

THE FATE OF COPPER AND CHROMIUM IN AQUATIC SYSTEMS

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CHAPTER I

INTRODUCTION

Human beings, unlike any other animal, know few population restrictions. As the population increases, so do the environmental problems. Among the many detrimental effects of pollution, none may be more important than that on water. An ever increasing population demands more water and in turn produces more wastewater. The expanding population exerts varied demands on production and a diversified production, to meet consumer demands, has increased both the amount of pollution and the number of pollutants.

In recent years, trace metals have become increasingly important. Sources of metal pollution are varied and industries responsible include galvanization, metal plating, and metal fabrication (1). Additional sources of metals to aqueous systems, although minimal comparatively, may be the atmosphere, road runoff, boat traffic, and sewage input (2). High concentrations may also be found in the sediment and/or the water surrounding natural deposits of these metals (3). The need to treat waters and wastewaters to remove these metals is essential. Natural water systems act as treatment systems, but these trace metals can cause many problems upon entering the system. Every increasing concentration of metals cannot be assimilated.

Sources indicate that there are 14 essential trace elements for humans. Copper and chromium are among the 14. However, the excessive addition of

copper and chromium to water supplies may result in increased uptake of these metals by all who use the supply. In addition to the previously mentioned sources of pollution, copper is used commercially to control aquatic growth, and chromium is used in boiler waters which can ultimately contribute to metal pollution of water supplies. There is evidence that deficiencies or excesses of these metals are related to health problems. Chromium may be related to the glucose tolerance factor. Deficiencies may be a causal factor in some cases of diabetes mellitus (4). Some trace metals are suspected of being related to cancer. Presently, correlations between water supplies and cancer mortality show no significant chromium-cancer relationship (4). Chromium concentrations of 10 ppm inhibit and may kill aquatic plants, thus altering the water's ecosystem (5).

Copper, upon entering an aquatic system, will have adverse effects on fish, zooplankton, cladocerae, rotifers, algae, and diatoms (2, 6). Bioaccumulation of copper, which is recognized for trace metals (7), may be a problem with these organisms.

The purpose of this study was to determine the amounts of divalent copper and hexavalent chromium removed from an aquatic system. The systems were divided into three fractions: natural water, sediment, and algae. The ability of each fraction to remove the metals from water was explored. In addition, the assimilative capacity of combined systems--containing water, sediment, and algae--for copper and chromium was examined.

CHAPTER II

LITERATURE REVIEW

Current conditions with respect to heavy metal concentrations vary with aquatic systems. In general, sea waters contain less chromium than most rivers or wells. Mertz (8) states that chromium concentrations in 15 rivers of North America range from 0.7 to 84 ppb. Soils across North America show a range from a trace to 250 ppm as Cr_2O_3 . Neither the water nor the soil shows any geographical distribution patterns. In 1962, a study was conducted on the chromium concentration in municipal drinking water in North America. The results showed a range from nondetectable amounts to 35 ppb. The established permissible level is 50 ppb as hexavalent chromium (8).

An extreme example of chromium in sediment is New Bedford Harbor, Massachusetts, which shows levels up to 2146 ppm chromium in the top 20 centimeters (9). Soil profiles show varying concentrations with varying depths (2, 9, 10). In the New Bedford Harbor example, the 0 to 5 cm core showed 218 ppm chromium, the 0 to 10 cm core showed 439 ppm chromium, and the 0 to 20 cm core showed 2146 ppm chromium. The presence of the metal is thought to be from the dumping of industrial waste into the harbor for the past 80 years (9).

Algae from the Susquehanna River in New York show concentrations from 0.01 to 10 ppm chromium (5). Mertz (8) states that chromium is regularly detected in vegetation if the analysis is sensitive. There is a wide

variety of concentration of chromium observed in plants, and this is probably dependent on species, soil, water, and during which season the plant was harvested (8).

Copper concentrations in lakes, streams, and springs in the Yukon Territory of Canada range from 0.001 to 50 ppm copper (3). The Ottawa River in Ontario has no detectable copper (7). In the high water lakes of the northwest territories of Canada, copper concentrations of 0.056 ppm are noted. In central Chile, the Andean streams show a high of 1.2 ppm copper (3). It is not uncommon in the quest for copper that suspect areas are tested for copper in the water. In these waters surrounding copper deposits, concentrations as high as 2,100 ppm are reported (3). Throughout the United States, it is not unusual to have copper concentrations as high as 20 ppb (11, 12). Concentrations over 2 ppm are considered a high level of pollution (13).

Concentrations of copper in sediments are considerably higher than those typical of water systems. The Ottawa River sediment has levels up to 50 ppm (7). New Bedford Harbor has levels up to 6000 ppm copper (9). The Gulf Coast region has a range of copper concentrations from 2 to 157 ppm (14). The sample sites included San Antonio Bay, Galveston Bay, Houston Ship Channel, Texas City Ship Channel, and the Mississippi River Submarine Delta. Copper concentrations in sediments vary from one body of water to another body of water. Copper concentrations also vary with the depth of soil (2, 9, 10, 14, 15). Lake Monona, Wisconsin, is an excellent example of the copper concentration varying with depth of the sediment. The maximum copper content was found at the 60 cm depth. Above and below this depth the concentration decreased rapidly (15).

The copper concentration in the aquatic environment of the algae

will dictate the availability, hence the copper uptake by the algae. The amount of copper uptake by algae varies from specie to specie.

Copper and Chromium in Sediments

There are several properties of soil that affect copper fixation. The size and concentration of clay particles are important factors. Clays have a physical attraction for copper. Stoffers (9) examined different grain size fractions to see if the metals are associated with fine-grain particles. The analyses were performed on the clay fraction smaller than 2 μm . Different types of clays have different adsorption capabilities for copper (9, 16, 17, 18, 19, 20). Kaolinite, illite, and montmorillonite are clays in increasing order of adsorption. This is also the order of increasing cation exchange capacity (19). The cation exchange capacities of a sediment are said to be a valid index of heavy metal ion sorption (7).

The amount of organics in the soil also affect the soil's ability to hold copper. Soil organics react with copper to form strong bonds. Two excellent examples are humic and fulvic acids which are end products of the decomposition of organic residues. Humic acid is the greater absorber of the two (19).

The adsorption of copper by sediments may be inhibited by various competing ions and reactions. Divalent ions will compete for sites on clay particles (17). Calcium in soluble or insoluble forms will compete with copper for binding locations. Copper readily forms CuCO_3 and Cu(OH)_2 if favorable conditions exist (21). Aluminum (+3) will compete more than either the copper or the calcium for these clay binding sites. Leggett (22) reports that Si(OH)_4 reacts with copper at a pH of six or

higher to form a precipitate. Anions will also affect the diffusion rate of copper in montmorillonite. Nitrates (NO_3^-), chlorides (Cl^-), sulfates (SO_4^{2-}), and acetate (OAc^-) are examples of these ions (18).

