CONTROL OF POLLUTION IN WATERS
CONTAINING HEAVY METALS

By

Don F. Kincannon
Marcia H. Bates
Richard N. DeVries
School of Civil Engineering

OKLAHOMA STATE UNIVERSITY

ABSTRACT

This study provided an integrated set of experiments encompassing the fate of chromium and copper in biological wastewater treatment processes, aqueous environments, and soil systems. The rotating biological contactor and activated sludge were used as the wastewater treatment processes. Water and sediments were used from several bodies of water in the Stillwater, Oklahoma area. Sandy and red silty clay soils were used as the soil systems. It was found that chromium was not generally removed by biological treatment processes or by algae but was removed by the lake and river sediments. Copper was removed by all systems. The removal efficiency of the metals was very dependent upon operating and environmental conditions.

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INTRODUCTION

Heavy metal pollution of the environment is becoming a problem of increasing concern. Metals are being derived from numerous point and non-point sources including wastewater effluents, atmospheric contributions, mining wastes, industrial discharges, runoff, leachates from landfills and hazardous waste disposal sites, pesticides, sewage sludges and natural geochemical leaching.

Copper and chromium, two of the heavy metals polluting the environment, are primarily derived from plating industries. In addition, another major source of copper is the use of copper sulfate as an algicide. In high concentrations both of these metals are undesirable. The bioaccumulation of either metal by primary producers, such as algae or fish, could result in the movement of the metals through the food chain (Laube et al, 1979) where they subsequently could become available for human consumption. Increased levels of copper in fresh water can affect both fish and zooplankton populations (Purves, 1977) and, as demonstrated by McIntosh and Kevern (1974), cladoceran and rotifer populations have been depressed in ponds with copper levels of 3 mg/l. Chromium is correlated with the glucose tolerance factor and is possibly a factor in some cases of diabetes mellitus (National Academy of Science, 1974). In addition, chromium is listed as a carcinogenic metal (Strain et al, 1975).

One of the major concerns with respect to the prevalence of copper and chromium in the environment is the distribution of these metals in

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water supplies. Although both metals may be derived from nonpoint sources, point sources such as industrial and domestic wastes may contribute heavily to metal loadings. Metals from wastewater effluent can ultimately contaminate both ground waters and surface waters. The amount of the contamination may somewhat be lessened by the fact that metals can be removed by soils as water percolates to the aquifers or be precipitated or adsorbed onto sediments in surface water supplies.

Proper management of metals in the environment includes the development and utilization of effective wastewater treatment practices and the investigation and subsequent understanding of the fate of metals in aquatic and soil systems. The purposes of this study are threefold. The ability of activated sludge systems and rotating biological contactors to remove copper and chromium will be evaluated concurrently with a study of the effects of these metals on the performance of the biological systems. The fate of the metals in aquatic systems with respect to uptake by algae and sediments or precipitation with ions in the aqueous phase will be examined. Sediment fixation of the metals and precipitation from the aqueous phase will be correlated with sediment characteristics and water quality parameters respectively. The third purpose of this study is to investigate the mobility of copper through soil columns and to study some of the factors affecting metal retention by soils.

The results from this study should further elucidate the behavior of copper and chromium in wastewater treatment processes and in soil and water systems. In addition, the investigation will yield information necessary for the proper management of heavy metals in the environment.

Effects of Chromium and Copper on Biological Treatment Processes

Chromium

The effects of heavy metals on biological treatment processes have been studied to varying degrees.

Ingols (1953) reported that the toxicity effect of chromium depends upon (a) the amount of organic matter present, e.g., strength of the sewage and type of organisms (autotrophic, heterotrophic); (b) state of oxidation of the chromium (the valance of chromium); (c) the presence or absence of oxygen. Ingols and Kirkpatrick (1952) concluded that the hexavalent chromium is much more toxic under anaerobic conditions than under aerobic conditions; however, trivalent chromium is relatively more toxic under aerobic conditions than under anaerobic conditions. Ingols also showed that hexavalent chromium seems to be 100 times more toxic than is trivalent chromium.

Moore and McDermott (1963) in their observations on COD removal showed that hexavalent chromium (Cr^{+6}) concentrations were present in the influent. When Cr^{+6} was fed at 20 mg/l it was occasionally found in small quantities in the effluent. With 5 mg/l and higher chromate feeds, variable but increasing amounts of Cr^{+6} passed through the system to ' emerge as either hexavalent or reduced chromium in the effluent. They also found that chromate noticeably restrained the development of odor in the primary clarifier and the development of Sphaerotilus in the mixed liquor.

Jenkins and Hewitt (1942) studied the effect of chromium on nitrification. They found that when activated sludge which was able to oxidize 40-50 mg/l ammonia nitrogen to nitrate within 12 hours at 18-19°C was subjected to 10 mg/l potassium chromate, the activated sludge failed to produce nitrate (NO_3^-) in 20 hours; however, nitrite (NO_2^-) formed instead. Within 48 hours following a second addition of sewage containing 10 mg/l of potassium chromate, formations of nitrite (NO_2^-) and nitrate (NO_3^-) were halted. Another experiment by Graham (1943) showed that inhibition depends considerably upon the nature and concentration of the heavy metals, the frequency and duration of their discharge, and probably also on the operational conditions in the plant. Influence on nitrifying bacteria is due, probably, to metal being either precipitated, adsorbed or chelated by constituents of the sludge.

Ingols and Fetner (1961) indicated that the presence of chromates will tend to cause a bulky sludge; that is, molds or Sphaerotilus will develop in preference to the zoogleal masses in the presence of chromate. This development of a filamentous sludge was observed in attempts to obtain the comparison of toxicity with acclimated sludge over non-acclimated sludge. Results indicate that mold mycelium have been seen at 500 mg/l concentration of sodium chromate, but no bacteria. Chromate at 500 mg/l concentration prevented the growth of bacteria to an extent that they did not compete for the food and space in the agar plate. Molds, however, are sufficiently resistant to the chromate at a concentration of 500 mg/l. In aerobic studies, Ingols and Hilly (1956) found that sludge having a predominance of Sphaerotilus, or zoogleal masses, responded differently to the same concentration of chromate. They conducted an

experiment to measure respiration by determining the CO_2 produced and the number of viable organisms which could be placed on nutrient agar. E. coli (bacterium) and Saccharomyces elliposideus were chosen for the experiment, because they produce CO_2 under aerobic conditions. Results indicated that with a sodium chromate concentration of 10 mg/l there was no effect on the respiration of either E. coli or S. ellipsoideus.

Stone (1961) found that potassium chromate at a concentration of 1 ppm reduced oxygen uptake by 18 percent. Studies by Dawson and Jenkins (1950) indicate that trivalent chromium is more toxic to activated sludge than is hexavalent chromium. Krieger and Moore (1949) reported that both trivalent and hexavalent chromium are toxic at 1 or 2 ppm in the BOD test, but the trivalent form is generally more toxic.

Moore (1961) showed that 10 mg/l of chromium would not interfere with conventional activated sludge treatment or anaerobic digestion of the sludges and that concentrations of the chromium in the effluent were reduced by over 50 percent.

Jenkins and Hewitt (1940) studied the effect of chromate on bacterial filters. They found that 0.1 part of Cr as K_2CrO_4 per 100,000 parts of sewage has little effect on the oxidation of organic matter or nitrification activity; one part of Cr per 100,000 parts of sewage slightly increased the amount of organic matter in the effluent and reduced the nitrification activity; 10 parts of Cr per 100,000 parts of sewage decreased nitrification 66 percent and 78 percent in two experiments, and still further increased the amount of organic matter in the effluent. They also found that the upper part of the filter receiving 10 parts of Cr contained about twice as much deposited solid matter as

did the control filter receiving no chromate. They also reported that, in sewage containing 2.6 ppm chromium as K_2CrO_4 (0.7 ppm as Cr), the BOD was decreased appreciably. Monk (1939) found that a suspension of A. aerogenes in contact with neutral chromium plating waste containing 5.2 ppm of Cr killed 16 percent of the organisms in two hours while 26 ppm Cr killed 46 percent. He also concluded that 50 ppm chromates as CrO_3 (26 ppm as Cr) might be permitted in sewage without affecting treatment efficiency. Jenkins and Hewitt (1942) studied the effect of potassium chromate on the purification of sewage by activated sludge. Their findings indicated that 1 ppm of hexavalent chromium has no effect on the activity of nitrifying bacteria; 2 ppm concentration of Cr^{+6} caused some depression of nitrification, 10 ppm of Cr^{+6} destroyed the respiration activity of the sludge. A study concerned with the effects of metal finishing waste containing potassium chromate on percolating filters showed that potassium chromate, equivalent to 1 ppm hexavalent chromium, had a perceptible effect on the BOD of the effluent and also reduced nitrification. The effect on the BOD of the effluent and nitrification was more severe at a 10 ppm concentration of chromium; 100 ppm of Cr^{+6} markedly reduced the oxidation of organic matter and ammonia. Gellam (1952) in his investigation dealing with metals, noticed two important points. First, when the concentrations of metal and sewage were decreased in the same proportion, the toxic effect of metal remained approximately constant. Second, the toxicity of the metal depends upon the pH of the solution. Thus, there was a marked drop in the toxicity of added trivalent chromium between pH 6 and 7. A trivalent chromium concentration up to 10 ppm was demonstrated by Heukelekian and Gelman (1955) to have little effect on

O_2 utilization, while 25 ppm concentrations caused an 80 percent reduction in a 24-hour period, and 14 percent reduction for a 5-day BOD. At 50 mg/l of trivalent chromium, inhibition of O_2 utilization was 27 percent for the 5-day period. Addition of 75 ppm chromium inhibited O_2 utilization after the first day. The effect of increasing concentrations of hexavalent chromium on O_2 utilization of sewage up to a concentration of 100 ppm is not sufficient to exert a complete toxic effect, because observations have shown that O_2 utilization was 67 percent of the control sample after a 5-day period. At Grand Prairie, Texas, Wells (1943) found that poor settling of activated sludge and low treatment efficiency were caused by the presence of chromium in the aeration liquor. Also high dissolved oxygen values were found in the activated sludge. Spencer (1939) concluded from a study on a trickling filter that chromates ranging from 3.5 to 67.5 ppm stopped biological action. Bozich (1959) found that nitrification begins to be retarded between 0 and 1 ppm concentrations of hexavalent chromium, and nitrification is completely retarded at 4 ppm of hexavalent chromium. Also the percentage of chromium removed by activated sludge is independent of concentration, with 1.5 to 3 percent of the metal fed being removed at concentrations from 1 through 24 ppm.

Copper

Shumate and Moulton (1963) found that the respiratory activity of sewage organisms is significantly affected by low copper concentrations. He concluded that copper at 45 mg/l is not sufficient to halt biological activity in aerobic biological waste treatment processes. His experiments show that adding copper continuously to the influent sewage results

in a linear decrease in respiratory activity. Heukelekian and Gelman (1955) noted that several factors affecting the toxicity of metal ions to activated sludge are pH, substrate concentration, and the amount of biomass. To this, Sawyer, Frame and Wold (1955) added the factor of temperature. They showed that increasing temperature decreased the toxicity of the hydroxyl ion. Dawson and Jenkins (1950) reported that Cu^{++} depressed respiration more than did Ni and CN^-. Barth and Ettinger (1965) found that a continuous copper concentration of 0.4 mg/l did not appreciably increase the effluent COD, but copper at 1.2 mg/l increased the effluent COD significantly. The findings of these studies also showed that continuous doses of copper at 10 mg/l caused failure in combined sludge digestion. According to Sierp and Fransemeier (1933), copper had a detectible effect in increasing turbidity and decreasing nitrification at 1 ppm, and had a slight effect on the BOD of the effluent from laboratory-scale activated sludge units.

Gellman (1952) showed that, at copper concentrations of 0.05 ppm, a 20 percent BOD reduction was noted using both manometric and dilution techniques. The concentration of copper which had a detectible effect on the activated sludge process was reported as 1 ppm. He also found that the toxicity of copper decreased between pH 5 and 6.5. This could be expected because the solubility of copper decreases with increasing pH of the solution. Southgate (1933) concluded that washes from the pickling of copper retarded or stopped biological action in trickling filters. Placak, Rucchoft, and Snapp (1949) showd that copper has an extreme effect on BOD. The results indicated that concentrations as low

as 0.01 ppm caused detectible reduction in BOD, and at 0.05 ppm copper
BOD was decreased by about 23 percent. Copper concentrations at 1 ppm
will permit only about a 34 percent BOD recovery. Copper concentrations
above 0.05 ppm inhibit nitrification completely.

Gerald, McDermott et al (1963) reported that the effluents of the
activated sludge units receiving 10, 15, and 25 mg/l copper fed as copper
sulfate were generally of lower quality than those of the control units.
They observed that the turbidity increased with increasing copper concen-
tration and a maximum copper concentration which had no significant ef-
fect on effluent turbidity was 0.8 mg/l. They also found that the maxi-
mum concentration of copper that did not have a detectible effect on BOD
and COD of the effluent was 1 mg/l.

Fate of Copper and Chromium in Aquatic Systems

Levels of both copper and chromium in sediments of aquatic systems
have been increasing. Hamilton-Taylor (1979) reports a recent copper
enrichment of sediments in Windermere, England, and Stoffers et al (1977)
report copper and chromium levels in New Bedford Harbor to be 5-10 times
higher than they were 50-100 years ago. Iskandar and Keeney (1974) have
studied copper and chromium concentrations in lake sediment cores of
several Wisconsin lakes and have compared them to precultural levels.
The concentrations of both metals have increased with time and the in-
crease in copper in Lakes Monona and Kegansa was attributed to the use
of copper sulfate as an algicide. Copper treated lakes were found to
have surficial sediment concentrations of 229-438 µg/g of copper. Sedi-
ment from untreated lakes had 16-71 µg/g copper.

With respect to chromium, Iskandar and Keeney (1974) observed that the concentrations in Lakes Mendota, Monona and Waubesa were 2-5 times higher than precultural levels. In these lakes, concentrations of chromium ranged from 1-42 μg/g. Ranges as high as 20-120 μg/g and 60-250 μg/g have been reported in Lake Michigan and upper Peoria Lake.

Trefly and Presley (1976) investigated the distribution of several heavy metals in the San Antonio-Guadalupe River system and observed copper concentrations that were 10% to 50% higher than natural levels. The increase in the copper concentration over the natural levels was attributed to the proximity of the sample site to large industrial and population centers.

With copper and chromium contamination becoming a more prevalent problem, it becomes necessary for researchers to understand the fate of these heavy metals in aquatic systems. Metals added to rivers or lakes may be incorporated into the sediment, be taken up by suspended algae and bacteria, be chemically precipitated by components of the water or may remain soluble in the aqueous phase.

Metal Uptake by Soils

Metal uptake by sediments may occur as the result of adsorption, precipitation, ion exchange, or reaction with organic matter. All of these reactions are influenced by soil type, soil texture, cation exchange capacity, pH and oxidation reduction potential.

Soil type is a major factor in retention of heavy metals. Clays are extremely important in adsorption reactions and the type of clay mineral is also a governing factor. In addition, soils high in humus

or other organic matter exhibit good exchange capability and a high
retention of metals. Metal retention tends to be high in finely tex-
tured soils such as clays and low in coarser textured soils such as
sands.

Copper readily reacts with silicates in soils causing a rapid
decrease in the free concentration of copper through precipitation
(Leggett, 1978). The copper ion also complexes strongly with humic and
fulvic acid fractions of soils (Cavallaro and McBride, 1978).

The reactions of copper in acid and calcareous soils have been
studied by Cavallaro and McBride (1978) Acid soils were found to fix
less metal than neutral soils. It was also suggested that, in calcareous
soils, calcium may be competing with copper for available adsorption
sites. Analyses of copper adsorption in the presence of 0.01 M $CaCl_2$
showed reduced fixation of copper.

The retention of copper by clays has been studied by several re-
searchers. Bingham et al (1964) observed copper retention on H-mont-
morillonite and found that cation exchange was the major mechanism.
However, as the pH began to increase above 6.5, additional copper was
removed by precipitation as $Cu(OH)_2$.

Ellis examined copper uptake and mobility in kaolinite, illite,
montmorillonite and vermiculite. He found that the rate of diffusion
of copper through the clays was kaolinite > illite > montmorillonite >
vermiculite. Using only kaolinite, illite and montmorillonite, Misra
and Tiwari (1966) observed greater retention in the montmorillonite
soil than in the kaolinite or the illite clay. These authors attributed
the higher fixation capacity of the montmorillonite to the higher NH_4^+
exchange capacity which it exhibited.

Korte et al (1976) have studied the retention and mobility of several metals, including copper and chromium, as related to soil texture, surface area and percentage of free iron oxides. The majority of the clay soils examined retained the metals. An exception to this occurred with chromium and a clay soil containing free $CaCO_3$. Chromium was not retained and was found to be mobile. Chromium, however, was retained by the clay soils having the highest concentration of free iron oxides and manganese.

Stoffers et al (1977) related the uptake of heavy metals in sediments to the particle size. These researchers showed that metals, including copper and chromium, were associated with the fine grained particles and that the largest amounts of some of the metals studied were found in the clay fraction smaller than 2 μm. Within the sediments, copper was distributed between the fine clay fractions, insoluble mineral detritus, the organic fraction and the authigenic phases which were composed mainly of iron sulfides. The distributional pattern exhibited by chromium was different than that found for copper. Eighty-five percent of the chromium was found in the authigenic fraction and eight percent in the leachate resistant fraction composed largely of the insoluble mineral detritus.

Aqueous Phase Chemistry of Copper

The maximum solubility of copper in a natural water system is a function of the chemical characteristics of the water since the formation of numerous organic and inorganic compounds and complexes are possible (Mann and Neutscher, 1977). Copper in natural waters may

form soluble organic complexes with humic and fulvic acids and amino acids and polypeptides. In solutions that are acid or near neutral in pH, copper solubility is dependent on the chloride, sulfide and carbonate ion activities. In the pH range of most natural waters, copper may form a soluble copper-carbonate species ($CuCO_3$) or be precipitated with phosphate and sulfides (Stiff, 1971). The most important precipitation reactions of copper in unpolluted waters lead to the formation of cupric oxide (CuO) and malachite ($Cu_2(OH)_2CO_3$) (Stiff, 1971). The end product which is formed is pH dependent and in the range of 6-8.5; malachite is the only precipitated species. In fact, Sylva (1976) states that the precipitation of malachite is the most significant process by which free copper (II) is removed from aqueous systems.

Copper in Aquatic Systems

Several authors have investigated the fate of copper in ponds and lakes with respect to uptake by sediments and precipitation reactions. Their results correlate well with those obtained from studies of copper interactions with soils and water. Sylva (1976) states that adsorption processes, both biotic and abiotic, can be expected to remove copper from solution and that abiotic adsorption will be considerable at pH values greater than 6.5. McIntosh (1975) reports that sediments act as the ultimate sink for copper added to an aquatic system and that copper is primarily removed by precipitation and adsorption. Sanchez and Lee (1978) agree with McIntosh that sediments act as a sink for copper but state that complexation and precipitation are the reactions controlling the soluble copper concentration in natural waters.

Reimer and Toth (1970) conducted investigations concerning the uptake of copper by clay, humic acids and muds. The results from their studies indicated that the amount of organic matter in the bottom sediments in addition to the nature of the clay minerals present would largely determine the amount of copper fixed by bottom materials. High amounts of limestone may also affect copper removal by sediments.

Reimer and Toth (1970) noted in their study that copper is adsorbed rapidly by pond bottoms. According to Reimer and Toth (1970), the copper fixed by the bottom sediments is rather strongly retained.

Sanchez and Lee (1978) examined the environmental chemistry of copper in Lake Monona, Wisconsin, a thermally stratified lake which has received over 1.5×10^6 pounds of copper sulfate in the last 50 years, for algae control. These authors concluded that the factor controlling copper concentrations in the lake under oxic conditions was the precipitation of copper as a basic carbonate. In the hypolimnion where anaerobic or anoxic conditions prevail, copper solubility is governed by the precipitation of cupric sulfide.

The assimilative capacity of natural waters for copper has been discussed by Sylva (1976) and Reimer and Toth (1970). Sylva concludes that the chemical conditions of most natural waters are appropriate for the reduction of relatively large levels of copper to extremely low values through the reactions of hydrolysis, precipitation, complexation and adsorption. Reimer and Toth also conclude that the clay minerals and humic acids present in sediments should completely adsorb the small

amounts of $CuSO_4 \cdot 5H_2O$ normally used for the control of algae.

Algae Uptake of Copper and Chromium

Trace metals such as copper and chromium can control algae growth by serving as micronutrients or as toxicants. Copper in the form of copper sulfate has been used for many years as an algicide. However, there is current evidence that some aquatic plants are capable of adsorbing and concentrating large quantities of copper (McIntosh, 1975). This is possibly accomplished by the release or secretion of extracellular metabolites that alter the metal speciation in the aquatic system and therefore reduce the toxicity of the metal species added (McKnight and Morell, 1979; Steemann and Wium-Anderson, 1971). Work done by Fogg and Westlake (1955) indicated that extracellular polypeptides of Anabena cylindrica could complex and detoxify copper. McKnight and Morell (1979) reviewed the copper complexing capacity of the organic compounds produced by 20 different species of algae. These authors specifically concluded that eucaryotic algae in the stationary growth phase produce micromolar concentrations of extracellular weak organic acids that are capable of complexing copper. Similarly, blue-green algae also produce these weak acid complexing agents but, in addition, produce very strong complexing materials during the latter growth phases of batch cultures. McKnight and Morell (1979) express the opinion that extracellular algae products may alter metal speciation in aquatic systems.

