CADMIUM AND ZINC IN THE AQUATIC SYSTEM

By

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CHAPTER I

INTRODUCTION

The fate of heavy metals in the aquatic environment has become an
area of increasing concern in recent years because most heavy metals are
able to bioaccumulate in the food chain or, in their simple ionic form,
can be toxic to aquatic life. The concern with heavy metals is exempli-
fied by the fact that EPA has specified 12 heavy metals as priority pol-
lutants. A priority pollutant as defined by EPA is any disease-causing
pollutant which, when assimilated into an organism can cause death,
disease, cancer, behavioral abnormalities, or derformation in off-spring
(1).

Two of the metals considered as priority pollutants are zinc and
cadmium. Zinc is a fairly abundant metal and at low levels is essential
to plant and animal metabolism but may become toxic to some animals at
higher levels. However, most toxicity problems encountered with zinc
are due to cadmium associated with zinc. Cadmium is a much rarer element,
which is not known to be essential to life processes, but it is highly
toxic to aquatic organisms and man. Although these metals are natural
constituents of aquatic environments, additional quantities introduced
by man's activities may result in the altered chemical composition of
aqueous and sediment phases. This can have a detrimental impact upon
the aquatic environment.

The purpose of this study was to examine the fate of zinc and

cadmium in three different aquatic systems under several different environmental conditions.  Sediments and water were obtained from Lake Carl Blackwell, Sooner Lake, and the Arkansas River.  The removal of soluble metals from systems containing natural lake or river water, sediments in distilled water, and sediments in natural lake or river water were determined.  The uptake and release of both metals in three combined systems, containing sediments and water from each of the three sources were  then determined under acidic and alkaline conditions and at low and high concentrations of dissolved oxygen.

CHAPTER II

LITERATURE REVIEW

Levels of cadmium and zinc in the environment as well as many other heavy metals have increased. The average background levels for zinc and cadmium in freshwaters are 10 micrograms per liter (2) and .01 micrograms per liter (3), respectively. Durum (4) has reported concentration as high as 42,000 micrograms per liter for zinc and cadmium levels as high as 130 micrograms per liter in the waters of Mineral Creek in Arizona.

The major portion of cadmium and zinc in surface waters tends to be accumulated in the sediments. Wentzel and Berry (5) found the cadmium content in the clay sediments of Palestine Lake, Indiana, a small recreational fishing lake, to be 2,678 ppm which is an enrichment of about 7,000 times that of the unpolluted clay sediments. In Coer d'Alene Lake, Idaho, researchers examined sediment cores with zinc concentrations up to 13,000 ppm (6).

The presence of zinc and cadmium in aquatic ecosystems may be due to natural causes or human activity. They may enter streams and lakes from a number of sources, such as geologic weathering, mining effluents, industrial effluents, domestic wastewater and urban stormwater runoff (7).

Not only are these metals widely distributed in the aquatic environment, but they also tend to remain in the ecosystem. They may be temporarily removed from the water phase in their divalent form by adsorption

onto suspended matter and bottom sediments or be taken up by the aquatic biota. However, the metal is still present in the system and it becomes available again when the organsim dies and decays or when it is desorbed from the solid phase upon changes in physical and/or chemical conditions.

## Cadmium and Zinc in Natural Waters

Zinc and cadmium are found in most natural waters. In their simple ionic form, they can be toxic to aquatic life. Processes such as complexation with inorganic and organic ligands, adsorption onto colloidal particles and precipitation all act together to regulate the aquatic concentration of the free metal ion (8).

The speciation of the metal usually depends upon the pH, redox potential and the chemical constituents of the water. The concentration of heavy metals in aqueous systems is usually controlled by the solubility of the hydroxides, oxides, sulfates, sulfides, and carbonates (9). Zinc and cadmium may also form complexes with silicate which is readily found in all natural waters. Zinc silicate is relatively insoluble whereas the cadmium silicate species is soluble (10).

