking the mixtures were allowed to stand at room temperature (22-24°C) for five days. The solutions were then analyzed for copper. Cobalt was tested for log Q in the same manner as copper. The concentrations of Co were 2, 5, 10, 20, and 50 mg.

In one last test, the time dependency of the log Q values of the Cu^{++} and Co^{++} reactions were investigated. For this test the results of the rates of reaction test given above were used. In Appendix, Table A11, A12, and A13, the error of the method and the fit of the data to the results is developed.

Pathways of Cu^{++} Within the Sediment

To test for the various forms (phases) of Cu in the sediment Cu^{++} was added to wet Houghton Lake sediments (Table 1) in a concentration of 443 mg/500 ml sediment (6.569g dry weight) and extracted after two hours and again after nine days. The sediment contained 60 µgCu/gm as background but this was considered negligible in affecting the general trends, since the added Cu was 6.74 mg Cu/gm of sediment. The Cu^{++} was intimately mixed into the sediment with a magnetic stirrer. A fraction was extracted, split into four nearly equal 20 ml portions and centrifuged. A resulting supernatant pore water was decanted and collected. The sediment was then washed four times with a 5 percent KCl solution followed by a single washing with distilled H_2O to remove surface adsorbed Cu^{++} (Mortland, personal communication, 1971). The washings were collected in four volumetric flasks and diluted to volume. Four washings with 0.01M Na-EDTA were then completed and collected in volumetric flasks. Na-EDTA is a very strong chelating agent of Cu^{++} and will extract Cu^{++} from weaker complexes such as natural metal-organic complexes (Knesek, personal communication, 1971). The samples were then dryed at 110°C, and weighed.

Finally, 5 g of $KMnO_4$ and 5 ml of sulfuric acid was added to each sample, and the mixture was digested for 30 minutes to solubilize the remaining Cu^{++}. The percent variation between the four samples in the three extractions is (1) KCl = ± 2%, (2) EDTA = ± 5%, and (3) $KMnO_4$ = ± 4%. The error and confidence limits of the various extractions is developed in Appendix, Table A14.

RESULTS AND DISCUSSION

Heavy Metal-Organic Interactions in Sediment Pore Water

Solubility of the Organics

The sediment organic matter-heavy metal reactions were studied by investigations on the reactions of the organic compounds in pore water. The pore water organic compounds were utilized to study the organic-metal interaction because they are; (1) representative of the sediment organic matter, (2) are highly reactive chemically, and (3) have fluorescent, absorbant and light scatter properties. Some of the properties of the pore water organics were studied by utilizing their changing response to ultraviolet light with changing chemistry.

Light scattering which is a function of the size and quantity of particles, was used in determining the solubility of the organics in the pore water solution containing a variety of electrolytes. First, the effect of pH on organic solubility was tested (Methods I, Light Scatter of Pore Water Interactions). Organic-rich pore water (92 µg C/ml) was extracted from Burke Lake sediment by centrifugation. The pH of the resulting series of pore water samples was adjusted in the range 2 to 10 and a light scatter spectrum having a peak intensity (Φ) at 330 mu was obtained from each sample

The relationship of light scatter peak height at 330 mµ to pH change suggests that solubility of organics in solution is inversely related to an increase in pH (Figure 4). The organic molecules and colloidal surfaces are negatively charged (Neihof and Loeb, 1972) and thus, OH^- effectively flocculates the organic molecules. As flocculation begins many nuclei form, and molecules begin to floc together. The increase in size and number of particles increases the light scatter.

The effect of increased concentration of divalent heavy metals on organic molecule solubility was then tested using Cu^{++}. Light scatter showed that as the concentration of Cu^{++} increased, the flocculation of the organics increased (Figure 5). The flocculation increased until an endpoint was reached and no further change in light scatter occurred with increasing Cu^{++} concentration. Thus, either the affects of increased Cu^{++} concentration increased ionic strength, or both caused flocculation of pore water organics. The increase in ionic strength was only about 10^{-5} so it is suggested that increased Cu^{++} concentration is the major factor causing flocculation.

The results shown in Figures 5 and 6 are similar to those relationships found by Krauskopf (1967) for the effect of electrolytes on colloids. These are: (1) divalent and trivalent ions are more effective in coagulating colloids than are univalent ions, (2) H^+ and OH^- although univalent are especially effective as coagulants, and

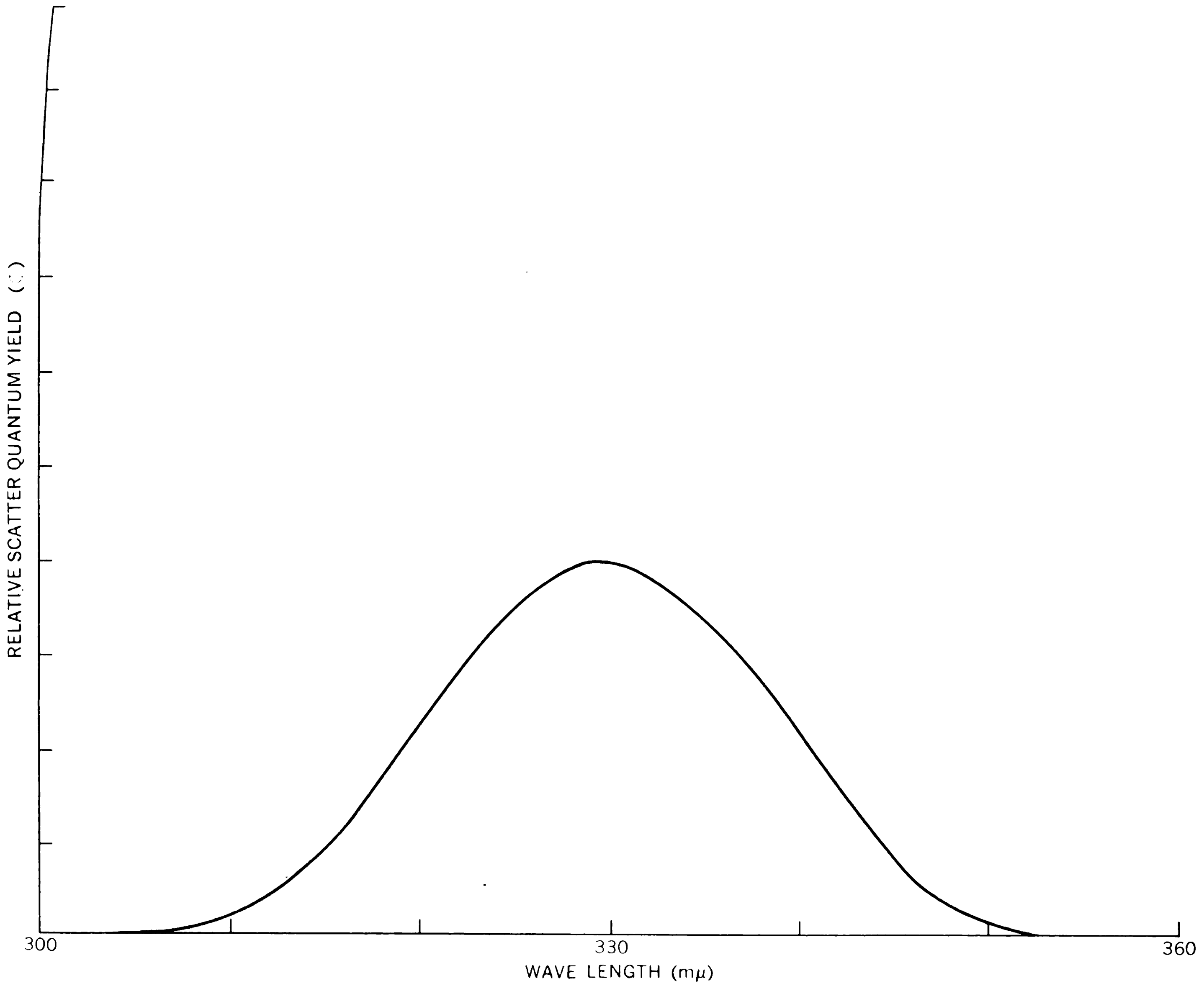


Figure 3. Sample light scatter output

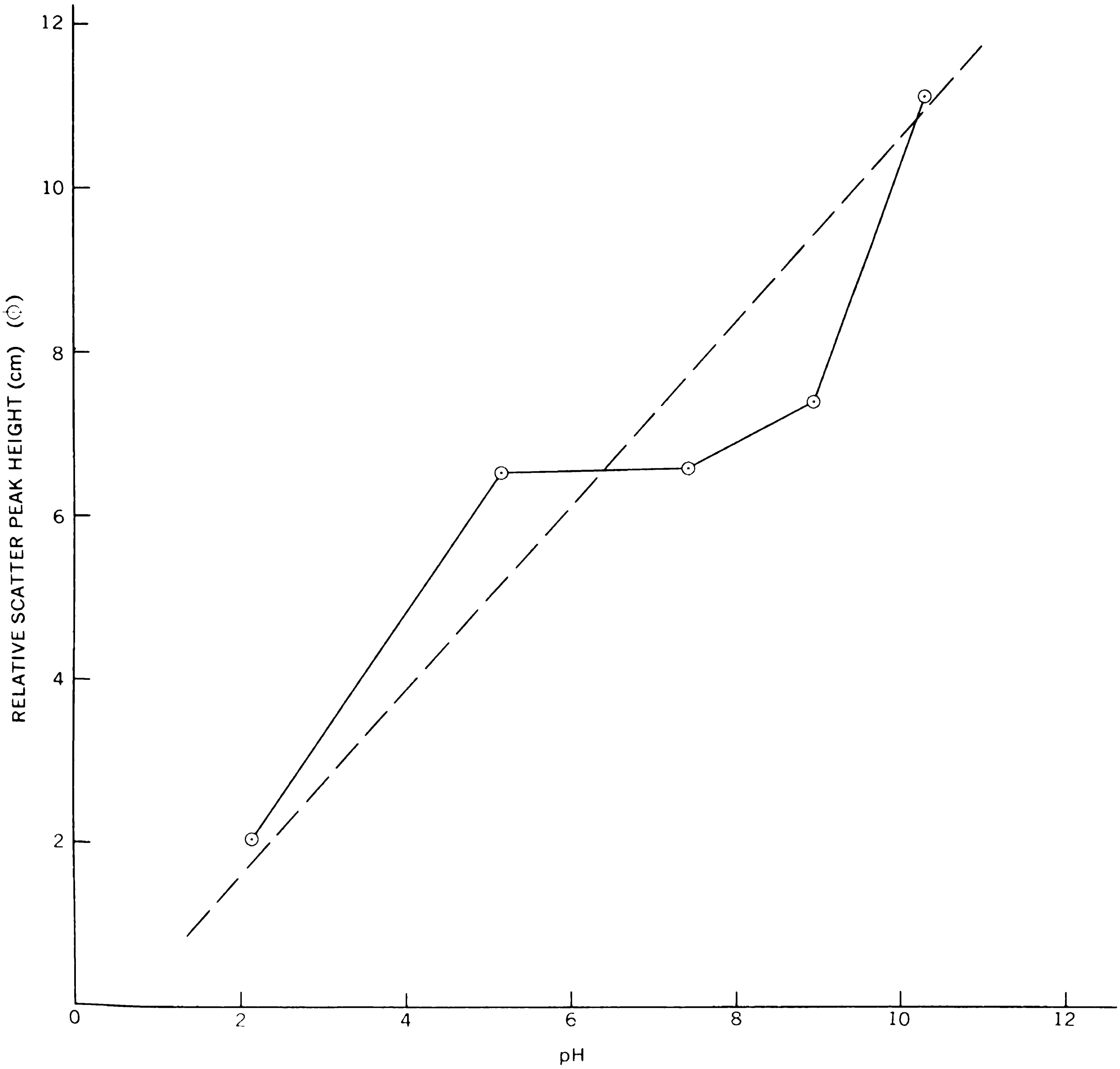


Figure 4. Dependence of organic solubility on the pH of the solution as shown by light scatter. The dotted line represents the data linearly. (Data in Table A1, Appendix)

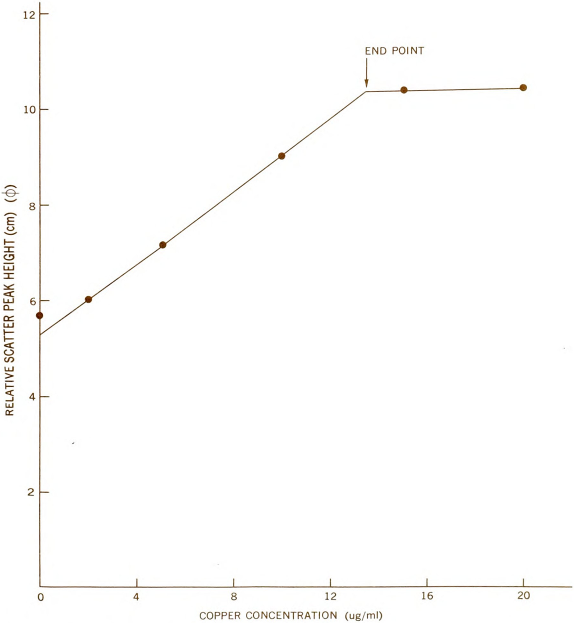


Figure 5. Effect of Cu^{++} concentration on organic solubility-light scatter. The data are derived from light scatter output at 330 mμ. A reaction end point occurs at 13 ug/ml of Cu^{++} in the organic rich solution. (Data in Appendix, Table A2)

(3) some electrolytes (some divalent transition metals) are more effective as coagulants than other equally charged electrolytes.

Specific Gravity of Organic Floc

The specific gravity of the flocculated organics was investigated to find what effect this might have on the sedimentation or mobility of a metal contained in the floc. The specific gravity of the organic floc is an average 1.6. When the flocculating agent is Cu^{++} at 20 µg/ml of pore water, the specific gravity of the resulting floc is an average 2.1. Cline, et al. (1973) have shown that the heavy metal, Hg^{++}, is also incorporated by the organics in pore water and a heavy metal-organic floc results which has a low specific gravity. A heavy metal-organic interaction could result in heavy metal mobilization as part of a low specific gravity organic floc.

Even as a precipitate, natural organics can be quite mobile in the aquatic environment. Clays are the last inorganic sediment to settle from a dynamic environment due to their small size, platy shape, surface charge, and a specific gravity ranging from 2.1 to 2.9 (Mason and Berry, 1968). The specific gravity of the organics is less than that of clays which means that they and associated substances such as heavy metals will be easily and quickly mobilized in a system with minimal turbulence and demobilized only in very quiet aqueous environments.

Order of Reactivity of Hg^{++}, Cu^{++}, and Co^{++} With Organic Molecules

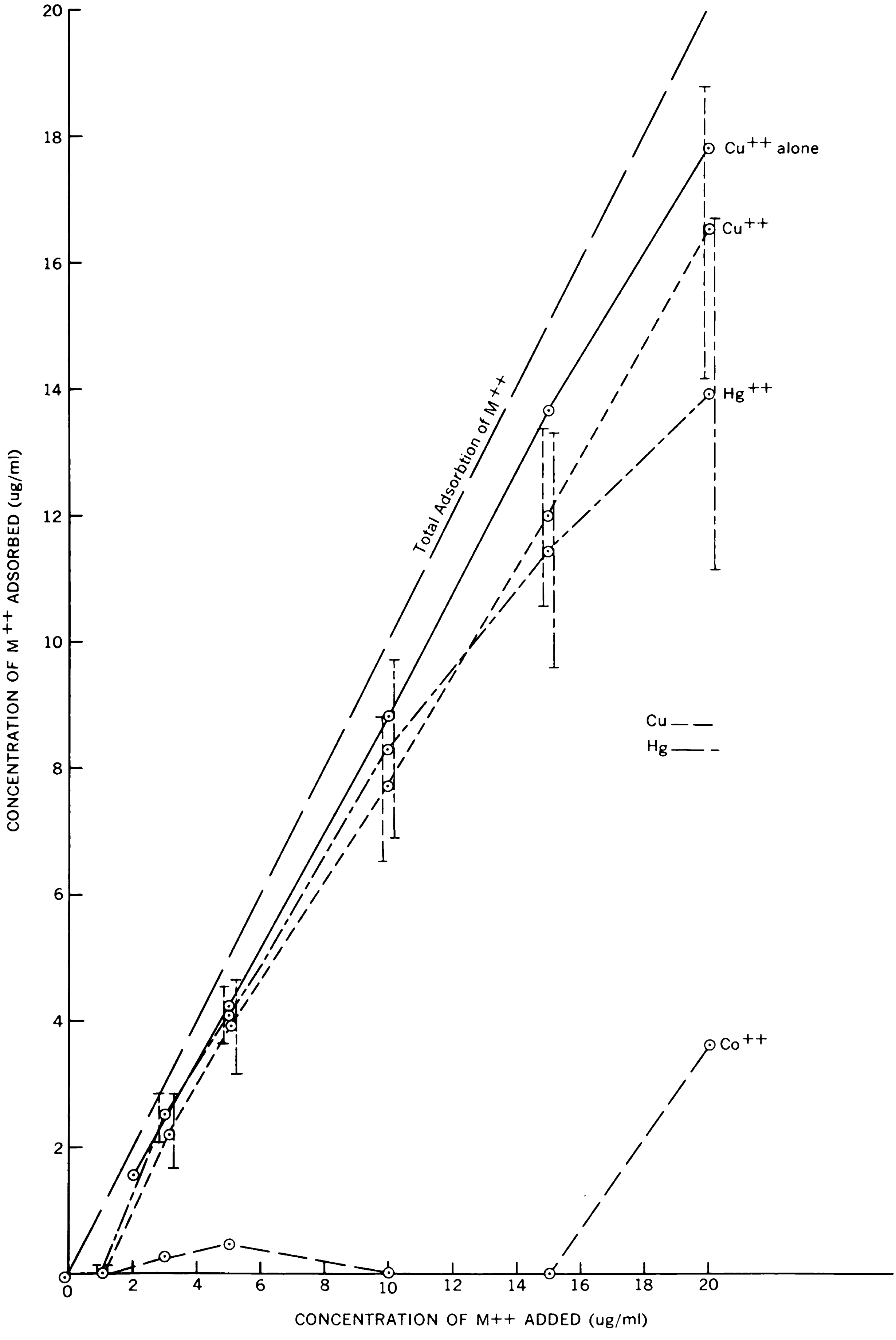
The interaction of a heavy metal with an organic molecule depends not only on the chemistry of the organic compound but to a large extent on whether a heavy metal can be complexed. The extent of reaction of different metal ions with organic complexing agents is related to the size, configuration, and charge of the ions. The relative reactivities of the heavy metals are listed with soil organics (Kononova, 1966; Schnitzer and Skinner, 1966; Broadbent, 1957) and with natural and synthetic chelating agents (Knesek, unpublished; Weast, 1968). To understand the significance and intensity of the Cu^{++}-organic reaction, it is necessary to compare its reaction with natural organic compounds to that of other heavy metal cations.

The reactivity of Cu^{++} with natural organics as compared to the reactivity of Hg^{++} and Co^{++}, was determined by means of a competition experiment using Burke Lake sediment as a source of natural organics. When only Cu^{++} was added to the pore water solutions (Figure 6), it was adsorbed (adsorption here is any metal-organic bond) in greater concentration than in the solution which contained Hg^{++}, Co^{++}, and Cu^{++} (Figure 6). The range of the data points in Figure 6 are ± 0.1 µg/ml or within the circles around each point. (See Appendix, Table 3A). These metals (Hg^{++}, Co^{++}, Cu^{++}) compete for available sites, supressing the adsorption of each other in varying degrees. For an unknown reason the metals do not suppress adsorption of each other to the extent that the total adsorption of Hg^{++}, Cu^{++}, and Co^{++} in the mixture adds up to the adsorption of Cu^{++} when it alone is in solution. Each type of metal ion may be adsorbed by sites specific to only that ion and not the others. Cobalt does not successfully compete with either Cu^{++} or Hg^{++} for organic adsorption sites, but Cu^{++} and Hg^{++} compete with each other. Mercury (Hg^{++}) suppresses Cu^{++} uptake and is adsorbed by the organics in approximately equal concentrations to Cu^{++}. Copper likely suppresses Hg^{++} uptake also. At about 15 to 20 µg/ml of Hg^{++}, Cu^{++}, and Co^{++} the total metal ion concentration in solution is a high 45 to 60 µg/ml and inorganic precipitation and/or inorganic colloid formation may cause the apparent changes in adsorption character. Inorganic colloids may be filtered by Millipore filtration (0.45 µ) and may cause the apparent increase in Co^{++} adsorption and continuing increase in Cu^{++} adsorption while Hg^{++} drops off. The following order of reactivity of the three heavy metal ions results:

$$Hg^{++}, Cu^{++} \gg Co^{++}$$

The above order of reactivity is in general agreement with that of the same ions with EDTA (Stary, 1964). At 25°C EDTA has a log K_s with Hg^{++} of 21.8, with Co^{++} 16.6 and with Cu^{++} 18.8. Cobaltic ion is much less reactive than Cu^{++} with the natural organics and is less reactive than would be predicted from the EDTA stability series. Mercuric ion and Cu^{++} are not only more strongly chelated than cobalt by given organic sites, but they also have more types of sites available to them for reaction. As an example of this, Broadbent (1957) showed by chromatography that the effluent of an acid washed column containing Cu^{++}- and Ca^{++}-organic complexes show four elution peaks with copper and two with calcium as acidity is increased. He concluded that there is a retention of copper by functional groups which do not combine with calcium. Cobalt cannot react with as many functional groups as metals higher in the stability series because it is not of favorable size for maximum chelate substitution. Charge is important, but in this case all three ions are equally charged. Of the three metal ions then, Co^{++} is an example of a weak reactor and Cu^{++} and Hg^{++} strong reactors with organic ligands. It follows that any study on Cu^{++} in a natural environment must account for its strong reaction with natural organic ligands.

Figure 6. Competition between Hg^{++}, Co^{++} and Cu^{++} for adsorption sites on organics in pore water. A comparison is made of the mixed metal ion (Hg^{++} + Cu^{++} + Co^{++}) adsorption and the non-competitive adsorption of Cu^{++} onto the organics. The closer a metal is to being totally adsorbed by the organics, the closer it will come to the "Total Adsorption of M^{++}" line. The range in determinations is shown by the bars on the data points (See data in Appendix - Table 3A).


20
18
16
14
12
10
8
6
4
2
0
0
2
4
6
8
10
12
14
16
18
20
CONCENTRATION OF M ++ ADSORBED (ug/ml)
CONCENTRATION OF M++ ADDED (ug/ml)
Total Adsorbtion of M++
Cu++ alone
Cu++
Hg++
Co++
Cu
Hg

Test of Chelation of Cu^{++} By Natural Organics

The bonding or association between a heavy metal and an organic molecule is often due to chelation of the cation. Cupric ion was allowed to react at varying values of pH with Burke Lake pore water to test for chelation (Methods I, Test of Chelation of Cu^{++} by Natural Organics). It was found that the percentage of total Cu^{++} that becomes bound to the filterable substances, such as the larger particulate and colloidal organic material, increases in direct response to a pH increase (Figure 7, curve a). At a pH greater than 7.5 a copper hydroxide precipitate may also form but the increasing reactivity of the organics likely minimizes this reaction (Krauskopf, 1956). Thus, the reaction between the natural organic compounds and heavy metals is pH dependent.