Mangi et al (1978) have investigated the effects of chromium on aquatic plants and found that the growth of all plants was inhibited by chromium concentrations greater than 10 mg/l. Studies conducted with

respect to chromium uptake by dead cells led these researchers to con-
clude that adsorption is the major mechanism responsible for uptake.
Work by Richards (1936) which was later supported by Mangi et al (1978)
indicated that the adsorption takes place on the cell walls. Mangi et al
further conclude that benthic and planktonic algae, through the adsorp-
tion of chromium on their cell walls, may remove large concentrations of
the metal from water.

Summary: Copper and Chromium in the Aqueous Phase

There is a fairly good distribution of literature on the behavior
of copper in the environment. However, there seems to be an almost com-
plete lack of material on the chemistry of chromium in aquatic and soil
systems. Both metals are taken up and retained by clays and organic
matter and, as far as copper is concerned, this seems to be the major
mechanism of retention in sediments. In addition, algae exhibit require-
ments for both copper and chromium. Some algae are even capable of com-
plexing and detoxifying copper and large amounts of chromium can be re-
moved by adsorption onto cell walls. The aqueous chemistry of copper has
been well defined and precipitation of copper with components of the
aqueous phase provides a major mechanism for the control of soluble copper
in natural water.

Behavior of Copper in Soil Systems

Heavy metals are introduced into the environment by several mechanisms.
It is important to determine the source, whether man-made or natural and
to study the movement or retention of the metal as it passes through the

soil to the ground water system. The pollutant is subject to many
reactions with the soil and its constituents. Heavy metals can undergo
processes of sorption, chemical complexing and chemical alteration.

Soils differ in basically two ways. These differences can affect
the manner in which the heavy metal is adsorbed, chemically complexed,
or chemically altered. The two ways soils differ are in the colloid
content and pH. Colloidal content will be discussed as organic and
inorganic. As reported by Leeper (1978) the organic colloid may have
five times the retention capability as compared to the inorganic. In
addition to the colloid content and pH, the microbial population in soil
systems may also affect the mobility of metal cations.

Organic Colloids

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

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

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

was satisfied by the addition of small amount of Cu. The reasoning is that Cu can circulate in an anionic form (Himes and Barber, 1957).

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

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

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

Inorganic Colloids

The subsurface and subsoil can remove large portions of a heavy metal after the reaction with the surface. The subsoil is composed primarily of inorganic colloids (i.e., clays) as compared to organic

matter. All soils contain negatively charged colloids. The range of inorganic colloids vary from 0% (pure sand) to over 50% for a heavy clay. Cu is adsorbed onto negative surfaces in soils. The ability of these surfaces to remove added cations from the soil is referred to as its cation exchange capacity. Typical values for an inorganic clay may range from 10-50 meq/100 g. As mentioned previously, the greater the C.E.C. the stronger the metals are adsorbed (Leeper, 1978).

Adsorption on clay minerals and quartz are increased with an increase of pH. As a result of raising the pH it was found that the Cu was more firmly fixed and thereby less toxic (Muller, 1959). Reuther and Smith found that at pH of 6 general toxicity begins (Reuther and Smith, 1954).

Soil pH

Soil pH also affects copper retention and/or mobility. Copper generally becomes less soluble and less exchangeable as the soil pH increases from 5 to 7. Bingham et al (1964) and Menzel and Jackson (1940) have reported an increase in the retention of copper with an increase in soil pH. The greater fixation at higher pH values may be the result of the precipitation of copper as $Cu(OH)_2$ or as a carbonate (Bingham et al, 1964).

Biological Activity

The subsurface environment contains sufficient quantities of organic matter to sustain microbial growth. Microbial growth becomes limited when the level of tolerance of two basic physical properties are exceeded, these being hydrostatic pressure and temperature (McNabb & Dunlap,

1975). Contaminants can also limit or destroy microorganisms if levels
of toxicity are exceeded.

The significance of a microbial population in the subsurface is
its ability to decompose a metal-chelate complex thus affecting the
chelate stability. In addition, microbial activity can result in a de-
crease in the oxidation-reduction potential which could increase the
solubility of copper.

MATERIALS AND METHODS

Biological Waste Water Treatment Processes

Rotating Biological Contactor

The Rotating Biological Contactor used in this study consisted of a plexiglass tank divided into six stages with four polyethylene discs in each stage. Each disc was 1/8 inch thick and 6 inches in diameter. This resulted in a total disc surface area of 9.42 square feet or 1.57 square feet per stage. The volume of the liquid in the reactor was 7.65 liters. This provided a forty percent submergence of the discs. The hydraulic flow rates to the RBC were maintained through the use of a constant head tank which received a continuous flow of tap water. The flow from the constant head tank was regulated by a valve combined with a flow meter on the tank outlet line. Water from the constant head tank was fed by gravity into a wet well, where it was mixed with the concentrated synthetic waste to achieve the desired organic concentration. The synthetic waste was pumped to the wet well using a Cole Parmer Masterflex pump. From the wet well, the mixture flowed by gravity into the first stage of the RBC. The rotational speed of the discs was maintained at 10 rpm.

The synthetic waste used in this study contained glucose as the sole carbon source. All required nutrients were added in excess so that carbon was the limiting growth factor. The COD of the influent wastewater was maintained at 450 mg/l.
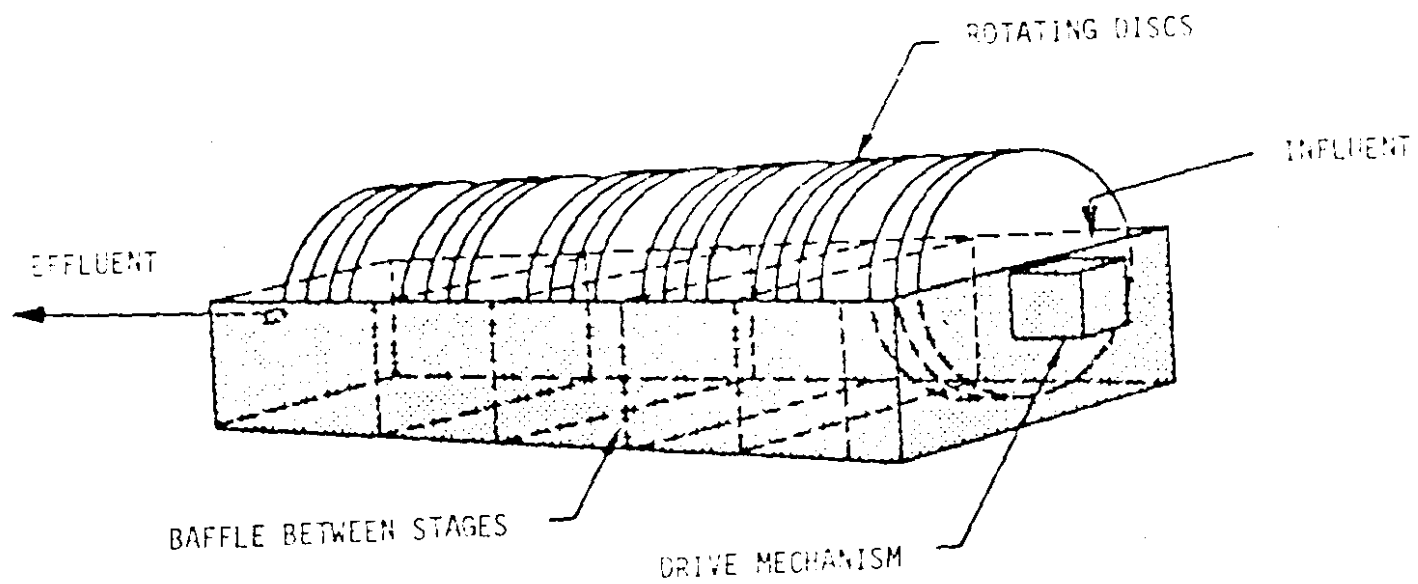
ROTATING DISCS

INFLUENT

EFFLUENT

BAFFLE BETWEEN STAGES

DRIVE MECHANISM

Figure 1. Schematic Diagram of Laboratory Scale Rotating Biological Contactor (RBC)

The RBC was initially seeded with effluent from the primary clari-
fier of the Stillwater, Oklahoma wastewater treatment plant. The RBC
was allowed to operate as a batch unit for three days and then operated
as a continuous flow reactor. The RBC was operated in this manner for
two weeks to allow the development of a biological growth. After the
development of a biological growth the heavy metal was added to the
wastewater. In the short term studies the RBC was allowed two weeks to
become acclimated to the heavy metal and then samples for analyses were
collected. In the long term studies samples were collected after one
day and then at various time periods.

Activated Sludge

The bench activated sludge unit used in this study was the internal
recycle type. The system consisted of a glass feed tank in which the
wastewater was pumped to the reactor. The reactor was constructed of
plexiglass and consisted of a 2.8 liter aeration tank and a 1.96 liter
settling compartment. The effluent from the reactor flowed to a glass
collection vessel. The wastewater fed to the reactor consisted of ethy-
lene glycol, ethyl alcohol, acetic acid, glutamic acid, glucose and
phenol as the carbon source. The COD of the wastewater was maintained
at approximately 550 mg/l. The reactor was operated at a hydraulic
detention time of eight hours and a sludge age of ten days. The following
procedure was used for daily operation of the bench activated sludge unit.

The adjustable baffle was set at a level that provided good return
flow of the return solids. This meant adjusting the baffle several times
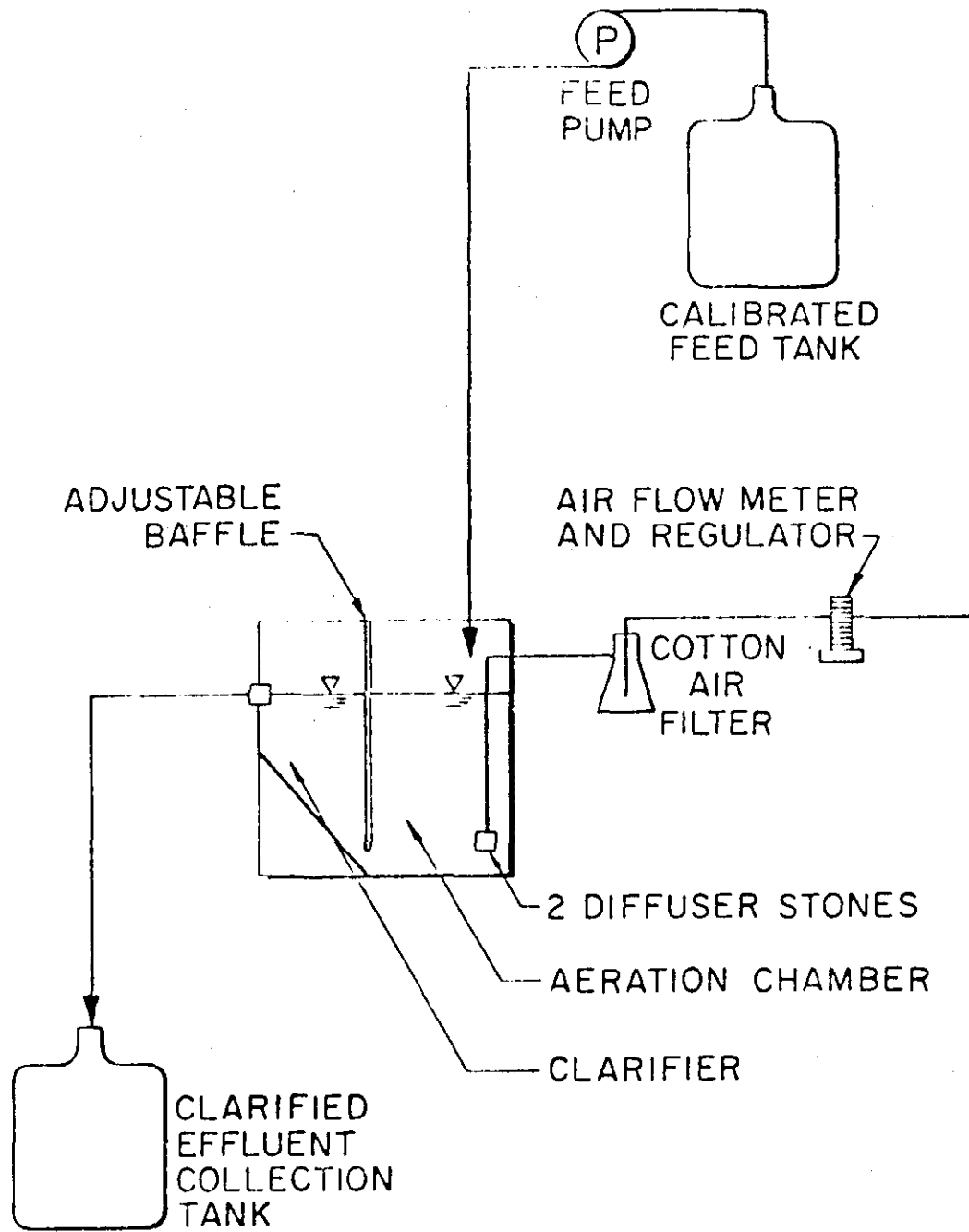per day.

Figure 2.   Laboratory pilot plant activated sludge unit with internal sludge recycle

Once each week solids were wasted and samples were collected for analyses. The following procedure was used for this operation.

1. Collect sample from effluent for COD, BOD, and TOC analysis.

2. Pull baffle and allow aeration chamber and clarifier to mix.

3. Take sample for MLSS analysis.

4. Waste required amount of biological solids.

5. Reset baffle.

6. Check flow rate.

7. Continue operation.

Fate of Copper and Chromium in Aquatic Systems

Procedure

For this experimental work, sediments were collected from Lake Carl Blackwell, Sooner Lake and the Cimarron River. Lake Carl Blackwell is a warm, monomictic eutrophic lake that serves as the water supply for the city of Stillwater, Oklahoma. The lake, which is also used for recreation, is located approximately seven miles west of Stillwater. Sooner Lake is a new lake having only been filled for two years. Its primary purpose is as a source of cooling water for the Sooner power generating facility which is a coal fired power plant. The lake is also used for recreational purposes and is located 30 miles north of Stillwater on Highway 177. The Cimarron River flows west-east through the state of Oklahoma to its confluence with the Arkansas River. It is an intermittent river and only contains water throughout its entire channel several times a year. Sediments were collected from the Cimarron River under the Highway 177 bridge

just south of Perkins, Oklahoma.

In all cases, sediments were collected from under approximately three feet of water. They were returned to the lab where as much water as possible was decanted and then stored in refrigerators until needed.

Metal uptake was determined for sediments and algae individually and then in combined systems containing sediments, algae and the appropriate lake or river water. Initially, sediment uptake was determined in systems containing distilled water. Lake and river waters were not used at this time because the precipitate formed on the addition of copper coated the sediments and hindered uptake by the sediment phase. Similarly, BOD water (Standard Methods, 1975) was used for the initial studies of algae uptake of copper and chromium. The BOD water provided available nutrients for the algae while precluding the formation of large amounts of copper precipitate. However, some precipitate was formed and therefore, control units containing only BOD water and the metals were observed. Metal removal by the algae was then calculated as the difference between metal disappearance in units containing BOD water and algae and the uptake in the controls. All experimental units were run in duplicate.

Final experiments examining the uptake of each metal included four units and their duplicate for each sediment-water type. The units studied for Lake Carl Blackwell were two units containing only filtered water from the lake plus metal, two units containing filtered lake water, metal and algae, two units containing filtered lake water, metal and sediments, and two units containing all three phases and the appropriate metal. Similar systems of four units and their duplicates were set up for sediments and water from Sooner Lake, and sediments and water from the Cimarron River.

The algae used in these studies were obtained from a laboratory grown culture which was seeded from a sample from Theta Pond, a small eutrophic pond on the Oklahoma State University campus. The algae culture was predominantly composed of blue green algae, green algae, and diatoms.

The experiments were run in glass gallon jars to which 900 grams of air-dried sediment were added. This gave a sediment depth of 2" for Cimarron River, 2-1/4" for Sooner Lake, 2-1/2" for Lake Carl Blackwell and an exposed surface area of 29.41 in^2. The total liquid volume in each jar was 3 liters. In studying algae uptake, a dry weight of 48 mg/l of algae was added to the copper systems to give 88 percent T when measured on the Bausch and Lomb Spec. 20. For chromium uptake investigations, a dry weight of 56 mg/l was added which also gave 88 percent T. In all units using actual lake or river water, in addition to algae, 208 mg/l (dry weight) of algae were added which gave 50 percent T.

All of the systems were capped to minimize evaporation. Air was bubbled through the jars to maintain aerobic conditions and, therefore, prevent possible metal speciation which could occur in an anaerobic environment. The pH was determined periodically using an Orion digital pH meter.

All units and duplicates were analyzed daily except for the chromium system containing actual lake or river water. At the end of the experimental period, when it was discovered that some of the remaining containers of chromium powder pillows used for analyses were not of the same composition as those currently being used, the frequency of analyses was reduced to every other day. This allowed the completion of the study using the original batch of chemicals.

Behavior of Copper in Soil Systems

Models

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

Columns differed in the soil that was used as the percolation media. Soil filled the column to six inches from the top. Two withdrawal ports were spaced at one foot intervals from the bottom of the column. In addition to the side ports, samples could be removed from the bottom.

Air diffusers were used as a means of drawing the solution from the column. The diffusers prevented soil from being pulled into a sample bottle when a vacuum was applied. The bottom of the column was gravel packed to prevent clogging by the finer sediments.

Soils

Soils were clayey-sand and red silty clay. These soils were selected on the basis of their representation of the general soil type in Oklahoma. The clayey-sand was taken from the Cimarron River at the Cimarron River bridge one mile south of Perkins off U.S. 177, Payne County, Oklahoma. The red silty clay was taken from the Brush Creek drainage basin in Stillwater, Oklahoma. Both soils were removed from their respective sites at a depth of approximately two feet beneath the surface.

Once in the laboratory, the soils were dried. After drying, the soils were crusted to reduce the volume. Crusting or grinding the soil aided in packing the soil in the columns. The soil, once in place, was saturated with distilled water and vibrated.

The volume of soil occupied and weight of dry soil in columns were calculated using weight-volume relationships.

Flowrate and Solution

Milton Roy pumps were used to apply a copper sulfate solution containing 200 mg/1 copper to the columns. Hydraulic loadings were adjusted so as not to exceed the permeability of the soils used.

Frequency of Withdrawal

Samples were withdrawn initially on a daily basis and then once every two or three days when the experimental period increased beyond a month. Sample sizes of 5 ml to 25 ml were taken. The sample size varied, based on the levels of concentration within the column. Because the allowable range of the spectrophotometer was no greater than 3.0 mg/1, samples needed to be diluted prior to analyses.

Analyses

All analyses for copper and chromium were conducted using the Hach dr/2 Spectrophotometer and the methods of the Hach Chemical Company. COD, suspended solids, hardness, and alkalinity were analyzed for in accordance with the procedures in Standard Methods (1975). TOC analyses were performed using a Beckman 915 Total Carbon Analyzer. All other water quality analyses were made using Hach Chemical Company methods. Soil samples were analyzed in the Oklahoma State University Soils Laboratories.

RESULTS

Biological Waste Water Treatment Studies

Rotating Biological Contactor

The rotating biological contactor (RBC) was subjected to wastewaters containing various concentrations of $K_2Cr_2O_7$, K_2CrO_4, and $CuSO_4$. The response of the system was determined by measuring its ability to remove the organic material present in the wastewater. This organic material was measured as Chemical Oxygen Demand (COD).

Figure 3 shows the response of the RBC to various concentrations of copper at a hydraulic loading of 0.7 gpd/ft^2. The COD of the influent wastewater was 450 mg/l. It is seen that copper concentrations up to 4.0 mg/l caused very little difference in the response of the system. However, a concentration of 10.0 mg/l did show an inhibitory effect during the first four stages. However, at the sixth stage the COD removal was the same for all concentrations of copper.

Figure 4 shows the COD removal by the RBC when subjected to copper concentrations of 3.0 and 10.0 mg/l and a hydraulic loading of 2.0 gpd/ft^2. It is seen that there was a difference in the ability of the two systems for removing COD.