Hem (10) reviewed the chemistry of cadmium and zinc in surface waters. He found that the solubility of zinc and cadmium is relatively high below pH 7 under oxidizing conditions. Zinc carbonate is then the stable phase for zinc until the pH reaches 8.3. Above 8.3, zinc hydroxide occurs.

For cadmium, the solubility is mainly governed by the carbonate phase. However, the chloride complex of cadmium can be significant if chloride concentrations exceed 350 mg/l. In addition, there may be some influence from the cadmium sulfate ion pair if the sulfate concentration exceeds 1,000 mg/l. These species would probably not be competitive with

hydroxide complexes in the minimum solubility region above pH 8 (10).

Other ligands such as ammonia and nitrate may form weak complexes with

cadmium but are normally present in such low concentrations in fresh

waters that their effect is insignificant (11). No evidence has been

found of zinc and cadmium complexes with phosphate (9).

Under anaerobic conditions and in the presence of sulfide, zinc and

cadmium both will form sulfide complexes which have a very low solubility.

The sulfide complex is practically insoluble at a neutral pH and is sta-

ble over a wide pH range (7).

Leckie and James (12) showed that trace metal adsorption onto parti-

cles is largely pH dependent and that adsorption typically increases

sharply over a narrow pH range of one to two pH units. Both zinc and

cadmium are adsorbed by Fe/Mn hydrous oxides (13), alumina (14), organi-

cally coated minerals (15), humic and fulvic acids (16, 17), clay minerals

(18), and by algae (7).

Organic species present in the the natural water can form complexes

with both zinc and cadmium. Cadmium is not as strongly complexed as zinc

by most organic ligands. However, the binding ability of these metals

appears to be chiefly controlled by the inorganic species rather than the

organic species (8).

The pH may play a deciding role in the formation of organometallic

complexes in fresh water since increasing pH usually promotes the forma-

tion of metal chelates (7). At a lower pH, Florence (19) found no

evidence for organic complexing of zinc in several freshwaters. In a

study by Allen et al. (20) using trace levels of cadmium (1 ug/l) and

keeping the pH constant at 8, it was found that complexes of cadmium with

soluble organic matter were slow to form, but the metal was more strongly

bound to organic compounds than to colloidal or particulate matter.

The hardness of the natural water can also play an important role in the binding of metals to humic material. Calcium and magnesium are both strong competitors for complexing sites in humic material (21). Experimental evidence has shown that cadmium in natural water tends to stay in the ionic form rather than becoming bound with the organic ligands. In soft waters, a certain degree of complexation is achieved at lower dissolved concentrations of humic acid due to less competition with the calcium and magnesium ions. Truit and Weber (8) concluded that the concentration of both organic and inorganic species in water samples strongly affect their metal-ion binding ability.

Cadmium and Zinc in Sediments

The major portion of dissolved zinc and cadmium in natural water systems is rapidly incorporated into the sediments. This can be accomplished through several different mechanisms which include ion exchange, sorption onto iron and manganese oxide coatings, precipitation or coprecipitation of an insoluble phase and complexation with insoluble organic matter (22). Factors that may influence these mechanisms are soil type, soil texture, pH, oxidation-reduction potential, and cation exchange capacity.

Soil type and texture are important. Researchers have found that the heaviest enrichment occurs in soil textures that are finer grained, usually the clays (7). In studies with montmorillonite, illite, chlorite and kaolinite clays, zinc and cadmium adsorption trends often followed the cation exchange capacity of the clay with montmorillonite > illite >

chlorite > kaolinite. This trend also corresponds with the reduction of particle size and the related increase in surface area.

The amount of metal adsorbed onto clay depends on pH, time of reaction and the concentration of the metal according to Tiller and Hodgson (23). Farrah and Pickering (24) noted that adsorption on kaolinite, illite and montmorillonite varied with clay, pH, concentration of competing ion and nature of ligands present.

The pH value may dominate the adsorption of heavy metals onto clay minerals. The H+ ion will compete with heavy metal cations for exchange sites in the system, thereby partially releasing the latter. Therefore, under extreme acidic conditions, the heavy metal ion is completely released (7). McDuffie et al. (25) reported that trace cadmium was extensively adsorbed by river sediments at a pH of 7.5, and completely released at a pH of 3.