To find if the uptake of Cu^{++} by the organic molecules is reversible, each pH adjusted solution was brought back to the original pH of 7.3. The quantity of copper remaining in solution or the percent of copper in all of the solutions is approximately the same (Figure 7, curve b). The metal reaction with the organics is thus reversible. Therefore, the natural organic compound-heavy metal reaction in the aquatic environment and in the model fulfills the theoretical requirements of complex compounds (Martell, 1971; Stevenson and Ardakani, 1971) proving that natural organic molecules complex and may chelate the heavy metals.

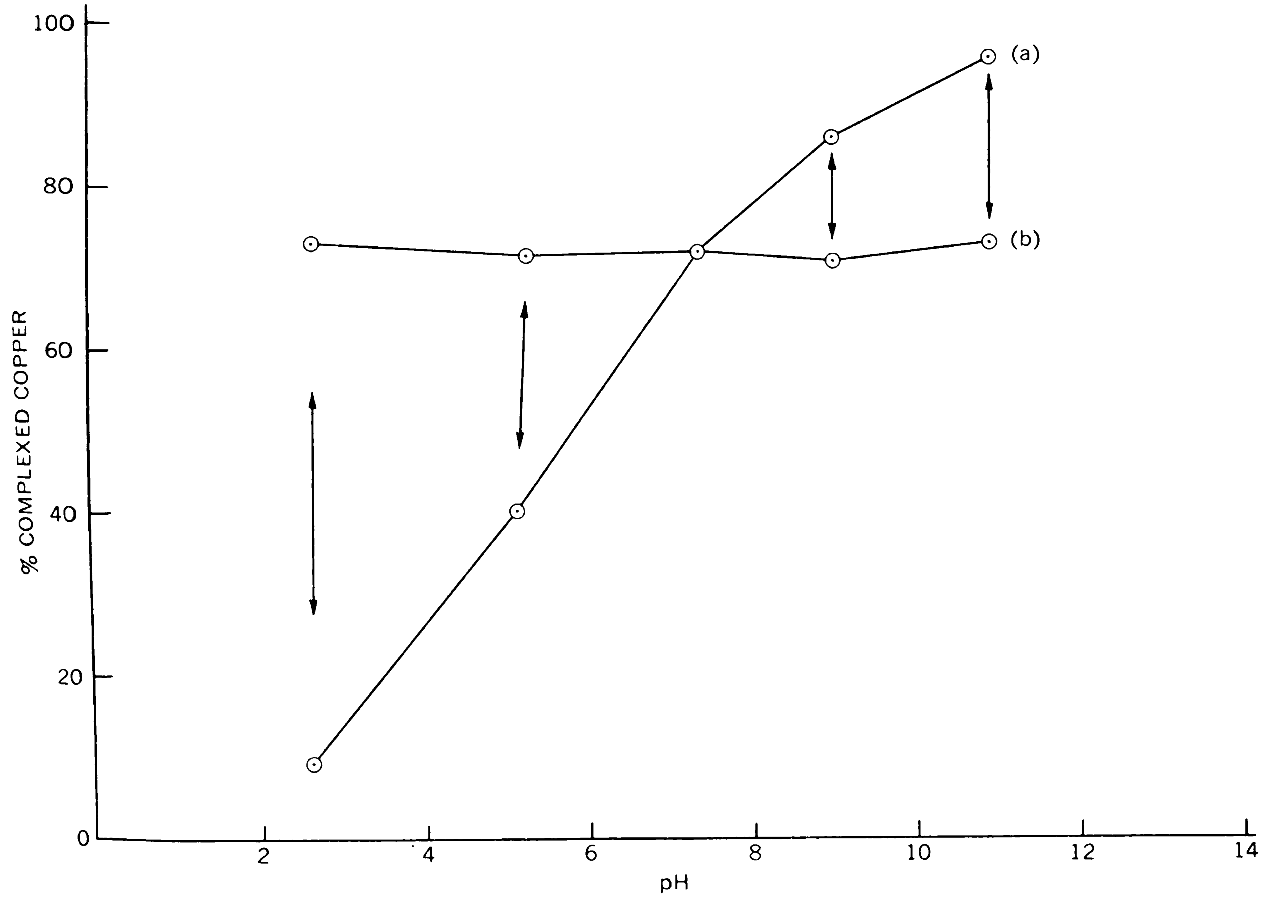


Figure 7. Equilibrium of Cu-organic chelate shown by pH adjustments. Curve (a) is a plot of percent of Cu^{++} uptake by organics versus pH of the solution while curve (b) is a plot of the percent Cu uptake of each sample after readjusting to a pH of 7.39 ± 0.03. (Data in Appendix, Table A4)

The natural metal-organic complexes can usually act as metal chelates, depending on their stability. A test on a complex to find if it is a chelate is to find if a dilution will cause release of metal ion from the complex (Martell, 1971). Most natural waters are deficient in heavy metals even though their sediments may be enriched with heavy metals. Thus the complex or chelate in the sediments is stable even in dilute solutions of heavy metals such as natural waters. As the Cu^{++} concentration decreases in an organic-rich solution (Figure 6, Cu^{++} alone), the percent of Cu^{++} in solution does not increase. Thus, dilution does not cause a release of metal ion from natural organic complexes indicating that the complexes are chelates.

Extent of Organic-Metal Reaction in Pore Water Solution

The heavy metal-organic interactions in solution were studied by means of the fluorescent and absorbant properties of organic compounds found in pore water (Methods I). Example fluorograms and absorbance spectra of Burke Lake pore-water solutions containing increasing quantities of Cu^{++} are shown in Figure 8. The quantity of organic molecules, pH, temperature and machine operating conditions (Holland, 1971) are the same for each example. The emission energy for each is set at 380 mµ. Each solution is individually excited by a source of energy through wavelengths ranging from 250 to 360 mµ. The intensity

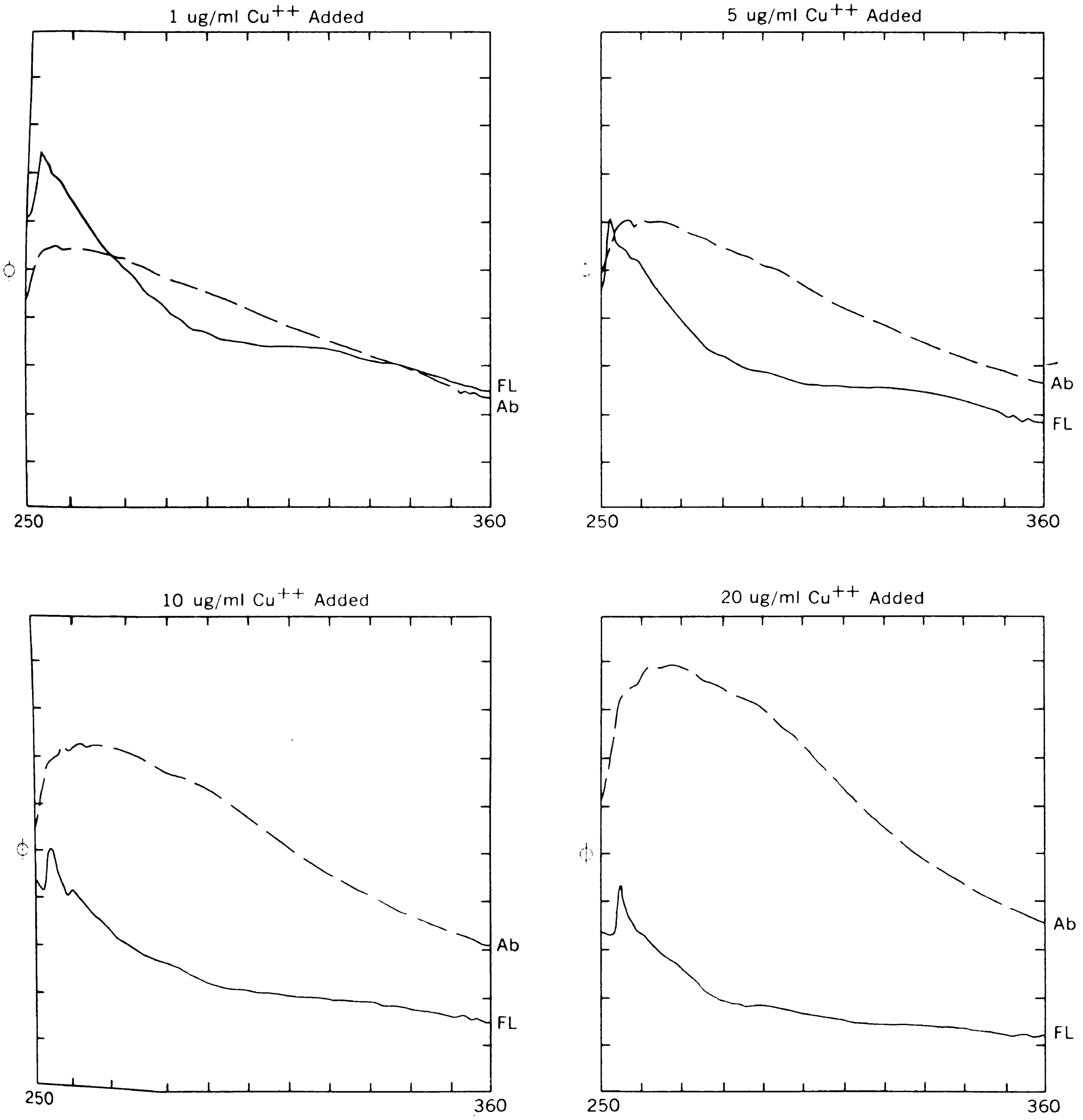


Figure 8. Example fluorograms of an organic rich pore water solution containing a constant carbon content and an increasing concentration of Cu^{++}. Fluorescence (FL) and absorbance (Ab) are simultaneously measured and recorded as shown. The vertical scale is in relative quantum units (Φ) while the horizontal scale is in wavelength (mμ) of emission.

of absorbance and corrected fluorescence emissions (Holland, 1971) or quanta are simultaneously measured throughout the scan.

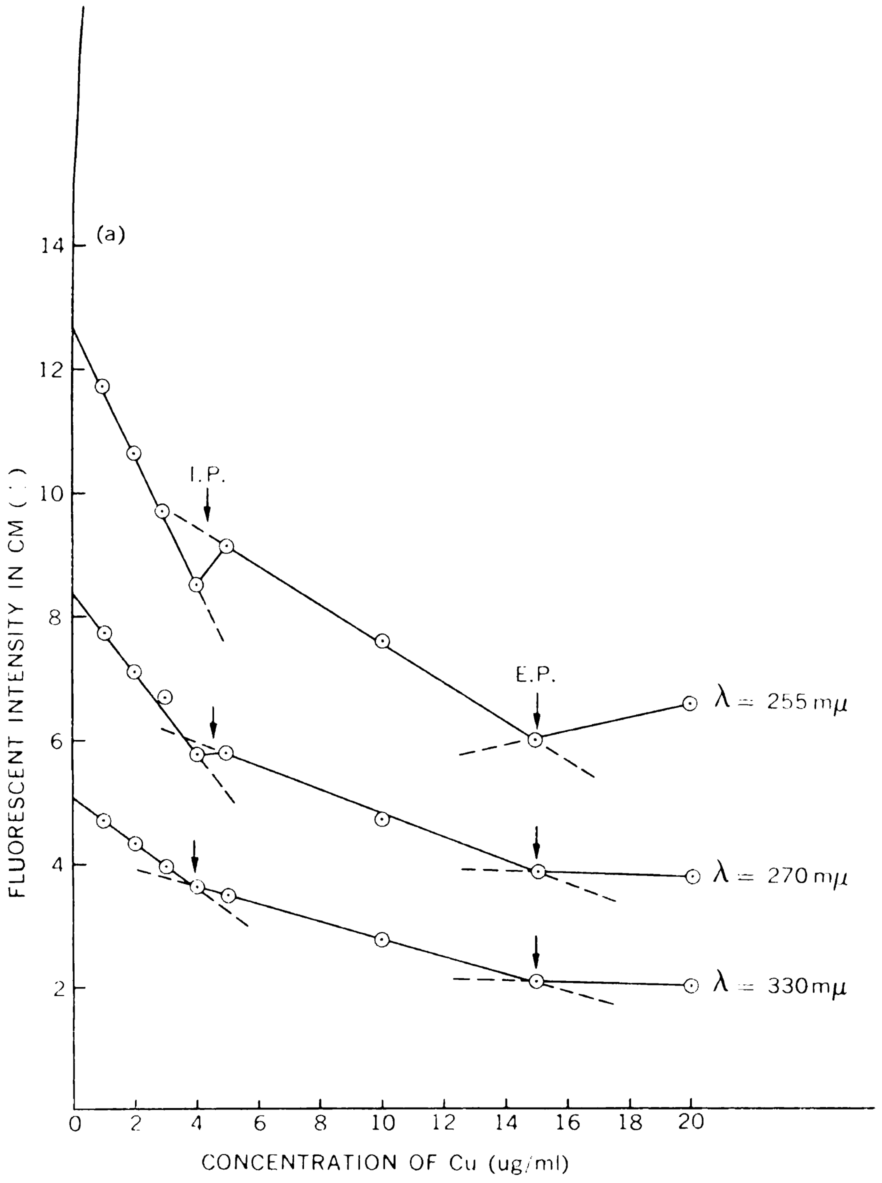
Figure 8 shows that each entire fluorescence spectrum decreases in intensity while the entire absorbance spectrum increases as copper concentrations are increased. A heavy metal causes a decrease of organic fluorescence in three ways: (1) the metal ion can cause the fluorescing organic to precipitate from solution; (2) when the metal ion reacts with the fluorescing molecule it stabilizes the resonating electrons of the fluorescing molecule; and (3) it can, without reacting, dampen fluorescence by its closeness to the electrons of the fluorescing molecule (Holland, personal communication, 1972). Absorbance often acts in an opposite manner to fluorescence. Every molecule must absorb before it can fluoresce. Non-fluorescing species however, can also absorb. Often, when a ligand makes bonds with a cation, absorbance will increase. Thus as reactions such as the cation-organic ligand reaction occur with fluorescing molecules, fluorescence will decrease while absorbance usually increases. If a cation is only surface adsorbed and no reaction occurs, absorbance will not increase (Holland, personal communication, 1972). But, when no bonds are made, fluorescence will still decrease due to close association of the metal ion to the resonating electrons of the organic molecules.

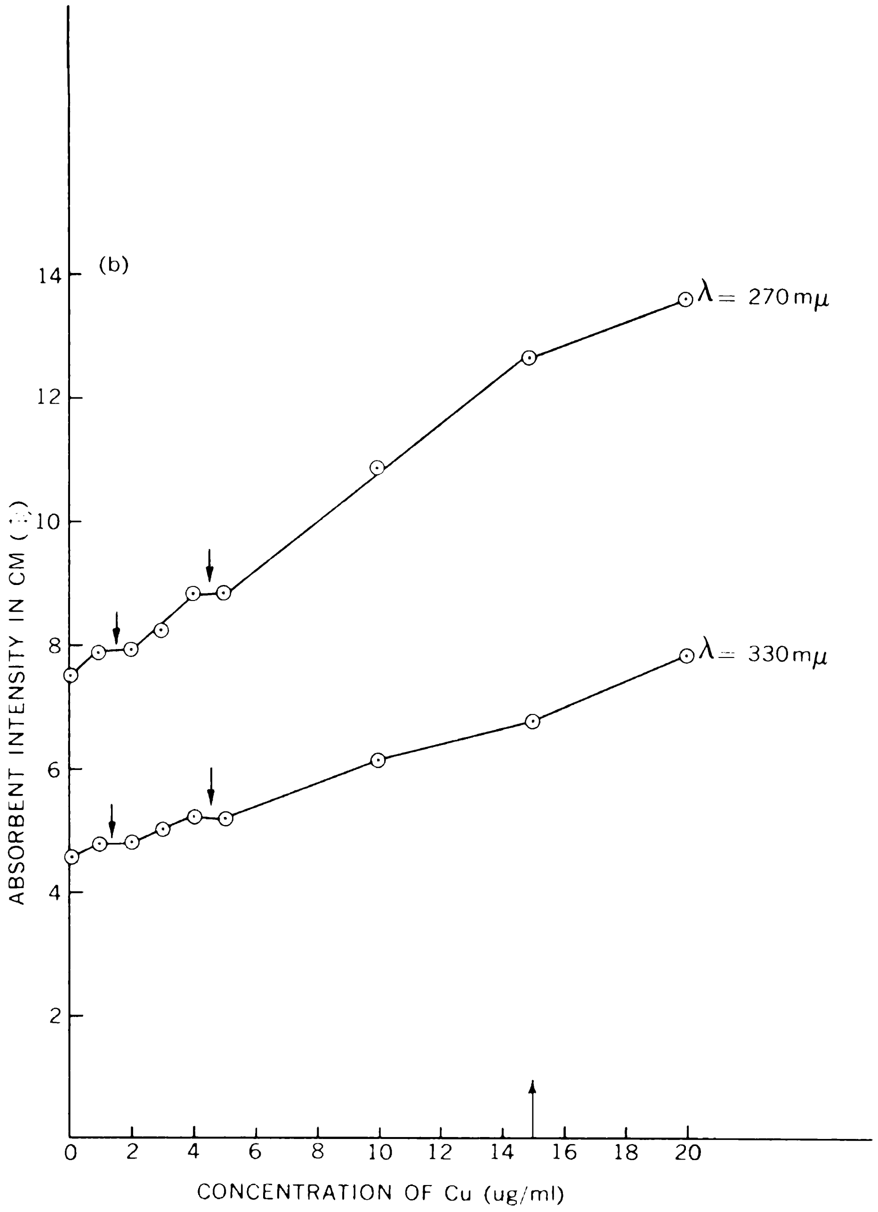
In comparing the four spectra in Figure 8, the affect of copper concentrations on the intensity of fluorescence is observed. At low concentrations, Cu^{++} is surrounded by a maximum number of ligand functional groups. After the more highly reactive sites are occupied, the Cu^{++} must fill less desirable sites where it is surrounded by waters of hydration (Martell, 1971). Then, at a cation/ligand ratio at which the cation is only weakly complexed, it should no longer affect the fluorescence of the molecules and an endpoint is reached.

Each spectrum in Figure 8 is a result of a mixture of fluorescing species, many of which are in the same molecule. At every wavelength in the entire spectrum the intensity of fluorescence decreases as the fluorescing species react or as concentration decreases due to precipitation. The change in fluorescence is slightly different at each wavelength because the character of the fluorescing molecules varies. Thus, to observe heavy metal organic reactions in the following experiments, changes in fluorescence are measured at a series of specific wavelengths.

Figure 9 relates the intensity of fluorescence (Figure 9, a) and absorbance (Figure 9, b) at specific wavelengths versus the total concentration of copper. The initial rapid decrease in fluorescence indicates that Cu^{++} is interacting with a maximum number of organic molecules. The inflection at 4 to 5 ug Cu^{++}/ml suggests a reaction endpoint of copper with highly reactive, organic functional

Figure 9. Change of fluorescent (a) and absorbent (b) intensity of dissolved organics in pore water at specified wavelengths (λ) with an increase in Cu^{++} concentration. E.P. = endpoint. I.P. = inflection point. (Data in Appendix, Table A5).


(a)
FLUORESCENT INTENSITY IN CM ( )
14
12
10
8
6
4
2
0
2
4
6
8
10
12
14
16
18
20
CONCENTRATION OF Cu (ug/ml)
I.P.
E.P.
λ = 255 mμ
λ = 270 mμ
λ = 330 mμ


(b)
ABSORBENT INTENSITY IN CM ( )
14
12
10
8
6
4
2
0
2
4
6
8
10
12
14
16
18
20
CONCENTRATION OF Cu (ug/ml)
λ = 270 mμ
λ = 330 mμ

group. The decrease in slope after 5 µg Cu^{++}/ml implies that copper is not incorporated as energetically because the most stable bond sites are occupied. At concentrations greater than 5 µg/ml, the Cu^{++} is not surrounded by a maximum number of functional groups and thus it cannot affect the organic fluorescence to as great an extent. The final change in slope at approximately 15 µg Cu^{++}/ml is likely due to saturation of most of the stable bond sites of the organic molecules. The Cu^{++} no longer affects the fluorescence of the organic compounds after this concentration and an endpoint is reached. The endpoint on the absorbance curve is not as apparent because with increased Cu^{++} concentration, some residual reaction causing non-fluorescent related absorption even though the organic-metal reactions are essentially complete as shown by fluorescence.

To calculate the quantity of organics that had reacted with the Cu^{++}, comparisons were made between results from Figure 9 and a standard organic curve (Figure 10) (Methods I). The fluorescent intensity of the standard organic solutions was plotted for three wavelengths versus the known percentage of pore water or concentration of organic carbon in solution. All of the metal containing solutions originally contained 50 percent pore water or 46 µg C/liter. As the metal ions react with the organics, the fluorescence of the solutions decreases to some intensity. Comparison of this new intensity to the standard plot at a specific wavelength, will give a measure of the percent unreacted pore water or percent unreacted carbon remaining in solution. The percent pore water or quantity of organic carbon that has reacted at an inflection point or an endpoint can then be calculated.