Figure 5 shows the response of the RBC to various concentrations of copper at a hydraulic loading of 3.0 gpd/ft^2. Again it is seen that the 10.0 mg/l copper concentration was much more inhibitory than the other copper concentrations.
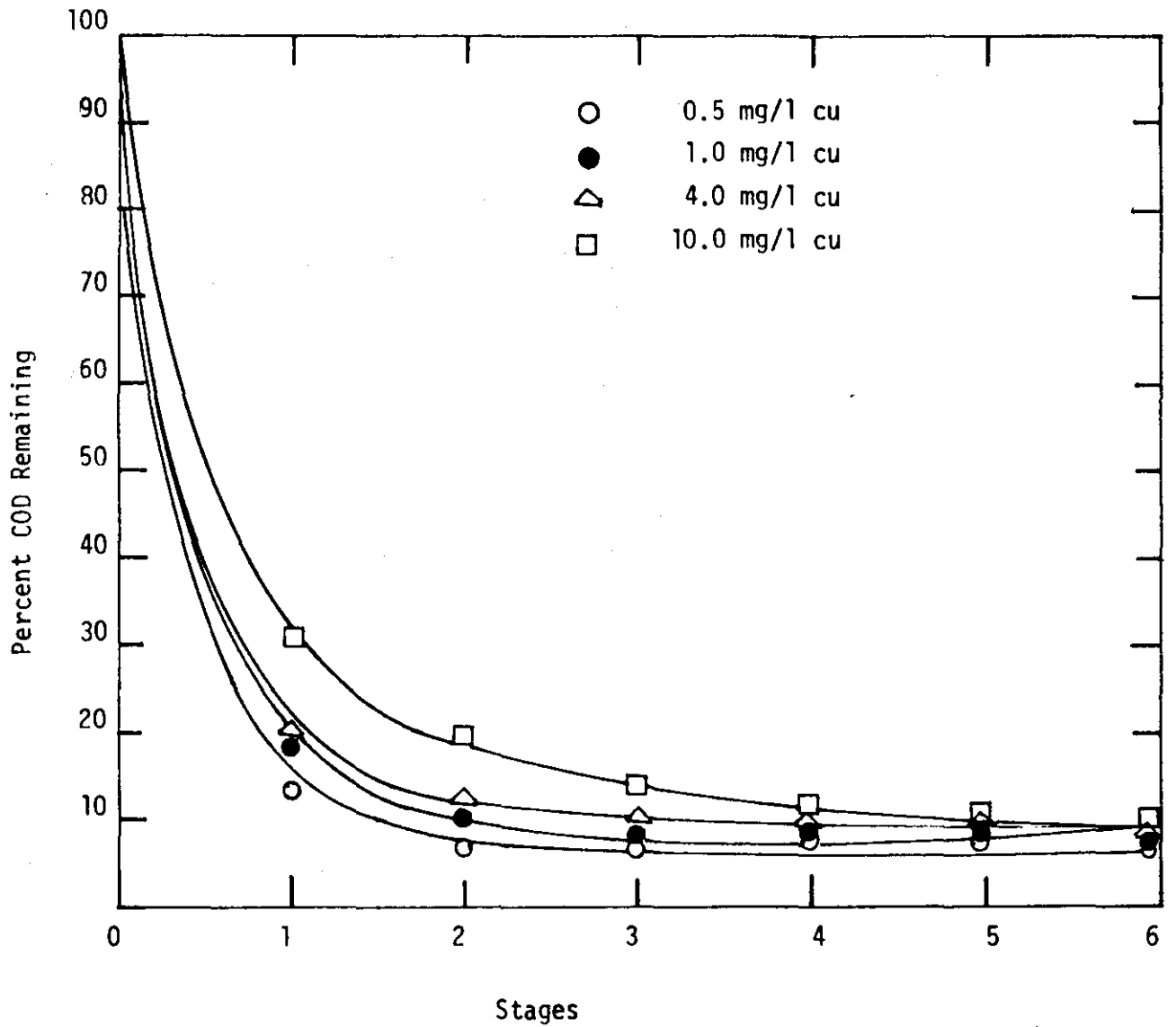
Figure 3. COD Removal by RBC at a Hydraulic Loading of 0.7 gpd/ft^2 and Various Concentrations of Copper.
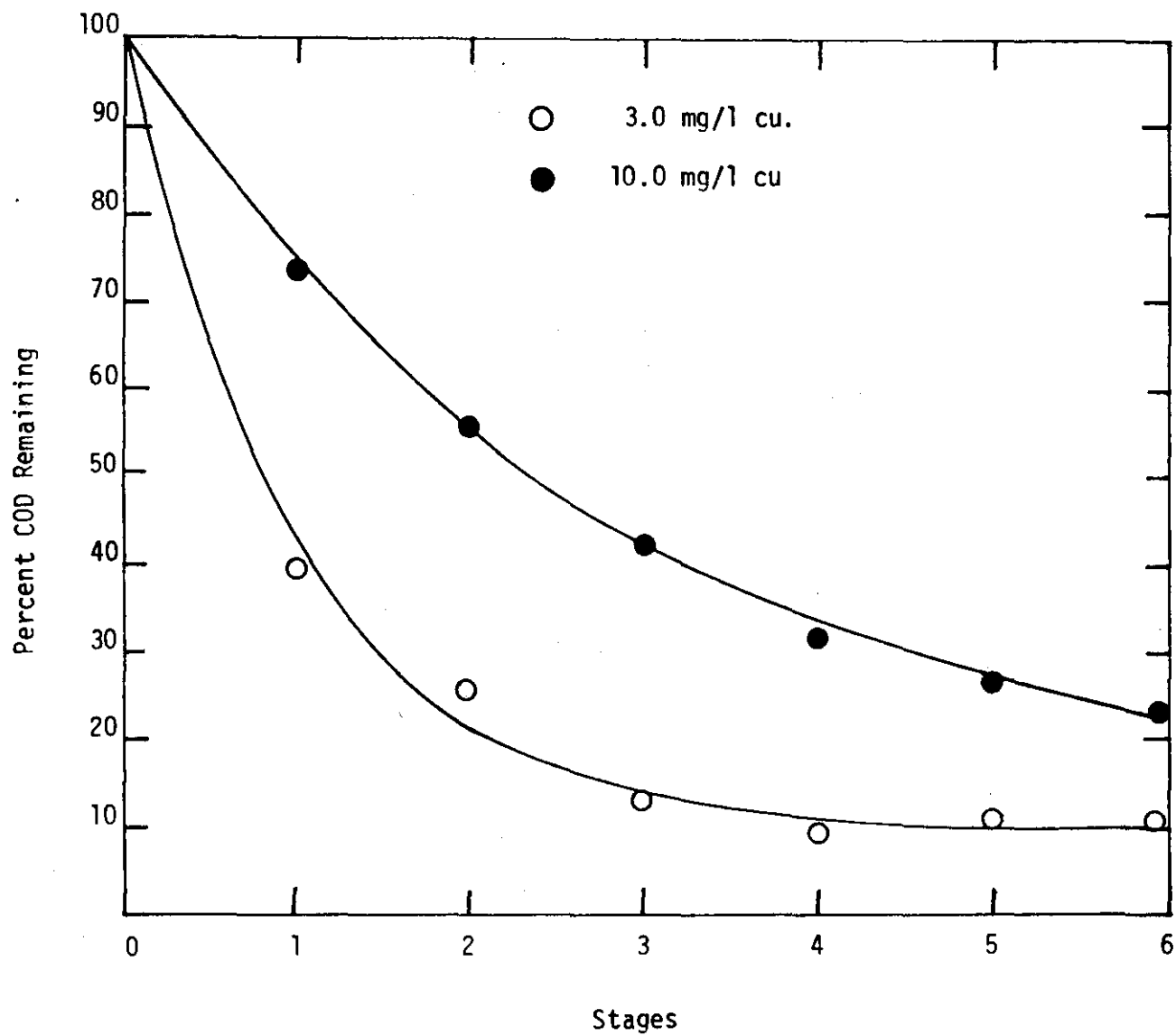
Figure 4. COD Removal by RBC at a Hydraulic Loading of 2.0 gpd/ft^2 and various concentrations of Copper.
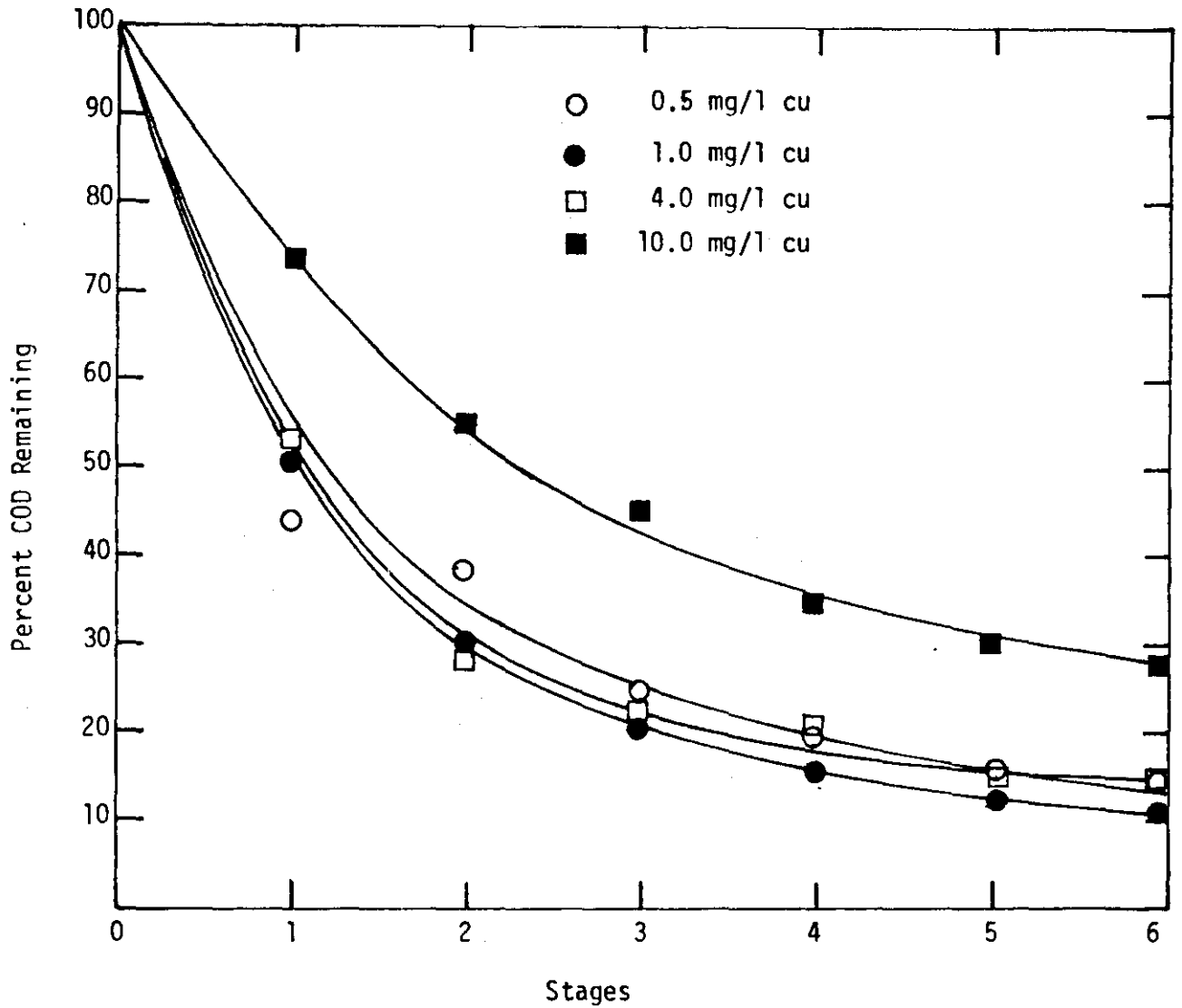
Figure 5. COD Removal by RBC at a Hydraulic Loading of 3.0 gpd/ft^2 and Various Concentrations of Copper.

One method for comparing treatment efficiency for various hydraulic
loadings is to plot the treatment efficiency as a function of the food to
microorganism ratio. The food to microorganisms ratio is determined by
multiplying the influent COD by the influent flow rate and dividing by the
mass of microorganisms. The mass of microorganisms on the RBC were calcu-
lated by using the active film theory. It is evident that an accurate
estimate of the amount of biological solids present on the discs and actively
participating in the substrate removal is not easy to make. The mass of
microorganisms was calculated by multiplying the disc surface area times the
density of the microorganisms, times the active film thickness. The density
of the microorganisms was taken as 95 mg/cm^3 and the active film thickness
as 200 μ. The biomass per stage would be 1.57 ft^2/stage x 929 cm^2/ft^2 x
95 mg/cm^3 x 0.02 cm = 2771 mg/stage and the food to microorganism ratio may
be calculated for various stages and flow rates. Figure 6 shows a plot of
treatment efficiency as a function of the food to microorganism ratio for
the RBC system receiving a wastewater containing copper. It is seen that
one relationship was obtained for zero copper and copper concentrations up
to 4.0 mg/l. Another relationship was obtained for the 10.0 mg/l copper
studies. Figure 6 shows that copper concentrations up to 4.0 mg/l had no
effect on the RBC. It also shows that 10.0 mg/l of copper had an inhibitory
effect on the RBC system.

Figures 7 and 8 show the effects of various concentrations of chromium
$(K_2Cr_2O_7)$ at hydraulic loadings of 2.0 and 2.8 gpd/ft^2. These figures
show that, except for 1.0 and 2.0 mg/l Cr, all other concentrations of
chromium had varying effects on the RBC system. This is also shown in
Figure 9 where the treatment efficiency is shown as a function of the food

Figure 6. Treatment Efficiency as a Function of Food to Microorganism Ratio for an RBC Receiving Various Concentrations of Copper.

Figure 7. COD Removal by RBC at a Hydraulic Loading of 2.0 gpd/ft^2 and Various Concentrations of Cr as $K_2Cr_2O_7$.

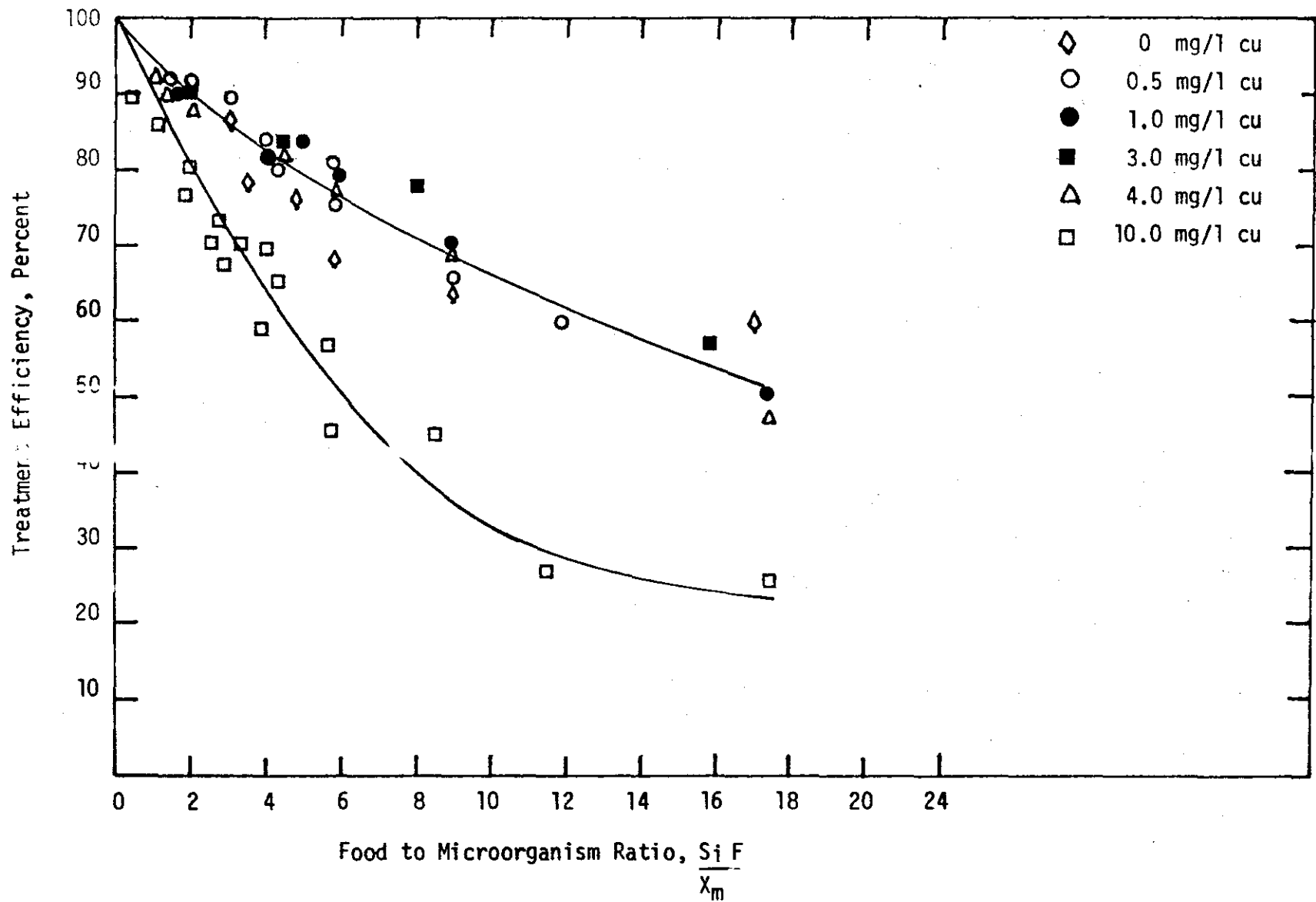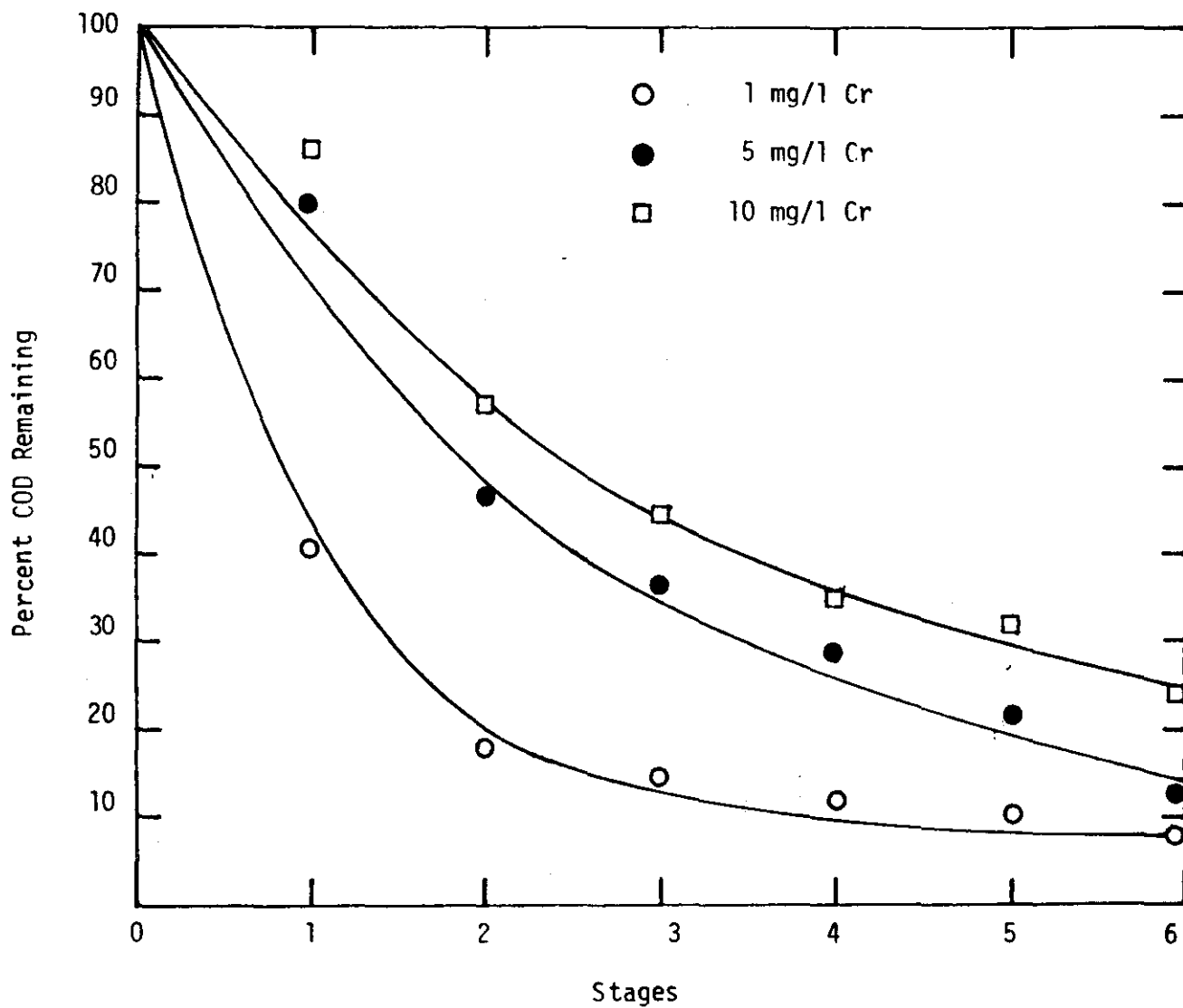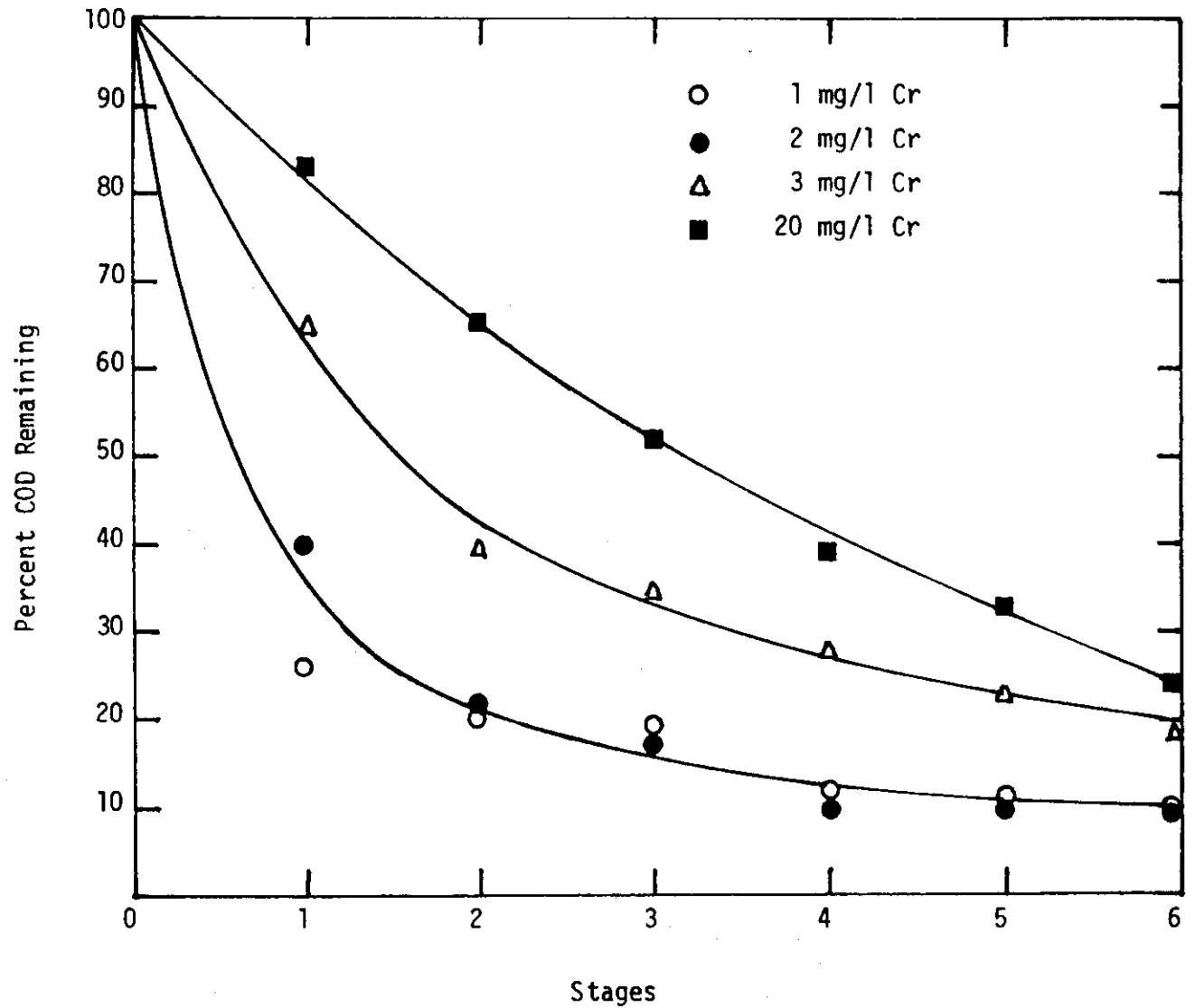Figure 8. COD Removal by RBC at a Hydraulic Loading of 2.8 gpd/ft^2 and Various Concentrations of Cr as $K_2Cr_2O_7$.
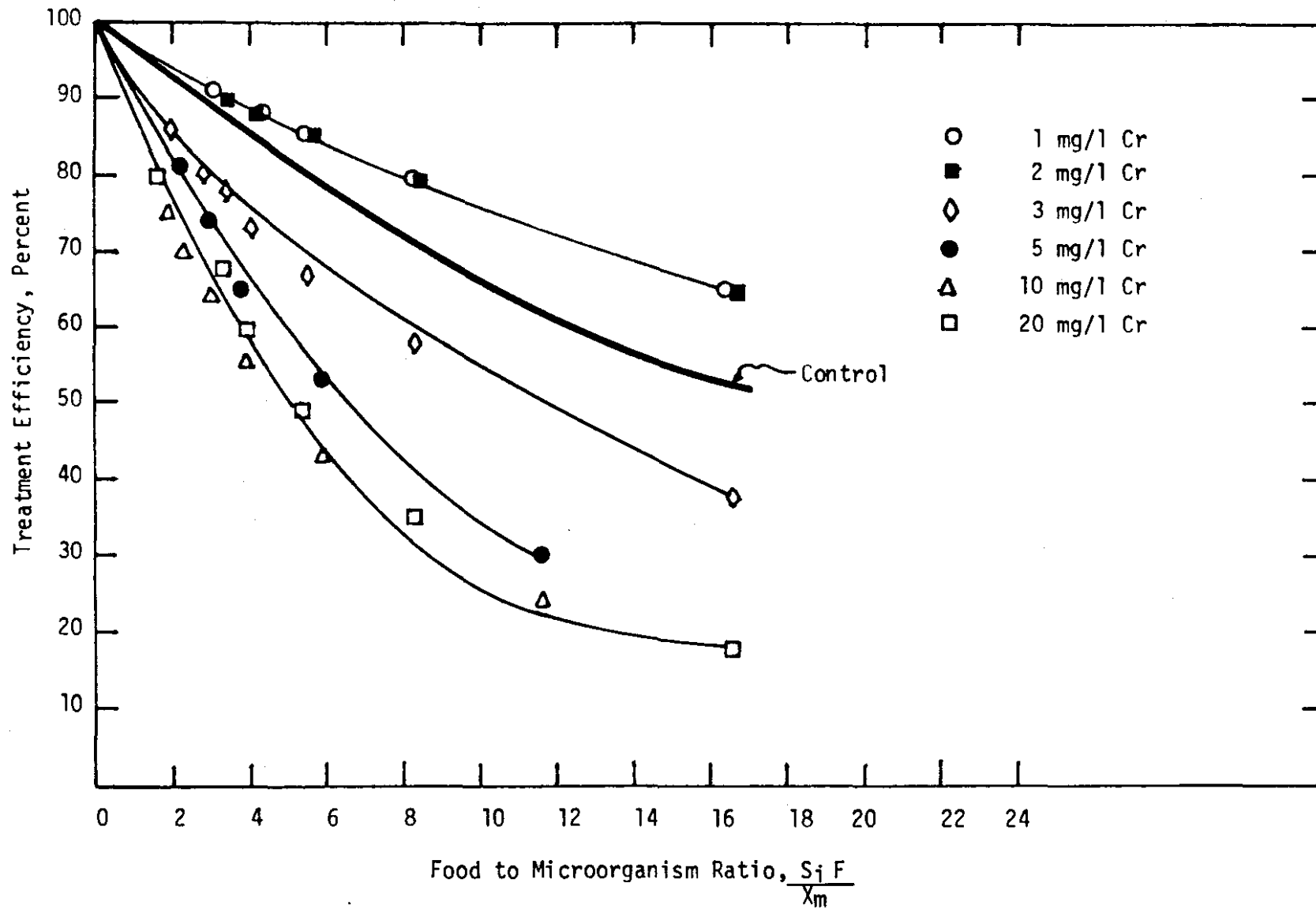
Figure 9. Treatment Efficiency as a Function of Food to Microorganism Ratio for an RBC Receiving Various Concentrations of Cr as $K_2Cr_2O_7$.