Shuman (26) found that soils high in clay or organic matter had higher adsorptive capacities and bonding energies for zinc than sandy soils low in organic matter. He also studied the effect of pH on the adsorption of zinc, which revealed that a low pH reduced zinc adsorption more for sandy soils than for those soils high in colloidal size material. With acid soils, Saeed and Fox (27) noted that at a pH > 7, the amount of zinc in solution increases in soils with high organic matter contents. This could be attributed to dispersion of the organic matter which either releases complexed zinc or provides chelating groups that reduce precipitation or adsorption.

Phosphate has been reported to increase zinc uptake by the soil. Dhillon (28) theorized that this may be due to phosphorus adding ligands to sites in the organic fraction, which aid in bonding zinc. Silicate

ions have also been found to increase zinc adsoprtion onto clay by creating additional active sites (29). This reaction is believed to take place primarly at the edge sites (30).

Cation exchange capacity, pH and organic carbon content are the parameters chiefly responsible for the fixation of cadmium in the sediments according to Singh (31). He found that cadmium is very strongly bound to the sediments with high organic carbon contents and a high cation exchange capacity.

High temperatures can also increase the amount of zinc and cadmium being adsorbed by the sediments by increasing the number of adsorption sites and reducing the bonding energy coefficient (32). The increased activity of microorganisms at higher temperatures may also have some effect on the uptake of heavy metals.

The hydrous oxides of aluminum, iron, and manganese constitute a significant sink of heavy metals in aquatic systems. These hydroxides and oxides readily sorb or coprecipitate cations and anions. Harding and Whitton (33) recognized that zinc fixation significantly correlated with the levels of iron in the sediments of the Derwent Reservoir in Northern England. They suggested binding by the hydrous oxide or coprecipitation with iron as a possible pathway into the sediment. Cadmium in comparison was a weak competitor for adsorption onto the hydrous metal oxide.

Chubin and Street (34) found that aluminum and iron hydroxides had a greater affinity for cadmium than the montmorillonite and kaolinite clays. With the addition of organic ligands to the system the hydroxides were not influenced, but in the silicate clay systems, enhanced adsorption

was noted. This is probably due to the formation of an organo-clay complex with a high affinity for cadmium.

Lion (35) found that the adsorption of cadmium may be controlled to a greater extent by organic coatings than by iron and manganese oxide coatings. While in a study by Luoma and Bryan (36), zinc was found to be primarily associated with the hydrous iron oxide. Benjamin and Leckie (37) noted that the complexation of cadmium by chloride and sulfate can decrease adsorption onto oxide surfaces.

In a study by Nriago and Coker (17) less than 5 percent of cadmium and zinc were found to be bound to the organic matter of Lake Ontario sediments. This could be due to the inability of these metals to compete effectively with copper and iron for binding sites in humic acid or displacement in the binding site by copper or iron.

Carbonate precipitation may be an important sink for cadmium and zinc in sediments high in bicarbonate and alkaline in reaction. Under slightly reduced to oxidized conditions, the solid carbonate fraction is a major control mechanism. The solubility of carbonates in aqueous solutions is highly dependent on the carbon dioxide partial pressure. The carbonate tends to be more soluble in the presence of carbon dioxide. Precipitation, primarily of hydroxides, sulfides and carbonates will occur within the water body when the corresponding solubility product is exceeded (7).

It has been noted that the redox potential of a sediment water system is a controlling factor in regulating the chemical form of the metal whereas pH influences the stability of the various forms (38). A change in redox conditions can also affect the solubility of zinc and cadmium. Metals associated with the oxides, hydroxides, and hydrous oxides of iron,

maganese and possibly aluminum present as coatings on clay minerals or as discrete particles which tend to sorb or coprecipitate metals under oxidizing condition will be released under reducing conditions (38). On the other hand, in the presence of sulfide under reduced conditions, zinc and cadmium will precipitate and under oxidizing conditions will be released (39).