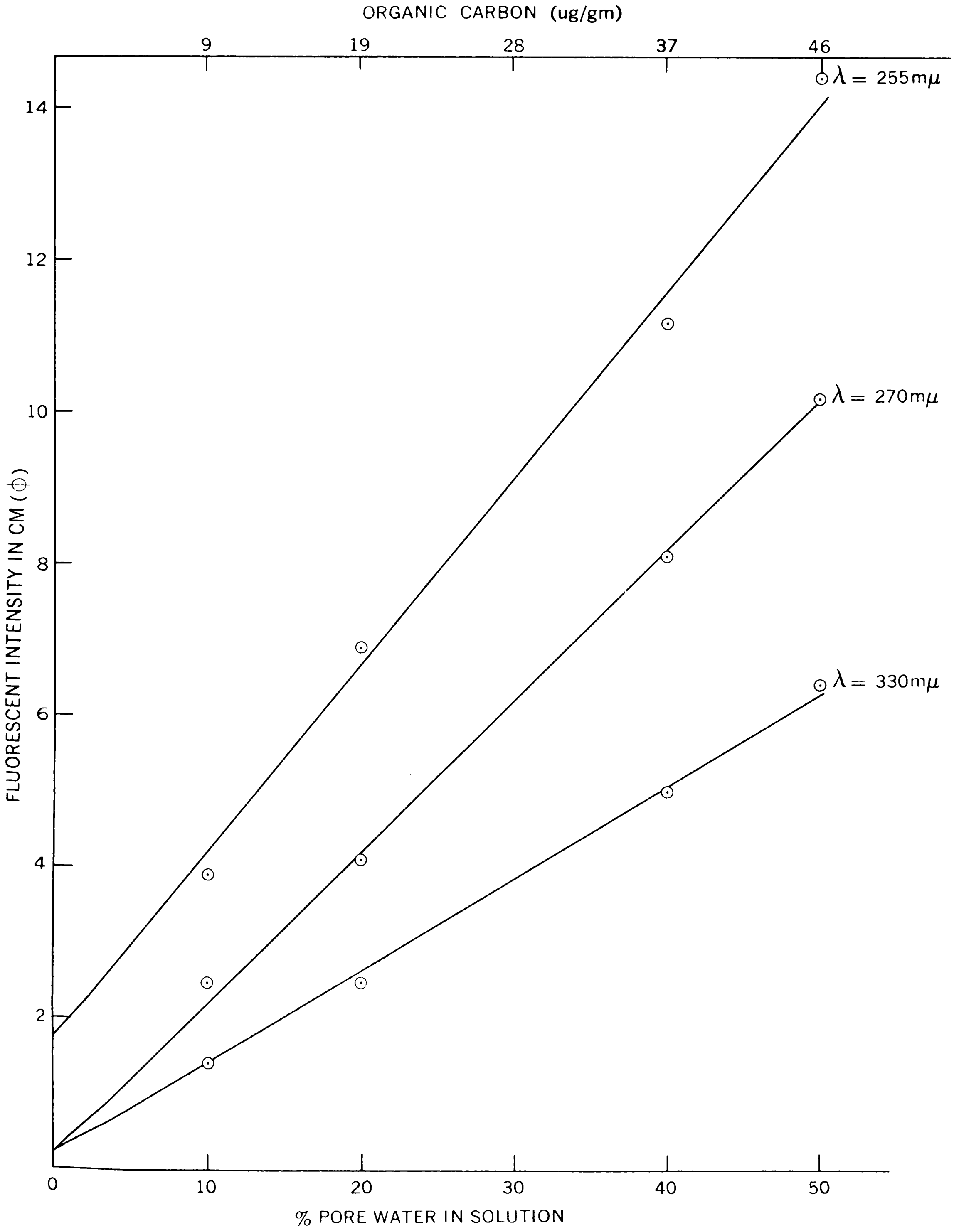
In the Cu^{++}-organic reactions (Figure 9) an inflection point occurs at 4 - 5 μg Cu^{++}/ml in solution. A comparison of the intensity of fluorescence at this wavelength, to the intensity of fluorescence of the standard curves show that approximately 29 percent of the organics from the original 50 percent pore water solution are still fluorescing. Thus 29/50ths or 58 percent of the organics in solution no longer fluoresce or fluoresce at a lower wavelength.

The quantity of fluorescing organic carbon dropped from 46 μg C/ml to 27 μg C/ml or 19 μg C/ml. At the second inflection point or apparent endpoint, 30 μg C/ml had stopped fluorescing or fluoresce at a lower wavelength.

Only 5 μg Cu^{++}/ml reacted with 19 μg/ml of organic carbon while it took three times as much Cu^{++} (15 μg/ml) to react with only 11 μg/ml more of the organic carbon. Probably, 66 percent of the organic molecules in Burke Lake pore water had functional groups capable of reacting with Cu^{++} but 42 percent of the organics had functional groups strongly reactable with Cu^{++}.

Figure 9 also gives information on the absorbance change of the copper-pore water solutions. The absorbance data show a possible reaction step function as Cu^{++}

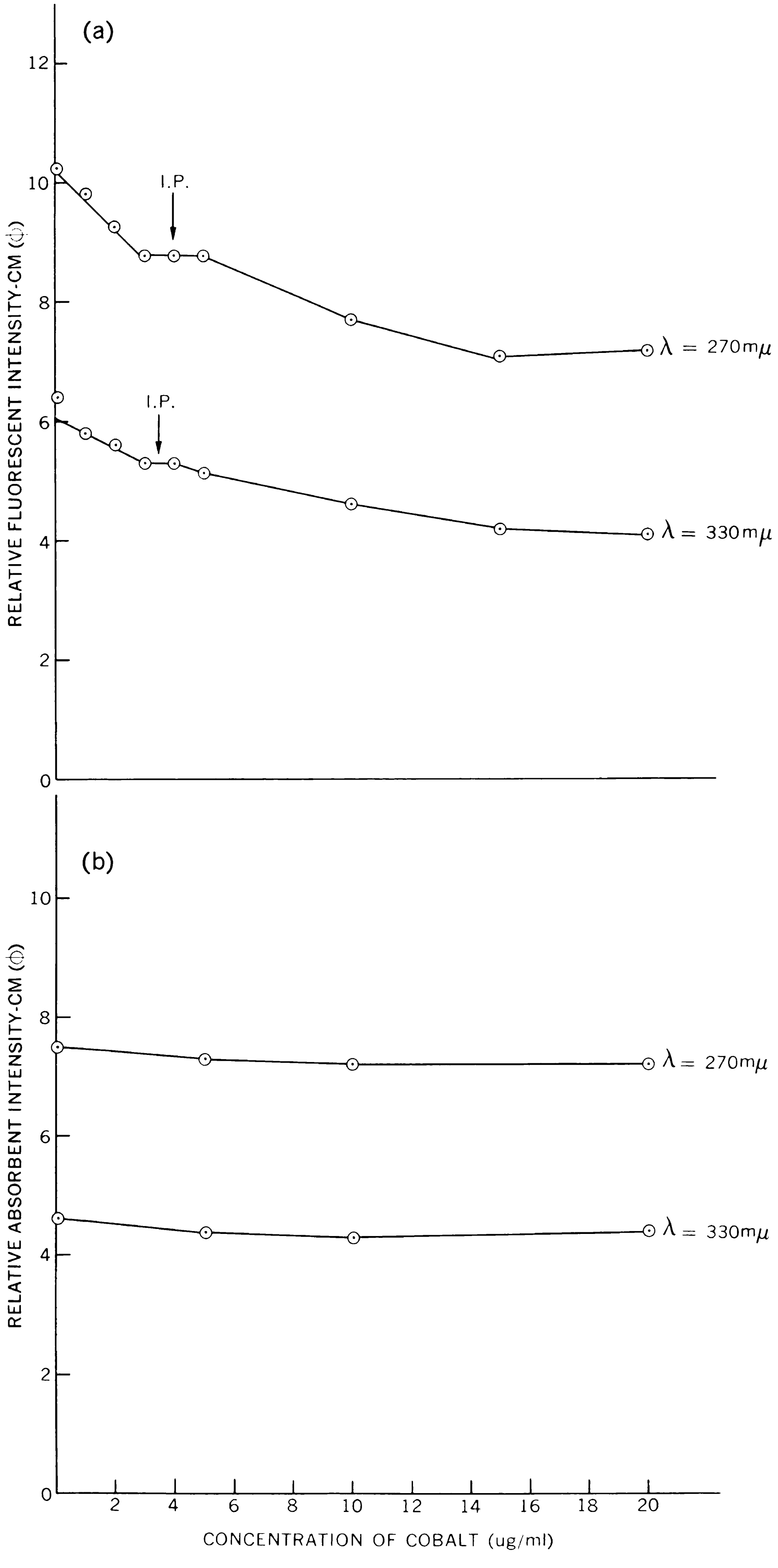
Figure 10. Standard organic fluorescent curves at specified wavelengths (λ). These lines are used to calculate the amount of organics still fluorescing in the heavy-metal, organic reactions. The peak height is measured on the fluorograms of the metal containing solutions. The percent pore water still fluorescing is found from these curves. (Data in Appendix, Table A6).


ORGANIC CARBON (ug/gm)
9
19
28
37
46
λ = 255mμ
λ = 270mμ
λ = 330mμ
FLUORESCENT INTENSITY IN CM (ϕ)
14
12
10
8
6
4
2
0
10
20
30
40
50
% PORE WATER IN SOLUTION

concentration increases. This step function reaction, especially the fluorescence step function, gives further evidence that Cu^{++} is being chelated by natural organics. Stevenson and Ardakani (1971) postulate that chelate reactions occur in a stepwise manner. Cupric ions appear to react with the natural organic compounds in a stepwise manner. This, together with former evidence (reversibility and pH dependency of the metal-organic reaction) reinforces the hypothesis that Cu^{++} is not only complexed but chelated, to a large degree, by natural organics in solution.

The fluorescence and absorbance changes of the pore water solutions to which Co^{++} are added (Figure 11) are different than Cu^{++} induced changes. A weak inflection in the fluorescence curve (Figure 11, curve a) occurs at 3 - 5 µg/ml of added Co^{++}, a broad endpoint at approximately 15 µg/ml of added Co^{++} and a decrease of slope occurs after each inflection. Unlike the copper-organic reaction only 6 µg/ml of organic carbon (13 percent) had reacted with Co^{++} at the inflection point and 27 µg/ml of organic carbon (29 percent) had reacted at the endpoint. In comparison to Cu^{++} then, Co^{++} reacts with fewer organic molecules and/or fewer functional sites. With an increase in Co^{++} concentration, fluorescence was slightly depressed but absorbance showed no change. This indicates that either weak bonds or no bonds are formed between the Co^{++} and the organic ligands. Co^{++} depresses the

Figure 11. Effect of Co^{++} concentration on organic fluorescence (a) and absorbance (b). A fluorescence endpoint (E.P.) appears at 15 µg/ml of Co^{++} while an inflection point (I.P.) in the slope of the curve occurs at 3 to 5 µg/ml Co^{++} added. (Data in Appendix, Table A7).


(a)
12
10
8
6
4
2
0
I.P.
I.P.
RELATIVE FLUORESCENT INTENSITY-CM (ϕ)
λ = 270mμ
λ = 330mμ
(b)
10
8
6
4
2
0
RELATIVE ABSORBENT INTENSITY-CM (ϕ)
λ = 270mμ
λ = 330mμ
2
4
6
8
10
12
14
16
18
20
CONCENTRATION OF COBALT (ug/ml)

fluorescence of the organic molecules weakly due to its closeness or physical adsorption to them and not reaction with them. Cobalt ion has a much lower tendency toward covalent bonding character than Cu^{++}. It is hypothesized that the association of Co^{++} with natural organic molecules in solution is by surface adsorption.

Formation of Metal-Organic Flocs

The effect of Cu^{++} and in comparison, Co^{++}-organic reactions on the solubility of the organic molecules in pore water was investigated by means of light dispersion (Holland, 1971). Colloids, like those in pore water solutions, disperse light to a greater or lesser degree depending on the size and number of the colloidal and flocculated particles. The effect of the heavy metals Cu^{++} and Co^{++} on the solubility, size and/or number of colloidal particles is demonstrated by the results of light scatter spectra shown in Figure 12. As Cu^{++} concentration increases an increase in light scatter results. This effect of Cu^{++} on the organics in solution is due to increased particle size (flocculation), an increase in the number of particles in solution, organic-metal colloid formation, and/or precipitation of suspended organics in solution. An endpoint in flocculation occurs at 13 µg Cu^{++}/ml (Figure 12). This agrees closely with the absorption and fluorescence data (Figure 9) in which an endpoint occurred at 15 µg Cu^{++}/ml. The chelation

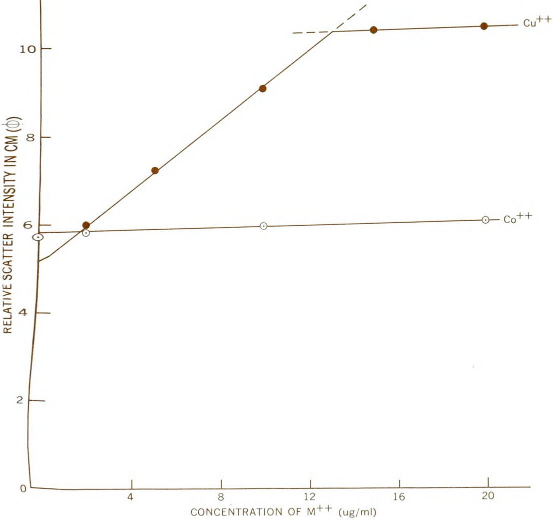


Figure 12. Comparison of Co^{++} and Cu^{++} effect on organic solubility in pore water using light scatter. Increased light scatter of solutions caused by formation of colloids or floccules yielding increased scatter. (Data in Appendix, Table A8).

of Cu^{++} by the organic molecules thus causes flocculation and will result in eventual precipitation of a metal-organic complex. Cobalt interaction with the organics (Figure 12) has no apparent affect on organic particle size and number at less than 20 µg/ml in these pore water solutions. Therefore, the Co^{++} does not cause flocculation and/or precipitation of an organic heavy-metal floc as readily as Cu^{++}. It does not strongly attract organic ligands and will not readily cause a flocculation. These data support the assumption that the less reactive Co^{++} is only surface adsorbed onto the organics while Cu^{++}, with its strong covalent bonding character, is chelated by the same organics and flocculates them. Since Co^{++} is not incorporated in the same manner as Cu^{++}, it does not cause organic flocculation with the possible exception of very high concentrations where ionic strength is the governing factor. It should be noted that the highest concentration of Cu^{++} used was only $3.2 \times 10^{-6}\underline{M}$ and Co^{++} was $3.3 \times 10^{-6}\underline{M}$. The increase in ionic strength due to these metals was negligible. Thus, if a heavy-metal interaction with soluble organic molecules is a strong chemical interaction as with Cu^{++}, and not merely a weaker interaction like physical adsorption as with Co^{++}, the metal ion can cause a precipitation of a metal organic floc at very dilute concentrations ($3.2 \times 10^{-6}\underline{M}$).

The consequence of the Cu^{++} organic reaction is a control on the dispersion of the heavy metal depending on the energy of the system. If heavy metal-organic interaction occurs in a turbulent system such as a river, it could have a mobilizing affect on the heavy metal due to the relatively low specific gravity of the organic precipitate or due to the solubility of some organic-metal complexes. Conversely, in a non-turbulent situation the reaction could have a demobilizing affect on the heavy metals. In any case, Cu^{++} readily reacts with organic molecules in solution, causes a flocculation of a metal organic complex, and eventually becomes incorporated in the bottom sediments.

Sediment-Heavy Metal Interactions

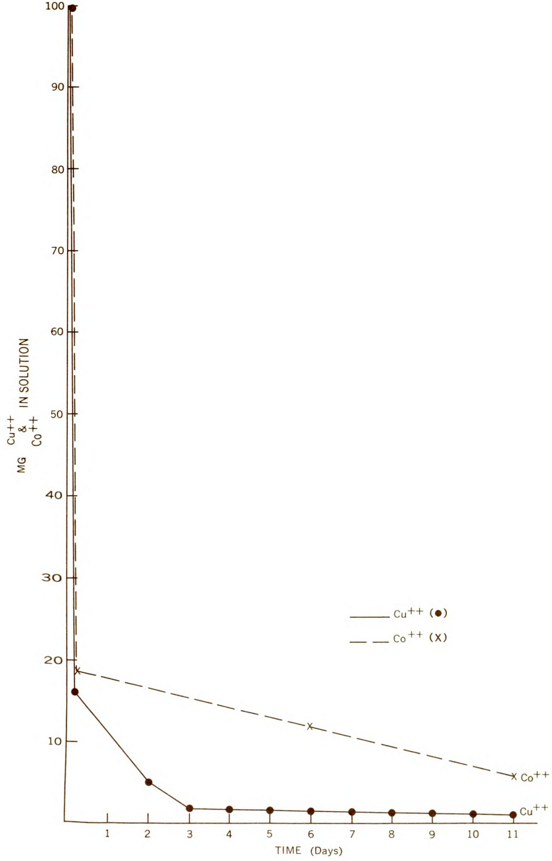
Rates of Reaction

The time dependency of Co^{++} and Cu^{++} uptake into sediment is demonstrated (Figure 13) by the two solutions most highly concentrated in their heavy metal (Methods II). The initial metal-sediment reaction rate could not be measured. During the first two hours approximately 85 percent of the metals are removed from solutions by chelation, adsorption, or inorganic precipitation. For the next 11 days each metal is slowly removed from solution in a probable diffusion dependent rate. Copper appears to react with and diffuse into the sediment at a faster rate than Co^{++}.

Cotton and Wilkinson (1968) have found that the rate of reaction for a given ion has little or no dependence on the identity of the ligands. The rate of reaction, then for Cu^{++} with the natural organic ligands would be approximately 10^8/sec and for Co^{++} 10^5/sec (Cotton and Wilkinson, 1968) which is the same rate of substitution of various aquo ions.

To determine the rate constants of Cu^{++} and Co^{++} uptake and diffusion into the sediment (Table 2) and the order of the reactions, first and second order rate equations were employed. In a first order reaction

Figure 13. Time dependence of Cu^{++} and Co^{++} reaction with organic rich bottom sediments. Up to 84.5 percent of the metal ions react immediately. After 11 days 94 percent of the Co^{++} and 99.5 percent of the Cu^{++} is no longer in solution. (Data in Appendix, Table A9).


100
90
80
70
60
50
40
30
20
10
MG Cu++ & Co++ IN SOLUTION
Cu++ (●)
Co++ (X)
Co++
Cu++
1
2
3
4
5
6
7
8
9
10
11
TIME (Days)

the rate depends on a single species reacting to form a product (Castellan, 1966) or on one species of an interacting pair which is much more concentrated than the other. Thus, the products are not involved in the rate law. If a is the original concentration of the reactants (A) and c the reactant concentration at time t, the first order rate reaction (Denbigh, 1968) is:

$$2.303 \log (c/a) = - Kt$$

The concentration of A decreases exponentially with time. A plot of log (c/a) versus t will be linear if the reaction is first order and the slope of the line will equal K, the rate constant.

The second order rate reaction (Castellan, 1966) is:

$$1/c = 1/a + Kt$$

A plot of 1/c versus t should yield a straight line if the reaction depends on the concentration of both species and is second order.

Both equations are related since the first equation is the limit of the second equation. In other words, in a second order reaction involving the concentration of two species, if one of the species becomes very dilute in comparison to the other, the rate will appear to be first order (Castellan, 1966; Denbigh, 1968).

When diffusion dependent uptake of Cu^{++} is plotted versus time, the 0.5 mg Cu^{++}, 5 mg Cu^{++} and 25 mg Cu^{++} solutions are first order and yield first order rate constants (Table 2). A first order plot of data from the

TABLE 2. Rates of diffusion dependent Cu^{++} and Co^{++} reaction with sediment. First and second order rate constants (day^{-1}) are shown (See Appendix - Figures A1 and A2 for the rate plots used to find the K's).

Cu (mg)/25 ml sediment	Order	K (day^{-1})
0.5	1	0.262
5.0	1	0.259
25.0	1	0.252
100.0	2	0.195
	Av. K =	0.242

Co (mg)/25 ml sediment	Order	K (day^{-1})
5.0	1	0.201
25.0	1	0.104
50.0	1	0.128
100.0	1	0.112
	Av. K =	0.136

100 mg solution is non-linear, but a second order plot (1/c versus time) yields a second order rate constant. The first order rate equation therefore applies only to dilute concentrations of Cu^{++}, though not enough data was taken to be certain. The rate of the diffusion dependent uptake of Co^{++} is only half as great as that of Cu^{++} (Table 2), but is a relatively constant first order reaction. Cupric ion maintains a nearly constant rate of uptake but unlike Co^{++}, Cu^{++} follows the second order rate law at high concentrations because the copper-organic diffusion reaction begins to depend not only on organic molecule concentration but also on copper concentration as predicted by theory (Castellan, 1966). The results in Table 2 show general trends and are not to be considered as repeatable in detail in another natural environment.

In summary, Cu^{++} diffuses approximately twice as rapidly as Co^{++} into Burke Lake sediments but both react rapidly at first as would be predicted (Cotton and Wilkinson, 1968). In the general model in Figure 1, then, this would mean that a high percentage of the heavy metals are immediately taken up by sediments but complete adsorption or uptake may be diffusion dependent and take several days.

Quantitative Aspects of Uptake

The metal uptake by bottom sediment is rapid and likely irreversible due to the strong organic and inorganic reactions with the sediment. The extent of the heavy metal-sediment reaction is important for a quantitative estimate of the pathways of a heavy metal. Thus, the stability constants of the heavy metal-organic reactions will be derived and the end point of reaction between sediments and a heavy metal enriched solution shown.

To describe the adsorption of ions from a liquid onto a solid surface, the equation developed by Freundlich (1926) is

$$\log (X/M) = (1/n) \log C + \log Q$$

where X/M = the quantity (meq/100 gm) of ions adsorbed per unit weight of adsorber (sediment in this case).

C = The equilibrium concentration (meq/l) of the adsorbate after adsorption has occurred (Cu^{++}, Co^{++} in this case)

Q = The equilibrium constant

n = A constant

A plot of log (X/M) versus log C should yield a straight line with an intercept of log (X/M) equal to log Q where log C = 0. A high value for Q would result from a high value of product or metal-complex versus the uncomplexed metal left in solution.

The result of a plot of log (X/M) versus log C for the Burke Lake pore water - Cu^{++} mixture is shown in Figure 14. The adsorption of Cu^{++} by pore water organics is a linear plot in the range of concentrations used and thus follows Freundlich theory. The total organic plot was derived for comparison of results to literature by using an assumed value of 640 for molecular weight of fulvic acid (Schnitzer, 1971) instead of 12, the molecular weight of carbon. The data do not intercept log C = 0 but the calculated log Q values of 5.10 for a copper-organic carbon complex and 5.38 for a hypothetical fulvic acid complex of copper were derived by least squares derivation (Appendix, Table A11, A12, and A13). This high stability constant shows that the organic-Cu complex is quite stable in natural pore water solutions and would be shown as irreversible in the generalized model (Figure 1).

When Cu^{++} was allowed to react with Burke Lake sediment a slightly different, but analagous result to the pore water reaction was attained (Figure 15). The Freundlich Isotherm is not linear through the range of Cu^{++} concentrations employed. A point of saturation or Cu-sediment equilibrium may have been reached where the inflection point occurs. Riley (1939) obtained a similar nonlinearity. The log Q value calculated by linear regression was 4.29 while the graphically derived log Q would be 1.55. Since the sediment apparently became saturated before the concentration of Cu^{++} reached

Figure 14. Freundlich Isotherms for the reaction of Cu^{++} with pore water from Burke Lake sediment. In one case the weight of carbon that reacted with a given concentration of Cu^{++} was used in the calculation of log Q. In the second case the weight of carbon in solution was multiplied by 1.92 and the ratio (X/M) calculated. (Data in Appendix, Table All).