to microorganism ratio. It is seen that treatment efficiencies greater than those achieved in the control were obtained with chromium concentrations of 1.0 and 2.0 mg/l. However, treatment efficiencies less than the control were achieved for all the other chromium concentrations.

Figure 10 shows the COD removal achieved by the RBC when the wastewater contained various concentrations of chromium in the form of K_2CrO_4. Figure 11 again shows that chromium concentrations of 1.0 and 2.0 mg/l produced treatment efficiencies better than the control, whereas, chromium concentrations of 3.0 and 4.0 mg/l produced treatment efficiencies less than the control.

If the data in Figures 6, 9, and 10 are plotted on semi-log paper, a straight line results. This indicates that a first order relationship exists between the treatment efficiency and the food-to microorganism ratio. This relationship can be described as

$$\ln \frac{E_0}{E_1} = K \left[\left(\frac{S_i F}{X_m} \right)_1 - \left(\frac{S_i F}{X_m} \right)_0 \right]$$

and the reaction rate constant K can be calculated for each case. The result reaction rate constants as a function of the chromium or copper concentration in the wastewater are shown in Figure 12. This data shows that chromium concentrations of 2.5 mg/l or less stimulate the biological activity of the RBC. Whereas, chromium concentrations greater than 2.5 mg/l show an inhibitory effect. It is also seen that copper shows no effect up to 4.0 mg/l. This value may be even greater. However, no studies were conducted at copper concentrations between 4.0 mg/l and 10.0 mg/l. A copper concentration of 10.0 mg/l was very inhibitory to the RBC system.
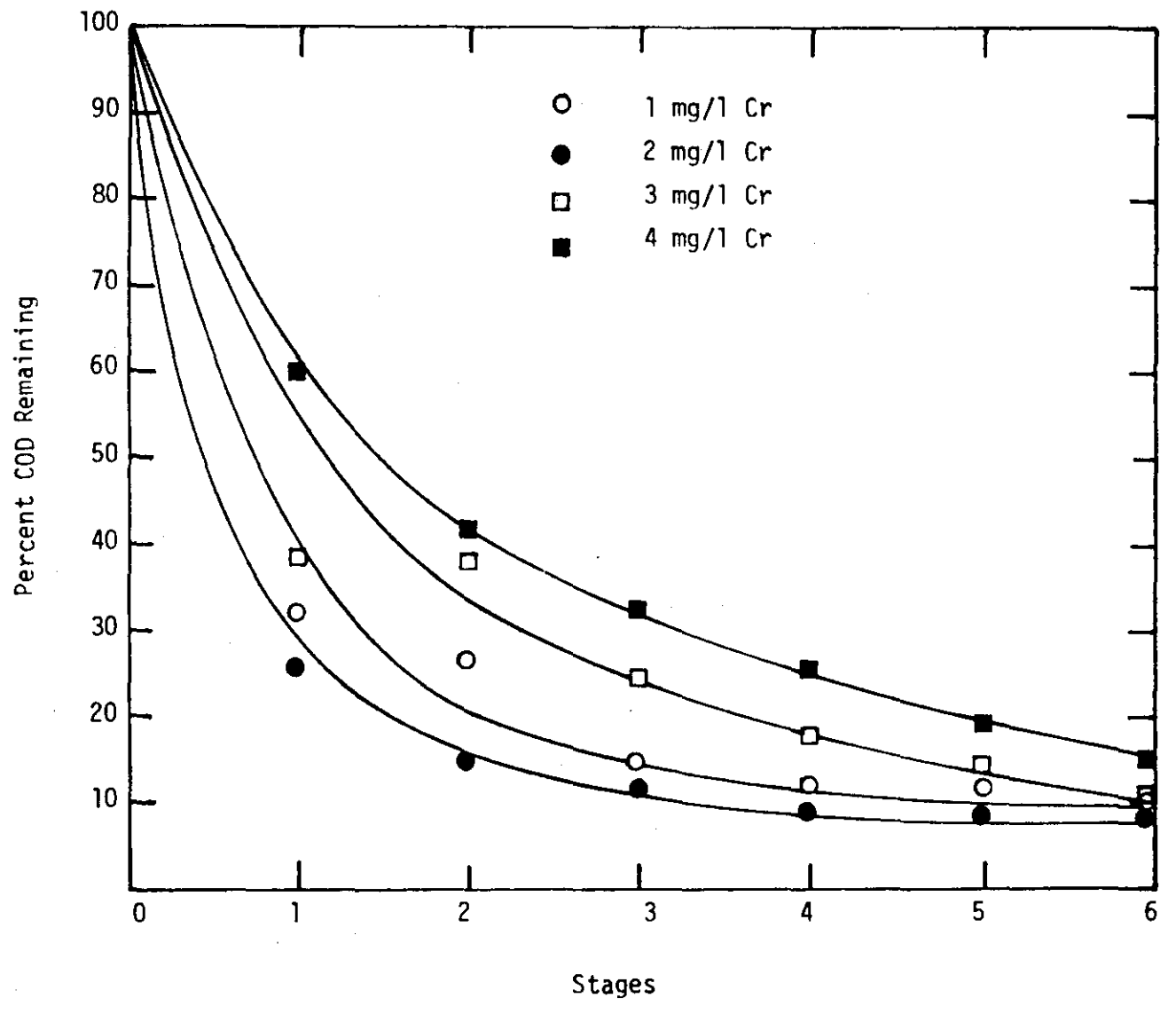
Figure 10. COD Removal by RBC at a Hydraulic Loading of 2.8 gpd/ft^2 and Various Concentrations of Cr as K_2CrO_4.
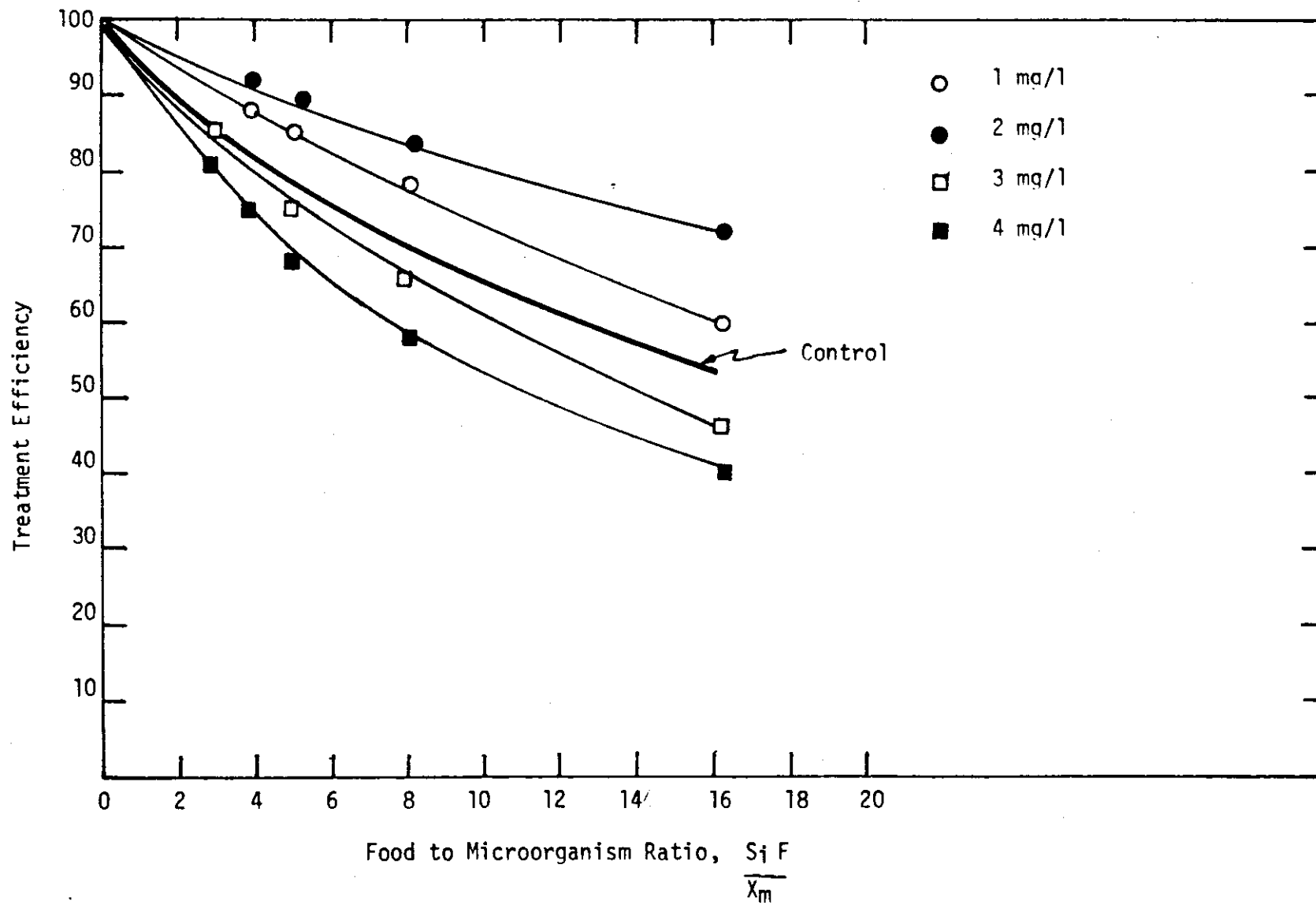
Figure 11. Treatment Efficiency as a Function of Food to Microorganism Ratio for an RBC Receiving Various Concentrations of Cr as K_2CrO_4.
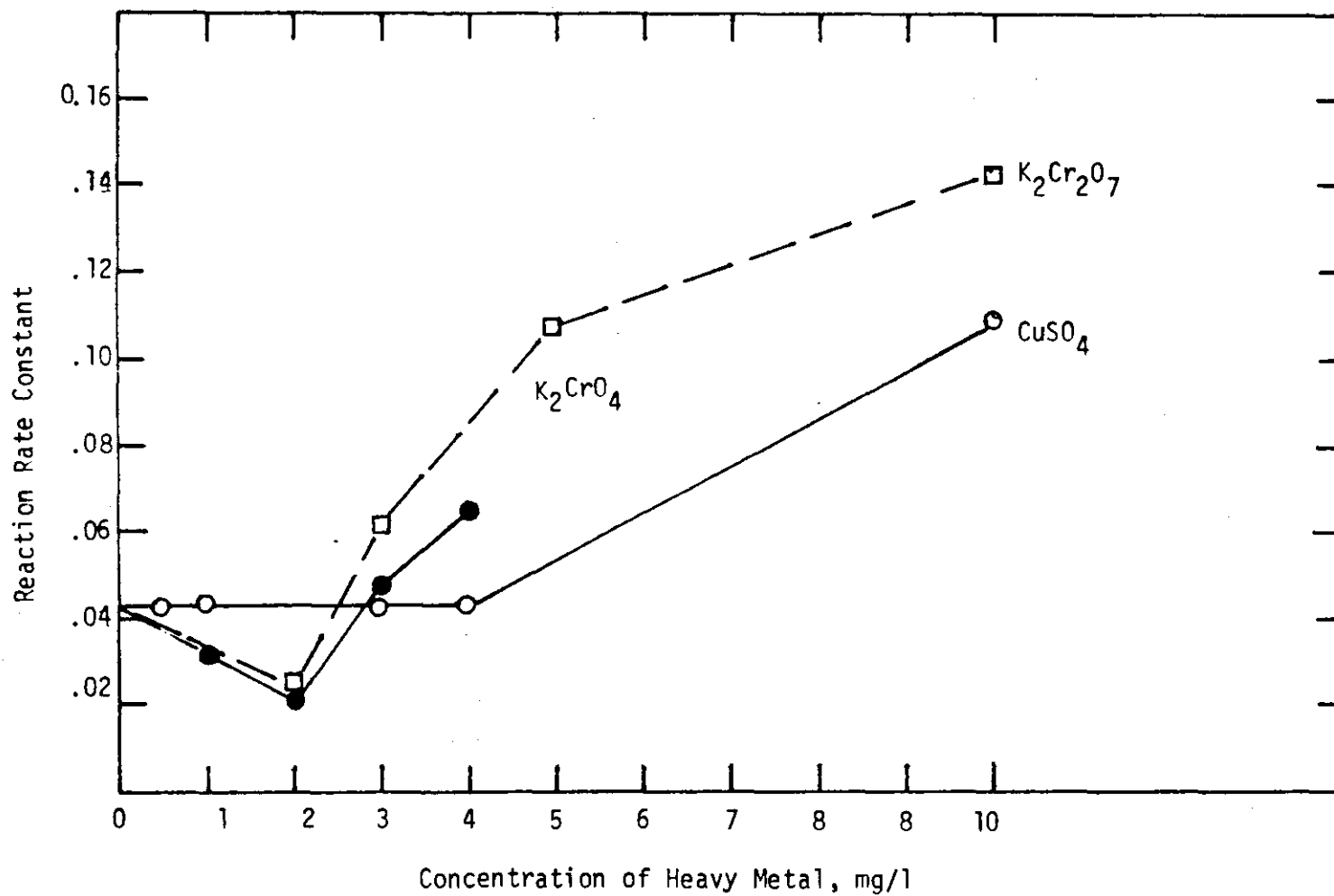
Figure 12. RBC Reaction Rate Constant as Function of Heavy Metal Concentration.

This study was also interested in the long term effects of chromium and copper on the RBC system. In these studies the COD removal capabilities of the RBC were measured at various time periods after the chromium or copper was introduced into the wastewater. During the periods of time that these studies were conducted, no difference in COD removal capabilities were observed as a result of time of exposure to the heavy metal.

Tables 1 and 2 show the removal of chromium and copper that was achieved by the RBC system. It is seen that fairly high levels of chromium removal were achieved by the RBC except at 4.0 mg/l and 20.0 mg/l concentrations at the 2.8 gpd/ft^2 hydraulic loading.

Table 2 offers some interesting results. The low hydraulic loading produced very low removal levels of copper. When the hydraulic loading was increased, the amount of copper removed increased.

Table 1. Chromium Removal by RBC

Hydraulic loading gpd/ft^2	Influent concentration mg/l	Effluent concentration mg/l	Recent removal
2.0	1.0	0.08	92.0
	5.0	0.10	98.0
	10.0	1.00	90.0
2.8	1.0	0.00	100.0
	2.0	0.08	96.0
	3.0	0.60	80.0
	4.0	1.51	62.3
	20.0	6.90	65.5

Table 2. Copper Removal by RBC

Hydraulic loading gpd/ft^2	Influent concentration mg/l	Effluent concentration mg/l	Recent Removal
0.7	0.5	0.5	0
	1.0	0.64	36
	4.0	2.73	31.7
	10.0	8.5	15.0
2.0	3.0	0.50	83.3
	10.0	0.10	99.0
3.0	0.5	0.02	96.0
	1.0	0.11	89.0
	4.0	0.25	94.0
	10.0	2.00	80.0

Activated Sludge

Figures 13-19 show the continuous operation of the activated sludge unit during this study. Figure 13 shows the performance of the system before the heavy metals were introduced to the wastewater. This data provides the baseline values for this study. Figure 14 shows the response after the chromium is no longer present in the wastewater. Figure 15 shows the response of the system when receiving 10.0 mg/l of chromium and Figure 16 gives the performance of the system after the 10.0 mg/l chromium is no longer present in the wastewater. Figure 17 shows the response of the system to 5.0 mg/l of copper in the wastewater. Figure 18 shows the response of the system after the 5.0 mg/l of copper is removed and when 20.0 mg/l is introduced to the wastewater. Figure 19 continues the 20.0 mg/l copper study.