## Cadmium and Zinc in Algae

Algal populations have been demonstrated by several researchers to be effective in reducing metal concentrations to lower levels. Removal rates appear to be related to soluble metal concentration and pH. However, zinc and cadmium can be toxic to algae. The toxic level varies with different algal species and environmental factors such as temperature, pH, light, complexing capacity, water hardness, interaction with other metals, nutrient levels, oxygen concentration and sediment concentration (40).

Growth and development of Selenastrum capricorntum, a green alga, was adversely affect by 700 ug/l zinc and 650 ug/l cadmium, according to Bartlett (41). He also found that 100 ug/l zinc inhibited growth in stream studies. A concentration of 2.4 mg/l zinc reduced the growth of Chlorella vulgaris by 50 percent (42). At zinc concentrations of 1.0-1.4 mg/l, Bringmann (43) found a median threshold effect for Scenedesmus. He also found that Scenedesmus exposed to 100 ug/l of cadmium was adversely affected. The U.S. Environmental Protection Agency has established guidelines (44) for the protection of aquatic life or 4-12 ug/l for cadmium and .01 x (96 hr LC 50) for zinc.

CHAPTER III

MATERIALS AND METHODS

Sample Collection and Preservation

Samples of water and sediment were taken from three different sour-
ces in Oklahoma, Lake Carl Blackwell, Sooner Lake and the Arkansas River.
Lake Carl Blackwell is located 7 miles west of Stillwater, and serves
primarily as a water supply for the City of Stillwater.  Samples were
taken at a point on the south end of the lake.  Sooner Lake is a man-
made lake which supplies cooling waters for the Sooner Power Plant.  It
is located 20 miles north of Stillwater.  The sample site was also locat-
ed at the south end of the lake.  Both lakes are also used for recreation-
al purposes.  The Arkansas River flows in the northern half of Oklahoma
on a southeast course.  The river flows through the city of Tulsa,
Oklahoma, and samples were taken at a site south of Tulsa on the east
bank below the Jenks Bridge.

Sediments were collected at a water depth of approximately 2 feet
and placed in plastic tubs.  The standing water was decanted and the
sediments were allowed to air dry at room temperature.  After drying, the
sediments were passed through a 20 mesh sieve to provide uniformity.
The pH of the sediments was determined and the sediments were analyzed
for cadmium and zinc and the total organic carbon content.

Waters from the lakes and river were collected in acid washed, 25
liter glass bottles.  The waters were then filtered through a .45 micron

filter and stored at 4 degrees celcius. The pH of the waters was deter-
mined and the waters were analyzed for sulfate, nitrate, phosphate,
silicate, chloride, magnesium, calcium, zinc, cadmium, alkalinity and
total dissolved solids.

## Experimental Systems and Procedure

Initial studies were conducted to determine the uptake of the metals
by the three sediments in the absence of any competition. The metals
were dissolved in distilled water instead of using the natural lake or
river water. The aquatic systems were set up by placing 1,000 grams
(dry weight) of each of the sediments into 5,000 ml 3 necked flasks.
The flasks were then filled with 4,000 mls of distilled water and metal
to obtain an initial metal concentration of 100 mg/l. Controls
were also set up of distilled water and metal to determine if sorption
of the metal onto the glass was significant. All systems were kept
aerobic by means of continuous aeration using compressed air. The flow
rate of the air was controlled to prevent turbulence and suspension of
the sediments. Aqueous samples were sampled periodically for soluble
metal.

The uptake of cadmium and zinc by the natural river and lake waters
in the absence of sediments was also determined. These studies allowed
the assessment of the uptake or removal of metals as a function of the
aqueous chemistry. Systems were again set up in the 3-necked round bot-
tom flasks. Water obtained from each source and then filtered was plac-
ed into the flasks. The units were kept aerobic. Initial zinc
concentrations used were approximately 100 mg/l, whereas the initial
cadmium concentration was increased from that used in the previous

studies to about 300 mg/l to prevent all the cadmium from preciptating out the first day of the study.