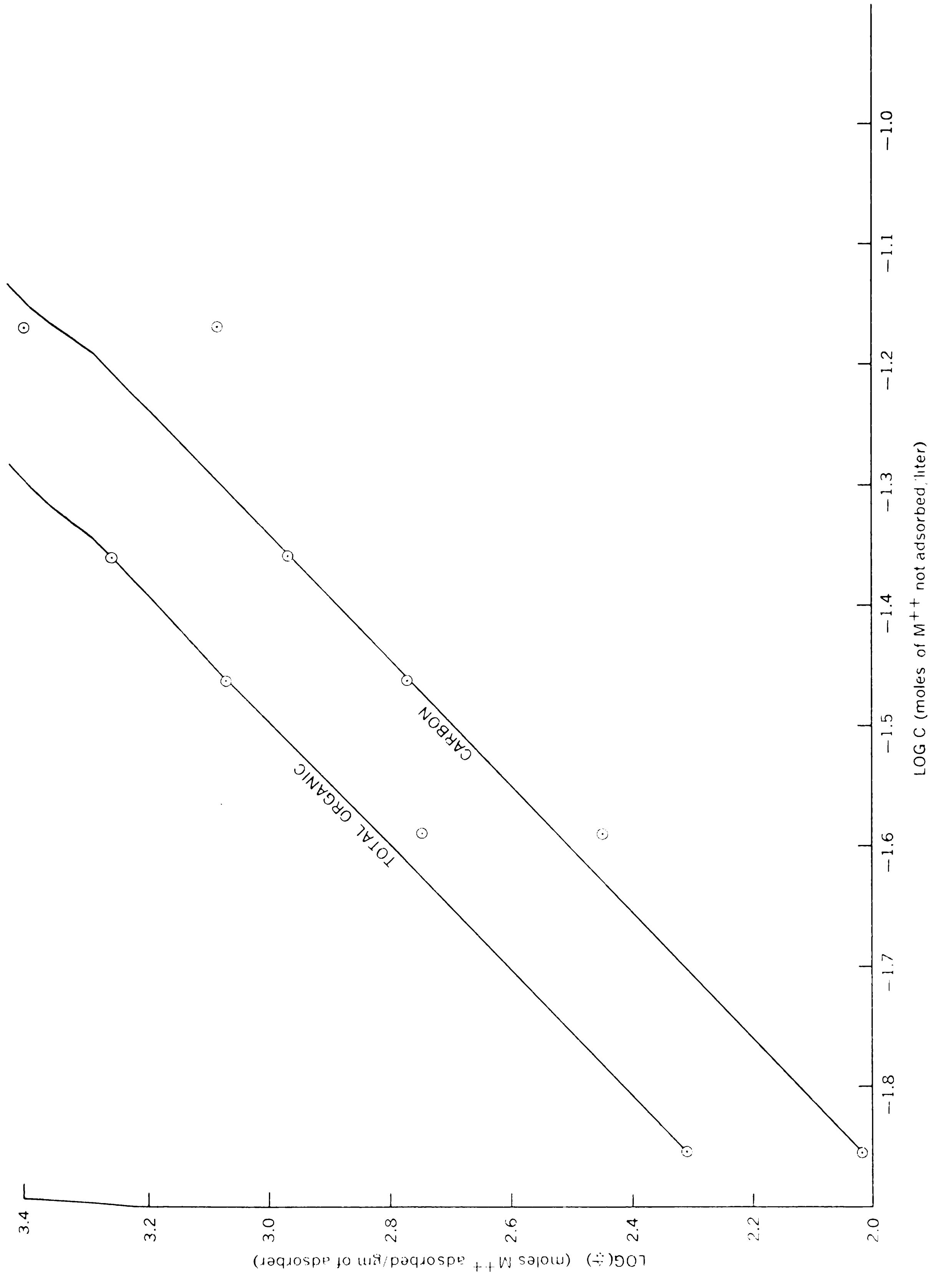
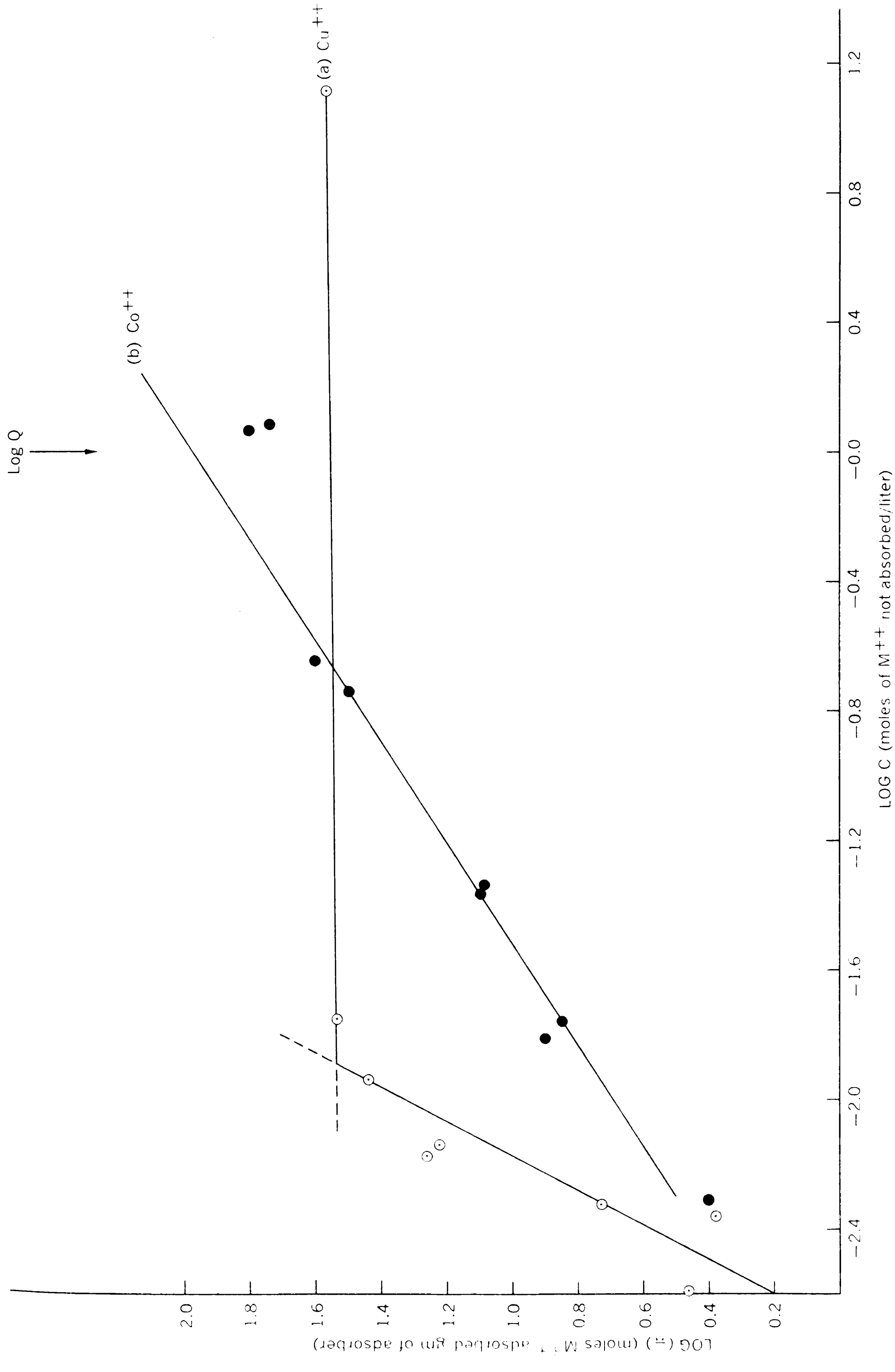

CARBON
TOTAL ORGANIC
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
LOG($\frac{x}{m}$) (moles M^{++} adsorbed/gm of adsorber)
−1.8
−1.7
−1.6
−1.5
−1.4
−1.3
−1.2
−1.1
−1.0
LOG C (moles of M^{++} not adsorbed/liter)

Figure 15. Freundlich Isotherms comparing the fit of data and the stability of reaction of Cu^{++} (o) and Co^{++} (●) with Burke Lake sediment. The dotted line connects the data but is represented by only one point and is therefore not necessarily a valid interpretation. (Data in Appendix, Table All).


(a) Cu^{++}
(b) Co^{++}
Log Q
LOG C (moles of M^{++} not absorbed/liter)
LOG (μ) (moles M^{++} adsorbed gm of adsorber)
−2.4
−2.0
−1.6
−1.2
−0.8
−0.4
−0.0
0.4
0.8
1.2
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

the intercept (log C = 0), the extrapolated log Q value of 4.29 is thought to be more realistic.

When Co^{++} was tested with the Burke Lake sediment under the same conditions as Cu^{++}, it followed the Freundlich Isotherm closely (Figure 15). Graphically it intercepts log C = 0 at approximately the same log (X/M) value as Cu^{++} but it is not as highly adsorbed as Cu^{++} initially. Cobalt concentrations do not reach a point where the adsorbant becomes saturated. Since the Freundlich Isotherm was derived for gas adsorption in a single layer onto a solid, then an aqueous ion such as Co^{++} that is only adsorbed onto a solid surface would closely approximate the isotherm. On the other hand, if the molecules also chemically react with the surface, an endpoint in the apparent high adsorption should occur as shown by the change of slope of the Cu^{++} curves. Thus, the hypothesis derived earlier that Co^{++} is associated with natural organics by surface adsorption while Cu^{++} reacts with the organic molecules is further reinforced.

Assuming that the log Q values for Co^{++} and Cu^{++} sediment interaction are time dependent, calculations for log Q were made for solutions with reaction times ranging from 2 hours to 11 days (Figure 16) (Methods II). Table 3 summarizes these results plus those log Q values attained in the two previous experiments. The log Q values increase with time and reach an apparent maximum after 11 days. The maximum log Q of 8.99 for Cu^{++} compares favorably with

TABLE 3. Equilibrium constants (log Q) for Cu^{++} and Co^{++} interactions with bottom sediments from Burke Lake. The calculated values of log Q were obtained by linear regression on the Cu data before the break in the curves. The graphic stability constants are extracted directly from the figures. The contact time of the metal ions with the sediment are given. (Data in Appendix, Tables All, A12, A13)

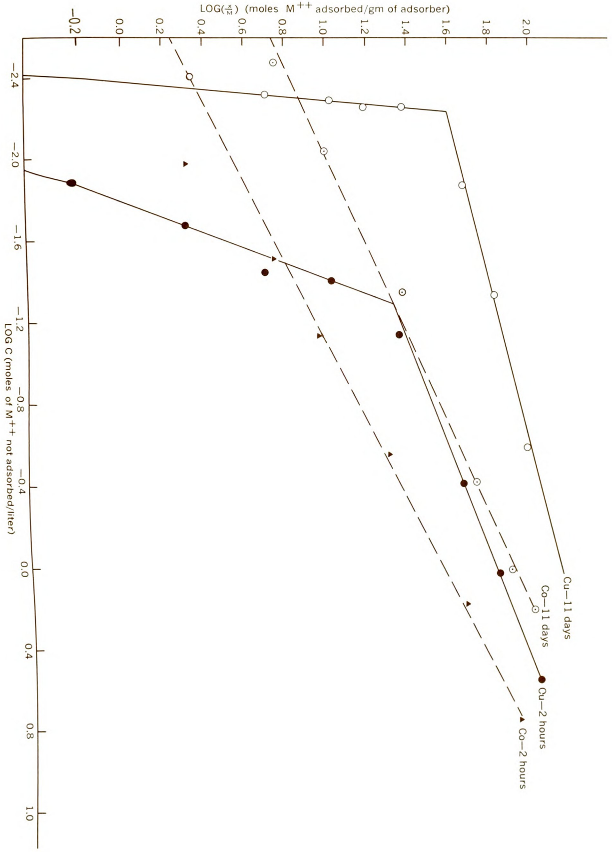
Figure	Adsorbant	Ion	Log Q values
16	pore water	Cu^{++}	5.10***
17	sediment	Cu^{++}	4.29**
17	sediment	Cu^{++}	1.55*
17	sediment	Co^{++}	1.78*
18	sediment (2 hours)	Co^{++}	1.63*
18	sediment (11 days)	Co^{++}	1.91*
18	sediment (2 hours)	Cu^{++}	4.59**
18	sediment (11 days)	Cu^{++}	8.99**

* 1. The value of Log Q is obtained by interpolation from the given figure

** 2. The Log Q value is calculated before any breaks in the curve by regression analysis.

*** 3. The Log Q of the pore water solution is calculated by regression analysis using the weight of organic carbon for the adsorbant weight.

Figure 16. Freundlich Isotherms comparing the reactions of Cu^{++} (———) and Co^{++} (- -) with Burke Lake sediment after two hours (●) and after 11 days (o). The log Q values for Cu^{++} were calculated using the slope of the solid lines before the break instead of where they intersected LOG C = 0. (Data in Appendix, Tables A9, A13).


LOG($\frac{x}{M}$) (moles M^{++} adsorbed/gm of adsorber)
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
-2.4
-2.0
-1.6
-1.2
-0.8
-0.4
0.0
0.4
0.8
1.0
LOG C (moles of M++ not adsorbed/liter)
Cu—11 days
Co—11 days
Cu—2 hours
Co—2 hours

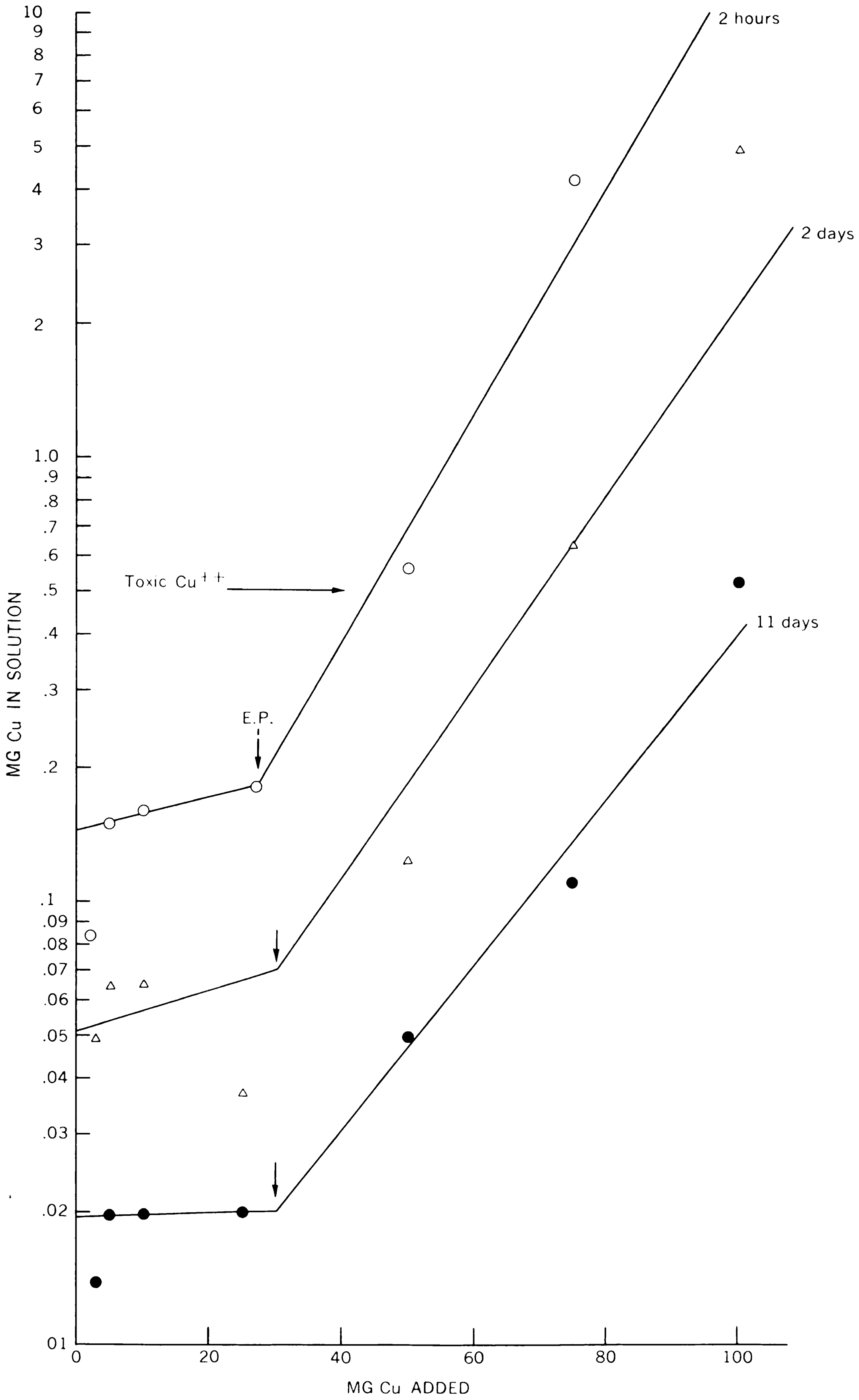
a log K value of 8.69 obtained by Schnitzer and Skinner (1966) who used fulvic acid extracts from soil as the adsorbent. The log Q values of Cu^{++} and Co^{++} are much less if the heavy metal has been in contact with the sediment for a short time and a steady state is not reached.

Brief and variable metal-sediment contact time is probably more the case in nature because fresh solutions and fine grained sediments are continually passing over the sediment. Pore water-heavy metal contact is not so variable and the log Q of 5.1 for Cu^{++}-pore water is a viable estimate to be used in a model which represents a variety of non-equilibrium situations in natural aqueous systems. Cu^{++} was found to have higher stability constants than Co^{++}, as expected, but still, the constants for both are sufficiently high to show that both will nearly quantitatively react with the bottom sediments and remain there. In the model then, Cu^{++} and Co^{++} have high enough stability constants with the bottom sediments that the overall trend is a quantitative uptake by the sediments.

Endpoints of Heavy Metal Reaction with Sediments

An endpoint of metal-sediment adsorption is determined for periods of metal-sediment contact (Figure 17). The endpoints are shown at 35 mg Cu added to 100 ml solution plus 25 g sediment or a concentration of 8070 µg Cu/gm dry sediment. (Methods II). With time the endpoint

Figure 17. End points for Cu^{++} reaction with Burke Lake sediment through time. The breaks in the curves are the approximate endpoints. At 0.5 mg Cu in solution, the Cu is toxic to small aquatic organisms. (Data in Appendix, Table A9).

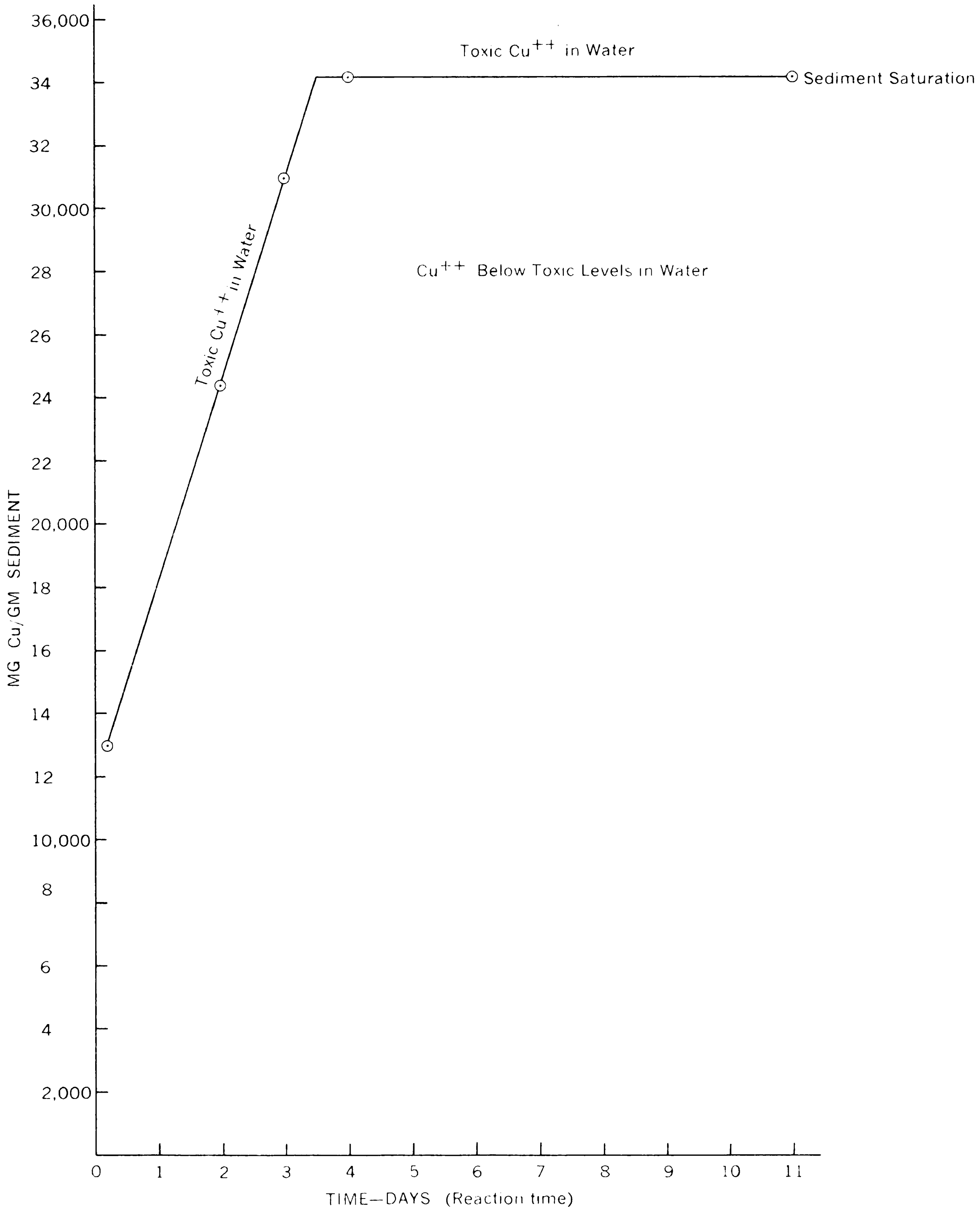

10
9
8
7
6
5
4
3
2
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.09
.08
.07
.06
.05
.04
.03
.02
01
MG Cu IN SOLUTION
0
20
40
60
80
100
MG Cu ADDED
2 hours
2 days
11 days
Toxic Cu^{++}
E.P.

remains the same but the total Cu^{++} in solution decreases. If at least 5 µg Cu/gm remain in solution, then, the solution is toxic to most aquatic organisms (Riley, 1939; Federal Water Pollution Control Association, 1968; Upchurch, 1973). As shown in Figure 17, if less than 40 mg Cu are in the sediment or 12,900 µg Cu/gm dry sediment is present the solution is immediately detoxified. More adsorption of Cu^{++} through time causes detoxification of solutions containing greater and greater concentrations of copper as will be demonstrated in detail later. The endpoints in Figure 17 show a trend which can be extrapolated in general to other environments but the actual numbers are good only under the given set of conditions (Methods II). In general, Figure 17 demonstrates that sediments can quantitatively remove high concentrations of Cu^{++} from solution. Then even after apparent sediment saturation with Cu^{++}, the Cu will be adsorbed even though the Cu^{++} concentration in solution is very low.

When Cu^{++} was let stand for nine days with Houghton Lake sediments in the same manner as with the Burke Lake sediments, an endpoint occured at 7,500 µg Cu/gm in the sediments (Cline, In Press). This comparatively smaller adsorption capacity of Houghton Lake sediment is likely a result of the larger average grain size, the greater quantity of inert sand, and the smaller percentage of organics (Table 1).