Figure 13. Response of Activated Sludge Unit from Feb.8 to March 11, 1980

Figure 14. Response of Activated Sludge Unit from March 12 to April 11, 1980.
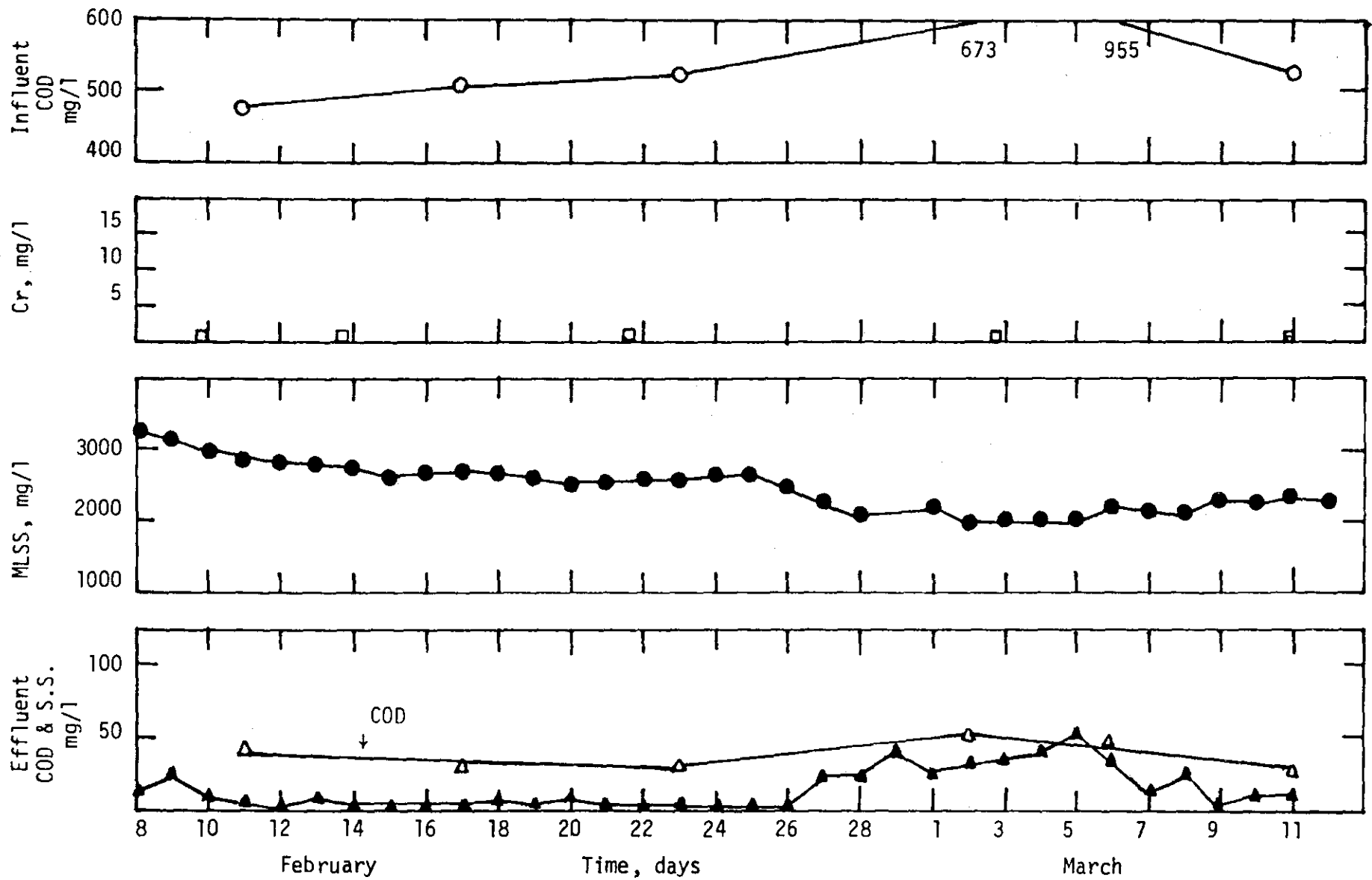
Figure 15. Response of Activated Sludge Unit from April 12 to May 12, 1980.

47
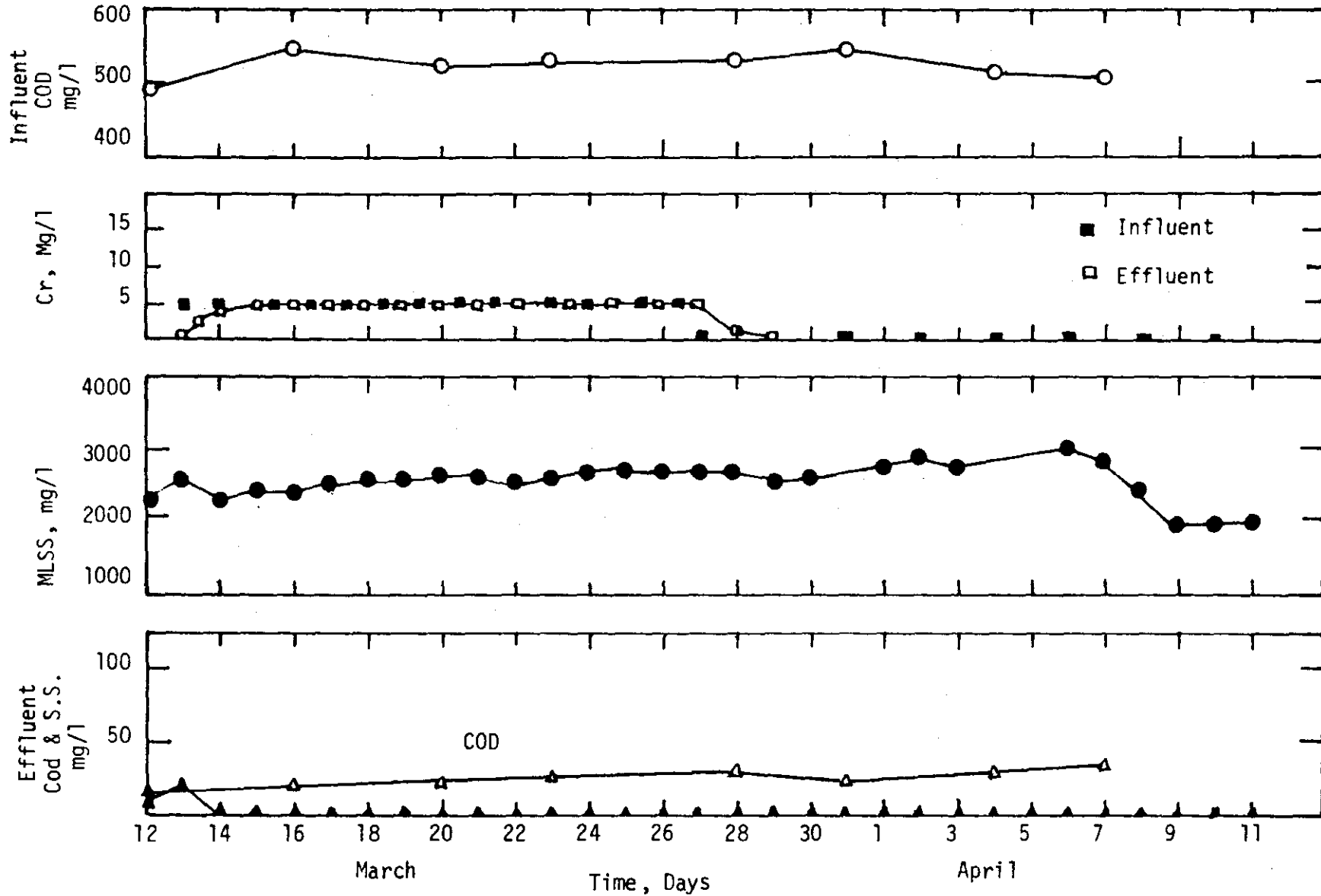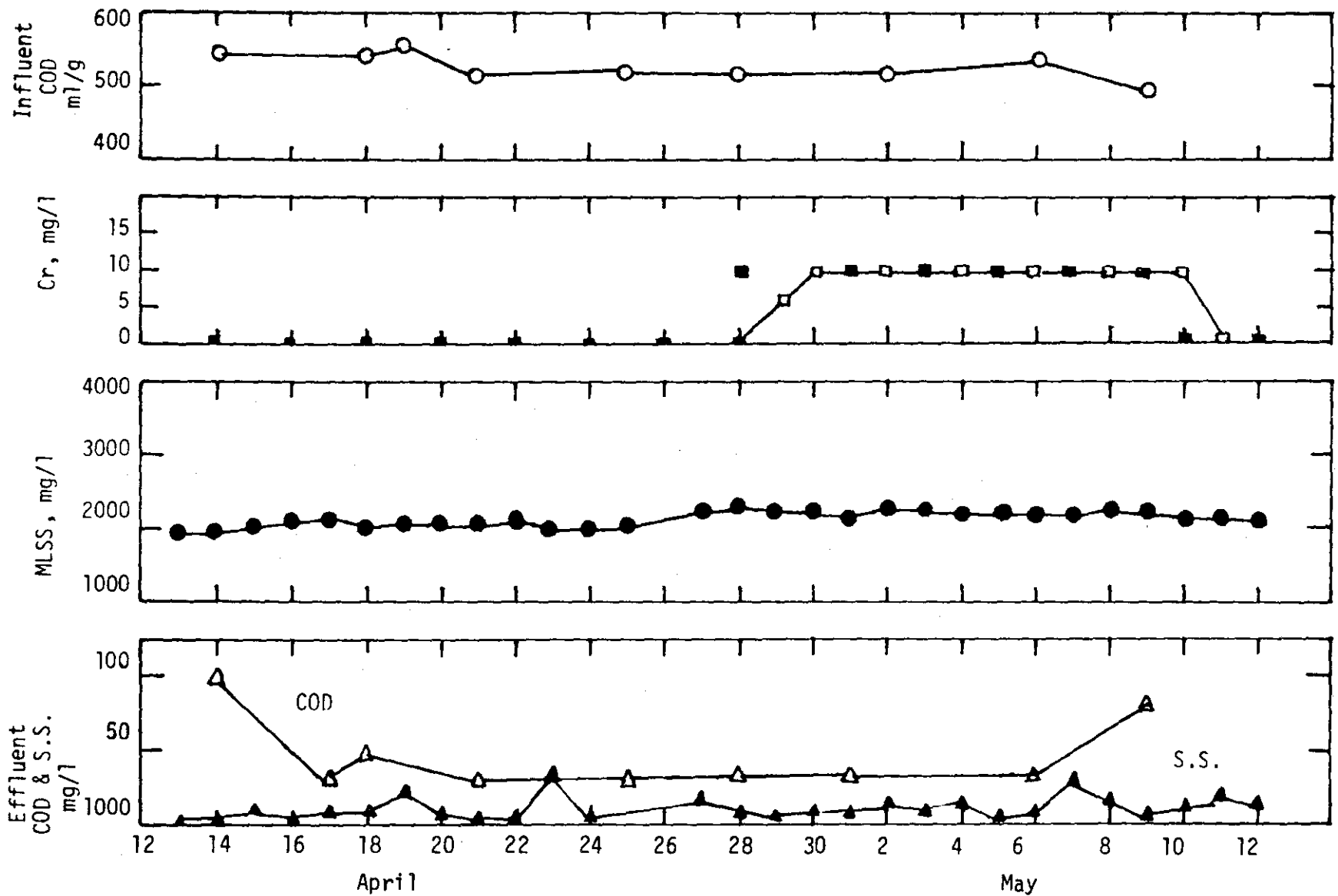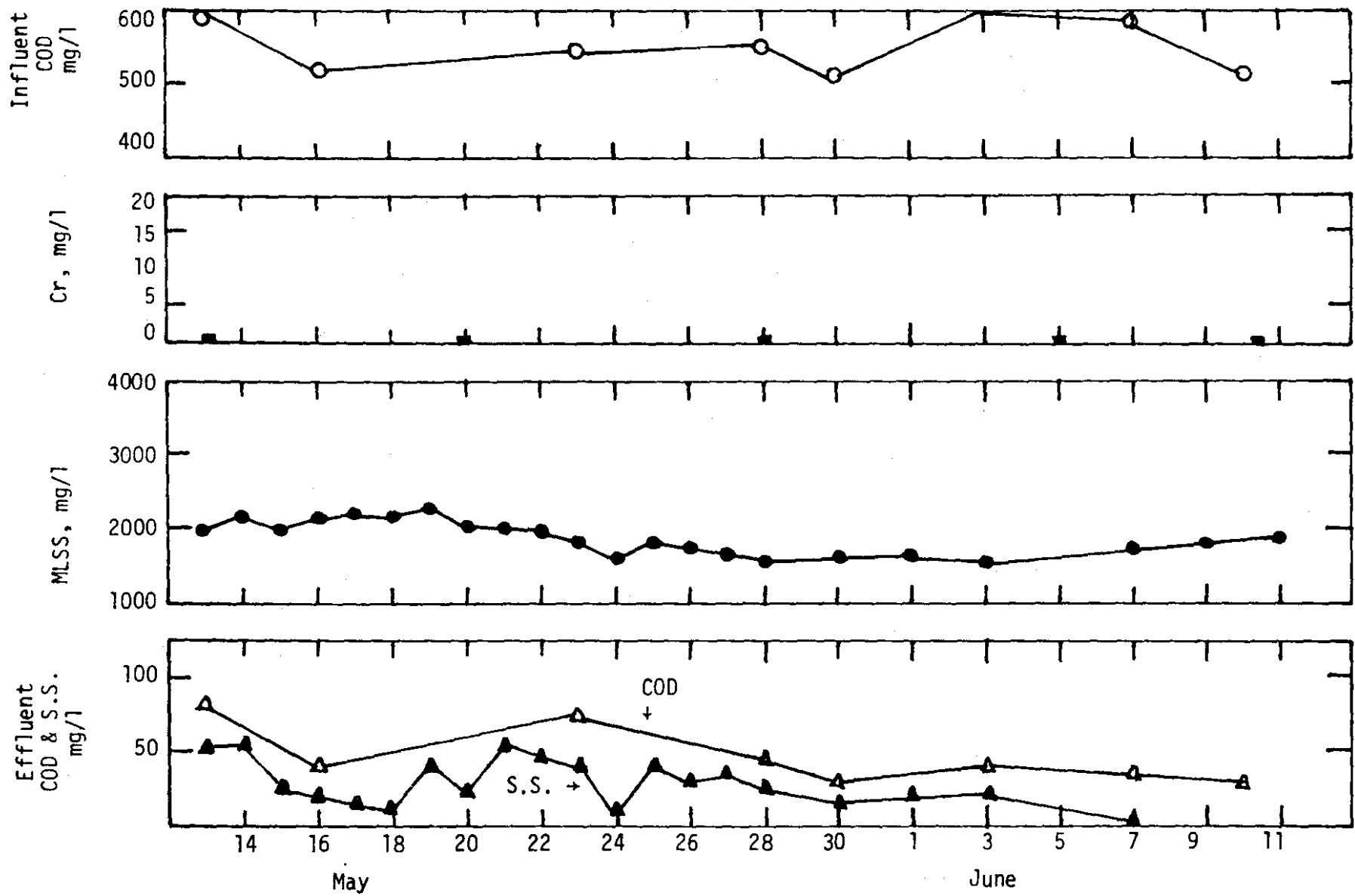
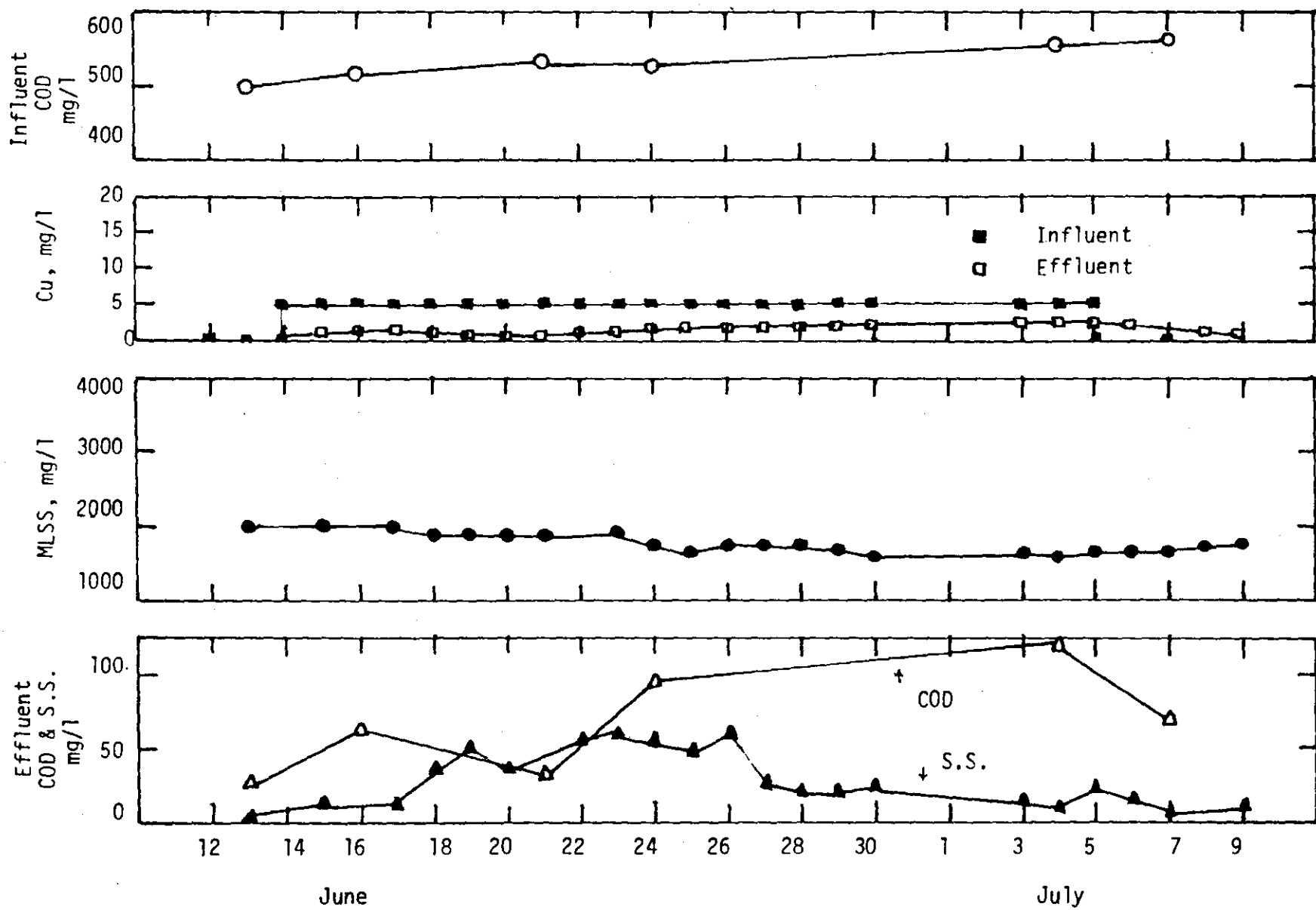Figure 16. Response of Activated Sludge Unit from May 13 to June 11, 1980.