The pH of a soil is a major factor affecting copper uptake (16, 17, 19, 20, 21, 22). Generally, it can be stated that acid soils retain less heavy metals than neutral soils. The pH strongly influences the selectivity of clays for copper (17). Chemical reactions may also be dictated by pH. The reaction of silicon with copper is an example. The silicons reacting are primarily monomeric silicic acid $\text{Si}(\text{OH})_4$ (22). Misra (21) states that in black (pH 8.1) and alkali (pH 10.9) soils, retention of copper is dependent on the pH value and the presence of carbonates. At high pH values the retention is probably due to the hydrolysis of divalent copper to monovalent hydroxylated copper ions (CuOH^+).

An additional factor influencing the assimilative capacity of a sediment for copper is its surface area, which is directly related to the sediment's texture class. Typical texture classes include loamy sand, sand, clay, silty clay loam, and various combinations. The predominant clay minerals of the different texture classes are of great importance in determining surface area. The relationship between surface areas and metal fixation is best related to divalent cations (20).

The ability of a soil to retain chromium is far less understood. It appears chromium concentrations in sediment are dependent upon its solubility, the presence of competing elements, the organic composition of the soil, and the chemical binding of the element (20). The mobility of chromium in soils containing clays shows little influence by the clays. The calcium content does not affect chromium's mobility either. However, pH of the sediment does have an influence on the mobility of chromium,

but it is overshadowed by the presence of free iron and manganese oxides. Both iron and manganese oxides hold chromium in the sediment (20). There is currently no geographical pattern for chromium distribution, but high concentrations of chromium are often seen in soils of basalt and serpentine origin (8).

Copper and Chromium Uptake by Algae

There are many examples of copper uptake by algae. Copper occurs naturally in water and is considered an essential plant nutrient. The amount of copper taken up by algae is affected by several factors. Algae will compete with soil for copper. Different species of algae will accumulate different concentrations of copper. Laube (7) reports that Anabaena accumulated 20 ppm copper in a 72-hour test period.

Several types of algae can release metabolites that complex metals and modify metal speciation in the water, controlling the metal availability and toxicity. Hydroxamic acids are known examples of metal-complexing agents released by algae (12). McKnight (12) states that Anabaena cylindrica produce extracellular polypeptides that complex and detoxify copper. Research has been conducted using synthetic chelators whose copper complexing properties are known. The results show that the toxicity of copper can be controlled by algae. Inside algae cells are copper binding lignins. Upon cell lysis these copper-bound lignins are released into the water. Binding sites for copper in algae are phosphates and numerous proteins (7). Growth rates are also stated as influencing copper uptake. During periods of rapid growth the highest levels of copper are consumed (11).

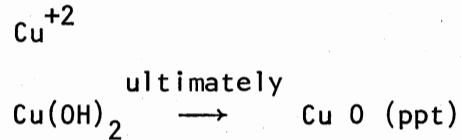
In a study of chromium uptake by algae and duck weeds, Mangi (5)

reports that growth of all the plants were inhibited by a chromium concentration of 10 ppm. During the test period, using a chromium concentration of 10 ppm, the unicells showed a decrease in cell numbers while the filamentous forms showed a weight loss. In these systems there remained a quantity of cells and filaments that were not affected and appeared healthy. Variations in plant tolerance range from 0.32 to 25 ppm. The uptake of chromium by the plants was a function of the initial concentration in the medium. This ratio of plant uptake to medium concentration is known as the enrichment factor. The uptake of chromium by the plants decreased as the concentration of chromium in the medium increased. This relationship is said to be approximately linear with the uptake varying as the concentration increases. The uptake of chromium occurs on the cell walls in both living and non-living cells. The uptake of chromium by dead cells suggest that adsorption is the removal mechanism (5).

Copper and Chromium in Natural Waters

In most natural waters copper may be found in several different forms. Speciation is variable from water to water and within the same water with respect to time. The form copper exists in is a function of pH and the chemical constituents of a water. In a pH range of 4 to 9 probable forms of copper would include (13):

	$\text{Cu}(\text{OH})_2$	(ppt @ pH >6.8)
	CuCO_3	(No ppt.)
Malachite →	$\text{Cu}_2(\text{OH})_2\text{CO}_3$	(ppt. @ pH > 6.0)
Azurite →	$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$	(ppt. @ pH > 6.2)
	$\text{Cu}_2(\text{OH})_2$	



As noted, some forms of copper are soluble at different pH values (13). The pH and ion activity may also affect the interactions of copper with the chemicals found in water.

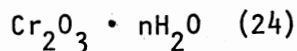
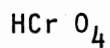
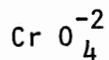
Substances found in water that may complex with copper are numerous. Organics such as humic and fulvic acids, polypeptides, and amino acids may complex copper (13, 15, 23). Phosphates, triphosphates, chlorides, and cyanide will also form copper complexes. The triphosphates will have little influence due to biological hydrolysis. The concentrations of triphosphate is small owing its existence to detergents. Cyanide would have to be available in the equivalent amounts of copper to form stable compound Cu(CN)_2 (23). The bicarbonate-carbonate ion activity will also influence copper speciation.

Stiff (23) states that anions such as silicates, sulfates, and nitrates are non-complexing species. Stiff's conclusions are different than those of Mann (3), who states that sulfates may contribute to the solubility and the form in which copper is found. Sylva (13) concludes that nitrogenous compounds derived from excretion products will complex copper. Concerning silicates, Leggett (22) states that at a pH of 6 or greater, $\text{Si(OH)}_4 + \text{Cu}$ forms a precipitate.

Particulates found in water (also constituents of soils) may also react with copper. Examples are clays and organics in suspension. It is seen that the role of copper in water is a complex function of many variables which can change daily in a natural body of water.

Chromium is present in most natural waters. Upon entering a body of water, hexavalent chromium can be reduced (8, 24). Likely forms would

include:



This reduction may result from an interaction with organic particles.

Chromium can be adsorbed onto particulate matter and settle. There are several substances that act as adsorbents and these are as follows:



Apatite

Clay

Plankton

Algae (living and non-living) (25).

Krauskopf (25) states that MnO_2 is the best adsorber and at low concentrations of chromium will adsorb up to 94 percent of the chromium. Curl (24) agrees with Krauskopf (25) that MnO_2 is an effective adsorbent but disagrees on the adsorbing capabilities of Fe_2O_3 , apatite, clay, and plankton which he considers to be ineffective adsorbents.