The uptake of zinc and cadmium by systems containing both water and sediment from each of the surface waters studied was also examined using the 3-neck round bottom flask. Each system, combining both the sediments and water from each source, contained 1,000 g dry weight of sediment and 4,000 ml lake or river water. The concentration of zinc used was 100 mg/l and the cadmium concentration was 300 mg/l. Aerobic conditions were maintained and the soluble metal concentration in the aqueous phase was measured periodically.

The effects of reducing the DO concentration were determined by setting up sediment, natural water and metal systems for each of the metals. The systems were first aerated for a period of time to provide oxidizing conditions. Nitrogen gas was then bubbled into the systems to lower the DO. The pH and the DO were measured before and after bubbling nitrogen into the system. Samples were pulled daily from all of the systems and analyzed for soluble metal.

The uptake and release of each metal under acidic and alkaline conditions was determined for each sediment-natural water combination. For each system, 150 grams of sediment, 500 ml of lake or river water, and a metal concentration of 100 mg/l was used. All units were set up in duplicate. Metal uptake by the systems was determined over a four day period. At that time, concentrated nitric acid was added to each system to reduce the pH to below 3. Ammonium hydroxide was added to the system duplicates to raise the pH to above 10. Systems were then analyzed over a three day period for soluble metal present in the water.

Zinc was supplied to all the systems in the form of zinc sulfate

and cadmium in the form of cadmium bromide.  Stock solutions were made

up to provide easier addition of the metal to the system.

## Methods

The Perkin Elmer Atomic Absorption Spectrophotometer Model 5000

(AA) was used for determination of cadmium, zinc, magnesium and calcium

present in the waters.  Soil samples were digested with nitric acid and

also analyzed for initial metal content using the AA.  Standards were

prepared using standard solutions.  Samples were diluted in order to

remain within the linear range of the AA.

The pH and the dissolved oxygen of the water were measured using

probes from Orion Research.  Methods provided by the Hach Chemical

Company (45) were used for the determination of sulfate, nitrate, phos-

hate and silicate present in the waters using the Hach dr 2 Spectrophoto-

meter and specified reagents.  Chlorides were determined by tritration

with mercuric nitrate.  The alkalinity and the TDS of the waters was

found using the procedures outlined in Standard Methods (46).

The sediments were classified into sand, silt, and clay fractions by

using the U.S. Standard Seive Series and the Fisher Hydrometer.  The

total organic carbon content of the sediments was determined by oxidiz-

ing the sediment with potassium persulfate, sealing it in vials and heat-

ing to produce carbon dioxide and analyzing it using an Oceanographic

International Total Carbon Analyzer.  Sediment pH was determined by

placing 10 grams of dried sediment into 25 mls of distilled water.  The

mixture was allowed to stand for 30 minutes and then the pH was measured.

CHAPTER IV

RESULTS AND DISCUSSION

The uptake of zinc and cadmium by the sediments used in this study
is best illustrated in Figures I and 2, respectively. The systems in-
vestigated contained distilled water, sediment, and metal. The use of
distilled water, allowed an assessment of the uptake capacity of the
sediments in the absence of any competition from the chemical components
of the natural river or lake waters. The trends for the uptake of both
cadmium and zinc appeared to be the same. With both metals, Lake Carl
Blackwell sediments fixed more of the metal faster than Sooner Lake or
the Arkansas River. However, over a ten day period, the sediments of
both lakes removed over 95 percent of the metal added, whereas a lesser
amount was removed by the river sediment.

In the zinc systems (Figure I), the total amount of zinc added
(400 mgs) was fixed by Lake Carl Blackwell sediments. Sooner Lake fixed
96 percent (384 mgs) of the zinc while only 26 percent (104 mgs) was
fixed by the Arkansas River sediments. For the cadmium sediment systems
(Figure 2), Lake Carl Blackwell fixed 98 percent (392 mgs), Sooner Lake
fixed 97 percent (388 mgs) and the Arkansas River fixed 56 percent (224
mgs) of the cadmium over a ten day period.