Figure 18 shows the quantity of Cu that must be in Burke Lake sediment as residence time increases, before toxic levels (5 µg/ml) of Cu are reached in solution. In a dynamic environment (2 hours residence time) containing organic rich sediments, more than 12,000 µg Cu/gm can accumulate in the sediments before toxic amounts of Cu^{++} will remain in solution (Figure 18). In a stagnant situation with greater than 4 days residence time, up to 34,000 µg Cu/gm can be bound in the sediment without toxic levels of Cu^{++} escaping back into solution. Mackenthun and Cooley (1952) exposed a variety of bottom-dwelling animals to bottom muds from Lake Monona, Wisconsin containing known quantities of precipitated $CuSO_4$. Their tests indicate that the toxic effects of Cu become apparent around 9000 µg Cu/gm sediment. This figure compares, in general, with endpoints for copper adsorption in the dynamic, non-equilibrium environment of the Burke Lake sediment (8070 µg/ml) and the Houghton Lake sediment endpoint of 7,500 µg Cu/gm. Thus, in the generalized model (Figure 1), heavy metals react rapidly and quantitatively with bottom sediments resulting in detoxified aquatic solutions.

Figure 18. Concentration of Cu^{++} necessary in Burke Lake sediment before toxic concentrations remain in solution as a function of reaction time. Toxic Cu^{++} is considered to be 5 µg/ml in solution.


Toxic Cu++ in Water
Sediment Saturation
Toxic Cu++ in Water
Cu++ Below Toxic Levels in Water
MG Cu/GM SEDIMENT
36,000
34
32
30,000
28
26
24
22
20,000
18
16
14
12
10,000
8
6
4
2,000
0
1
2
3
4
5
6
7
8
9
10
11
TIME—DAYS (Reaction time)

Pathways of Cu^{++} Within the Sediment

After only two hours of Cu^{++}-sediment contact, the Cu^{++} was approximately 88 percent readily exchangeable as KCl exchangeable, surface adsorbed; EDTA extractable organic complexes; and pore water phases of Cu (Table 4) (Methods II). The KCl extractions removed 27 percent of the sediment bound Cu^{++} showing that a high percentage was only sufrace adsorbed onto organic and inorganic sites. The EDTA extraction removed 60 percent of the total sediment bound Cu^{++}, showing that Cu^{++} was complexed by organic ligands in the sediment. These data indicate in general that the initial Cu^{++}-sediment reactions are adsorption and complexation. These percentages are trends and can only approximate results under different conditions.

TABLE 4. Change of Phase of Cu in Houghton Lake Sediment with Time. (See Appendix, Table A14, for raw data and estimate of error.)

Phases	% Cu^{++} after 2 hours	% Cu^{++} after 9 days
Pore Water	2.8	0.2
EDTA extractable-organic complex	60.0	33.0
KCl exchangeable-surface adsorbed	27.0	5.0
$KMnO_4$ digestible-precipitated Cu	11.8	61.0

The original quantity of Cu^{++} bound in pore water, as surface adsorbed, complexed, and precipitated Cu^{++}, continuously changes with time (Table 4). The precipitated, $KMnO_4$ digestible Cu^{++} increased from 9.8 percent to 66.9 percent of the total sediment Cu^{++} in nine days while the other forms of Cu^{++} all decreased in quantity. The difference in each of the four extracted forms of Cu^{++} is a difference in the amount of energy of the Cu^{++} sediment bonds. In pore water, Cu^{++} is in a soluble and/or colloidal form as a result of sediment exchange and organic complexes that are soluble or colloidal. The Cu^{++} defined as surface adsorbed is the weakly bound Cu^{++}; complexed Cu^{++} is fairly strongly bound. Thus, the forms of Cu^{++} change from initially weaker bonds of adsorption and chelation to strong bonds of precipitates through time. After the heavy metal is taken into the sediments, as shown in the generalized model (Figure 1), the percentage of it that becomes tightly bound increases with time and/or burial.

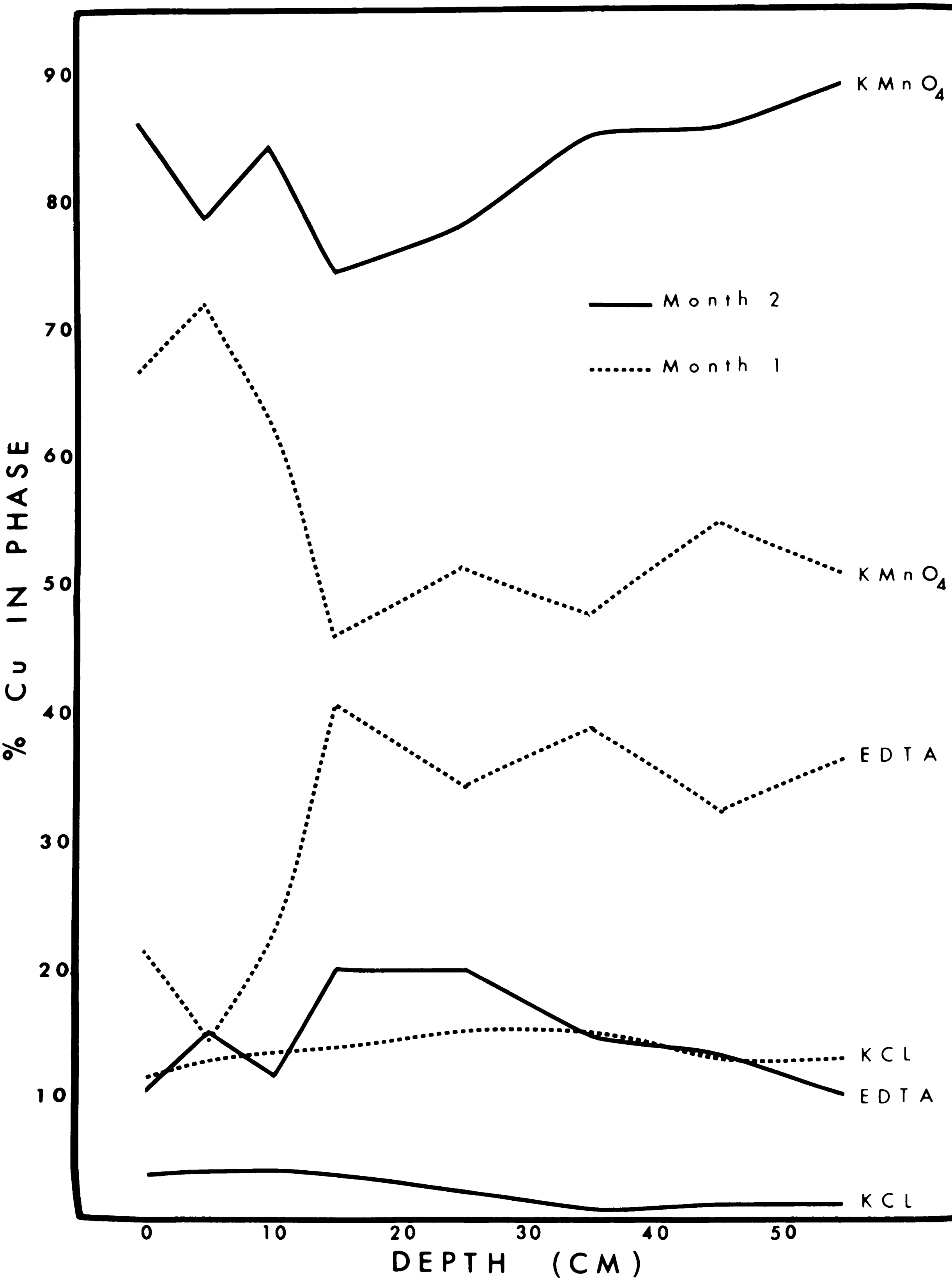
Through time the changing chemistry of the sediment due to bacterial action can cause a phase shift of heavy metals and possibly a cycling within the sediment column. To test for cycling of a heavy metal in the sediment, Cline and Upchurch (1973) mixed Cu^{++} (as $CuCl_2$) with organic rich sediment from Burke Lake, homogenized the solution, poured it into glass tubes, corked them on the bottom, inserted them into the sediment for 1 week to 3 months, pulled them as a function of time, and analyzed them with depth. Cline and Upchurch (1973) showed that there was a rapid upward migration of Cu. After one week they found little difference in the Cu concentration throughout the sediment column, but by the end of four weeks, the Cu was highly concentrated in the top of the core as compared to the bottom. It was suggested that the observed migration could be a result of compaction and dewatering, directional ion migration (diffusion), or decay of organics by bacteria and release of complexed copper.

Three different mechanisms for the rapid migration of copper in the tubes were suggested: (1) In tests on sea foam it was shown by Wallace (personal communication, 1973), that bubble surfaces are extremely reactive. Trace constituents such as heavy metals, phosphates and nitrates are concentrated many fold by the bubble surfaces. Therefore, it seems that the gases released by bacteria to form bubbles in sediment could act as a transport mechanism for heavy metals within the sediment. (2) There are bacteria that methylate mercury and cause its mobilization (Wood _et_ _al_., 1968). No other heavy metals form a dimethyl or methyl gas but maybe gaseous organic chelates are formed. (3) Szalay and Szilazi (1968) found that Se and As migrate as hydrogen-metal gases in the sediment and undergo ion exchange with the iron in humates in the upper few cm of sediment, become sulfide precipitates and remain in the top layer of sediments. A similar type of gaseous migration may happen with other heavy metals although no other metals are known to form the hydrogen-metal gas.

To determine the phases in which the Cu is found and possibly identify the transport mechanism, Cline and Upchurch (1973) chemically partitioned cores taken after one and two months. Figure 19 compares percent Cu in the KCl exchangeable adsorbed form, the EDTA extractable complexed form, and the precipitated form-$KMnO_4$ digestion (Cline and Upchurch, 1973). The quantity of Cu in pore water is insignificant and not included. Month 1 core shows an enrichment of the $KMnO_4$ digested phase of Cu in the upper 10 cm of the core. This indicates that as the copper migrates upward, it is reincorporated into the sediment (likely as sulfide, oxide, organic complex or carbonate) when it reaches the biologically active oxidized portion of the sediment.

A comparison of the extractions on the core from month 2 to the core from month 1 (Figure 19) show that the residual, $KMnO_4$ extracted, form or Cu increases at the expense of the less strongly bound adsorbed and complexed Cu with time. Thus, as found previously, the percentage of total Cu in the sediment that becomes tightly bound increases. In the sediment of the generalized model, the results of the Cu interactions and cycling

Figure 19. Comparison of Cu phases within a sediment column and with time of cores at months 1 and 2. The time comparison shows the change in percent of Cu phase through 60 cm of core. (From Cline and Upchurch, 1973).



90
80
70
60
50
40
30
20
10
% Cu IN PHASE
0
10
20
30
40
50
DEPTH (CM)
Month 2
Month 1
KMnO$_4$
KMnO$_4$
EDTA
KCL
EDTA
KCL

indicate a tendency of a heavy metal such as Cu to remain at the sediment-water interface, and become more tightly bound at the interface through time.

TESTS OF THE LABORATORY RESULTS IN NATURAL ENVIRONMENTS

Houghton Lake Copper Study

To test the previous laboratory results and conclusions concerning Cu^{++}-sediment interactions, Houghton Lake, a real environment containing Cu, was used as a sampling site (Figure 20). The south and southwest shores of the lake have been treated for swimmers itch with $CuSO_4$ since 1948 (Michigan Department of Natural Resources, 1971). In 1971, 13,620 kg of $CuSO_4$ was dumped into the lake (Michigan Department of Natural Resources, personal communication, 1972). The south and lower west shores of the lake are directly contaminated by copper as $CuSO_4$.

The copper distribution with depth of sediment was investigated by coring the bottom sediments (Figure 20) using a one meter piston corer. The cores were frozen with dry ice, immediately returned to the lab and sectioned. The sections were stored in glass jars until they were analyzed for Cu and organic carbon. The samples were digested in nitric acid (Environmental Protection Agency, 1971) and the solutions analyzed with a Perkin Elmer 303 atomic absorption spectrophotometer. The

error of the total method of digestion, sample handling and analysis is an average of ± 5%. Organic carbon was measured on an Envirotech carbon analyser (variability = ± 2 µg/gm or 2%, whichever is greater). Size analyses were made with a settling tube for the coarse particles and a Coulter Counter (after sonic disagregation) for the fine particles (repeatability is ± 1%). The resulting "size" of a sediment is an average.

Concentrations as high as 67 ± 3. µg Cu/gm sediment (dry weight) were found in the upper strata of sediment and in most cores there was a rapid decrease with a copper concentration as low as 5 ± 0.5 µg/gm at a depth of 50 to 80 cm (Table 5). In agreement with the previous laboratory finding and projected results in a natural system, the upper few centimeters of sediment were often found to be enriched with copper even though copper has been dumped into the lake for 26 years and rapid sedimentation may have been occurring in some of the sample locations (i.e. station 7) (Novi, personal communication, 1971). Organic carbon and sediment grain size were found to closely correlate with high Cu concentrations (Table 5). Thus, as predicted from the laboratory data, the distribution and concentrations of the heavy metal Cu seems to depend on organic carbon concentration and sediment texture.

TABLE 5. Copper concentrations, percent organic carbon (O.C.), and size with decreasing depth in eight cores taken in Houghton Lake. The sediment sizes were not all measured but are quite similar within each core.

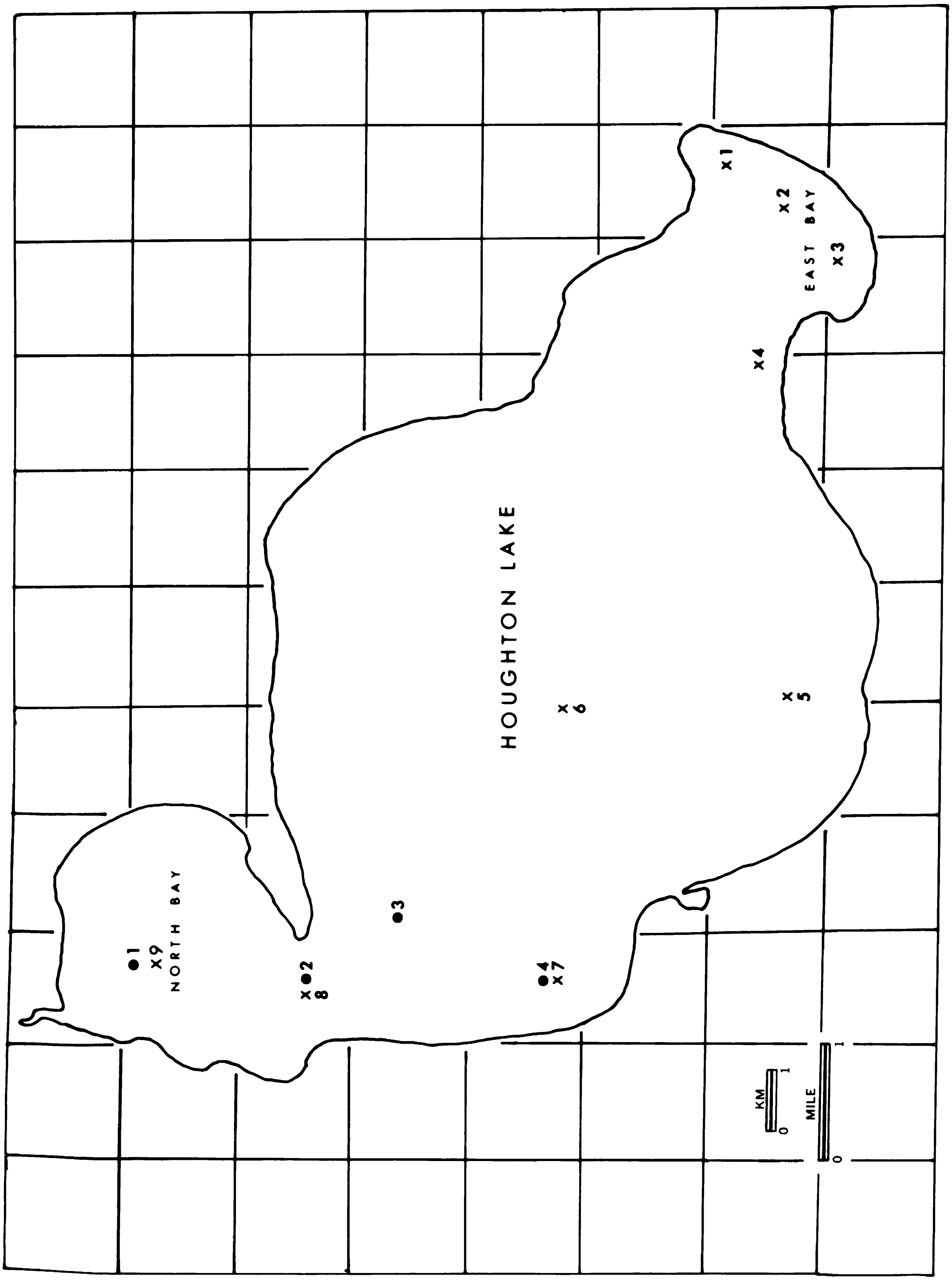
T = top of core.

Sample	Description	Length (cm) section	Length (cm) core	μg Cu/gm Sediment	% O.C.	Mean Size (μ)
1-4 T	Clean sand	5.0	0.0-5.0	6.4	0.18	200
1-3	Clean sand	5.0	5.0-10.0	4.5	0.10	---
2-5 T	Dirty sand	7.5	0.0-7.5	5.7	1.10	250
2-4	Dirty clay	15.0	7.5-22.5	32.0	1.70	---
3-7 T	Clean sand	7.5	0.0-7.5	1.6	0.08	250
4-4 T	Clean sand	7.5	0.0-7.5	16.0	0.13	250
4-3	Clean sand	15.0	7.5-22.5	3.2	0.10	---
4-2	Dirty sand	15.0	22.5-37.5	4.5	0.06	---
5-4 T	Organic clay	7.5	0.0-7.5	14.0	32.7	3-4
5-3	Organic clay	7.5	7.5-15.0	26.0	28.9	---
5-2	Organic clay	30.0	15.0-45.0	6.8	28.8	---
5-1	Organic clay	30.0	45.0-75.0	5.9	27.0	---
6-5 T	Organic clay	7.5	0.0-7.5	28.0	27.0	3-4
6-4	Organic clay	7.5	7.5-15.0	8.6	25.1	---
6-3	Organic clay	15.0	15.0-30.0	3.3	15.0	---
6-2	Organic clay	15.0	30.0-45.0	5.1	14.0	---
6-1	Organic clay	30.0	45.0-75.0	3.4	12.6	---
7-5 T	Organic clay	10.0	0.0-10.0	16.0	11.4	3-4
7-4	Organic clay	10.0	10.0-20.0	68.0	22.5	---
7-3	Organic clay	15.0	20.0-35.0	25.0	21.3	---
7-2	Organic clay	15.0	35.0-50.0	11.0	22.6	---
7-1	Organic clay	30.0	50.0-80.0	9.6	15.9	---
8-4 T	Clean clay	5.0	0.0-5.0	33.0	0.16	4-5
8-3	Clean clay	5.0	5.0-10.0	35.0	0.55	---

The cation exchange capacity (CEC) of Houghton Lake sediment was evaluated before and after removal of the organics by H_2O_2 digestion to find if indeed the sediment organic matter might contribute to the high copper concentration in the organic rich area. The CEC in meq/100 gm sediment was determined in triplicate by washing with Ca^{++} as $CaCl_2$ followed by Mg^{++} as $MgCl_2$ (Mortland, M.M., personal communication, 1971). The average CEC of the natural sediment is 22.0 ± 0.5 meq/100 gm. The average CEC of the same sediment after H_2O_2 digestion is 7.0 ± 0.5. The sediment is 19 percent organic matter by weight yet the decrease in the CEC of the sediment due to the organic removal is 65 percent. The overall exchange capacity of the sediment is low due to presence of inert substances, but a high percentage of that exchange capacity is due to naturally occurring organic compounds. Thus organic matter contributes to sediment cation adsorption and in this case is the major metal adsorbant in the sediment.

Eighteen water samples at nine sample sites (x) were collected during the fall of the year (Figure 20). Four samples at four stations were collected in March (●) (Figure 20). The samples were collected during one day when the temperature was 11°C. The wind was 3 m/sec and the pH of the water was 7.8 ± 0.1. The samples were collected at the sediment-water interface and at the water surface at each location by divers. Half of each sample

Figure 20. Diagram (in 2.604 sq. Km or 1 sq. mi.) of Houghton Lake showing the eight coring locations (x), nine fall water sample locations (x), and the four winter water sample sites (●).


HOUGHTON LAKE
NORTH BAY
EAST BAY
x 1
x 2
x 3
x 4
x 5
x 6
x 7
x 8
x 9
● 1
● 2
● 3
● 4
KM
0
1
MILE
0
1

was digested with $KMnO_4$ to release Cu^{++} from organic, particulate material. All samples were analyzed by atomic absorption spectrophotometry (sensitivity = ± 0.02 µg Cu/ml).

The concentrations of Cu in the water varied from 0.02 to 0.75 µg/ml. There was no significant variation in Cu concentration between the surface and bottom samples. As would be expected, the average concentration near the area of high loading (the southern and western shorelines) averaged 0.24 µg Cu/ml while the northern portions of the lake averaged 0.06 µg Cu/ml. A portion of the nondigested samples was filtered with Whatman #1 filter paper to remove large particulate matter. Copper concentrations decreased from an average 0.24 µg /ml in the solutions to an average 0.07 µg/ml in the filtrates. Millipore filtration (0.45 µ) of the same water samples removed all of the detectable Cu from every water sample. This indicates that the Cu was associated totally with particulate matter and colloids but to the highest degree with the large particulate matter.

Mobilization of organic particulate matter readily occurs in this large shallow unprotected lake due to wave action. Since copper is highly associated with the particulate matter, it also is mobilized by the particulate matter. As would be predicted from the derived laboratory results, the heavy metal, copper, is associated in solution with particulate matter, and is thus mobilized as a part of low specific gravity floccules.

Mobility and solubility in trace constituents is often affected by oxidizing or reducing conditions (Ruttner, 1962). To find if these conditions affected copper mobility, water samples were collected during March under 0.6 meters of ice at sites where the water column was either reducing (oxygen < 2 µgO/ml) or oxidizing. There was no disturbance of the sediment due to wave action and suspended particulate matter was at a minimum. The water sampling sites (●) (Figure 20) consisted of both aerobic (samples 2 and 3) and anaerobic (samples 1 and 4) environments. The oxygen concentrations in the water samples ranged from 1.76 mg/l at 1 (●) and 4 (●) to 8.35 at 2 (●) to 13.28 mg/l at 3 (●). Samples 1 (●) and 4 (●) smelled of H_2S upon collection. The water pH ranged from 7.3 at the anaerobic sites to 7.7 at the aerobic sites. The concentration of copper in the water at all of these sites was 0.00 µg/ml. Neither aerobic or anaerobic conditions in the water seemed to have an affect on Cu mobility in the water solution. Since anaerobic conditions do not have an apparent affect on Cu mobility in Houghton Lake water, then another factor must be governing the Cu mobility. Wave action was present during the Fall collection of water samples; but during the winter collection it was absent, and had been for a long time. Wave action, which causes intense bottom stirring in Houghton Lake and mobilizes organic particulate matter

(Riley, 1939) and associated Cu is apparently the major factor causing Cu mobilization in Houghton Lake.