CHAPTER III

MATERIAL AND METHODS

Water and sediment samples were taken from three sources surrounding Stillwater, Oklahoma. Two of the sources were Lake Carl Blackwell and Sooner Lake; the third was the Cimarron River. Lake Carl Blackwell (LCB) is a warm, monomictic eutrophic lake. The lake serves the dual purpose of water supply for Stillwater and a recreational lake. Lake Carl Blackwell is located seven miles west of Stillwater. A point on the south side of the lake served as the sample site. Sooner Lake is located 30 miles north of Stillwater on Highway 177. The lake was filled two years ago to supply cooling waters for the recently constructed Sooner power plant. The lake also provides a recreational area. The sample site was at the south end of the lake. The Cimarron River flows from northwest Oklahoma on an east-southeast course. The river converges with the Arkansas River at the head of Lake Keystone. The sample site was located 0.5 mile south of Perkins under Highway 177 bridge.

Sediments from each site were collected in a similar manner. The sediments were collected at a water depth of approximately three feet. An effort was made to remove the top 15 centimeters of sediment. Once collected the samples were placed in plastic tubs. The standing water was decanted and the samples were placed in the refrigerator to retard decomposition of organic matter.

A heterogeneous algae stock originating from Theta Pond on the

Oklahoma State University campus was kept in an aerated aquarium. Nutrients dissolved in tap water were added periodically to sustain life.

Lake or river water was collected just below the surface of the water. The water was stored in five gallon plastic containers.

Experimental Aquatic Systems

Initial systems containing distilled water and sediment were set up and run to determine the range of metal concentration to be used in the simulated aquatic models. The aquatic models using natural lake or river water and set up in duplicate were as follows:

1. Natural water + metal solution
2. Natural water, metal solution, and algae suspension
3. Natural water, metal solution, and sediment
4. Natural water, metal solution, sediment, and algae suspension

The aquatic models were set up identically with respect to weight of sediment, volume of water, and amount of algae. The models were set up in one gallon glass jars. The jars and all equipment involved were cleaned with a nitric acid solution.

Each model received 900 grams (dry weight) of sediment. The surface area was 29.41 square inches. However, the sediment depth varied. Lake Carl Blackwell depth was 2.5 inches, Sooner Lake, 2.25 inches, Cimarron River, 2.0 inches.

A total liquid volume entering the system was three liters. To obtain a three-liter volume the required amount of copper solution plus the algae suspension were subtracted from three liters. This difference was the amount of natural water added. Preparation of the natural water consisted of filtration through a Whatman number five filter.

A divalent copper concentration was achieved by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water. A standard solution of one gram copper per liter solution was used throughout the experiment. Identical models were set up using $\text{K}_2\text{Cr}_2\text{O}_7$ as the hexavalent chromium source. The standard solution used was 1 gram chromium per liter. Dilutions were made from these standard solutions.

When added, the algae suspension created a transmittance reading of 50 percent in three liters of water. The optical density proved to be a consistent method for providing uniform distribution of algae in duplicate models as well as the separate aquatic systems.

All systems were kept aerobic by means of a single stone air diffuser. To minimize evaporation lids were used. Aeration caused minimal sediment and algae turbulence. The systems were maintained at a room temperature of approximately 24°C . The models were in the presence of both natural and artificial light.

Analysis Performed

The sediment was placed in an oven at 103°C for drying purposes. The 900 grams of sediment used in the appropriate models were weighed on a Troemner triple beam balance. The organic content was measured by igniting a one gram sediment sample for 20 minutes at 600°C . The fixed fraction was then subtracted from the total to yield the volatile or organic content. The sediments were put through sieve analysis using a U.S. Standard Sieve Series sieve. The hydrometer analysis was accomplished using a Fisher Scientific hydrometer. Soluble metals in the sediment were measured by adding one gram sediment to 50 ml of distilled water and

mixing for one hour. The sample was then filtered through a 0.45 μm filter and the filtrate tested.

The algae stock suspension was examined microscopically to identify dominant forms of aquatic life. The transmittance of the algae suspension was measured using a Bausch and Lomb Spec. 20 spectrophotometer.

The natural waters were put through a series of tests. The pH of the natural waters were determined using an Orion Research model 701 pH meter. A Beckman 915 TOC analyzer was utilized to determine the organic content of the water. Methods outlined in Standard Methods (25) were used in the analysis of hardness, alkalinity, and acidity. The following tests were run on a Hach dr/2 spectrophotometer analyzer:

metal concentrations

phosphates

nitrates

sulfates

chlorides

The aquatic models were set up on day zero and maintained for a 14-day period. Testing began on day one. One test was run per model daily to determine the metal concentration in the water of that model. Dilutions were made as the concentrations dictated.

CHAPTER IV

RESULTS

The organic content of each of the three sediments was determined and the results obtained are shown in Table I. Lake Carl Blackwell sediment had the highest organic content, 71.8 mg/gm. Blackwell's sediment was followed by Sooner Lake, 64.7 mg/gm., and the Cimarron River sediment had the lowest concentration of organic matter, 4.3 mg/gm. The water soluble metal concentrations of the three sediments were similar. Each soil's leachable metal content was approximately the same as the distilled water blanks tested. The distilled water had a copper concentration of 0.1 mg/l and a chromium concentration of 0.01 mg/l. Table I summarizes these findings.

Using sieve and hydrometer analysis each sediment was divided in three general fractions. These fractions were sand, silt, and clay. Table II shows the percentage of each fraction.

The stock algae contained a variety of species. The predominant specie was the blue-green algae. Other life forms present included green algae, fungi, nematodes, and diatoms.

Results from water quality analyses of each natural water are given in Table III. Initial copper and chromium levels are extremely low and can be neglected considering the high concentrations used in the experiments.

The uptake of copper and chromium by each sediment was determined by applying metal dissolved in distilled water to each sediment. As seen

TABLE I
SEDIMENT ANALYSIS

Test	LCB	SL	CIM RIV
Organics	71.8 mg/gm	64.7 mg/gm	4.3 mg/gm
Soluble Copper in Sediment Filtrate	0.09 mg/l	0.05 mg/l	0.09 mg/l
Soluble Chromium in Sediment Filtrate	0.01 mg/l	0.01 mg/l	0.01 mg/l

TABLE II
SIEVE AND HYDROMETER ANALYSIS

Sample	Sand (%)	Silt (%)	Clay (%)
LCB	37	48	9
SL	16	68	16
CIM	70	30	

TABLE III
WATER QUALITY ANALYSIS PRIOR TO EXPERIMENT

Test (mg/l)	LCB	SL	CIM RIV
Alkalinity			
Total	137	133	159
Phenolphthalin	15	8	11
Acidity	0	0	0
Phosphates	2.5	17	3.5
Nitrates	1.0	1.0	1.0
Chlorides	21	250	2275
Sulfates	21	100	375
Copper	<0.01*	<0.01*	<0.01*
Chromium	0.03	<0.02	<0.02
Hardness	127	204	543
pH	8.0	7.5	6.8
Total Carbon	105	250	130
Inorganic	2	3	3
Organic	103	247	127

*Concentrations could not be read accurately below 0.01 mg/l

from Figure 1, Lake Carl Blackwell's sediment fixed the most copper and chromium, followed by Sooner Lake and Cimarron River sediments. This study allowed the determination of an adequate range for the concentration of metal to be used in the aquatic models.