Figure 17. Response of Activated Sludge Unit from June 12 to July 9, 1980.
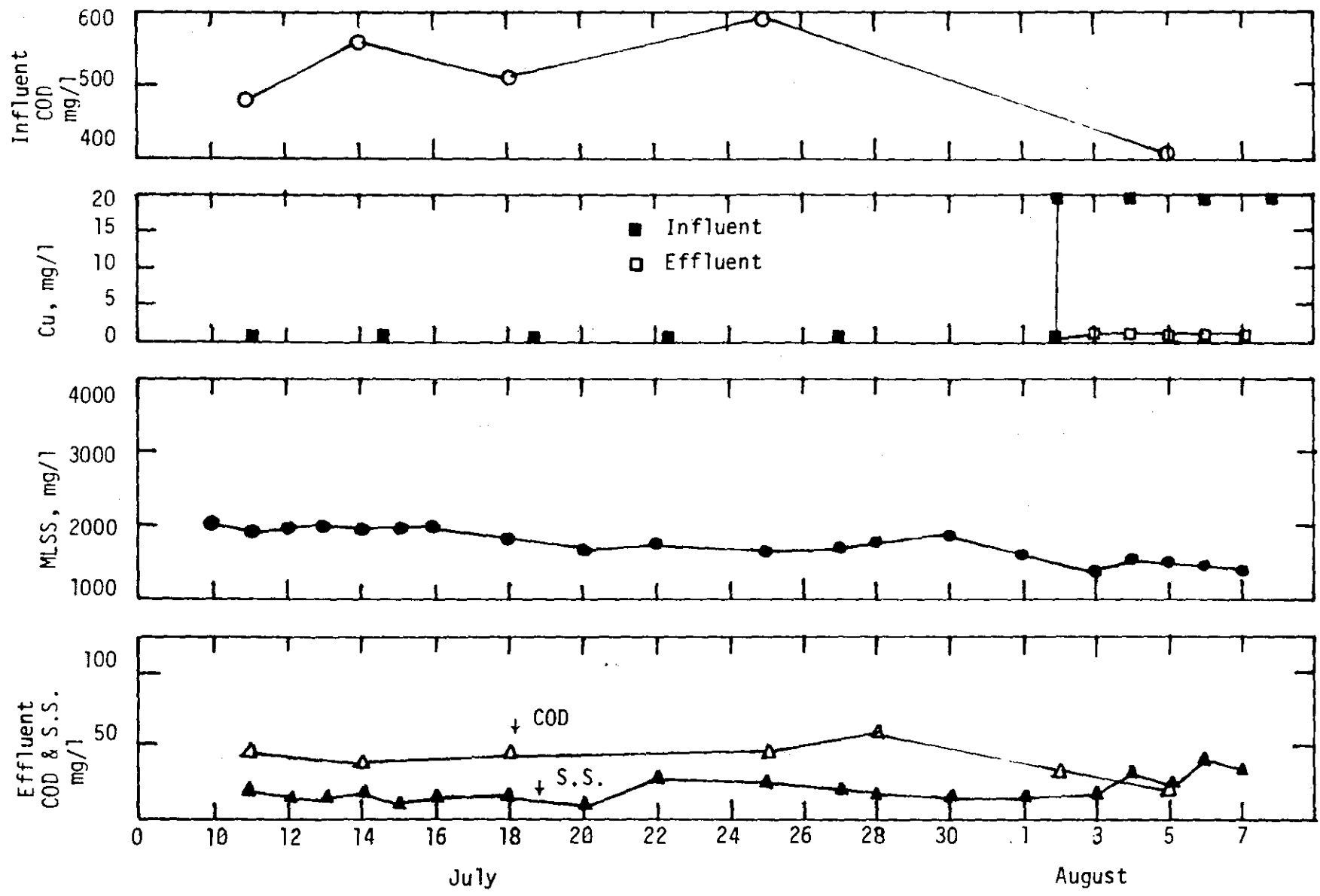
Figure 18. Response of Activated Sludge Unit from July 10 to August 7, 1980.
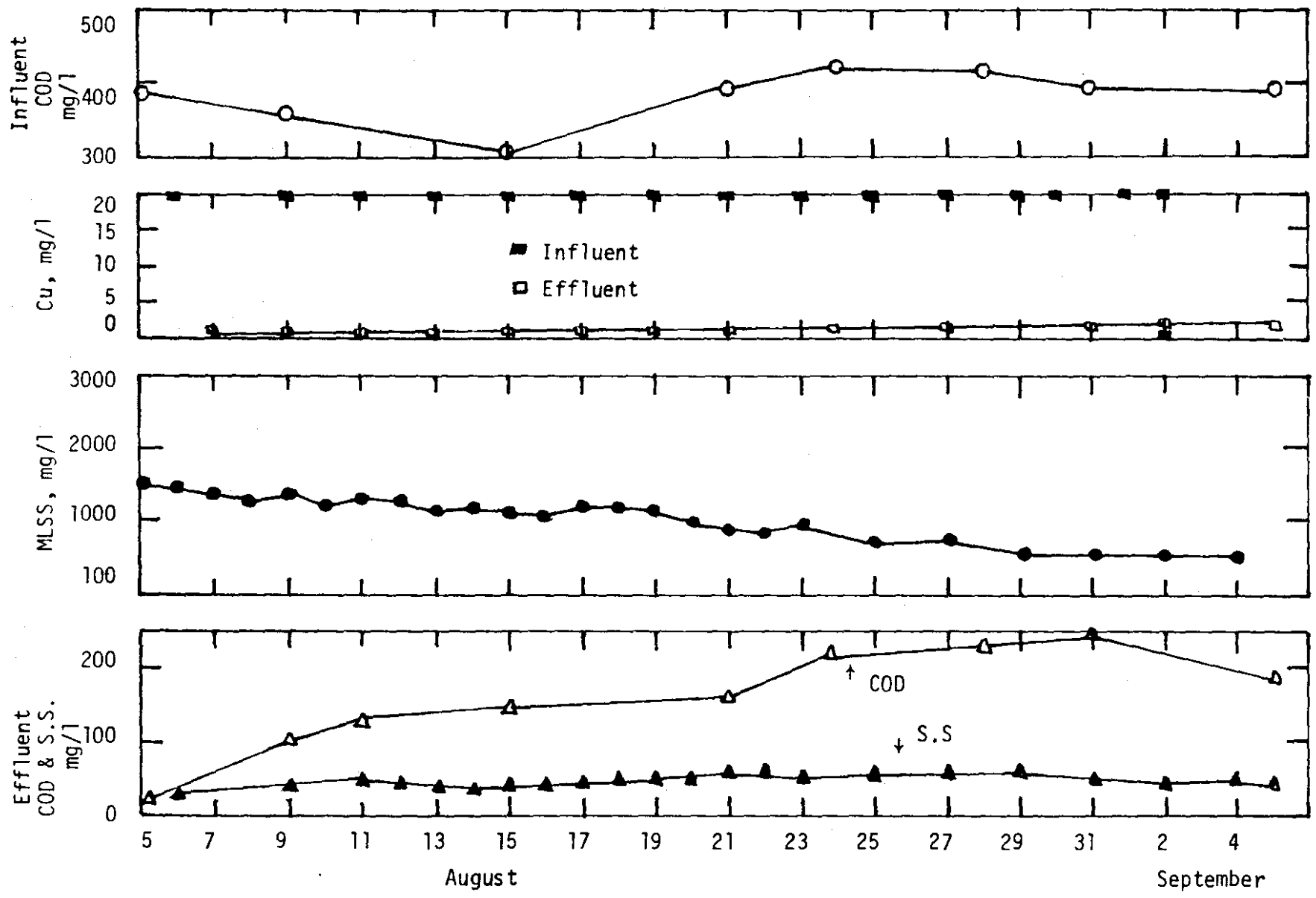
Figure 19. Response of Activated Sludge Unit from August 5 to September 5, 1980

There are several important factors to be observed in these figures. A chromium concentration of 5.0 mg/l shows no inhibitory effects. A chromium concentration of 10.0 mg/l shows a very slight inhibitory effect. The activated sludge system shows a worse response after it is no longer receiving the 10.0 mg/l chromium. The effect of 10.0 mg/l of chromium may have just occurred as the wastewater was returned to a zero chromium concentration and the bad response observed in Figure 16 may have been caused by the chromium.

Figure 17 shows that a copper concentration of 5.0 mg/l caused inhibition of the biological population. The effluent COD increased to over 100 mg/l and the mixed liquor solids decreased to 1500 mg/l. Figure 19 shows that a copper concentration of 20.0 mg/l was very inhibitory to the activated sludge process. The effluent COD increased to over 200 mg/l and the mixed liquor solids decreased to 500 mg/l.

Table 3 gives a statistical summary for the various time periods. A relationship that has been used for the activated sludge process is

$$\frac{S_i - S_e}{xt} = K\ S_e$$

where the reaction rate constant K is a measure of the treatability of a wastewater. The statistical data given in Table 3 was used to calculate reaction rate constants for a zero heavy metal concentration, 5.0 mg/l Cr, 10.0 mg/l Cr, 5.0 mg/l Cu and 20.0 mg/l Cu. Figure 20 shows these reaction rate constants as a function of the metal concentration. Figure 20 shows that a chromium concentration of 5.0 mg/l stimulated the biological system, whereas, a chromium concentration of 10.0 mg/l was slightly inhibitory. It also shows that both 5.0 mg/l and 20.0 mg/l of copper were inhibitory to the system.

Table 3. Statistical Data for Activated Sludge System

| Date	Parameter	S_i	S_e	X	X_e	θ_c
2/8-3/12	n	5	6	33	34	33
	$\bar{x}$	540	40	2488	14	8.6
	σ	69	9	308	15	1.0
	c.v.%	12.7	23.8	12.4	103.2	11.8
3/13-3/28	n	5	5	16	16	16
	$\bar{x}$	525	24	2535	3	9.1
	σ	19	6	133	6	0.5
	c.v.%	3.5	25.3	5.3	240.0	5.5
3/29-4/27	n	8	8	25	20	22
	$\bar{x}$	542	43	2312	6	8.7
	σ	18	23	349	9	0.8
	c.v.%	3.4	54.0	15.1	145.3	8.9
4/28-5/10	n	4	4	13	13	13
	$\bar{x}$	512	46	2222	12	8.2
	σ	21	22	47	6	0.5
	c.v.%	4.0	46.9	2.1	52.0	6.0
5/11-6/13	n	9	9	25	24	25
	$\bar{x}$	565	41	1887	28	7.1
	σ	65	15	224	16	1.1
	c.v.%	11.6	36.4	11.9	55.1	16.0
6/14-7/5	n	4	4	17	17	17
	$\bar{x}$	535	79	1779	33	6.5
	σ	13	34	130	18	1.06
	c.v.%	2.5	43.5	7.3	53.7	16.2
7/6-8/1	n	6	6	19	17	19
	$\bar{x}$	568	50	1800	17	7.5
	σ	65	11	127	5	0.4
	c.v.%	11.5	22.5	7.1	29.1	5.8
8/2-9/1	n	9	9	25	25	25
	$\bar{x}$	381	139	1088	43	4.8
	σ	54	72	342	11	1.05
	c.v.%	14.1	52.0	31.4	25.1	21.9
9/2-9/11	n	2	2	6	6	6
	$\bar{x}$	394	195	374	38	2.9
	σ	4	4	122	6	0.8
	c.v.%	1.1	2.0	32.7	15.5	27.8
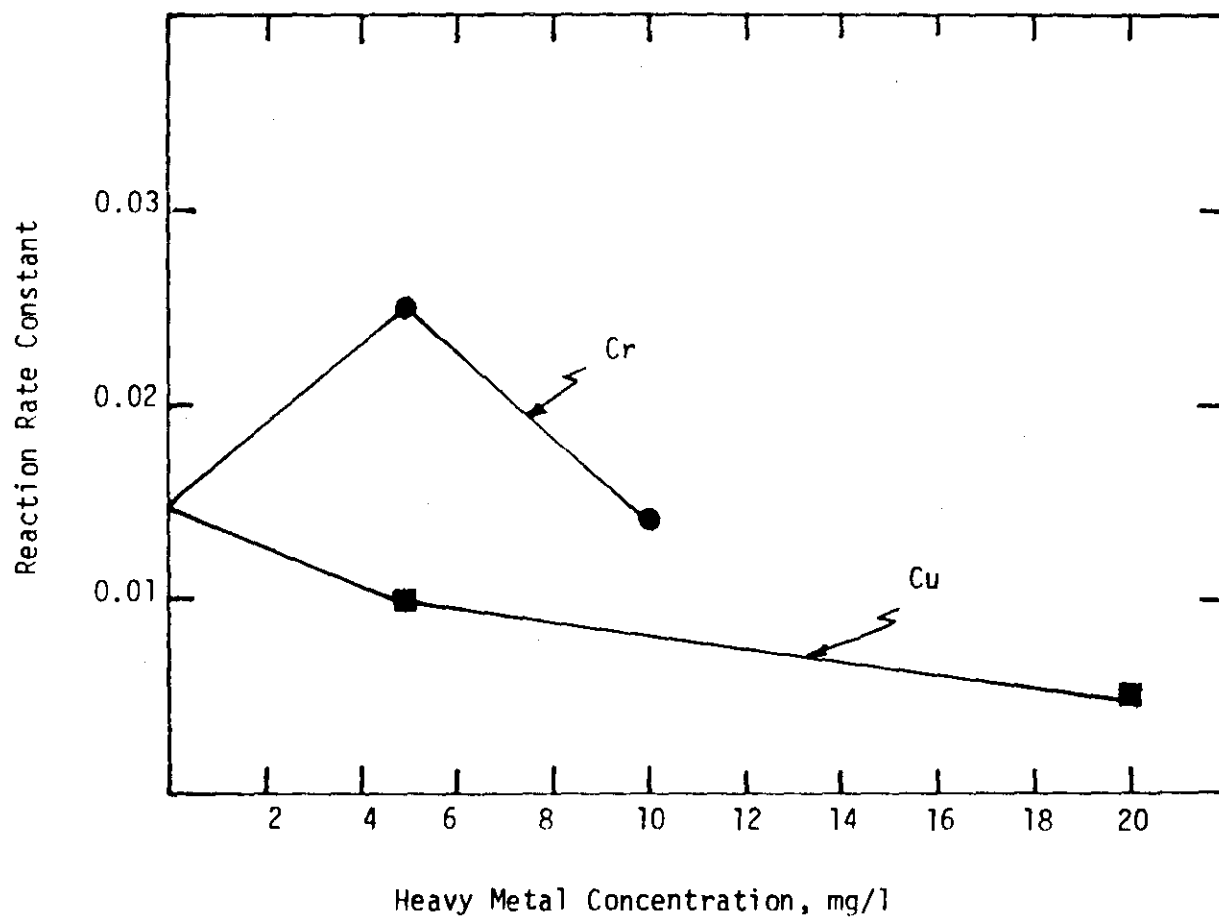
Figure 20. Activated Sludge Reaction Rate Constant as Function
of Heavy Metal Concentration

It is also interesting to note that no chromium was removed by the activated sludge system, whereas, high levels of removal were achieved for copper.

Fate of Copper and Chromium in Aquatic Systems

The results from the analyses of the three sediments with respect to clay, sand, silt and organic matter are presented in Table 4.

Table 4. The Percent of Clay, Sand, Silt and Organic Matter in the Sediments

Sediments	Clay	Silt	Sand	Organic Matter
Lake Carl Blackwell	9%	54%	37%	7.18%
Sooner Lake	16%	68%	16%	6.47%
Cimarron River	0%	30%	70%	0.43%

The data in Table 4 indicate that the sediments from the Cimarron River are largely composed of sand and the major fraction of the sediments of Lake Carl Blackwell and Sooner Lake is composed of silt. The organic matter composition of Lake Carl Blackwell is much higher than that of the Cimarron River and slightly higher than that of Sooner Lake.

Table 5 presents the chemical characteristics of the lake and river water. While alkalinity and pH measurements are similar for all waters, Sooner Lake and the Cimarron River have substantially higher chloride and sulfate concentrations than Lake Carl Blackwell. Sooner Lake has higher organic carbon and phosphate concentrations than Blackwell or Cimarron

River water, and the total hardness for Cimarron River water (542.6 mg/l) is significantly higher than that in Lake Carl Blackwell (127 mg/l) and Sooner Lake (204 mg/l).

Table 5. Chemical Characteristics of the Waters from Lake Carl Blackwell, Sooner Lake and the Cimarron River

Parameter	Lake Carl Blackwell	Sooner Lake	Cimarron River
pH	8.0	7.5	6.8
Alkalinity-mg/l as $CaCO_3$	137.0	133.0	159.0
Hardness-mg/l as $CaCO_3$	127	204	542.6
Copper-mg/l	<0.01	<0.01	<0.01
Chromium-mg/l	0.03	<0.02	<0.02
Phosphate-mg/l	2.5	17.0	3.5
Sulfate-mg/l	21.0	100.0	375.0
Chloride-mg/l	21.0	250.0	2250.0
Nitrate-mg/l	>1.0	<1.0	1.0
TOC-mg/l	103.0	347.0	127.0

The data obtained from the treatment of all three sediments with copper in the presence of distilled water are shown in Figure 21. The initial copper concentration was 200 mg/l. The data plotted in this and all subsequent graphs represent an average of the results obtained from duplicate systems. In all cases duplicate values, if not identical were very close and well within the range of experimental error. Although great care was taken to minimize any experimental error, samples had to be
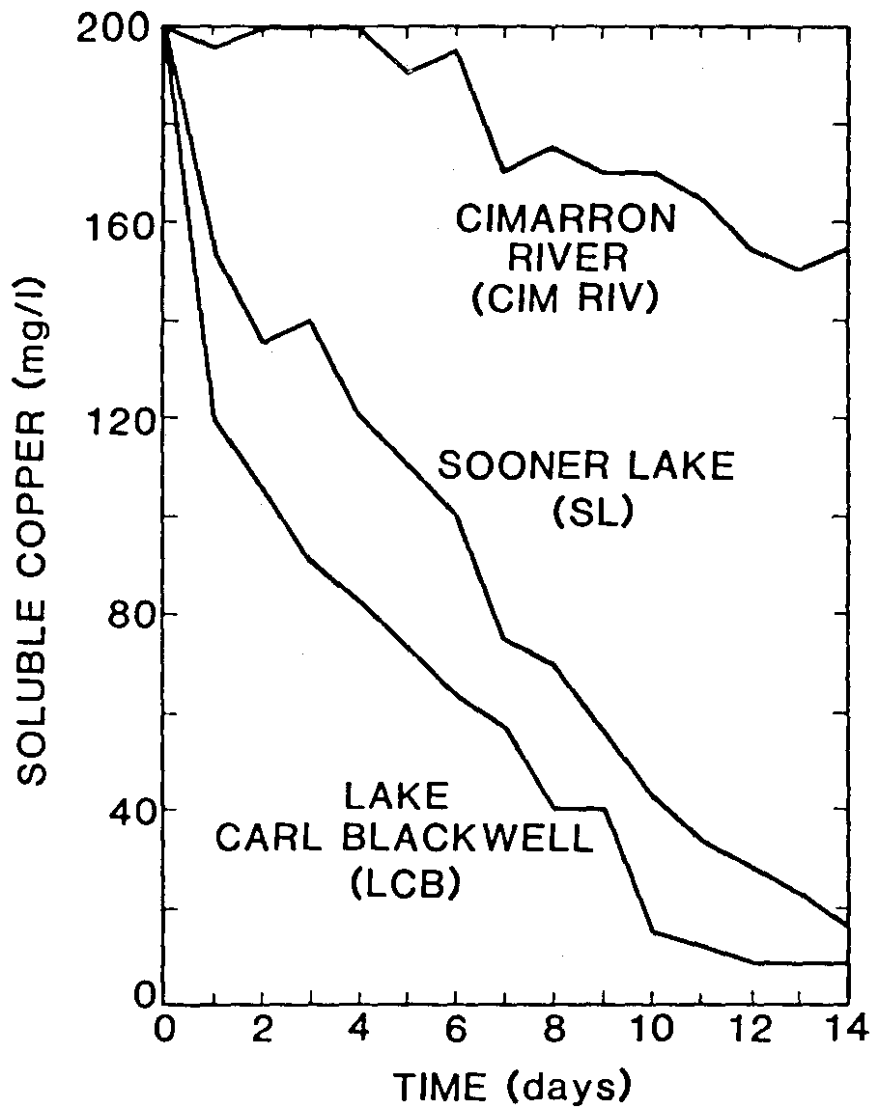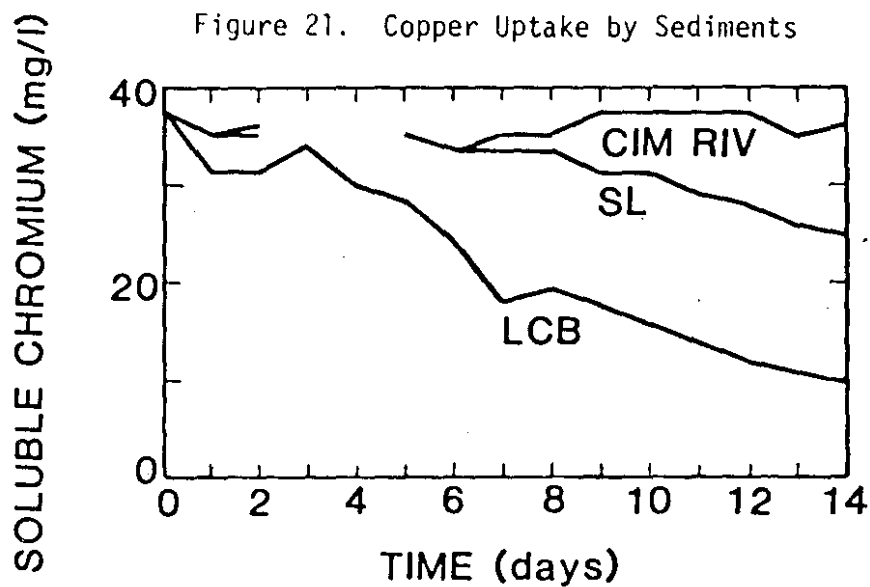
Figure 21.   Copper Uptake by Sediments

Figure 22.   Chromium Uptake by Sediments

diluted in many cases by a factor of 100 to utilize the Hach dr/2 for analyses. The smallest of variations when multiplied by 100 could cause noticeable error.

From Figure 21 it can be seen that the sediments of Lake Carl Black-well (LCB) took up more copper in the fourteen-day experimental period than did those of Sooner Lake or the Cimarron River. Blackwell fixed a total of 573 mg (191 mg/l) and Sooner Lake a total of 546 mg (182 mg/l). The sediments from the Cimarron River fixed much less copper with a four-teen day total of 135 mg (45 mg/l).

The sediments from all three sources had a higher affinity for copper than for chromium. Figure 22 indicates the uptake of chromium in a fourteen day period by the sediments. The initial chromium concentration was 37.5 mg/l. At the end of the experimental period, sediments from Lake Carl Blackwell had removed 82.5 mg (27.5 mg/l); sediments from Sooner, 37.5 mg (12.5 mg/l); and sediments from the Cimarron River, 4.5 mg (1.5 mg/l). Sediments from Lake Carl Blackwell fixed more copper and chromium than sediments from Sooner Lake or the Cimarron River.

Figure 23 represents the decrease in the soluble copper concentration in systems containing 30 mg/l copper and 48 mg/l (dry weight) of algae. In a fifteen-day period, the copper concentration was reduced 50 percent to a final concentration of 15 mg/l. The plotted data were corrected for the uptake of the BOD water control prior to graphing.