The removal of cadmium and zinc by the sediments can be correlated
with the grain size (Table I), the total organic carbon content (Table
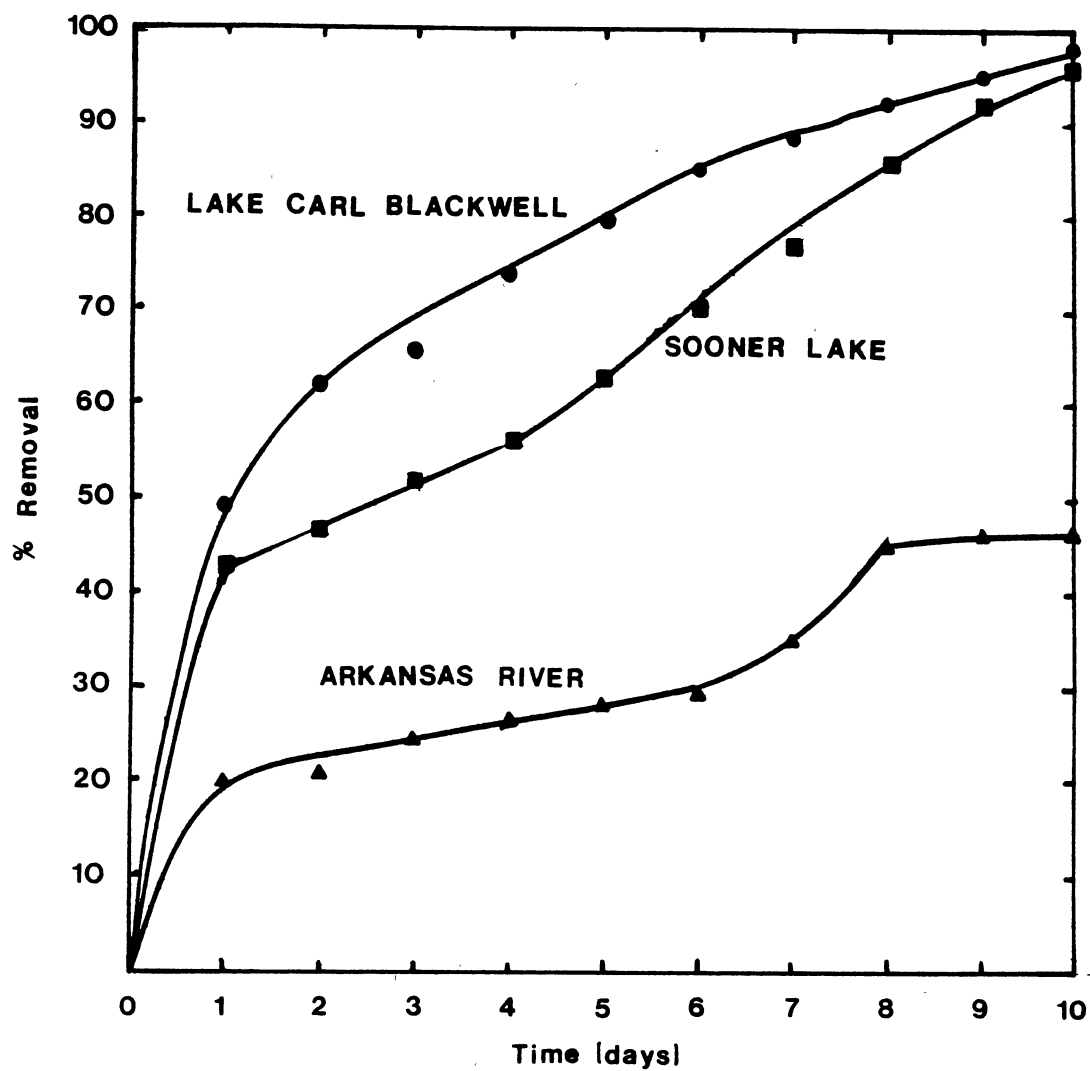II), and pH (Table II). As reviewed previously in the literature, metal