Using separate models for each parameter and a final combined model allowed separate and total system analysis. Lake Carl Blackwell's assimilation of copper is shown in Figure 2. The maximum assimilation occurred in the sediment and water system accounting for 140 mg/l removal of copper from the water. The combined system removed approximately 120 mg/l copper. The algae and water system was responsible for the removal of 80 mg/l of copper from the water. The water alone showed a decrease of about 40 mg/l copper.

The Sooner Lake models, Figure 3, showed similar tendencies with respect to the order of removal efficiencies. However, the amount assimilated by these models was considerably higher. The sediment and water model was responsible for approximately 158 mg/l copper removal from the water. The removals for the combined systems and the algae and water models were close with about 150 mg/l copper removal. The water model showed a depletion of copper from the water of about 132 mg/l.

The assimilation of copper by the Cimarron River is shown in Figure 4. All four models were close, separated by a maximum difference of 5 mg/l copper. The range of removal for the four systems was 160-165 mg/l.

During the test period a film or layer formed on top of the sediment. This layer varied in depth and the amount of the surface area it covered. Part of this layer was algae that had settled. Another part of this layer was copper that had precipitated. Lake Carl Blackwell's models had the least depth and surface area covered by this layer. None of the

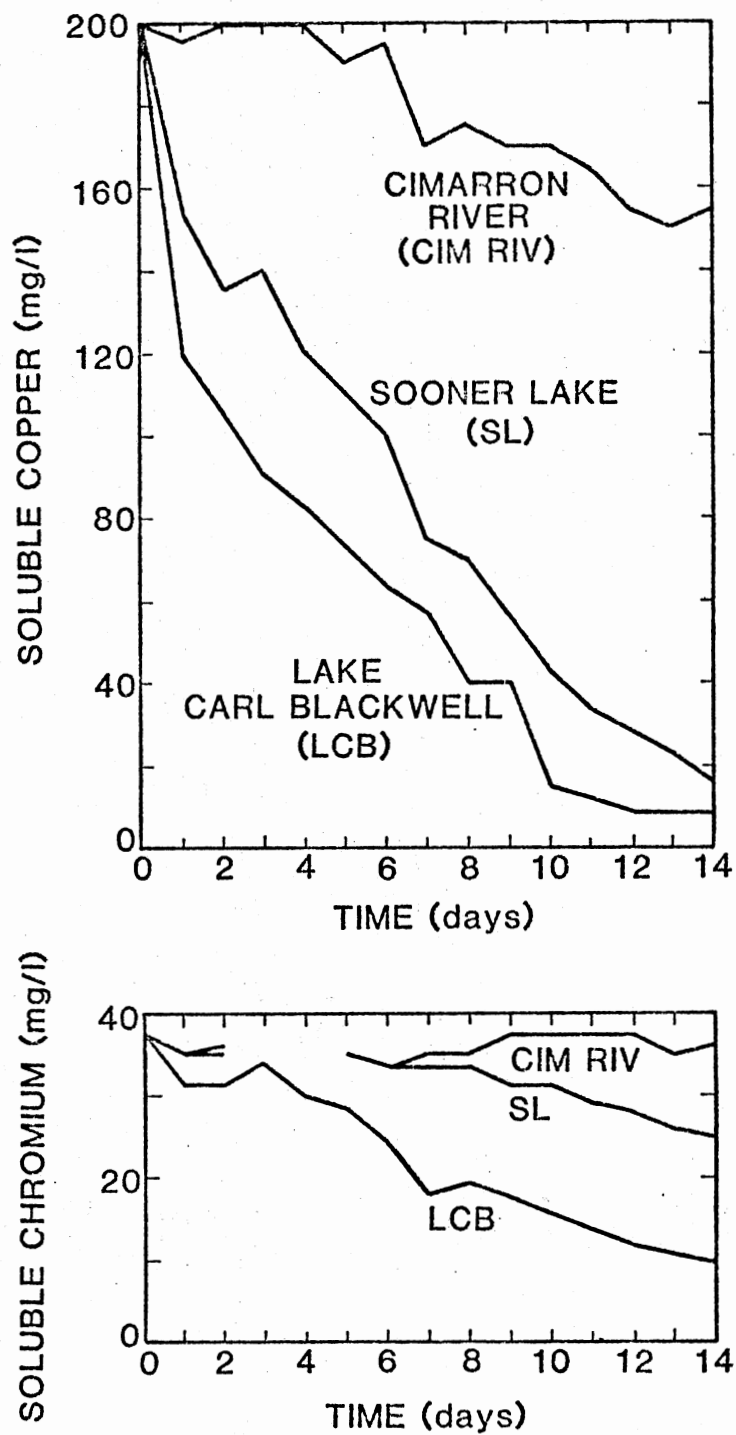


Figure 1. Soluble Copper Versus Time for Sediment from LCB, SL, and CIM Riv

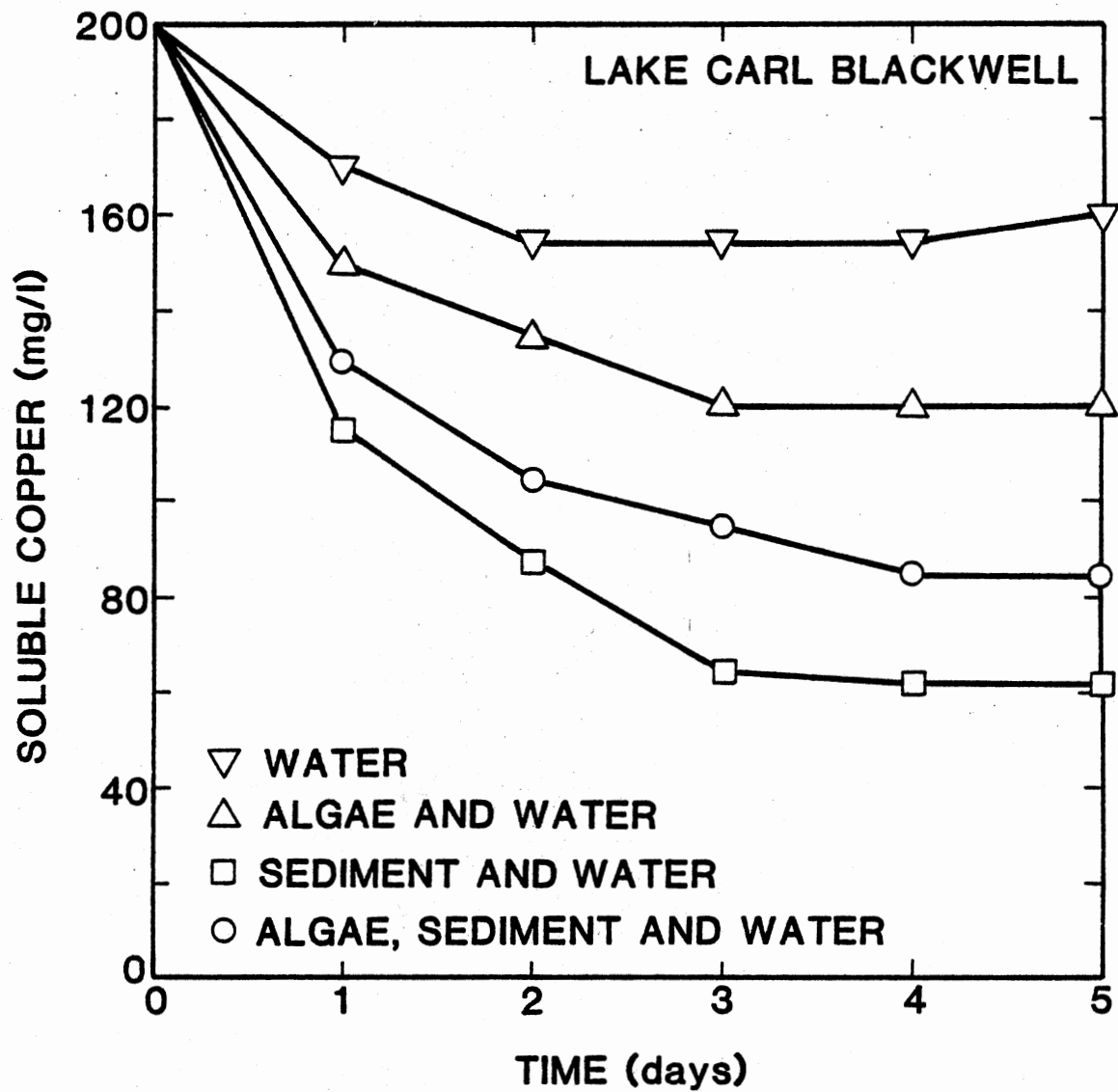


Figure 2. Soluble Copper Versus Time for Sediment, Natural Water, and Algae in LCB

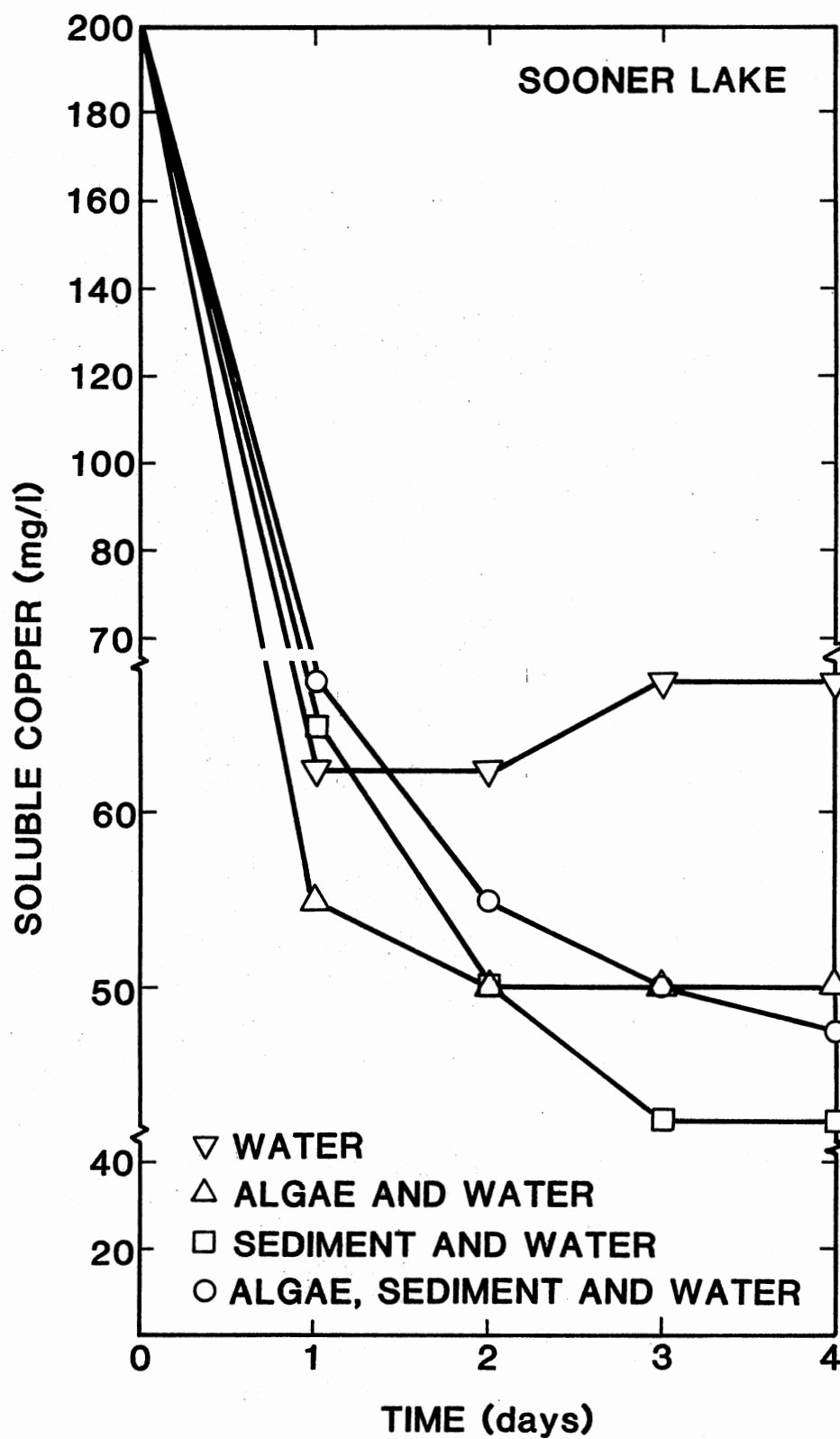


Figure 3. Soluble Copper Versus Time for Sediment, Natural Water, and Algae in SL