The systems containing only BOD water, algae and chromium showed no uptake of the metal by the algae. An initial concentration of 28 mg/l chromium was used for the studies with the addition of 56 mg/l (dry weight) of algae. The only uptake of chromium over a seven-day period could be attributed to the BOD water and was equal to 3 mg/l.
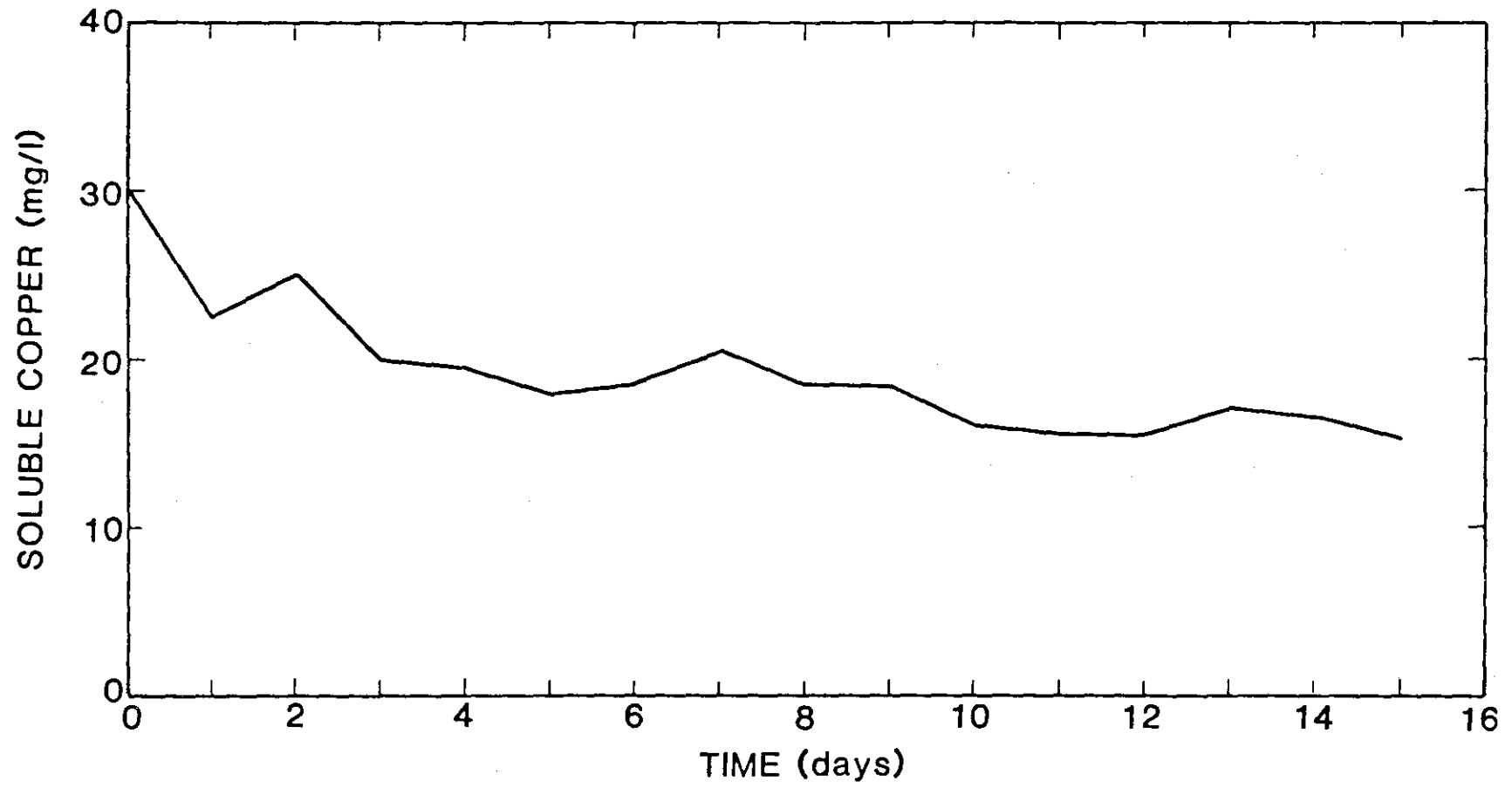
Figure 23.   Copper Uptake by a Mixed Algae Culture

Figures 24, 25, and 26 represent the uptake of copper by units containing water, algae and water, sediment and water, and a combined system containing algae and water and sediments for Lake Carl Blackwell, Sooner Lake and the Cimarron River respectively. For both Lake Carl Blackwell (Figure 24) and Sooner Lake (Figure 25), the units containing only sediment and water fixed more copper over the experimental period than even the combined units which contained algae in addition to the sediment and water. In all units containing actual lake or river water, a layer of precipitate formed and coated the sediments on the bottom of the jars.

Figure 27 shows the data obtained from studies of the uptake of chromium by water, algae, sediments and a combined system for Lake Carl Blackwell, Sooner Lake and the Cimarron River. The last two analyses for all of the Cimarron River systems show an ancrease in soluble chromium back to the original concentration. Prior to these analyses, the pipet used for taking all previous samples was broken and a new pipet was used. That, coupled with the 100:1 dilution factor, probably accounts for the discrepancy.

Behavior of Copper in Soils

The data obtained from studying the mobility of copper through soil systems indicate the copper uptake capabilities of various soils. Figures 28-30 represent the concentration of soluble copper in aqueous samples taken at various depths from a soil column containing sand. Figure 31 represents the data obtained from withdrawing and analyzing aqueous samples from two soil columns, one containing sand and one containing a red silty clay.
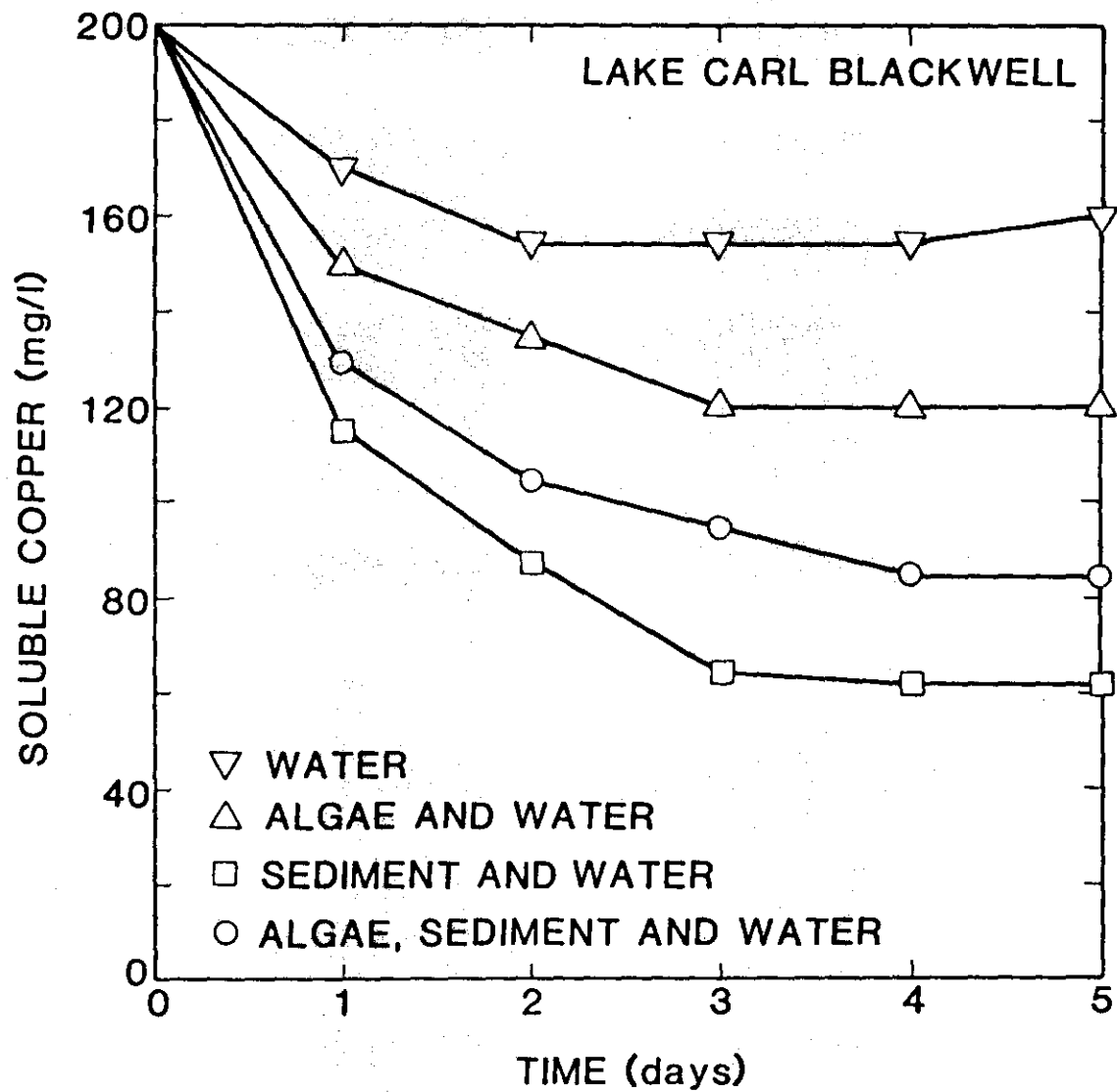
Figure 24. Copper Uptake by Algae and Water and Sediments
From Lake Carl Blackwell

Figure 26. Copper Uptake by Algae and Water and Sediments from the Cimarron River
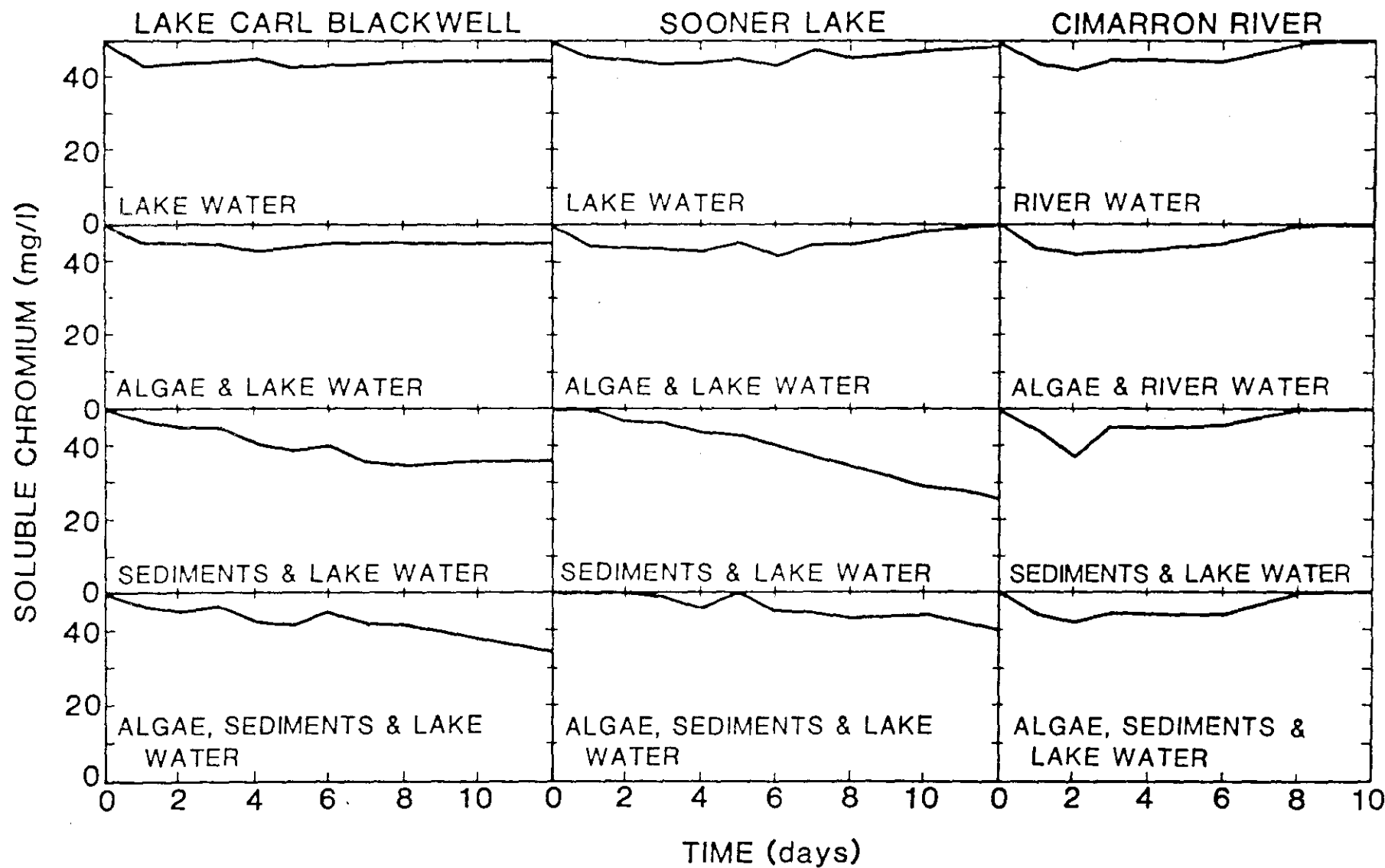
Figure 27. Chromium Uptake Studies Using Algae and Water and Sediments from
Lake Carl Blackwell, Sooner Lake, and the Cimarron River
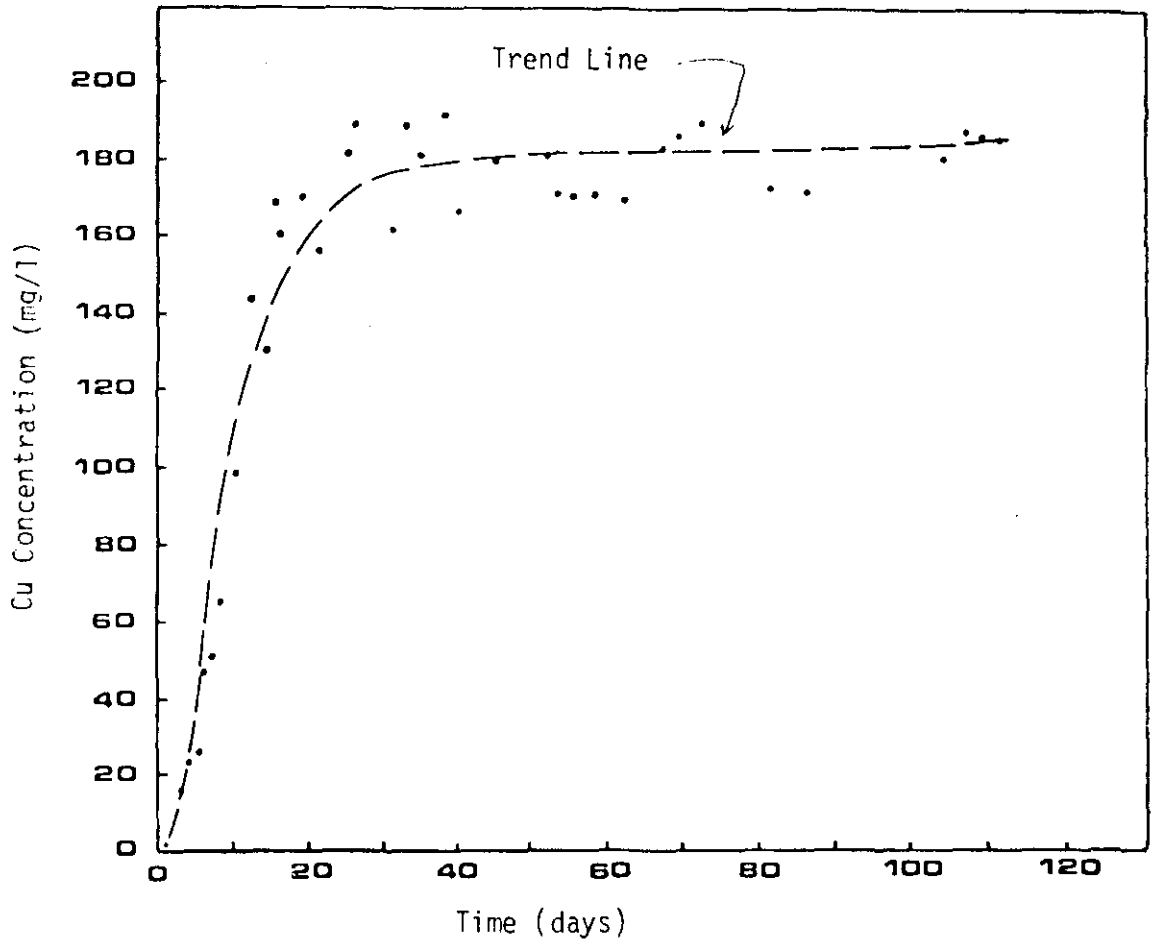
Figure 28. Soluble Cu in the Effluent at 6 inches below the
Soil Surface.
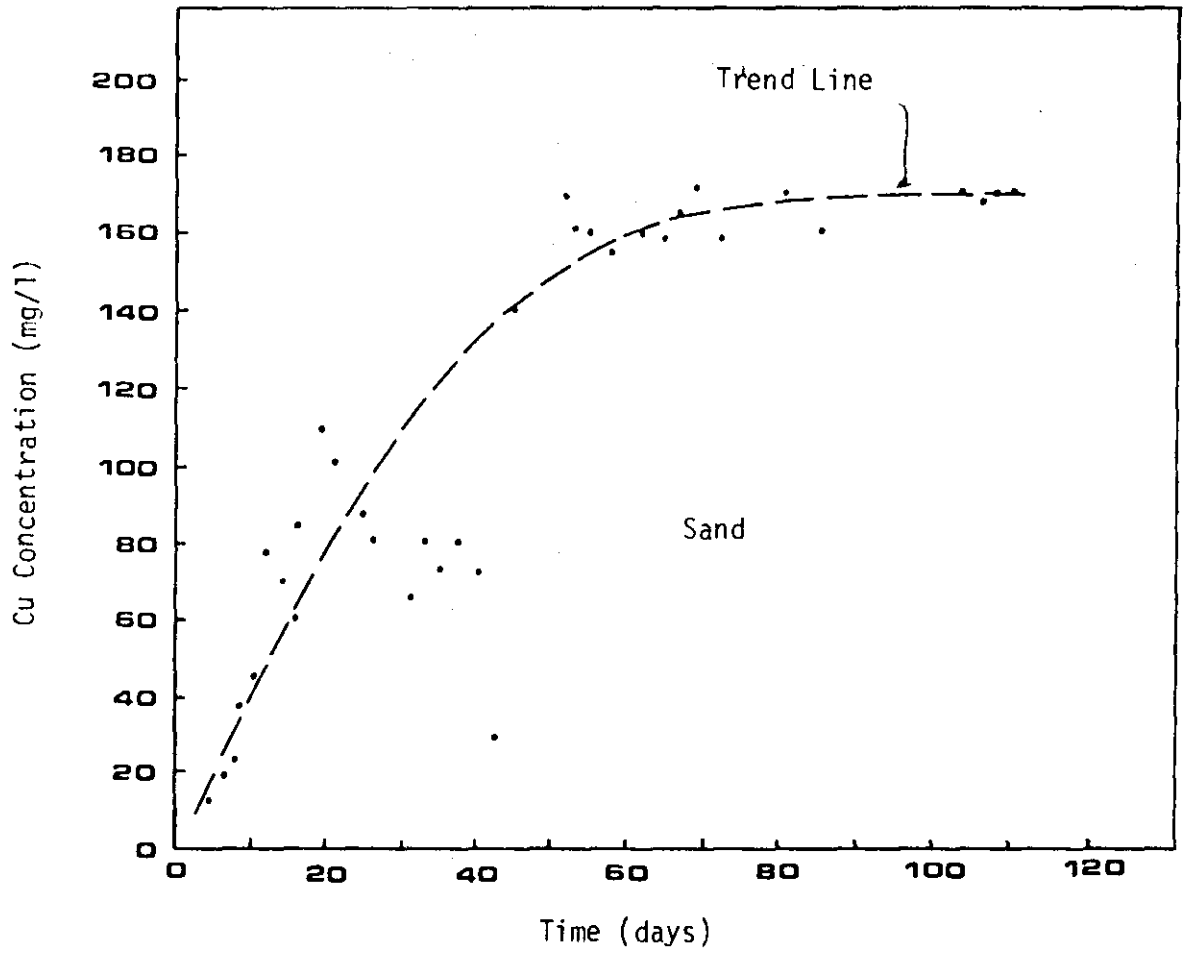
Figure 29. Soluble Cu in the Effluent at 18 inches below the Soil Surface.
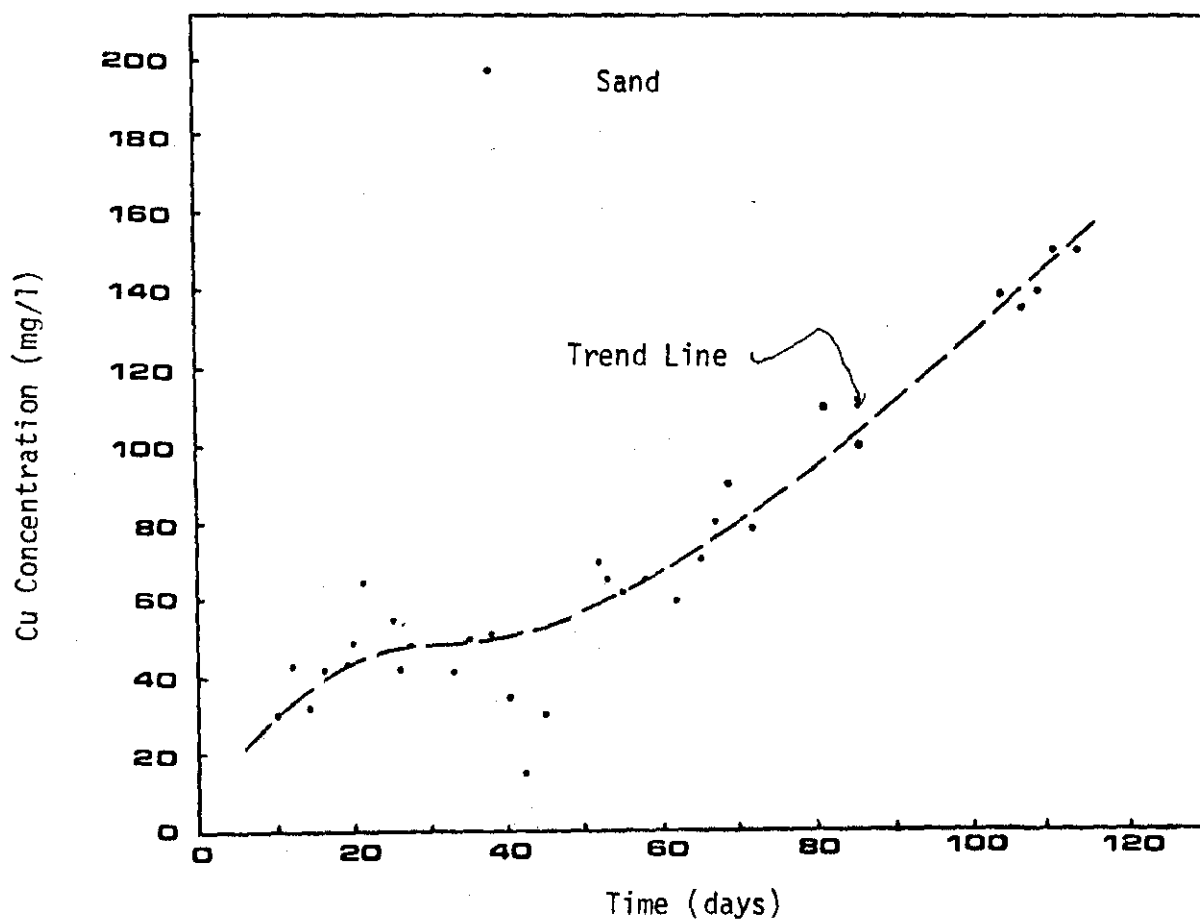
Figure 30. Soluble Cu in the Effluent at 30 inches below the Soil Surface.
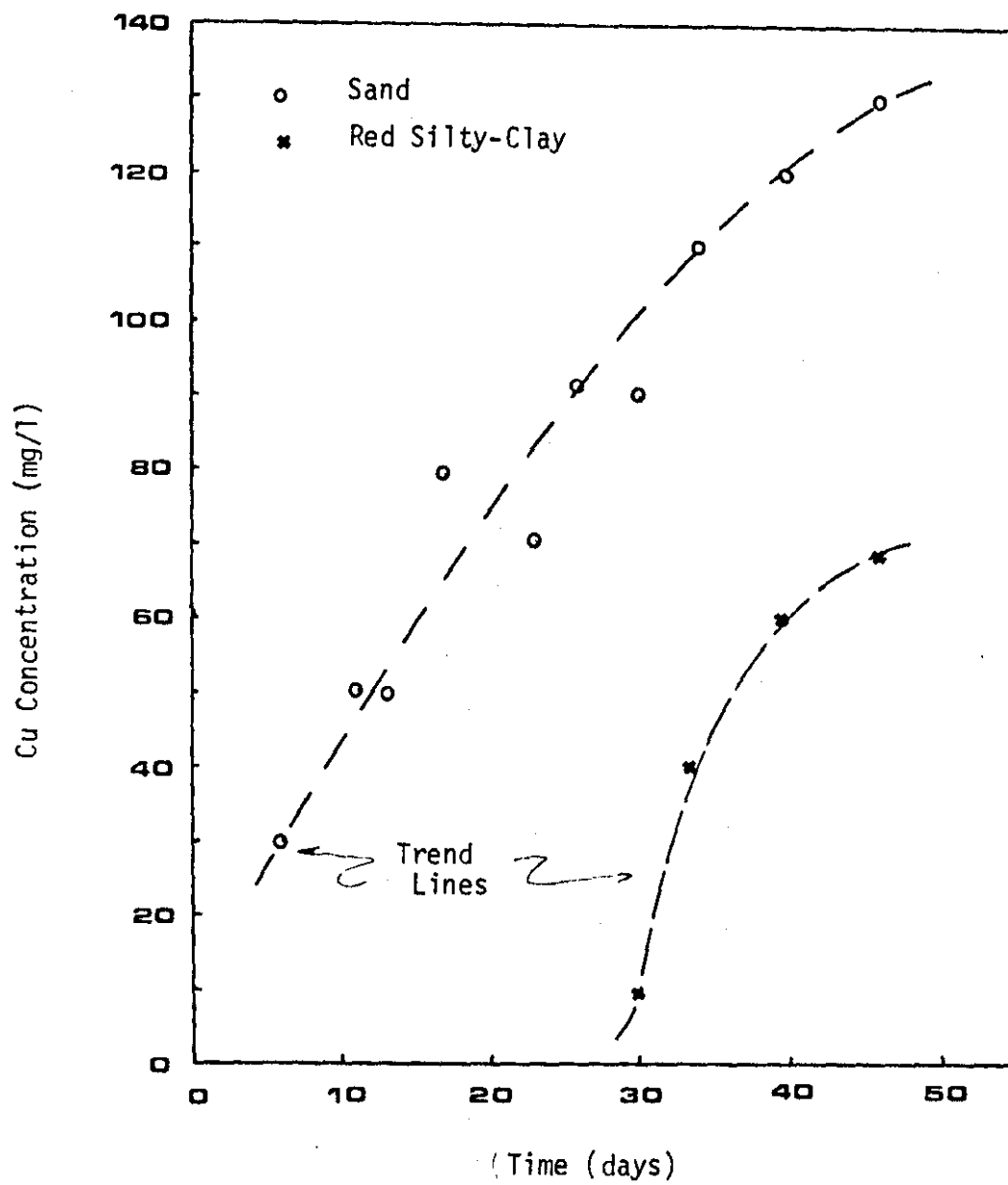
Figure 31. Soluble Cu in the Effluent at 30 inches below the Soil Surface.