The data show that the Cu in Houghton Lake is (1) highly associated with low specific gravity organic floccules and other particulate matter in the water, (2) associated with the sediment organic matter, (3) the most highly concentrated in the upper few centimeters of sediment and (4) quantitatively removed from solution by sediment reaction. These trends of Cu-organic reactions and pathways in the natural environment could be surmised from the previous laboratory results. The laboratory data and resulting conclusions are thus validated in a natural environment and could be developed into a more specific model of Cu pathways in sediments.

Related Studies from Literature

Riley (1939) did a survey on copper in three Connecticut lakes. He found that copper mobility was affected most by seasonal change when a high amount of bottom stirring occurred. By means of a series of multiple correlations he listed five factors that affect the copper content of lake waters: (1) precipitation, which lowers the copper content of lake waters; (2) sedimentation, the removal of copper from solution by adsorption on organic matter; (3) regeneration from the mud; (4) liberation of copper from littoral plants when they die and uptake when growing; (5) liberation of copper in the autumn by the decomposition of vegetation surrounding the lake.

Orzek, et al. (1972) collected sediment samples at Rochester Harbor, New York, down river from several sources of heavy metals. They analyzed the samples for organic and inorganic bound Cu, Co, Zn, Cr, and Na. The heavy metals Cu and Zn increased in concentration on the organic fraction of sediment as the percent organics increased in the sediment while the inorganic bound heavy metals remained constant. This study further substantiates the laboratory data by giving conclusive evidence that organic compounds govern the chemistry and physical mobility of heavy metals.

An accumulation of metals in the upper strata of sediment and a correlation of heavy metal concentrations to an increase in organic carbon was found in two studies. In Lake Michigan, Shimp et al. (1972) found an increase of heavy metals, such as Pb, Cu, and Hg in the upper strata of sediment. A rapid increase in concentration usually occurs in the upper 10 cm. The increase correlated with an increase of percent organic carbon. Walters et al. (1971) studied sediment cores from Western Lake Erie and collected water samples at the same locations. They analyzed the water for basic parameters such as turbidity, pH, alkalinity, specific conductance, and analyzed the cores for mercury. High mercury values were found in stagnant water zones having high organic carbon concentrations and were attributed to deposition of mercury-laden organic sediment. The mercury concentration in cores invariably decreased exponentially with depth. It was suggested that the increase of mercury in the surface sediments was due in part to an upward diffusion of mercury.

In the St. Clair River, Cline _et_ _al_. (1973) experimented with mercury laden sediments. Substantial amounts of the mercury were mobilized and transported either as soluble metal organic complexes or low specific gravity organic flocs at pH levels at which the mercury would otherwise be insoluble. The study showed that the heavy metal, mercury, quickly disappeared from solution in the St. Clair River, yet it was distributed far downstream in the sediment. The mercury load within the organic fraction of the sediment increased with an increase in mercury concentration while the mercury load in the inorganic fraction remained nearly constant. The mercury concentrations in the sediment were therefore directly correlated with the organic fraction of the sediment. Organic compounds thus play a prominent role in the reaction pathways of the heavy metal, mercury, in a natural water system.

The studies in the laboratory generated data could be used to predict the results of each of these studies; the heavy metal association with organic carbon,

high accumulations of the metals in the sediment, and marked upward increase in heavy metal concentrations in the sediment and high accumulation of the heavy metals in organic rich sediments. Since the laboratory results are substantiated by each individual study, a more specific model than the generalized model (Figure 1) is suggested.

SUMMARY AND CONCLUSIONS

A hypothetical model was constructed showing possible copper pathways through the aquatic environment. Copper exists in solution and as part of the sediment in many different phases. Partitioning of copper between these phases depends on changing environmental factors and the reactivity of the specific metal ion with organic and inorganic substances. In the lab different environmental conditions were simulated in order to trace copper-pathways in the subaquatic environment.

Sediments from Burke Lake were used to develop the hypothetical model in the lab. Burke Lake contains highly reactive organic rich sediment. The high reactivity is due to the high organic carbon content and small grain size (4 to 6 μ) of the sediments. The role that organic matter plays in the heavy metal equilibria was investigated with this sediment and its pore waters.

The solubility of organics is affected by pH, ionic strength, and heavy metal cations. The affect that these parameters have on the organics in pore water was investigated with a computer centered spectrofluorimeter-spectrophotometer. The organics react to an increase in ionic strength by showing an increase in light scatter emissions indicating a flocculation and precipitation. This precipitation can be caused by univalent ions but generally divalent ions and especially some heavy metal ions are very efficient due to their reaction with the organic molecules. An increase in pH or OH^- readily causes an increase in light scatter or number of particles/particle size and flocculation of an organic floc. Thus, the chemistry of soluble organic compounds is affected strongly by the inorganic substances in solution.

As heavy metals enter the aquatic environment, they react rapidly with bottom sediments and substances in solution. The capacity of the heavy metal ions to react with organics depends on the size, charge, electronegativity, and configuration of the metal ion. In a general agreement with the EDTA -M^{++} order of stability, the following order of reactivity of three heavy metals with natural organics was established: Hg^{++}, Cu^{++}, Co^{++} at less concentrations than 20 µg/ml. Thus, in developing the hypothetical model, Hg^{++} and Cu^{++} are considered strong reactors, and Co^{++} a weak reactor with bottom sediments and organic rich pore water.

Reactions of Cu^{++} and Co^{++} with organics in organic rich pore water from Burke Lake were studied by means of fluorimetry and absorbance using the computer centered spectrofluorimeter-spectrophotometer. Reactions of the organics in pore water are similar to the overall metal organic reactions of the sediment. The natural organics in solution could be studied because of their ability to absorb quanta of ultraviolet light and fluoresce. Changes in the fluorescent and absorbant emissions of the organics results from reaction with Co^{++} and Cu^{++}.

Cupric ion and Co^{++} were shown by fluorimetry to readily react with organics in pore water. Copper reacts strongly in a stepfunction with increasing metal ion/organic carbon ratios. In other words, the Cu^{++}/ organic carbon reaction ratio decreases in nonlinear steps with increased Cu^{++} concentration. The adsorption spectra of the Cu^{++}-organic reaction in pore water show that the Cu^{++}-organic reaction is chelation because, the reaction is not only a non-linear stepfunction but also is pH dependent, reversible and the complex formed is stable under dilute conditions. Cobalt, on the other hand, as shown by fluorescence, reacts weakly with the organic compounds, and as shown by absorption emmissions, does not form strong bonds with the organics, but is likely only surface adsorbed.

The copper-organic reaction can cause precipitation of an organic-metal floc as shown by light scatter emissions. The specific gravity of this floc is approximately 2.1 ± 0.1 at a concentration of metal which will just cause precipitation. The same floc has an approximate specific gravity of 1.6 ± 0.1 if no metal is involved.

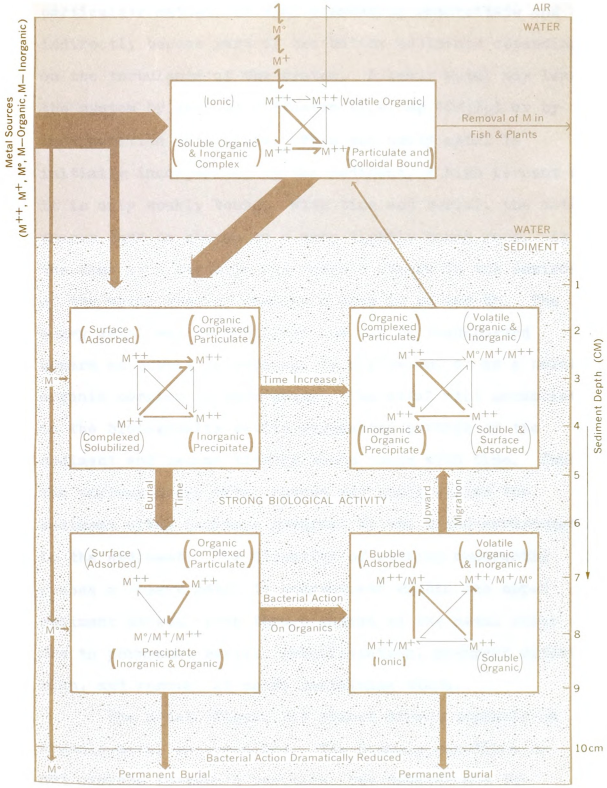
Both of these specific gravities are equal to or less than that of the clays. Thus, organic-metal flocs can be very mobile in the aquatic environment and contribute to heavy metal distribution.

The incorporation of Cu^{++} into the bottom sediments is quite rapid at first. This is caused by precipitation, rapid complexation by organics and rapid primary adsorption by organics and clays. After the primary reaction, heavy metals remaining in solution continue to be taken up by the bottom sediments but the rate is quite slow and probably is diffusion dependent. The Cu-sediment reaction was shown to be quantitative and essentially irreversible due to the high stability of the products. The stability constant (log Q) for the Cu^{++}-sediment reaction at a pH of 7.4 and 23°C is in the range of 2.0 to 8.9 compared to the stability constant (log Q) of approximately 2.0 for cobalt under the same conditions. The reaction is normally quantitative but if greater than about 7000 µg Cu/gm of Houghton Lake sediment or 8000 µg Cu/gm of Burke Lake sediment is reached, an adsorption endpoint results. The endpoint rate and stability constants are dependent on the sediment type, the chemistry of the environment and the reaction time, and, therefore, show only the dominant trends, not specific numbers to be extrapolated to other situations.

Copper continues to react within the bottom sediments and a cycling of the heavy metal may occur. When the Cu^{++} initially reacts with the sediments, it is approximately 65 percent bound by organic complexes and surface adsorbed, while approximately 35 percent is in a precipitated form. Then, as time and/or burial continues, 70 to 80 percent of the metal becomes bound in a precipitated form. At the same time a chemical change occurs due to the intense bacterial action in the surface layers of sediment. This together with diffusion, compaction, upward migrating bubbles, and water migration may cause a cycling and an upward accumulation of the Cu within the chemically active upper strata of the sediment.

These laboratory results suggest a more precise model than the generalized model (Figure 1) for the pathways and interactions of Cu and chemically similar heavy metals in the aquatic and subaquatic environment. The general trends found in contaminated natural aqueous systems together with the results and basic trends of the laboratory data are summarized in Figure 21, a model of heavy metal pathways and preferred reactions in aquatic sediments. Upon entering the aquatic environment, a heavy metal such as copper quickly and quantitatively becomes incorporated into the sediment. A metal ion will either react directly with the bottom sediments or will react with dissolved inorganic and/or organic constituents.

Figure 21. Model of heavy metal (M)-phase relationships and preferred pathways through the subaquatic environment. The boxes represent microenvironments and contain the heavy metal phases. The arrows between the boxes are relative and show the direction and magnitude of heavy metal movement. Within the boxes the arrows, by their thickness, show the direction of phase formation and the parenthesis around the phases represent by their thickness, the quantity of metal in that phase.


AIR
WATER
Metal Sources
(M++, M+, M°, M—Organic, M—Inorganic)
M°
M+
(Ionic)
M++
M++
(Volatile Organic)
(Soluble Organic & Inorganic Complex)
M++
M++
(Particulate and Colloidal Bound)
Removal of M in Fish & Plants
WATER
SEDIMENT
(Surface Adsorbed)
(Organic Complexed Particulate)
M++
M++
M°
M++
M++
(Complexed Solubilized)
(Inorganic Precipitate)
Time Increase
(Organic Complexed Particulate)
(Volatile Organic & Inorganic)
M++
M°/M+/M++
M++
M++
(Inorganic & Organic Precipitate)
(Soluble & Surface Adsorbed)
Burial
Time
STRONG BIOLOGICAL ACTIVITY
Upward
Migration
(Surface Adsorbed)
(Organic Complexed Particulate)
M++
M++
M°
M°/M+/M++
Precipitate (Inorganic & Organic)
Bacterial Action
On Organics
(Bubble Adsorbed)
(Volatile Organic & Inorganic)
M++/M+
M++/M+/M°
M++/M+
M++
(Ionic)
(Soluble Organic)
Bacterial Action Dramatically Reduced
M°
Permanent Burial
Permanent Burial
1
2
3
4
5
6
7
8
9
10cm
Sediment Depth (CM)

If a metal ion reacts with dissolved substances or mobile particulate matter, it will eventually precipitate and indirectly become part of the bottom sediments depending on the turbulence of the system. A heavy metal may leave the system by gaseous diffusion (i.e. Hg $(CH_3)_2$) or by incorporation into biota. When the heavy metal is initially incorporated by the sediment, a high percent of it is only weakly bound. With time and burial, the metal phases tend to change to a more tightly bound form. At the same time bacteria can cause a change in the environment of the metal species causing a drop in pH and Eh. The heavy metal may be mobilized and can be transported upward on bubble interfaces, by diffusion, or as a soluble organic complex in pore water. The metal will accumulate in the biologically active oxygenated portion of the sediment and become tightly bound there with time. Thus, the various heavy metal phases may cycle within the sediment along pathways governed by the micro-environments in the sediment. The direction of cycling apparently causes a heavy metal to concentrate within the upper sediment strata, even though losses of the metal occur due to permanent burial, solubilization, downward diffusion, and removal of metal containing biota.

The model (Figure 21) places strong emphasis on organic-metal interactions. The organic reactions do not exclude inorganic reaction, but demonstrate the importance and often the predominance of organic-heavy

metal interaction in most environments. The organic based model was shown to be operational with Cu in natural situations and is therefore a practical tool for predicting the reaction pathways in the aquatic environment of Cu and probably most heavy metals.

APPENDIX

TABLE A1. Data presented in Figure 4 concerning the dependence of organic solubility in pore water on pH of the solution. The relative intensity of light scatter in cm measured at 330 mμ are shown at the given pH's.

Relative Scatter Intensity (cm)	pH
2.0	2.2
6.5	5.2
6.6	7.5
7.5	9.0
11.1	10.4

The light scatter spectra were so reproducible that no difference between two spectra of the same metal-organic concentration could be measured. The instrumentation has an accuracy of ± 0.002 absorbance over the absorbance range 0-2.0 (Holland, 1971). This same accuracy is given for light scatter and fluorescent analyses. The error of the method will be developed further in Table A6.

TABLE A2. Effect of Cu^{++} concentration on organic solubility-light scatter as shown in Figure 5. The relative scatter intensity is measured in cm at 330 mμ for each concentration of Cu in μg/ml. The peak heights are measured to the nearest cm.

Relative Scatter Height (cm)	Cu Conc. (μg/ml)
5.7	0
6.5	3
7.3	5
9.0	10
10.4	15
10.4	20

TABLE A3. The data for the competition experiment shown in Figure 6 are presented below. The standards for atomic absorption analysis are given together with the relative percent of absorbance (Ab) and resulting concentrations of each metal in each sample after filtration. The percent absorbances for Cu^{++} and Co^{++} are given without decimals for ease of sample handling since the readings are all relative. The standard deviations (S) and confidence limits (a = 0.10) are given for the standards and the samples.

The standard deviation is given by $S = \frac{(Y-\bar{Y})^2}{N-1}$ (Krumbein and Graybill, 1965) for sample size less than 30; $\bar{Y}$ is the mean of a set of samples Y and N is the number of samples. The confidence limits (t) for the samples and the standards is given by the formula $\bar{Y} \pm t_a \frac{S}{N}$ where t_a will always represent the 90% confidence limit for this data. The confidence limits and resulting percent error is always calculated on absorbance.

Co Standards

Concentration (µg/ml)	Ab	± S (Ab)	$\bar{Y} \pm t$ (Ab)	
1.00	86, 99, 96	5.10	94	2.94
2.00	180, 178, 187	4.72	182	2.73
3.00	258, 265, 274	8.02	266	4.63
4.00	377, 382, 390	6.56	383	3.78

Average % S = 3.1

TABLE A3 Continued

Cu Standards

Concentration (µg/ml)	Ab	± S (Ab)	Ȳ ± t (Ab)	
1.00	68, 68, 65	1.9	64	1.6
2.00	128, 136, 137	4.9	134	2.8
3.00	206, 210, 200	5.0	205	2.9
4.00	260, 265, 269	4.5	264	2.6

Average % S = 2.9

Hg Standards

1.00	3.6, 3.9	0.21	3.7	0.21
2.00	10.1, 9.7, 9.5	0.31	9.8	0.179
3.00	14.9, 16.0, 16.0	0.64	15.6	0.369
4.00	21.9, 22.0, 22.8	0.49	22.2	0.283
5.00	28.1, 27.7, 28.0	0.17	27.9	0.098

Average % S = 2.9

Conc. Added (µg/ml)	Ab (Cu)	dil.	Average Remaining Conc. Cu (µg/ml)	Ab (Co)	dil.	Average Remaining Conc. Co (µg/ml)
1.00	40, 43	--	0.50	85, 95	--	1.00
3.00	55, 54	--	0.83	240, 243	--	2.78
5.00	74, 71	--	1.10	195, 206	1/2	4.60
10.0	152, 153	--	2.24	91, 91	1/10	10.0
15.0	206, 210	--	3.00	132, 140	1/10	15.0
20.0	236, 241	--	3.46	145, 140	1/10	16.4

Conc. Hg Added	Ab (Hg)	dil.	Average Remaining Conc. Hg (µg/ml)
1.00	23.0, 23.4	1/100, 1/2	0.93
3.00	23.9, 24.4	1/100	0.44
5.00	23.6, 22.8	1/100, 1/2	0.95
10.0	18.0, 17.5	1/100, 1/5	1.70
15.0	19.2, 19.1	1/100, 1/10	3.58
20.0	16.5, 16.0	1/100, 1/20	6.08

TABLE A3 Continued

Concentration of Adsorbed Metal

Conc. Begin (µg/ml)	Conc. (µg/ml) End			Conc. (µg/ml) Adsorbed		
	Cu	Hg	Co	Cu	Hg	Co
1	0.95	0.93	1.00	0.05	0.07	0.00
3	0.83	0.44	2.78	2.17	2.56	0.22
5	1.10	0.95	4.60	3.90	4.05	0.40
10	2.24	1.70	10.0	7.76	8.30	0.00
15	3.00	3.58	15.0	12.0	11.4	0.00
20	3.46	6.08	16.4	16.54	13.9	3.60

Standard deviations and confidence limits of relative percent absorbance of samples are given for the absorption.

Conc. M^{++} Added (µg/ml)	± s (Cu) (Ab)	± s (Co) (Ab)	± s (Hg)	± t (Cu)	± t (Co)	± t (Hg)
1.00	2.12	7.07	0.282	9.46	24	1.2
3.00	0.707	2.12	0.353	3.15	9.2	1.5
5.00	2.12	7.77	0.565	9.46	27	2.4
10.0	0.707	0.00	0.353	3.15	0	1.5
15.0	2.82	5.65	0.707	12.58	20	3.11
20.0	3.53	3.53	0.353	15.75	15	1.5

Then the total percent error (100 x confidence limit/mean) for the metals is the addition of percent error in measuring standards and percent error in measuring samples.

Conc. Cu Std. (µg/ml)	% error Standards	Conc. Cu Added (µg/ml)	% error Samples (t)	% error total (t)
1.00	4.3	1.00	9.9	14
2.00	5.3	3.00	5.7	9.6
3.00	3.5	5.00	12	16
4.00	2.4	10.0	2.0	5.9
		15.0	6.0	8.9
Average % error	= 3.9	20.0	6.5	10
			Average % error	= 10

TABLE A3 Continued

Conc. Co Std. (ug/ml)	% error Standards	Conc. Co Added (ug/ml)	% error Samples (t)	% error Total (t)
1.00	10.5	1.00	26	30
2.00	1.9	3.00	3.7	8.0
3.00	2.4	5.00	13	17
4.00	2.4	10.0	0	4.3
		15.0	14	18
Average % error =	4.3	20.0	10	14
			Average % error =	10

Conc. Hg Std. (ug/ml)	% error Standards	Conc. Hg Added (ug/ml)	% error Samples (t)	% error total (t)
1.00	8.2	1.00	5.1	10
2.00	4.6	3.00	6.4	11
3.00	8.3	5.00	10	15
4.00	3.2	10.00	8.5	13
5.00	.91	15.0	16	21
		20.0	9.2	14
Average % error =	5.0			
			Average % error =	14

The confidence limits and the resulting percent error derived for Cu, Co, and Hg are extremely high. These high results are due to having a small analyses number of two. The Student's t test and the standard deviation do not adequately describe the data at this low sample level. The analyses were not done for the purposes of statistical manipulation and therefore the sample size does not readily yeild applicable error analyses. The percent error of 10% for Cu^{++} analyses yeilds a range in concentration of 1.00 ± 0.1 ug/ml to 20 ± 2 ug/ml. These ranges of Cu^{++} precision are unreasonable since Cline (In press)

TABLE A3 Continued

has shown that the total accuracy in a similar Atomic Absorption study (that was statistically oriented) was ± 1 to 2%. Since the error in accuracy in this experiment is greater than the error in precision in Cline's (In press) work, it is suggested that the above tests of error, as suggested by the reviewer, do not adequately describe the data.

The total experimental accuracy is estimated to be less than ± 0.1 µg/ml, the confidence limit shown by the circles around the data points in Figure 6. The standard deviations and variability of Co, Cu, and Hg standards is essentially the same in the following data. It will therefore not be shown again.

TABLE A4. Data for Figure 7 showing the equilibrium between the Cu-organic chelate with pH adjustments. Four µg Cu/ml is in each solution with a constant 46 µg C/ml. Shown are the results of filtering the solution after pH adjustment from 7.36 to between 2.63 to 10.92 and again filtering the solutions after readjusting the pH's back to 7.36 ± 0.04.

Cu Standards

Conc. (µg/ml)	Absorbance	Standard deviation (S)
1.00	71, 66, 65	± 3.2
2.00	140, 137, 136	± 2.08
3.00	201, 195, 203	± 4.16
4.00	247, 259, 250, 263	± 7.5

Average % S = 2.7

The correlation (r) within the samples and the resulting sample variability are given below.