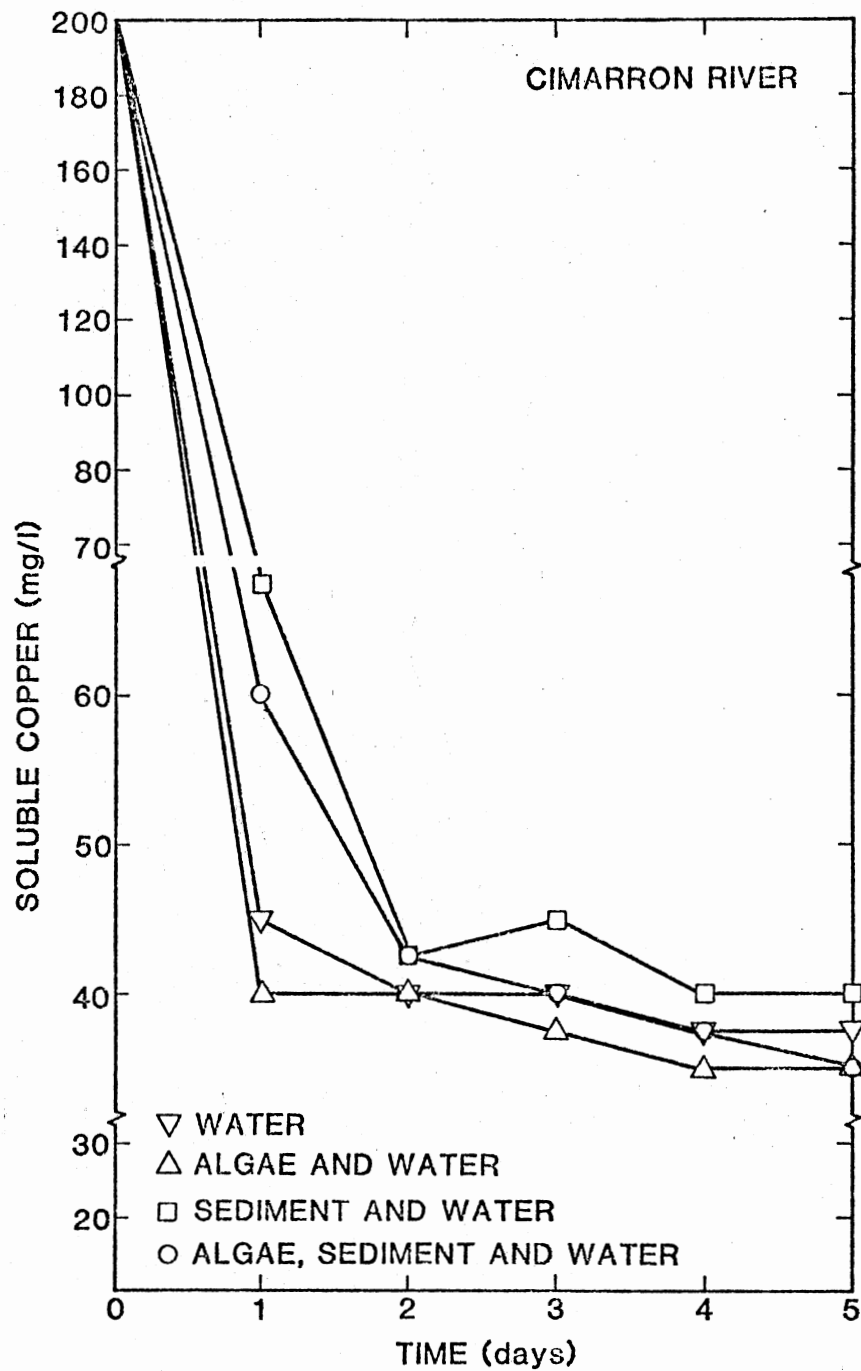


Figure 4. Soluble Copper Versus Time for Sediment, Natural Water, and Algae in CIM Riv

Lake Carl Blackwell models' complete surface area was covered. All of the Sooner Lake models had most of their surface area covered. The layer in these models ranged from a light film (ppt. only) to 3 millimeter (algae + ppt) in depth. The covering was not uniform due to currents caused by the aerator. The Cimarron River models had their entire surface area covered. The precipitated layer in the lake water and sediment model was approximately 4 millimeters deep. The precipitate and algae layer found in the algae and water model and the combined model ranged from 7 to 9 millimeters in depth.

Chromiums removal was considerable different from copper removal. Figure 5 shows the results from the 12 models. The Cimarron River models showed very little uptake of chromium from solution. On the eighth day an increase can be seen over the sixth day. The dilution process is believed to be responsible for this increase. In addition, the pipette used throughout the experiments broke after testing the Lake Carl Blackwell and Sooner Lake models on the eighth day. The use of a new pipette coupled with the 1:100 dilution may have been responsible for the increase observed. In the Sooner Lake models the greatest decrease in chromium, 25 mg/l, occurred in the sediment and lake water model. The combined model removed 10 mg/l chromium. The remaining two models showed a small decrease of 1-3 mg/l. These same two models show an increase on the tenth day again, possibly due to the previously mentioned broken pipette. All of the Lake Carl Blackwell models showed a decrease in the chromium concentration. The maximum metal assimilation, 16 mg/l, occurred in the combined model. The sediment and lake water model showed a decrease of approximately 19 mg/l. The algae and lake water model showed decreases of about 5 mg/l. Overall the majority of the metal stayed in solution.