DISCUSSION

Biological Waste Water Treatment Studies

These studies have shown that the rotating biological contactor
and activated sludge biological wastewater treatment processes are
affected in similar ways by chromium and copper. However, it appears
that the activated sludge process is more severely affected. Chromium
stimulated biological activity in both systems at lower concentrations,
whereas, both systems showed slight inhibition at higher chromium con-
centrations. Copper showed no effect on the RBC system at concentrations
below 4.0 mg/l. Copper showed inhibition to both systems at concentra-
tions above 4.0 mg/l. The inhibition of copper appears to be more severe
in the activated sludge system. This could be due to the fact that in
the RBC system the copper is removed in the first stages and would not
be present in the later stages. This would allow the later stages to
function without any inhibition. In the activated sludge system, this
staging is not possible and the entire biological population is affected.

The removal of chromium and copper by the RBC and activated sludge
provides some contrasting results. Both chromium and copper were removed
at fairly high levels in the RBC system. However, chromium was not re-
moved by the activated sludge process. Copper was removed by the activated
sludge. This study did not give any answers to why chromium would be re-
moved by the RBC biological population and not by the activated sludge.
However, one possible explanation is that the chromium is removed by

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adsorption and the RBC population is such that adsorption was accomplished by the slime layer. This slime layer did not exist in the activated sludge system.

Apparently copper is removed by a different mechanism than chromium. Fairly high removal of copper was achieved in the activated sludge process and also in the RBC system at hydraulic loadings of 2.0 and 3.0 gpd/ft^2. Low removal levels of copper were achieved in the RBC at a hydraulic loading of 0.7 gpd/ft^2. It would appear that copper is removed by metabolic uptake since copper was removed by both the RBC process and activated sludge. This would also account for the more inhibitory effect exerted by the copper. It does not explain why the low hydraulic loading was so inefficient in removing copper. The lower hydraulic loading provides a low food to microorganism ratio which in turn may foster a physiological condition of the microorganisms which would not readily take up copper.

Whatever the mechanism, this study has shown that the effect of heavy metals on biological wastewater treatment processes is dependent upon the type of treatment process and upon the operating conditions. This probably accounts for the various effects that are reported in the literature. Researchers have used different operating conditions to study the effects of heavy metals. Therefore, their results differ.

Fate of Copper and Chromium in Aquatic Systems

Heavy Metal Uptake by Sediments

Examining the uptake of copper by the three sediments in the presence

of distilled water (Figure 21) probably gives a more accurate representa-
tion of the sediments' capabilities for metal fixation than the results
obtained in the lake or river water systems. The sediments from Lake
Carl Blackwell fixed more copper (573 mg) than those from either Sooner
Lake (546 mg) or the Cimarron River (135 mg). However, the amount fixed
by Sooner Lake sediments was very close to that fixed by Lake Carl Black-
well sediment. The significant difference between the copper fixing
capabilities of the two lake sediments versus the Cimarron River sediments
was expected. As previously mention in the review of literature, heavy
metal fixation is high in soils containing clay, organic matter or small
textured particles. The sediments from Lake Carl Blackwell and Sooner
Lake are primarily composed of silt but have more clay and organic matter
than the Cimarron River sediments which are composed of sand (Table 4).

The trends exhibited by chromium (Figure 22) and the three sediments
in distilled water are very similar to those seen in Figure 21 for copper,
which again supports the fact that heavy metal uptake is favored in soils
containing clay and organic matter. However, chromium uptake by the sedi-
ments differed from that of copper in that sediments from Sooner Lake
took up much less chromium than those from Lake Carl Blackwell. Uptake
over the fourteen-day experimental period for Lake Carl Blackwell was
82.5 mg chromium whereas Sooner Lake sediments fixed only 27.5 mg. Clay
mineralogy also affects metal uptake and may have been responsible for
the significant difference observed between the chromium fixing capabilities
of Lake Carl Blackwell and Sooner Lake.

Heavy Metal Uptake by Algae

Copper sulfate has long been recognized and utilized as an algicide and chromium also has algicidal properties. The uptake of these two heavy metals by algae was examined individually in solutions containing BOD dilution water and algae. Over a fifteen-day experimental period, algae reduced the soluble copper concentration from 30 mg/l to 15 mg/l. Chromium showed no uptake by algae during the experimental period. This is converse to the results obtained by Mangi et al (1978) and Richards (1936) with respect to algae utilization of chromium. In addition, the lack of chromium removal from solution precludes adsorption onto cell walls which was the major mechanism of chromium removal in natural waters suggested by Mangi et al (1978).

Interaction with the Aqueous Phase

Very little chromium was removed by precipitation with the lake or river water (Figure 27). Removals throughout the experimental period averaged 16% for Lake Carl Blackwell water, 11% for Sooner Lake water and 9% for Cimarron River water.

Copper, however, readily reacted with components of the aqueous phases resulting in the precipitation of large amounts of copper. As can be seen from the data in Figures 24, 25, and 26, water from Lake Carl Blackwell was responsible for removing an average of 20% of the soluble inorganic copper from solution. Water from Sooner Lake removed 68% of the copper and water from the Cimarron River removed 80% of the

soluble inorganic copper from the aqueous phase. The results of the water quality analyses shown in Table 5 correlate well with the various copper removals observed in the aqueous phases. Sylva (1976) states that a pH above 6.5, abiotic removal of copper is a predominant mechanism and, according to Stiff (1971), copper reacts to form mala-chite, an insoluble copper species, in the pH range of 6.0 - 8.5 This chemical reaction could have occurred in all three systems since the pH of Cimarron River water was 6.8, the pH for Blackwell was 8.0 and the pH for Sooner Lake was 7.5. In addition, chloride also serves to control the soluble copper concentration in natural waters. The much higher chloride concentrations (Table 5) found in the Cimarron River and Sooner Lake waters as compared to Lake Carl Blackwell probably accounts for greater copper removals noted in these waters. Precipi-tation, as stated by Sanchez and Lee (1978) and McIntosh (1975) is definitely a primary mechanism in controlling the soluble copper concen-tration.

Metal Uptake in Simulated Systems

Copper and chromium uptakes in simulated aquatic systems containing algae, lake or river water and sediments were determined for Lake Carl Blackwell, Sooner Lake and the Cimarron River. Algae and sediment uptake were again determined individually; however, lake or river water was used instead of the BOD water and the distilled water used in the previous studies. The results from the copper uptake studies are shown in Figures 24, 25 and 26.

Looking at Figures 24, 25 and 26 and comparing the uptakes in the three combined systems, it can be seen that the combined system containing Cimarron River water sediments removed more copper (165 mg/l) than the Lake Carl Blackwell system (115 mg/l). In addition, the Sooner Lake combined system also removed more copper (152.5 mg/l) than the Lake Carl Blackwell unit. The higher combined removals seen with the Cimarron River and Sooner Lake units as compared to Blackwell can be attributed to the greater amounts of copper precipitated by the aqueous phase. In fact, the 165 mg/l removal in the combined Cimarron River system was only 2.5 mg/l greater than the copper removed in the unit containing Cimarron River water only. Similar results were seen with the Sooner Lake combined system in which the removal of 142.5 mg/l was only 10 mg/l higher than the uptake seen in the Sooner Lake water system.

It was previously determined that the sediments from the Cimarron River and Sooner Lake (Figure 21) were capable of removing soluble copper from solution. In the distilled water studies, Cimarron River sediments removed 45 mg/l and Sooner Lake sediments removed 182 mg/l. In addition, it was also previously determined that algae are responsible for removing some soluble copper from solution (Figure 23). If the amount of copper removed in the water only systems is subtracted from the total amount of copper removed in the Cimarron and Sooner combined systems, it appears that there was only very minimal participation by the algae and/or the sediments in the removal of the soluble copper. In addition, if the amount of copper removed in the water only system is subtracted from the

algae-water unit and the sediment-water units for Lake Carl Blackwell, Sooner Lake and the Cimarron River, it appears that the uptake of copper by algae and sediments in natural water is lower than in the previous BOD and distilled water studies.

In substracting the uptake of the water from all the other units to get the net algae and net sediment uptake, it is assumed that the water removed the same concentration of copper in all the units. This may not be a valid assumption. The amount of copper removal attributed to soluble components in the aqueous phase could be higher in the presence of algae and/or sediments. Extracellular components secreted by the algae or ions leached from the sediments could enhance the complexation or precipitation of copper in solution. If this did occur, however, it would further decrease the total amount of removal which could be attributed to the algae or sediments in the individual or combined units, and their uptake in natural water would still be lower than that observed in the previous studies.

There may possibly be several reasons for this decreased uptake by algae in the natural water systems. In the systems containing lake and river water, the experimental period was not fourteen days as with the BOD water-algae units but 5 days for Lake Carl Blackwell and the Cimarron River and 4 days for Sooner Lake. It is possible that with a longer experimental period uptake may have increased; however, analyses were stopped at these periods because uptake was not showing any experimentally significant difference from one day to the next. In addition, the copper

concentration in the systems with lake and river water was initially 200
mg/l; whereas, in the system with BOD water the initial concentration was
only 50 mg/l. The significantly higher copper concentration may have
inhibited algae growth or killed the algae and therefore reduced the total
copper uptake.

The formation of the copper precipitates is probably the major cause
of depressed copper removal by algae in the natural water units. In
addition to reducing the amount of copper available for algae uptake,
the precipitates removed the algae from solution as they settled and then
formed a protective layer on top of the algae at the bottom of the jar.

As with the algae, sediment uptake was hindered by the formation of
the copper precipitates which served to seal the sediments. The Cimarron
River sediments were sealed by a 5 mm layer of precipitates. Precipita-
tion in the Sooner Lake system was less than the Cimarron units but still
coated almost 100% of the exposed sediment surface area. Only minimal
precipitation was observed in the Lake Carl Blackwell units and complete
and uniform coverage of the sediments did not occur.

In the combined units, the algae that settled with the copper precipi-
tates also formed a seal on the sediments. Combined systems were chrac-
terized by a layer of green algae immediately on top of the sediments.
This in turn was covered with the copper precipitates. The algae layer,
in addition to the precipitate layer, probably accounts for the lower
copper uptake observed in the combined systems (Figures 24 and 25) as com-
pared to the uptake in the units containing only sediment and waters.

It is entirely possible that the capacity of the Cimarron River and Sooner Lake and even Lake Carl Blackwell systems for copper removal is much higher than that exhibited. In the actual lake or river situation, where the exposed sediment surface area and the volume of water are much larger, there would be little chance of the sediments being sealed with copper precipitates or algae. This should allow for more sediment inter-action in copper removal and increase overall uptake.

The uptake of chromium in the water, algae-water, sediment-water and combined systems for Lake Carl Blackwell, Sooner Lake and the Cimarron River is shown in Figure 27. The waters from all three sources fixed similar amounts of chromium (3 - 5 mg/l) over the experimental period and the amount removed by the water was minimal compared to the concen-trations of copper removed by the lake and river waters. The algae in all three waters fixed essentially no chromium as shown by the fact that chromium removals in the algae-water systems as compared to the water (only) units were equal or only differed slightly throughout the experi-mental period. These results agree with those previously obtained in the algae and BOD water systems.

The combined systems indicate that the chromium removals for the Cimarron River, Sooner Lake and Lake Carl Blackwell systems were 5 mg/l, 11 mg/l and 16 mg/l respectively. Chromium removal in these combined systems seems to be largely a function of the sediments. Total uptake of chromium in the sediment-water systems compared favorably with the total uptake seen in the combined systems for Lake Carl Blackwell and the Cimarron River. For Sooner Lake, more chromium was removed in the

sediment-water sytem than in the combined system.

It was pointed out that in the copper systems containing algae and sediments, the algae provided some sealing of the sediments which may have decreased sediment uptake of copper. It would therefore be expected that the same phenomenon would exist in the chromium systems containing algae and sediments. By the end of the experimental period, the algae had indeed settled onto the sediments. However, the algae in the chromium systems remained in suspension much longer than the algae in the copper systems. This in turn provided a longer period qf time for the sediment adsorption of chromium. The precipitate formed in the copper systems caused the algae along with the precipitates to settle and seal the sediments within a day.

Aquatic systems, as demonstrated by the simulated systems in this study, are capable of removing both copper and chromium from solution. Copper removal is largely a function of the water composition and the sediment; whereas, the sediments were the controlling factor in chromium removal. All three sediments and waters exhibited a much higher affinity for copper than for chromium. The Cimarron River removed more copper but less chromium from solution than did Lake Carl Blackwell or Sooner Lake. Conversely, Lake Carl Blackwell removed less copper but more chromium than Sooner Lake and the Cimarron River.

Although conclusive with respect to copper and chromium uptake, these results do not imply that the metals will be permanently retained by the sediments or be permanently precipitated as insoluble species. Changes in

pH and oxidation reduction potential could cause release of the metals

from the sediments and resolubilization of precipitated species. En-

vironmental changes in pH and redox potential should always be considered

in assessing the assimilative capacity of aquatic systems for heavy

metals.

Behavior of Copper in Soils

The combination of Figures 28 through 30 illustrate the copper up-

take capabilities of the soil as a function of depth. The plots show

soluble copper remaining in the effluent. At a time greater than zero,

the soils ability to adsorb the copper is decreased as evident of the

increase of soluble copper in the effluent.

Figures 28 through 30 demonstrate the importance of uptake capa-

bilities as the depth of allowable contact increases. The soluble copper

concentration in the effluent decreases as the distance from the source

increases.

Figure 31 clearly exhibits the adsorption capabilities of a red

silty-clay versus a sand. The soluble copper remaining in the effluent

at day forty is significantly lower for the silty-clay soil as compared

to the sand, thus implying the adsorption capability of the silty-clay

is much greater than that of the sand. This is supported by Leeper (1978)

who states that the cation exchange capacity of a soil increases as the

clay content increases.

CONCLUSIONS

The data obtained from all of the investigations conducted in this study trace the fate of copper and chromium through wastewater treatment processes, aquatic systems and soil systems. In general, the results indicated that copper is probably of less environmental concern than chromium since it is so readily removed by wastewater treatment systems, aquatic systems and soils. Copper is removed by microorganisms in activated sludge and rotating biological contactors and by algae in simulated aquatic systems. In addition, sediments and soils show a strong affinity for copper and the uptake of copper by both can be correlated with soil type. A final mechanism for the reduction of soluble copper in aquatic systems is the precipitation of copper as the result of the interaction with soluble anions in the aqueous phase.

Chromium behaved somewhat differently than copper. Chromium was removed only by the rotaing biological contactor and not in the activated sludge or algae systems. In addition, removal of chromium in aquatic systems seems to be primarily a function of sediment composition. The correct choice of treatment process and the operational conditions for the removal of chromium from wastewater streams is extremely important. Effluent chromium concentrations can be minimized by the use of rotating biological contactors versus activated sludge. It is essential that as much chromium be removed as possible from wastewaters since the assimilative capacity of aquatic systems for chromium is relatively low as

compared to copper.

Effluent streams from wastewater treatment facilities should contain relatively low copper concentrations and any copper discharged into an aquatic system should be readily precipitated or adsorbed. Similarly, copper applied to soils should be removed before it is transported to the groundwater providing the soil contains clay or organic matter.

Heavy metal contamination of the environment can be minimized by proper management practices. The correct choice of wastewater treatment processes and soil systems, coupled with an understanding of the fate of these metals in aquatic systems, should enable the reduction of copper and chromium pollution in the aqueous environment.

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