Data for First Filtration - Figure 7 - Curve (a)

pH	Absorbance (Ab)	Conc. Cu (µg/ml)	% Cu Adsorbed
2.63	240, 236	3.62	9.50
5.16	157, 161	2.40	40.0
7.36	77, 77	1.15	71.3
9.00	37, 39	0.57	85.8
10.92	14, 14	0.20	95.0

Cu Standards

Conc. (µg/ml)	$\bar{Y}$ (Ab)	± t (Ab)	% error
1.00	67	5.4	8.0
2.00	137	3.5	2.5
3.00	200	7.0	3.5
4.00	254	12.6	4.9

TABLE A4 Continued

Cu Samples

pH	$\bar{Y}$ (Ab)	± t (Ab)	± S (Ab)	% error (Ab)	% error Total (Ab)
2.63	238	4.7	2.82	2.0	6.7
5.16	159	4.7	2.82	2.9	7.6
7.36	77	0.0	0.00	0.0	4.7
9.00	38	2.4	1.41	6.3	11
10.92	14	0.0	0.00	0.0	4.7

Average % error = 6.9

Data for Filtration After Adjusting pH to 7.4 Figure 7 - curve (b)

pH original	pH back	Absorbance (Ab)	Cu Conc. (µg/ml)	% Cu Adsorbed
2.63	7.32	62, 59	0.97	75.8
5.16	7.42	74, 76	1.10	72.5
7.36	7.36	77, 77	1.13	71.8
9.00	7.36	50, 55	1.18	70.5
10.72	7.34	38, 39	0.99	75.2

Standard Deviation and Error of the pH Adjusted Solutions - Curve b

pH original	$\bar{Y}$	± S (Ab)	± t (Ab)	% error (Ab)	% total error (Ab)
2.63	60	2.12	3.6	6.0	11
5.16	75	1.41	2.4	3.2	7.9
7.36	77	0.00	0.0	0.0	4.7
9.00	52	3.58	5.9	11	16
10.72	38	0.707	1.2	3.1	7.8

Average % total error 9.5

The error in this experiment is 4.7% for the standards and a total of 6.9 and 9.5% for the total run. Since the original concentration of Cu was 4.00 µg Cu/ml, the error

TABLE A4 Continued

is 4.0 ± 0.27 µg/ml and 4.0 ± 0.38 µg/ml in the two sample sets. The accuracy of the experiment is dependent on filtration error and pipetting error. It is estimated that an accuracy of 0.05 µg Cu/ml for the experiments is much less than "precision".

TABLE A5. Data for Figure 9 - (a) and (b) giving the change in fluorescent (a) and absorbant (b) intensity measured in cm at various wavelengths (λ) in mμ as Cu concentration changes.

Fluorescence (a)

Conc. Cu (μg/ml)	Intensity in cm λ = 255	 λ = 270	 λ = 330
0	12.7	8.2	5.0
1	11.8	7.8	4.8
2	10.7	7.1	4.3
3	9.8	6.7	3.9
4	8.6	5.8	3.6
5	9.2	5.8	3.5
10	7.6	4.7	2.8
15	6.0	3.9	2.1
20	6.6	3.8	2.0

Absorbance (b)

Conc. Cu (μg/ml)	Intensity in cm λ = 270	 λ = 330
0	7.5	4.5
1	7.8	4.7
2	7.9	4.7
3	8.2	5.0
4	8.8	5.2
5	8.8	5.2
10	10.8	6.1
15	12.5	6.7
20	13.5	7.7

TABLE A5 Continued

The above results were repeatable in duplicate runs such that no difference could be measured. The measurement itself is good to the nearest 0.5 mm.

TABLE A6. Data for Figure 10 showing the intensity of fluorescence of diluted pore water solutions is measured in cm at three wavelengths (λ) in mu.

% Pore Water in Solution	Organic Carbon (µg/ml)	Fluorescent Intensity (cm) λ = 255	λ = 270	λ = 330
10	9.2	3.9	2.5	1.4
20	18.0	6.9	4.1	2.6
40	35.0	11.2	8.1	5.0
50	46.0	14.4	10.2	6.4

The variation of the data points from the theoretical linear line fit.

Line	Mean Variation of Line		Standard Deviation (S) of line
λ = 255	4.6%		2.2%
λ = 270	3.9%		5.5%
λ = 330	1.4%		1.9%
Grand Variation Mean	3.3%	Grand	Mean = 2.9%

The variation and standard deviation of the data points about the various lines are shown. Pipetting error or variation in pipetting is about 1 drop/25 ml or about 0.5%. The grand variation mean of 3.3% is attributed to machine variation and 0.5% attributed to sample handling. The same variation, 3.3%, can be expected in all of the fluorescence, absorbance and light scatter spectra.

TABLE A7. Data for Figure 11 (a) and (b) giving effect of Co^{++} on organic fluorescence (a) and absorbance (b) intensity in cm at two wavelengths (λ) in mu.

Conc. Co (µg/ml)	Fluorescent Intensity (cm)		Absorbant Intensity (cm)	
	$\lambda = 270$	$\lambda = 330$	$\lambda = 270$	$\lambda = 330$
0	10.2	6.4	8.5	4.6
1	9.8	5.8	---	---
2	9.2	5.6	---	---
3	8.8	5.3	---	---
4	8.8	5.3	---	---
5	8.8	5.1	8.3	4.4
10	7.7	4.6	8.2	4.3
15	7.1	4.2	---	---
20	7.2	4.1	8.2	4.4

The results are reproducible within the limits of the intensity measurement or to the nearest tenth of a cm. The variation of 3.3% can be expected for these results.

TABLE A8. Data for Figure 12 comparing Co^{++} and Cu^{++} affects on the light scatter of a pore water solution.

Conc. Cu (ug/ml)	Light Scatter Intensity (cm)	Conc. Co (μg/ml)	Light Scatter Intensity(cm)
2	6.0	0	5.7
5	7.3	2	5.8
10	9.1	10	5.9
15	10.4	20	6.0
20	10.5		

The light scatter spectra were reproducible within the measurement range of ± 0.5 cm. The variation of 3.3% is applicable to the above results.

TABLE A9. Data for Figure 13 showing the time dependence of Cu^{++} and Co^{++} reaction with organic rich sediments from Burke Lake. All data from the experiment are given though only the 100 mg M data are presented in Figure 13.

Time = 2 hours for Cu

Standards		Samples				
Cu (ug/ml)	Absorbance (Ab)	Conc. Cu Added (mg)	Dilution	Ab	Conc. (ug/ml)	mg in Solution
0.500	39, 41	0.500	---	35, 37	0.42	0.0525
1.00	74, 82	2.00	---	54, 58	0.67	0.0837
2.00	166, 168	5.00	---	99, 103	1.20	0.150
3.00	222, 234	10.0	---	105, 111	1.30	0.162
		25.0	---	118, 119	1.45	0.181
		50.0	1/50	19, 20	12.5	1.56
		75.0	1/50	54, 56	33.5	4.19
		100.0	1/50	193, 199	124.0	15.5

Time = 2 days for Cu

Standards		Samples				
Cu (ug/ml)	Ab	Conc. Cu Added (mg)	Dilution	Ab	Conc. (ug/ml)	mg in Solution
0.500	45, 52	0.500	---	9, 8	0.18	0.022
1.00	115, 104	2.00	---	40, 35	0.40	0.050
2.00	188, 180	5.00	---	51, 51	0.53	0.066
3.00	280, 291	10.00	---	48, 40	0.51	0.063
		25.0	---	44, 43	0.50	0.062
		50.0	---	94, 102	1.00	0.12
		75.0	1/25	25, 27	7.50	0.64
		100.0	1/50	73, 76	39.35	4.88

TABLE A9 Continued

Time = 3 days for Cu

Standards		Samples				
Cu (µg/ml)	Ab	Conc. Cu Added (mg)	Dilution	Ab	Conc. (µg/ml)	mg in Solution
0.500	32, 33	0.500	---	9, 10	0.20	0.024
1.00	68, 72	2.00	---	28, 30	0.45	0.054
2.00	135, 130	5.00	---	50, 47	0.80	0.096
3.00	176, 185	10.0	---	58, 55	0.92	0.11
		25.0	---	60, 64	0.95	0.11
		50.0	---	61, 59	0.81	0.097
		75.0	---	139, 146	2.05	0.25
		100.0	1/25	48, 48	20.0	2.40

Time = 4 days for Cu

Standards		Samples				
Conc. Cu (µg/ml)	Ab	Conc. Cu Added (mg)	Dilution	Ab	Conc. (µg/ml)	mg in Solution
0.500	39, 38	0.500	---	17, 17	0.20	0.024
1.00	78, 77	2.00	---	31, 32	0.30	0.036
2.00	150, 149	5.00	---	69, 67	0.82	0.098
3.00	210, 219	10.0	---	76, 79	0.96	0.12
		25.0	---	68, 72	0.87	0.11
		50.0	---	70, 71	0.87	0.11
		75.0	---	140, 144	1.94	0.23
		100.0	1/50	41, 43	15	1.80

Time = 5 days for Cu

Standards		Samples				
Conc. Cu (µg/ml)	Ab	Conc. Cu Added (mg)	Dilution	Ab	Conc. (µg/ml)	mg in Solution
0.500	39, 40	0.500	---	14, 14	0.10	0.012
1.00	74, 78	2.00	---	22, 21	0.21	0.025
2.00	150, 156	5.00	---	40, 42	0.50	0.059
3.00	212, 218	10.0	---	40, 43	0.50	0.059
		25.0	---	42, 49	0.55	0.066
		50.0	---	47, 49	0.56	0.066
		75.0	---	105, 109	1.42	0.167
		100	---	41 x 10	10.0	1.18

TABLE A9 Continued

Time = 6 days for Cu

Standards		Samples				
Conc. Cu (ug/ml)	Ab	Conc. Cu Added (mg)	Dilution	Ab	Conc. (ug/ml)	mg in Solution
0.500	38, 36	0.500	---	10	0.10	0.012
1.00	75, 55	2.00	---	28, 27	0.38	0.024
2.00	149, 154	5.00	---	31, 32	0.42	0.049
3.00	285, 279	10.0	---	36, 39	0.52	0.060
		25.0	---	40, 45	0.57	0.066
		50.0	---	71, 79	1.00	0.116
		75.0	---	131, 140	1.88	0.218
		100	---	64 x 10	8.80	1.02

Time = 8 days for Cu

Standards		Samples			
Conc. Cu (ug/ml)	Ab	Conc. Cu Added (mg)	Ab	Conc. (ug/ml)	mg in Solution
0.50	23, 25	0.5000	4	0.10	0.011
1.00	55, 54	2.00	9	0.20	0.023
2.00	109, 105	5.00	15, 14	0.30	0.034
3.00	148, 161	10.0	15, 15	0.30	0.034
4.00	197, 205	25.0	15, 16	0.30	0.034
		50.0	32	0.62	0.071
		75.0	61	1.13	0.127
		100	41 x 10	7.80	0.889

Time = 9 days for Cu

Standards		Samples			
Conc. Cu (ug/ml)	Ab	Conc. Cu Added (mg)	Ab	Conc. Cu (ug/ml)	mg in Solution
0.50	34, 37	0.50	0	0.00	0.000
1.00	68, 73	2.00	6	0.10	0.011
2.00	144, 138	5.00	8	0.12	0.014
3.00	200, 202	10.0	12, 11	0.18	0.020
4.00	259, 266	25.0	12, 12	0.18	0.020
		50.0	29, 31	0.42	0.047
		75.0	67, 62	0.80	0.090
		100	190 x 2	5.20	0.582

TABLE A9 Continued

Time = 11 days for Cu

Standards		Samples			
Cu Conc. (ug/ml)	Ab	Conc. Cu Added (mg)	Ab	Conc. Cu (ug/ml)	mg Cu in Solution
0.50	34, 33	0.50	0	0.00	0.000
1.00	65, 71	2.00	6	0.12	0.013
2.00	138, 137	5.00	10, 9	0.17	0.018
3.00	200, 211	10.0	10, 10	0.17	0.018
4.00	259, 270	25.0	11, 12	0.18	0.019
		50.0	29, 31	0.45	0.048
		75.0	65, 59	0.82	0.101
		100	167 x 2	5.13	0.513

Time = 2 hours for Co

Standards		Samples				
Co Conc. (ug/ml)	Ab	Conc. Co Added (mg)	Dilution	Ab	Conc. Co (ug/ml)	mg Co in Solution
0.50	24, 26	0.50	---	7	0.20	0.025
1.00	59, 49	2.00	---	14, 13	0.27	0.034
3.00	164, 157	5.00	---	42, 44	0.84	0.105
5.00	245, 243	10.00	---	95, 105	1.95	0.243
		25.00	1/2	179, 189	7.53	0.941
		50.00	1/50	39, 42	41.0	5.13
		75.00	1/50	87, 78	80.5	10.1
		100	1/50	159, 140	144	18.1

Time = 2.5 days for Co

Standards		Samples				
Co Conc. (ug/ml)	Ab	Conc. Co Added (mg)	Dilution	Ab	Conc. Co (ug/ml)	mg Co in Solution
0.50	31, 28	0.50	---	0	0.00	0.000
1.00	52, 62	2.00	---	19, 20	0.35	0.051
3.00	149, 165	5.00	---	31, 37	0.60	0.091
5.00	250, 259	10.0	---	48, 44	0.80	0.116
		25.0	---	140, 150	2.87	0.416
		50.0	1/70	94, 103	15.8	3.29
		75.0	5/50	199, 217	41.0	5.95
		100	1/50	109, 108	102	14.8

TABLE A9 Continued

Time = 6 days for Co

Standards		Samples				
Co Conc. (µg/ml)	Ab	Conc. Co Added (mg)	Dilution	Ab	Conc. Co (µg/ml)	mg Co in Solution
0.50	31, 33	0.500	---	0	0.00	0.000
1.00	66, 63	2.00	---	18, 19	0.32	0.039
2.00	128, 138	5.00	---	19, 19	0.33	0.039
3.00	192, 200	10.0	---	21, 27	0.40	0.049
4.00	258, 258	25.0	---	141, 151	2.30	0.281
		50.0	1/10	99, 84	1.50	1.83
		75.0	1/10	224, 234	3.58	4.37
		100	1/50	112, 113	90.0	10.98

Time = 11 days for Co

Standards		Samples				
Conc. Co (µg/ml)	Ab	Conc. Co Added (mg)	Dilution	Ab	Conc. Co (µg/ml)	mg in Solution
0.5	47, 49	0.500	---	0	0.00	0.000
1.0	85, 90	2.00	---	0	0.00	0.000
2.0	179, 175	5.00	---	8	0.10	0.012
3.0	258, 272	10.0	---	25, 26	0.27	0.032
4.0	312, 328	25.0	---	188, 192	2.15	0.258
		50.0	1/20	49, 52	0.56	1.30
		75.0	1/20	126, 139	1.50	3.48
		100	1/20	196, 213	2.33	5.40

TABLE A9 Continued

The weights of sediment or adsorber in each reaction flask are given below.

#Co (mg)	Wt. of App. (gm)	Wt. Beaker (gm)	Wt. Sediment (gm)
0.5	106.522	103.787	2.735
2	100.259	97.128	3.131
5	107.707	104.686	3.021
10	102.484	99.150	3.334
25	104.436	100.836	3.600
50	102.758	99.848	2.910
75	100.298	97.385	2.913
100	110.410	107.450	2.960

#Cu (mg)	Wt. of App. (gm)	Wt. Beaker (gm)	Wt. Sediment (gm)
0.5	106.913	104.519	2.394
2	103.238	100.331	2.907
5	103.300	100.402	2.898
10	100.727	97.846	2.881
25	99.641	96.530	3.111
50	99.593	96.400	3.193
75	106.907	103.805	3.102
100	107.715	104.779	2.936

Confidence Limits, Standard Deviation, and Percent Error for Cu after 2 Hours and 2 Days

Standards
2 Hours

Conc. Cu (ug/ml)	$\bar{Y}$ (Ab)	±S (Ab)	t (Ab)	% Error
0.50	40	1.4	6.3	15
1.00	78	4.2	18	23
2.00	164	1.4	6.3	3.7
3.00	228	7.1	31	14

Average % Error = 14%

TABLE A9 Continued

Standards
2 days

Conc. Cu (μg/ml)	$\bar{Y}$ (Ab)	±S (Ab)	t (Ab)	% error
0.50	43.5	2.12	3.1	7.1
1.00	111	3.56	16	14
2.00	184	4.24	19	10
3.00	285	4.94	22	7.7

Average % Error = 9.7%

Samples
2 hours

Conc. Cu Added (μg/ml)	$\bar{Y}$ (Ab)	±S (Ab)	t (Ab)	% error	% total error
0.500	36	1.41	6.3	17	27
2.00	56	2.82	12	21	31
5.00	101	2.82	12	12	22
10.0	108	4.24	19	17	27
25.0	118	0.707	3.2	2.7	12
50.0	19	0.707	3.2	16	26
75.0	55	1.41	6.3	11	21
100	196	4.24	19	10	20

Average % total error = 23%

2 days

Conc. Cu Added (μg/ml)	$\bar{Y}$ (Ab)	±S (Ab)	t (Ab)	% error	% total error
0.500	8.5	0.707	3.1	36	46
2.00	37	2.82	12	32	42
5.00	51	0.00	0.0	0.0	9.7
10.0	45	4.24	19	42	52
25.0	43	0.707	3.1	7.2	17
50.0	99	3.66	16	16	26
75.0	22	1.41	6.3	28	38
100	74	2.12	9.5	12	12

Average % total error = 30%

As in the earlier experiments the error calculated is extremely high due to the small sample size. The same results are obtained for the other repetitions of this experiment and are therefore not shown.

TABLE A9 Continued

These errors show the confidence level one can place in the determination by atomic absorption but, they do not account for the inaccuracy inherent in the experiment. The temperatures varied by ± 1.5°C, and the sediment mixtures, even though homogenized, were mixtures of many inhomogeneous compounds, colloids, etc. These sediments and their chemistries change by season and location. Thus, the machine error shown above is minimal compared to the variation in a natural system. The numbers and data given will show only trends, trends with confidence levels much exceeding the calculated machine error. The inherent error in these data will be given in Tables A10 and A13.

TABLE A10. Data and figures used to obtain the rate constants K (day^{-1}) in Table 2 of the Co^{++} and Cu^{++} reactions with Burke Lake sediment. The raw data are given in Table A9. The correlation coefficient (r) shows the fit of data to the line and the slope m is equal to the rate constant, K. The value σ^2 or $\% \sigma^2$ is defined as percent variability and represents the goodness of the fit of the data to the theoretical linear curve. The percent variability ($\%\sigma^2$) is given by $(100(1-r^2))$ (Wang Laboratories, 1970).

Data for Cu^{++} plotted in Figure A1, where $2.3 \log \left(\frac{N_o}{N_o-X}\right) = Kt$ is the first order plot.

Conc. of Cu^{++} added = 0.5 mg = N_o
X = conc. of Cu adsorbed

Time (day)	N_o-X	2.3 LOG (N_o/N_o-X)
0.2	0.053	2.25
2.0	0.048	2.35
3.0	0.024	3.04
5.0	0.023	3.11
6.0	0.012	3.75
8.0	0.012	3.75
9.0	0.011	4.78

Correlation coefficient (r) = 0.97
Slope (m) = 0.262
Intercept (a) = 2.05

Conc. Cu^{++} added = 5.0 mg = N_o
X = Conc. of Cu adsorbed

Time (day)	N_o-X	2.3 LOG (N_o/N_o-X)
0.2	0.150	3.50
2.0	0.130	3.66
3.0	0.096	3.96
4.0	0.098	3.93
5.0	0.059	4.44
6.0	0.049	4.62
8.0	0.031	5.08
9.0	0.014	5.89

r = 0.96
m = 0.259
a = 3.18
σ^2 = 7.8%

TABLE A10-Continued

Conc. Cu^{++} added = 25 mg = N_o
X = Conc. of Cu adsorbed

Time (days)	N_o-X	2.3 Log $(N_o/N_o\text{-}X)$
0.2	0.18	4.92
2.0	0.16	5.06
3.0	0.11	5.38
4.0	0.10	5.47
5.0	0.065	5.93
6.0	0.066	5.91
8.0	0.032	6.65
9.0	0.020	7.13

r = 0.97
m = 0.252
a = 4.64
σ^2= 6.0%

Conc. Cu added = 100 mg = N_o
X = Conc. of adsorbed Cu
c = N_o-X
This is a second order plot of 1/c vs t

Time (day)	N_o-X	1/c
0.2	15.5	0.064
2.0	4.88	0.20
3.0	2.40	0.42
4.0	1.80	0.56
5.0	1.18	0.85
6.0	1.02	0.98
8.0	0.77	1.30
9.0	0.52	1.92
11.0	0.51	1.96

r = 0.98
m = 0.195
a_o= -0.127
σ^2= 4.0%

TABLE A10--Continued

Rate data for Co. The first order rate equation LOG (N_o/N_o-X) where N_o = original Co concentration and X = adsorbed Cu is used.

N_o = 100 mg

Time (day)	N_o-X	2.3 LOG (N_o/N_o-X)
0.2	18.1	1.71
2.5	14.8	1.91
6.0	11.0	2.21
11.0	5.40	2.92

r = 0.99
m = 0.112
a_2= 1.64
σ^2= 1.9%

N_o = 50 mg

Time (day)	N_o-X	2.3 LOG (N_o/N_o-X)
0.2	5.13	2.27
2.5	3.29	2.71
6.0	1.83	3.31
11.0	1.30	3.66

r = 0.97
m = 0.128
a_2= 2.36
σ^2= 5.9%

N_o = 25 mg

Time (day)	N_o-X	2.3 LOG (N_o/N_o-X)
0.2	0.941	3.27
2.5	0.416	4.09
6.0	0.281	4.48
11.0	0.258	4.58

r = 0.89
m = 0.104
a_2= 3.50
σ^2= 20.8%

TABLE A10 Continued

$N_o = 5$ mg

Time (day)	N_o-X	2.3 LOG (N_o/N_o-X)
0.2	0.105	3.86
2.5	0.091	4.23
6.0	0.039	4.85
11.0	0.012	6.03

r = 0.99
m = 0.201
a = 3.75
σ^2 = 1.9%

The fit of data to each of the lines is given by percent variability σ^2. The average percent σ^2 for the Co runs are 7.62% and for the Cu runs 4.96%. This shows that the Cu data fit the theoretical curve better than the Co data.

The results of the listed data are plotted for Cu^{++} (Figure A1) and for Co^{++} (Figure A2) reaction rates with Burke Lake sediment.