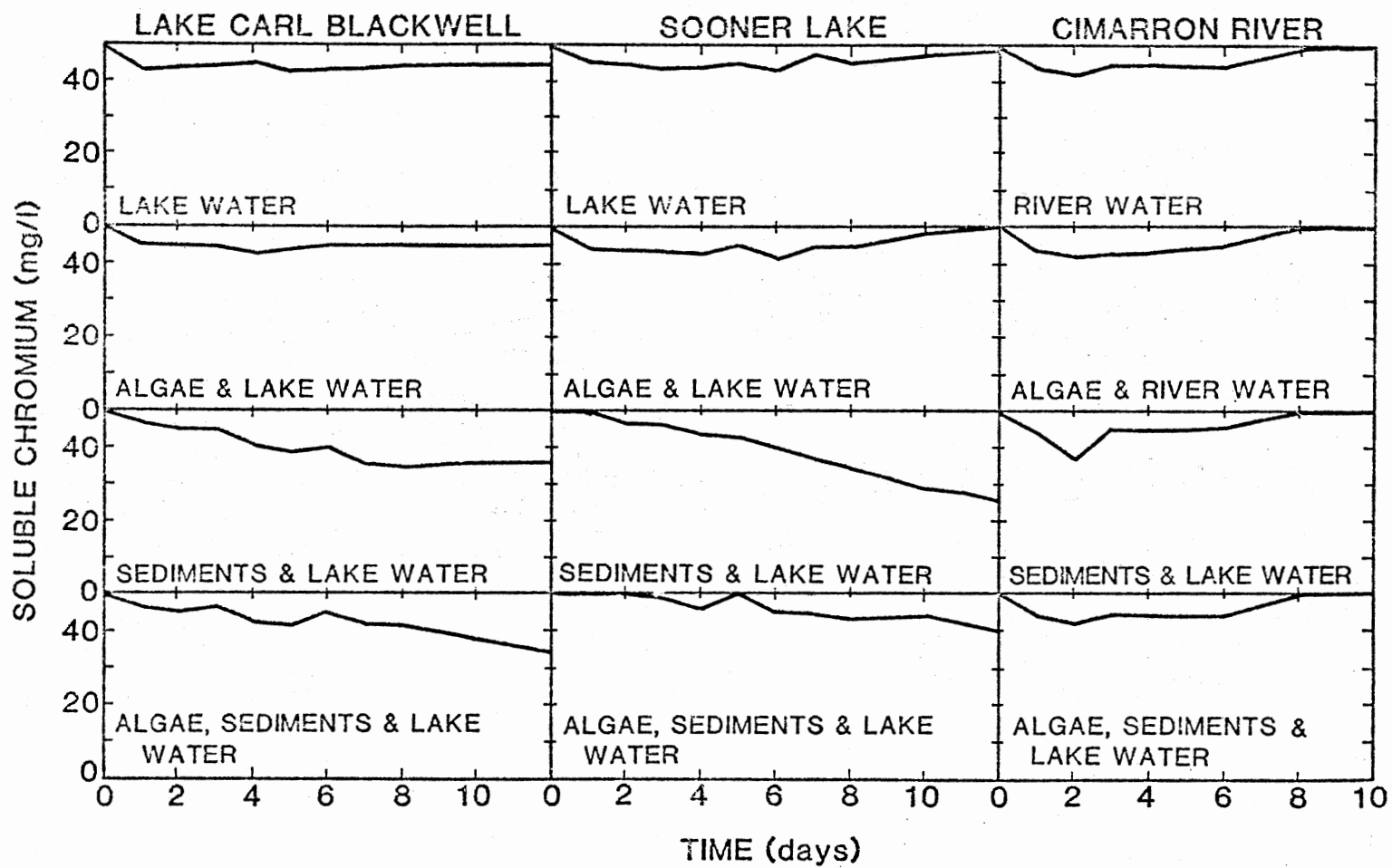


Figure 5. Soluble Chromium Versus Time for Sediment, Natural Water, and Algae in LCB, SL, and CIM Riv

CHAPTER V

DISCUSSION

The objectives of this experiment were to determine the fate of copper and chromium in an aquatic system. From the results presented in the previous chapter, it is seen that copper was readily removed from solution while chromium was fixed only in small amounts by the aquatic systems. This discussion will relate the results of the individual components and model analyses to the literature cited.

Several authors have stated that clays and organic matter will fix copper (16, 17, 18, 19, 20). As seen from Table II all the sediments have organic matter and all the sediments but Cimarron River sediments have clay present. From Figure 1 the fixation of copper from distilled water solutions, by the sediments, was highest in the Lake Carl Blackwell models, followed by Sooner Lake models, and then the Cimarron River models. Table II shows that Lake Carl Blackwell sediment had the highest organic content, followed by Sooner Lake sediment, and last the Cimarron River sediment. The relationship between the percentage clays and copper fixation did not follow the same trend. Sooner Lake sediment had the highest clay content, almost twice that of Lake Carl Blackwell sediment. However, Lake Carl Blackwell removed slightly more copper than the Sooner Lake systems. Copper fixation by clays is also a function of clay mineralogy which may have played a role in the higher uptake by Lake Carl Blackwell sediment. The Cimarron River sediment had no clay present. Comparing the removal

of copper by Lake Carl Blackwell and Sooner Lake sediments and the copper removal by Cimarron River sediment shows that the removal efficiency for Lake Carl Blackwell and Sooner Lake was three times as high. The fixation of copper by the combined action of the organic matter and the clays in Lake Carl Blackwell sediment and Sooner Lake sediment could have kept their removal efficiencies close to each other. The Cimarron River had no clays and little organic matter, therefore, fixing the least copper. This is in agreement with the supporting literature (17, 18, 19).

The removal of chromium from distilled water solutions (Figure 1) was highest in the Lake Carl Blackwell sediment, followed by Sooner Lake sediment, and then the Cimarron River sediment. This is the same trend found with copper. The clay content is said to have little influence on chromium fixation (20) and no correlation between the clay content of the sediment and chromium uptake could be established. The organic content is able to chemically reduce chromium (20). The Hach analysis for chromium was for hexavalent chromium; therefore, any chemical reduction of chromium would appear as a reduction in concentration. Table II shows that all three sediments had organic matter present. The reduction of chromium could also be attributed to iron and manganese oxides. No analysis for these compounds was made, but they are not unusual components of sediments.

The remaining discussion will include the results from models that had natural water present. The chemistry of the natural waters influences the removal of the metal and therefore is a factor in all the models containing natural water. There are many compounds in water that may react with copper. Table III shows the results of the analyses done on the natural waters. The carbonate, bicarbonate alkalinity can influence

the speciation of copper (23). The phosphates, nitrates, chlorides, and sulfates can complex copper (3, 23). Hardness may indirectly influence copper, resulting in precipitation at a particular pH (3, 13). The organic content can also affect the concentration of copper in water (13, 15, 23). In the natural water systems, the Cimarron River water was responsible for the largest copper depletion, followed by Sooner Lake and Lake Carl Blackwell water. Not knowing the chemical composition of the precipitate that formed in these models makes it impossible to determine what had the major influence. The Cimarron River water had the greatest total concentration of possible complexing agents, followed by Sooner Lake, and last by Lake Carl Blackwell. The greatest copper depletion occurred in the water with the greatest total concentration of possible complexing agents.

Chromium was far less reactive than copper in the natural water models, as seen from Figure 5. Lake Carl Blackwell's water had the largest depletion, followed by Sooner Lake and Cimarron River models. The maximum depletion of 6 mg/l exemplifies the fact that chromium was not very reactive. The depletion does not seem to follow any trend. There are factors that influence the fate of chromium in natural waters that were not analyzed in the initial testing. The hexavalent chromium may be reduced and settled out due to the adsorption onto organic particulate matter or the hydrolysis andolation of the chromium hexaaquo nucleus forming insoluble hydroxides (8, 24). There are several adsorbents of chromium including Fe_2O_3 , MnO_2 , apatite, clay, and plankton (25). From the results it is impossible to determine what exerted the major influence on the removal of chromium.