Figure I. Percent Zinc Removed from Distilled Water Systems vs.
Time by Sediments from Lake Carl Blackwell, Sooner
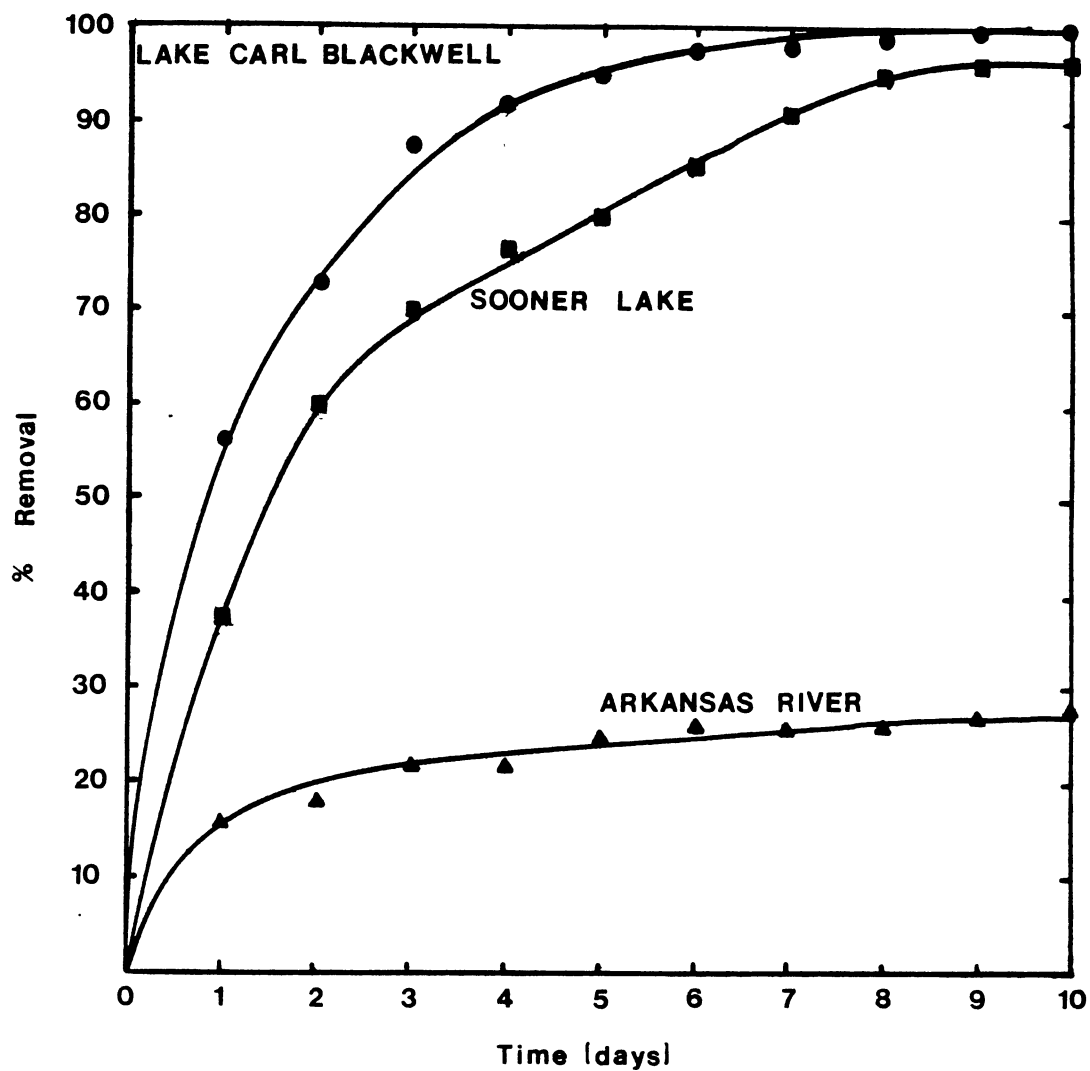Lake, and the Arkansas River

Figure 2.   Percent Cadmium Removed from Distilled Water Systems
vs. Time by Sediments from Lake Carl Blackwell,
Sooner Lake, and the Arkansas River