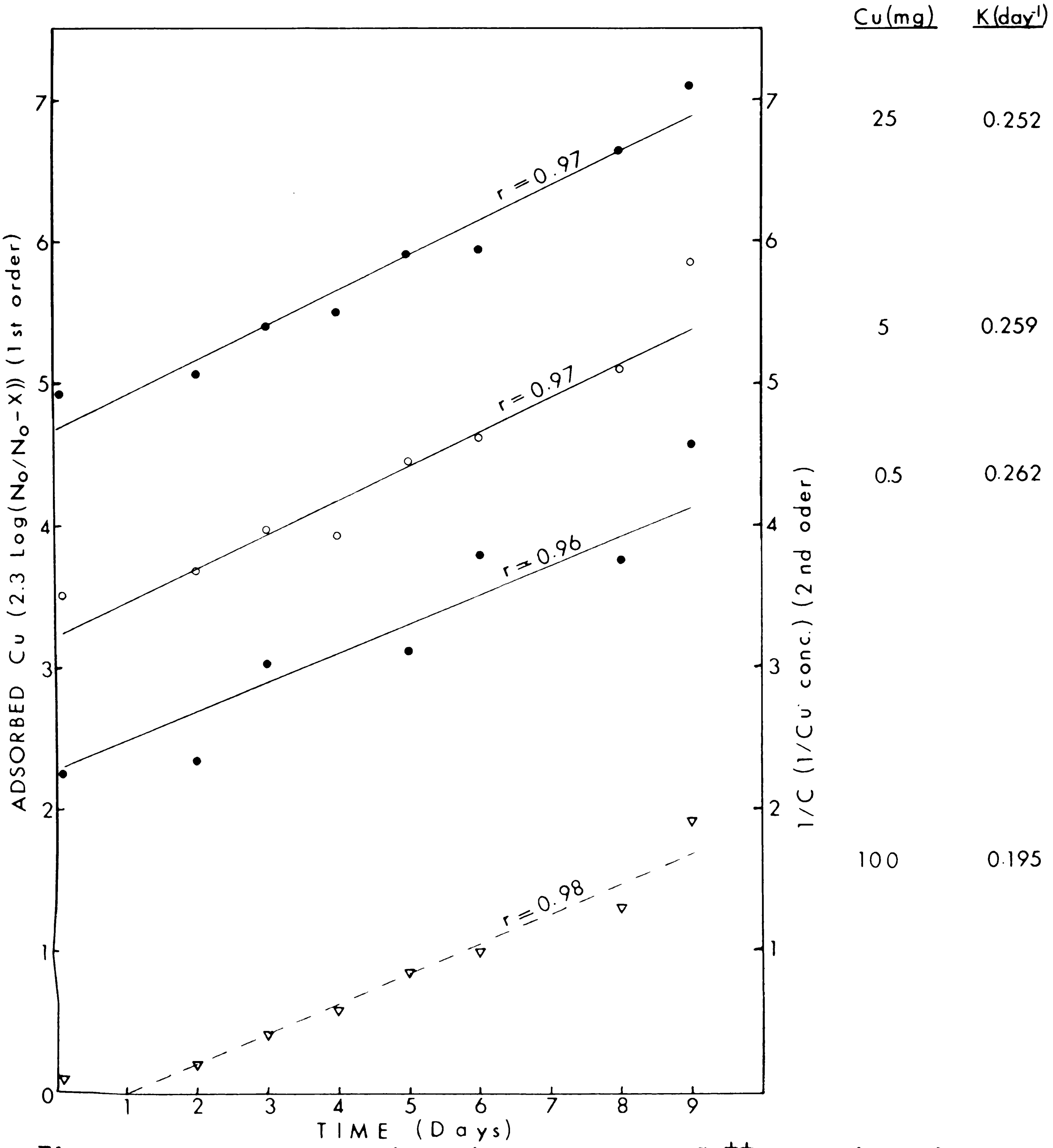


Figure A1. Rates of diffusion dependent Cu^{++} reaction with sediment. First (——) and second (- - -) order rate plots (day^{-1}) and constants are shown for diffusion of different concentrations of Cu^{++} into Burke Lake sediment. The vertical scale represents the log of the adsorbed Cu^{++}. N_{o} = original Cu^{++}. X = adsorbed Cu^{++}. 2 .3 corrects for the natural log conversion to $\log_{10}$.

Figure A2. Rates of diffusion dependent reaction with sediment. First order rate plots and constants (day^{-1}) are shown for diffusion of different concentrations of Cu^{++} into Burke Lake sediment.

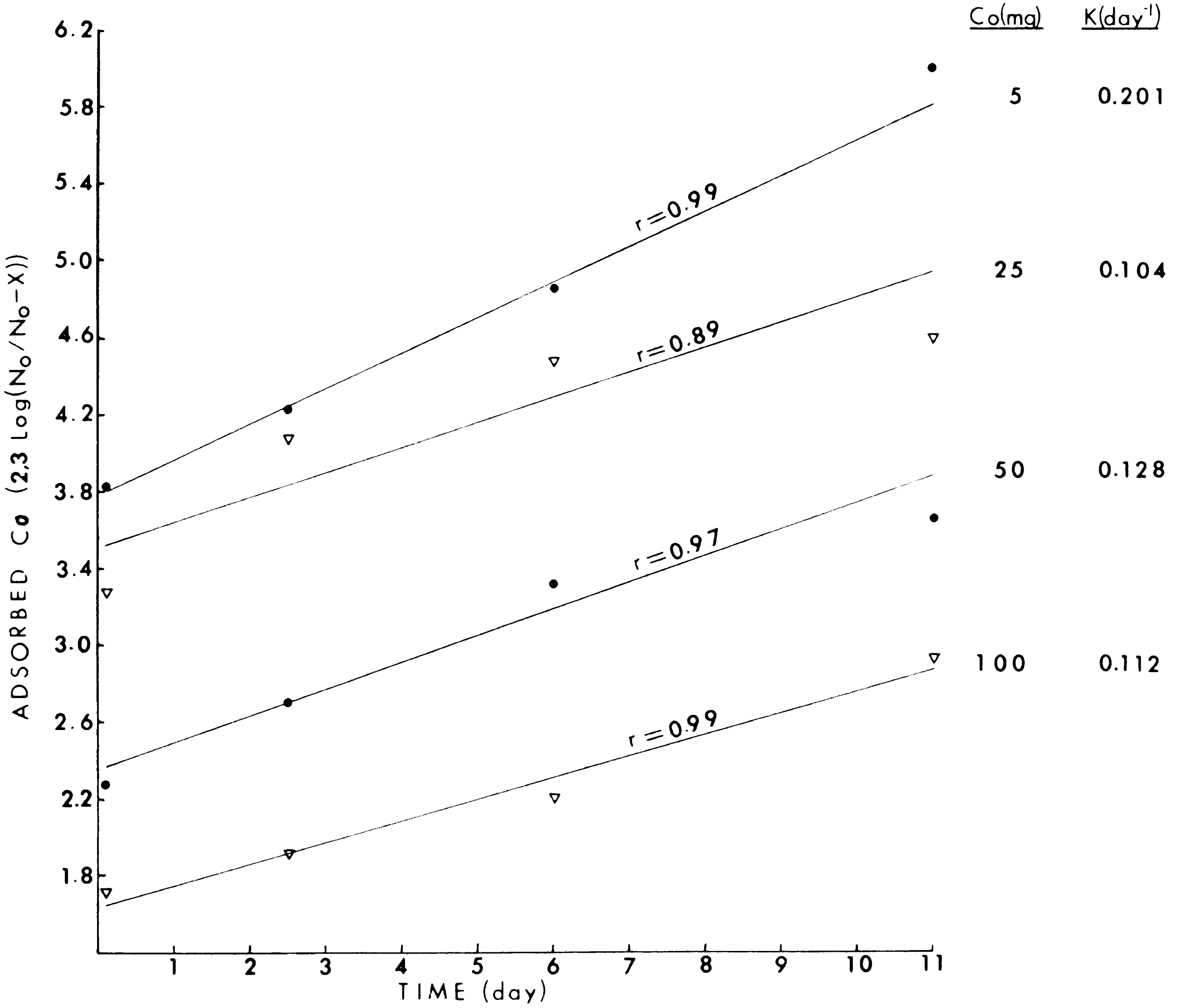

ADSORBED Co (2,3 Log(No/No-X))
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
TIME (day)
1
2
3
4
5
6
7
8
9
10
11
r=0.99
r=0.89
r=0.97
r=0.99
Co(mg)
K(day⁻¹)
5
0.201
25
0.104
50
0.128
100
0.112

TABLE A11. Data for Figure 14 giving two Freundlich Isotherms for one Cu^{++}-organic pore water reaction. The weight of organic carbon and the weight of organics (organic carbon x 1.92) that reacted with a given concentration of Cu^{++} are given. X = meq. Cu adsorbed, M = wt. of adsorber.

C = meq Cu/L left in solution, and M 46 µgC/ml and 91 µg organic/ml

Conc. Cu Added (ug/ml)	Ab	Conc. Cu Remaining (ug/ml)	Conc. Cu Adsorbed (ug/ml)	LOG$_2$ $\frac{X}{M}$	LOG$_1$ $\frac{X}{M}$	LOG C
2.0	34, 35	0.46	1.54	2.31	2.02	-1.853
5.0	62, 68	0.84	4.16	2.75	2.45	-1.588
10	81, 82	1.13	8.87	3.07	2.77	-1.462
15	99, 109	1.43	13.57	3.26	2.97	-1.358
20	162, 157	2.22	17.78	3.37	3.08	-1.168

A linear regression on the data yields an intercept (a_o) = LOG Q

Carbon		Organics	
	$r = 0.98$		$r = 0.98$
	$m = 1.64$		$m = 1.64$
	$a_o = 5.10$ = LOG Q		$a_o = 5.47$ = LOG Q
	$\sigma^2 = 4.0\%$		$\sigma^2 = 4.0\%$

Conc. Cu Added (ug/ml)	$\overline{Y}$	± S (Ab)	± t (Ab)	% error (Ab)
2.00	34	0.707	3.1	9.1
5.00	65	4.24	11	6.5
10.0	81	0.707	3.1	3.8
15.0	104	0.707	3.1	2.9
20.0	159	3.53	16	2.2

Average % error = 4.9

TABLE A12. Data for Figure 15 yielding Freundlich Isotherms of Cu^{++} and Co^{++} reaction with Burke Lake sediments. X = meq of M^{++} adsorbed/L, M = wt. of adsorber, $\frac{X}{M} = \frac{meq}{100\ gm}$, $C = \frac{mmole\ Cu}{L}$ remaining.

#	Conc. Cu Added (mg)	Ab	Conc. Cu µg/ml
13	2.172	5	0.14
14	2.172	4	0.10
31	5.430	6	0.16
32	5.430	-	-
15	10.86	16, 14	0.25
16	10.86	15, 15	0.24
27	27.15	23, 19	0.38
28	27.15	35	0.60
29	54.30	250, 256	4.18×10^2
30	54.30	253	4.18×10^2

#	Wt. Cu (mg)	Wt. Sediment (gm)	LOG $(\frac{X}{M})$	LOG (C)
13	0.00308	2.857	0.38	-2.38
14	0.00245	2.047	0.47	-2.60
31	0.00416	2.922	0.73	-2.32
32	-	-	-	-
15	0.00575	2.000	1.22	-2.11
16	0.00588	1.924	1.23	-2.13
27	0.03686	3.007	1.43	-1.93
28	0.04320	2.449	1.52	-1.75
29	36.784	1.484	-	-
30	32.395	2.007	1.56	1.12

$r = .931$
$m = 1.51$
$a_o = 4.29$ = LOG Q
$\sigma^2 = 13.5\%$

TABLE A12 Continued

#	Conc. Co Added (mg)	Ab	ml	Conc. Co (ug/ml)
3	2.000	0	21.2	0.00
4	2.000	0	23.0	0.00
5	10.00	43, 42	26.0	1.25
6	10.00	42, 44	20.5	1.23
17	5.000	17, 16	22.8	0.50
18	5.000	15, 16	26.0	0.45
19	20.00	218, 227	80.5	6.48
20	20.00	189, 183	83.0	5.20
21	50.00	118, 120 (x 10)	74.0	34.8
22	50.00	110, 122 (x 10)	79.0	34.0

#	Wt. Cu (mg)	Wt. Sediment (gm)	LOG ($\frac{X}{M}$)	LOG (C)
3	0.00	2.603	-	-
4	0.00	3.069	-	-
5	0.325	2.683	1.10	-1.37
6	0.252	2.439	1.10	-1.38
17	0.0114	2.524	0.90	-1.81
18	0.0117	2.077	0.83	-1.77
19	0.522	1.667	1.52	-0.66
20	0.432	2.047	1.60	-0.75
21	2.58	3.200	1.80	0.06
22	2.69	2.380	1.70	0.07

$r = .972$
$m = 0.489$
$a_0 = 1.78 = \mathrm{LOG}\ Q$
$\sigma^2 = 5.9\%$

The percent variability ($\%\sigma^2$) of 13.5% for Cu and 5.9% for Co show that the Cu-organic reaction compared to the Co-organic reaction is less linear and has more inherent error resulting from an inhomogeneous reaction.

TABLE A12 Continued

Standard deviation, confidence limit and % error in absorbance are given for Cu and Co reaction with sediment.

Cu

#	Conc. Cu Added (mg)	$\bar{Y}$	± S (Ab)	± t (Ab)	% error
13	2.172	5	0.0	0.0	0.0
14	2.172	4	0.0	0.0	0.0
31	5.430	6	0.0	0.0	0.0
32	5.430	-	-	-	-
15	10.86	15	±1.41	± 6.3	42
16	10.86	15	0.0	0.0	
27	27.15	21	±2.82	±13	62
28	27.15	35	0.0	0.0	0.0
29	54.30	-	-	-	-
30	54.30	253	±4.24	19	7.5

Average % error = 16

Co

#	Conc. Co Added (mg)	$\bar{Y}$	± S (Ab)	± t (Ab)	% error
3	2.000	0.0	0.00	0.00	0.0
4	2.000	0.0	0.00	0.00	0.0
5	10.00	42	0.707	3.1	7.4
6	10.00	43	1.41	6.3	14
17	5.000	16	0.707	3.1	19
18	5.000	15	0.707	3.1	20
19	20.00	222	6.36	28	12
20	20.00	186	4.24	19	10
21	50.00	119	1.41	6.3	5.3
22	50.00	116	8.48	38	32

Average % error = 12%

TABLE A12 Continued

The percent error or precision in the experiment are again high due to the low sample number. The precision or sensitivity of 0.02 ug Cu/ml and 0.05 ug Co/ml given in the A.A. instrument handbook are closer approximations.

TABLE A13. Data for Figure 16 yielding Freundlich Isotherms for Cu^{++} and Co^{++} reactions with Burke Lake sediment through time. The raw data is taken from table A9. $\frac{X}{M} = \frac{\text{meq Cu or Co}}{\text{100 gm}}$, $C = \frac{\text{meq of Cu or Co}}{\text{liter}}$

Cu after 11 days

LOG $(\frac{X}{M})$	LOG (C)
0.32	-2.41
0.71	-2.32
1.02	-2.29
1.39	-2.25
Break	
1.68	-1.87
1.83	-1.33
2.01	-0.60

Cu after 2 hours

LOG $(\frac{X}{M})$	LOG (C)
-0.13	-1.88
0.25	-1.68
0.70	-1.44
1.02	-1.40
1.37	-1.34
Break	
1.68	-0.42
1.85	-0.18
2.07	0.55

Co after 11 days

LOG $(\frac{X}{M})$	LOG (C)
0.75	-2.47
1.00	-2.04
1.36	-1.15
1.76	-0.42
1.93	0.00
2.05	0.40

$r = .99$
$m = 0.459$
$a_o = 1.91 = \text{LOG } Q$

Co after 2 hours

LOG $(\frac{X}{M})$	LOG (C)
0.33	-2.01
0.76	-1.54
1.00	-1.17
1.35	-0.59
1.74	0.12
1.88	0.45
1.98	0.70

$r = .99$
$m = .593$
$\text{LOG } Q = a_o = 1.63$

TABLE A13 Continued

Linear regressions are made on the Cu reactions before and after the break and total, while only a total linear regression is needed for Co.

	r	m	a_o (LOG Q)	$\%\sigma^2$
Cu, 11 day before	0.97	6.52	8.99	5.9
Cu, 11 day after	0.97	0.259	2.70	5.9
Cu, 11 day total	0.82	0.761	2.17	33
Cu, 2 hour before	0.96	2.55	4.59	7.8
Cu, 2 hour after	0.95	1.22	2.32	9.7
Cu, 2 hour total	0.90	0.821	1.90	33
Co, 11 day total	0.99	0.459	1.91	2.0
Co, 2 hour total	0.99	0.593	1.63	2.0

Average $\%\sigma^2$ Cu = 7.32
Average $\%\sigma^2$ Co = 2.0

The line fit using linear regression shows that Co is much better "behaved" than Cu. The fit of data to a theoretical linear curve seems to depend on the metal reactant and the linearity of the reaction.

TABLE A14. Data for Table 4 showing the change of phase of Cu^{++} as pore water Cu, KCl extractable Cu, EDTA extractable Cu and precipitated Cu.

Extraction after 2 hours Cu-sediment reaction
(Total Cu = 22 mg Cu/run)

Extraction	Dilution	Ab	Conc. Cu (ug/ml)	mg Cu	Water (gm) or wt. Sediment (gm)	% Cu in Phase
Cu^{++} pore water (a)	$\frac{35}{50}$, $\frac{2}{100}$, $\frac{1}{4}$	143	1.44	0.411	35.16	2.7
Cu^{++} pore water (b)	$\frac{34}{50}$, $\frac{2}{100}$, $\frac{1}{4}$	130	1.31	0.385	33.98	2.9
Cu^{++} (KCl) (a)	250, $\frac{2}{100}$	54	0.485	6.15	6.569	26.2
Cu^{++} (KCl) (b)	250, $\frac{2}{100}$	53	0.465	5.81	5.972	28.2
Cu^{++} (EDTA) (a)	250, $\frac{2}{100}$	110	1.11	13.9	6.569	60.7
Cu^{++} (EDTA) (b)	250, $\frac{2}{100}$	97,	0.98	12.3	5.972	59.8
Cu^{++} Unextractable						10.8

Standards

Conc. Cu (ug/ml)	Ab	$\overline{Y}$ (Ab)	± S (Ab)	± t (Ab)	% error
0.196	28, 30	29	1.41	6.3	21
0.490	55, 56	55	0.707	3.1	5.6
0.980	97, 97	97	0.00	0.0	0.0
1.96	190, 194	192	2.82	13	6.8

Average % error = 8.3

TABLE A14 Continued

Extraction after 9 days Cu-sediment reaction for 2.172, 10.86, 5.43 and 27.15 mg of Cu added to 25 ml sediment.

Surface Water

#	Volume (ml)	Ab	Conc. Cu (ug/ml)	Cu Wt. (ug)
13	22.0	5	0.14	3.08
14	24.5	4	0.10	2.45
15	23.0	16, 17	0.25	5.75
16	24.5	15, 15	0.24	5.88
27	97.0	21, 22	0.38	36.9
28	92.0	33, 37	0.60	43.2
31	26.0	6	0.16	4.16

Pore Water

#	Volume (ml)	Ab	Conc. Cu (ug/ml)	Cu Wt. (ug)
13	11.9	10	0.20	2.38
14	11.4	24, 25	0.43	4.90
15	11.8	47, 49	0.82	9.68
16	11.5	31, 32	0.55	6.32
27	10.0	49	1.05	11.2
28	10.0	65, 71	1.14	11.4
31	10.0	23	0.40	4.00

Standards

Conc. Cu (ug/ml)	Ab	$\overline{Y}$ (Ab)	± S (Ab)	± t (Ab)	% error
1.00	71, 71	71	0.00	0.00	0.00
2.00	148, 149	149	0.707	3.1	2.1
3.00	204, 215, 214	211	4.80	13	6.1
5.00	328, 330	329	1.41	6.3	1.9

Average % error = 2.5

TABLE A14 Continued

KCl Extraction

#	KCl dil.	Ab	Conc. Cu (ug/ml)	Wt. Cu (µg)
13	250	26	0.35	87.5
14	250	26, 27,	0.36	90.0
15	250	88, 89	1.25	312
16	250	100, 104	1.42	355
27	250	219, 231	3.22	805
28	250	273, 277	3.88	970
31	250	59, 59	0.81	203
32	250	57, 58	0.79	198

EDTA Extraction

#	EDTA dil.	Ab	Conc. Cu (ug/ml)	Wt. Cu (µg)
13	100, 1/20	25, 26	0.35 x 20	700
14	100, 1/10	47, 46	6.3	630
15	100, 1/20	109, 106	30.0	3000
16	100, 1/20	121, 117	1.65 x 20	3300
27	250, 1/50	59	1.82 x 50	10300
28	250, 1/50	69	1.10 x 50	13700
31	250, 1/20	23	0.32	1580
32	250, 1/20	---	---	---

% Extractable Cu in various solutions and sediment

Average phase	13 and 14	31 and 32	15 and 16	27 and 28
Total	34.9	32.7	32.2	47.6
Pore Water	0.167	0.073	0.073	0.041
Surface Water	0.127	0.076	0.053	0.147
KCl	4.09	3.68	3.07	3.27
EDTA	30.6	29.0	29.0	44.2

TABLE A14 Continued

Standard deviation, confidence limit and percent error in absorbance for Cu extraction from sediment.

Surface Water

#	$\bar{Y}$	± S (Ab)	± t (Ab)	% error	% total error
13	5	0.0	0.0	0.0	8.3
14	4	0.0	0.0	0.0	8.3
15	16	0.707	3.1	19	27
16	15	0.0	0.0	0.0	8.3
27	21	0.707	3.1	14	22
28	36	2.82	12	33	41
31	6	0.0	0.0	0.0	8.3
				Average total error =	17

Pore Water

#	$\bar{Y}$	± S (Ab)	± t (Ab)	% error	% total error
13	10	0.0	0.0	0.0	8.3
14	24	0.707	3.1	12	20
15	48	1.41	6.3	13	21
16	32	0.707	3.1	9.7	18
27	49	0.0	0.0	0.0	8.3
28	68	2.82	12.6	18	26
31	23	0.0	0.0	0.0	8.3
				Average total error =	16

KCl Extraction

#	$\bar{Y}$	± S (Ab)	± t (Ab)	% error	% total error
13	26	0.0	0.0	0.0	8.3
14	27	0.707	3.1	11	19
15	89	0.707	3.1	3.5	12
16	102	3.56	16	16	24
27	225	7.07	31	13	21
28	275	2.82	12	4.4	13
31	59	0.0	0.0	0.0	8.3
32	58	0.707	3.1	5.3	14
				Average total error =	15

TABLE A14 Continued

EDTA Extraction

#	$\bar{Y}$	± S (Ab)	± t (Ab)	% error	% total error
13	26	0.707	3.1	12	20
14	47	0.707	3.1	6.6	15
15	108	2.12	9.4	8.7	17
16	119	2.82	12	10	18
27	59	0.0	0.0	0.0	8.3
28	69	0.0	0.0	0.0	8.3
31	32	0.0	0.0	0.0	8.3
32	---	---	---	---	8.3
				Average total error =	13

Percent variation of confidence limits in mg for extraction of the phases of Cu when increasing quantities of Cu are added to a given quantity of sediment.

Phase	$\bar{Y}$	± S (mg)	± t (mg)	% variation in t
Pore Water	0.090	0.054	0.032	35
Surface Water	0.12	0.437	0.26	216
KCl	3.52	0.453	2.71	77
EDTA	3.32	7.37	4.42	13
Total	36.8	7.26	4.35	12

From the last set of confidence limits and percent variation in t, it is observed that increasing Cu concentrations has an affect on the percent of Cu in a given phase in the following order: surface water, KCl, pore water, EDTA, total extraction.

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