In the natural water and algae models the depletion of copper is

greater than that found in the natural water model which is as expected. The depletion follows the same pattern as the copper and natural water models. The greatest depletion occurred in the Cimarron River system (Figure 4), followed by the Sooner Lake system (Figure 3), and last the Lake Carl Blackwell system (Figure 2). The largest difference between the natural water model and the algae and natural water systems occurred in Lake Carl Blackwell system. The Cimarron River system took up an additional 2.5 mg/l copper over the amount removed by the natural water only systems. The Sooner Lake system took up an additional 17.5 mg/l and the Lake Carl Blackwell system took up an additional 40 mg/l copper. Laube (7) states that particular species of algae can take up to 20 ppm copper in a 72-hour test period. McKnight (12) reports that algae can produce extra cellular and intercellular copper complexing compounds. The addition of algae to the systems may therefore be accountable for the increased copper uptake seen in the natural water and algae systems. The differences in the amounts removed attributed to the algae may be a function of the amount of copper that precipitated. In the algae and natural water systems most of the algae settled to the bottom of the container. The flocculant precipitate that formed, settled on top of the algae. The precipitate may have formed a layer that restricted the contact between the water and algae. The model with the greatest amount of precipitate (Cimarron River) showed the smallest uptake by the algae. In addition, when the algae entered the Cimarron River water it may have experienced osmotic shock. The chloride concentration was very high in this water and the algae may have died or been damaged upon entering the system. This could also account for the small copper depletions by the algae in the Cimarron River system.

In the natural water and algae systems chromium again showed its non-reactive behavior. In the Cimarron River and Sooner Lake model, Figure 5, it is seen that most of the chromium stayed in solution. The Lake Carl Blackwell model (Figure 5) showed an uptake of 5 mg/l chromium, which is less than the Lake Carl Blackwell natural water model. The sample was diluted 100 times and this could have resulted in an error. In general, there was no significant uptake of chromium which could be attributed to the algae. According to Mangi (5) the cell wall will take up chromium if the cells are alive or dead. This uptake is affected by the concentration of chromium in solution. Research performed by Mangi (5) used a chromium concentration ranging from 0.1 to 10 ppm. At high concentration of chromium (10 ppm) the ratio of plant uptake of chromium to initial medium concentration was less than at lower concentrations. Increasing the chromium concentration in the medium causes a linear decrease in plant uptake of chromium (5). This could account for the lack of uptake by the algae in the experimental system since a concentration of 50.0 mg/l of chromium was utilized.

The next models to be discussed include the natural water and sediment systems. The copper depletion follows the same pattern as in the two previous sets of models. The Cimarron River model, Figure 4, took up the largest amount followed by Sooner Lake, Figure 3, and last by Lake Carl Blackwell, Figure 2. Comparing the natural water and sediment models, Figures 2, 3, and 4, to the distilled water and sediment models, Figure 1, shows that all but the Cimarron River model depleted less copper in the natural water and sediment systems. The Cimarron River natural water only model, Figure 4, exerted a larger influence than the sediment and distilled water model, Figure 1. This is the opposite of

the remaining models. The sediments of Sooner Lake and Lake Carl Blackwell fixed more copper in the sediment and distilled water model, Figure 1, than the natural water only model, Figures 2 and 3. The copper precipitates that formed may have formed a barrier that restricted contact with sediment as in the algae and natural water models.

The comparison of the natural water models and the natural water with sediment shows that the sediment in the Lake Carl Blackwell and Sooner Lake systems did have an influence on uptake. The greatest influence and least precipitate occurred in the Lake Carl Blackwell model, Figure 2. The sediment appears responsible for an uptake of 98 mg/l copper. The Sooner Lake sediment, Figure 3, shows a 25 mg/l copper removal. All of the Cimarron River models, Figure 4, are within 5 mg/l of each other and therefore no significant conclusion can be drawn. The addition of sediment to the natural water would result in a complex interaction of the copper with the sediment and water chemistry. Both the natural water and sediments show great affinity for copper. Together their effects do not appear to be accumulative, which is probably the result of influence of the precipitate layer. The competition for the copper between the sediments and the natural water could also be a factor.

Chromium activity in the sediment and natural water model is seen in Figure 5. The Sooner Lake model took up 24 mg/l of chromium, Lake Carl Blackwell model took up 14 mg/l and the Cimarron River model has an insignificant response. The organics found in the natural water and sediment could be responsible for these reductions in the chromium concentration (20).

The combined models concerning copper depletion show that the affinity for copper exhibited by each component does not result in an

accumulative effect. The three components, algae, natural water, and sediment, were expected to deplete the largest amount of copper. This was not the case in any of the models. As stated earlier the algae and precipitate layer may have acted as a barrier, restricting the contact between the sediment and water. This double layer varied in depth from system to system and model to model.

The chromium combined models were similar to the copper models. They did not show an accumulative effect. The algae layer may have been responsible for this.

CHAPTER VI

CONCLUSIONS

Copper was fixed by natural water, sediments, and algae. The natural waters and sediment accounted for the majority of the copper fixed. Chromium was less reactive than copper, and significant uptake could only be attributed to the three sediments.

The quantitative results obtained from this study will not be applicable to all natural water systems because of the variation in water, sediment and algae composition from one surface water source to another. In addition, the uptakes of the metals observed in laboratory models may not apply to Lake Carl Blackwell, Sooner Lake, and the Cimarron River especially in the case of copper. The precipitate layer that formed and covered the surface of the sediment in the aquatic models inhibited sediment uptake of copper. Although the precipitate would form in a lake or river, it possibly would not cover the sediment because of the larger surface area to volume ratio. Therefore, the total uptake in the actual lake or river could be higher. Even though the actual numerical results obtained from this study may not be universally applicable, the trends observed with respect to sediment, algae, and water uptake of metals, as well as the correlations established between sediment characteristics, water composition and metal fixation provide needed information with respect to the fate of metals in aquatic systems. This is especially true

for chromium for which available literature and information is very limited.

It should be pointed out that the results from this study pertain only to the uptake of copper and chromium in surface waters. The potential for release and resolubilization of the metals as the result of pH and oxidation-reduction potential changes was not investigated. However, this is a very viable possibility in a natural water system and the effective management of heavy metal pollution of aquatic systems should be based on an understanding of factors affecting both uptake and release.

CHAPTER VII

RECOMMENDATIONS

The recommendations are:

1. Work with lower chromium concentrations to see if the high concentration inhibited algae uptake.
2. Use larger aquatic models to reduce interference by precipitate layer.
3. Determine clay mineralogy and its effect on sediment fixation of copper and chromium.
4. Determine the iron and manganese oxide concentrations in sediments and their effect on the uptake of copper and chromium by the sediment.
5. Use atomic adsorption for analysis (not available at the time of this research) of sediments, algae, and waters.

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