TABLE I

SEDIMENT GRAIN SIZE

| Sample | % Med. Sand | % Fine Sand | % Silt | % Clay | USDA Class |
|--------|-------------|-------------|--------|--------|------------|
| LCB | 5 | 17 | 55 | 23 | Silt Loam |
| SL | 5 | 66 | 24 | 5 | Sandy Loam |
| ARK | 34 | 62 | 4 | 0 | Fine Sand |

TABLE II

SEDIMENT ANALYSIS

| Test | LCB | SL | ARK |
|------|-----|-----|-----|
| Total Organic Carbon | 6 mg/gm | 6 mg/gm | 1.1 mg/gm |
| Zinc | .58 mg/gm | .30 mg/gm | .23 mg/gm |
| Cadmium | .03 mg/gm | .04 mg/gm | .04 mg/gm |
| pH | 8.10 | 7.86 | 6.95 |

fixation is high in the finer grained sediments, primarily the clays and sediments with a high organic carbon content (24, 26, 31). Lake Carl Blackwell was primarily composed of silt and clay. The sediments of Sooner Lake were primarily composed of silt and fine sand, while the Arkansas River sediment was composed mainly of sand. The total organic carbon content (Table II) of the sediments from Lake Carl Blackwell and Sooner Lake was approximately the same, 6 mg/gram, while the Arkansas River sediment contained only 1.1 mg/gram. Therefore, as could be predicted by the literature and the results of the sediment analyses, the sediments from Lake Carl Blackwell and Sooner Lake had the highest metal fixation capacity. This trend was also observed by Huggins (47) who conducted similar studies with sediments from Lake Carl Blackwell, Sooner Lake, and the Cimarron River using copper and chromium. In addition, Shuman (26), whose research was with zinc, also noted that soils high in clay or organic matter had higher adsorptive capacities than sandy soils low in organic matter.

The pH of a soil may also be correlated with metal fixation by sediments. The pH controls sorption desorption reaction and precipitation-solubilization reactions. In addition, the cation exchange capacity of soils generally increases with an increase in pH, and heavy metals tend to form insoluble or slightly soluble precipitates in the neutral to high pH range. For this study, Lake Carl Blackwell sediment had the highest pH at 8.1 followed by Sooner Lake with a soil pH of 7.86 and the Arkansas River sediment with a pH of 6.95. It would, therefore, be expected that Lake Carl Blackwell and Sooner Lake sediments would fix more cadmium and zinc than the sediments obtained from the Arkansas River.

Metals may also be removed from solution in aquatic systems by pre-
cipitation when their solubility product is exceeded. This occurred in
the combined systems of sediment, natural water and metal as well as in
the natural water and metal only systems (Figures 3-8). Precipitant was
formed with all the natural waters for both metals. A floc type precipi-
tant was observed in the zinc systems whereas a more granular precipitant
was observed for the cadmium systems.

For both zinc and cadmium, the waters obtained from Sooner Lake were
responsible for the highest amount of precipitation (Figures 4 and 7).
With respect to the quantity of metal removed, the water from Sooner Lake
was followed by Lake Carl Blackwell water and then the water obtained
from the Arkansas River. The amounts of zinc and cadmium removed by the
natural waters from all three sources can be correlated with the alka-
linities and pH values of the waters. Precipitation of the metal proba-
bly occurred as the carbonate species. The pH of the waters, as seen in
Table III was too low for the formation of the metal hydroxide species (7).
The water from Sooner Lake had the highest alkalinity and pH which prob-
ably accounts for the higher removals of both metals. Other factors such
as sulfate, nitrate, phosphate, chloride and silicate may have also had
a slight influence on the solubility of the metal. Again, Sooner Lake
water, as compared to water from Lake Carl Blackwell and the Arkansas
River had the highest concentrations of silicate, sulfate, nitrate,
phosphate, and chloride (Table III).

In the Lake Carl Blackwell and the Arkansas River systems the amount
of metal removed were relatively close, with Lake Carl Blackwell slightly
fixing more metal than Arkansas River. This can be mainly attributed to
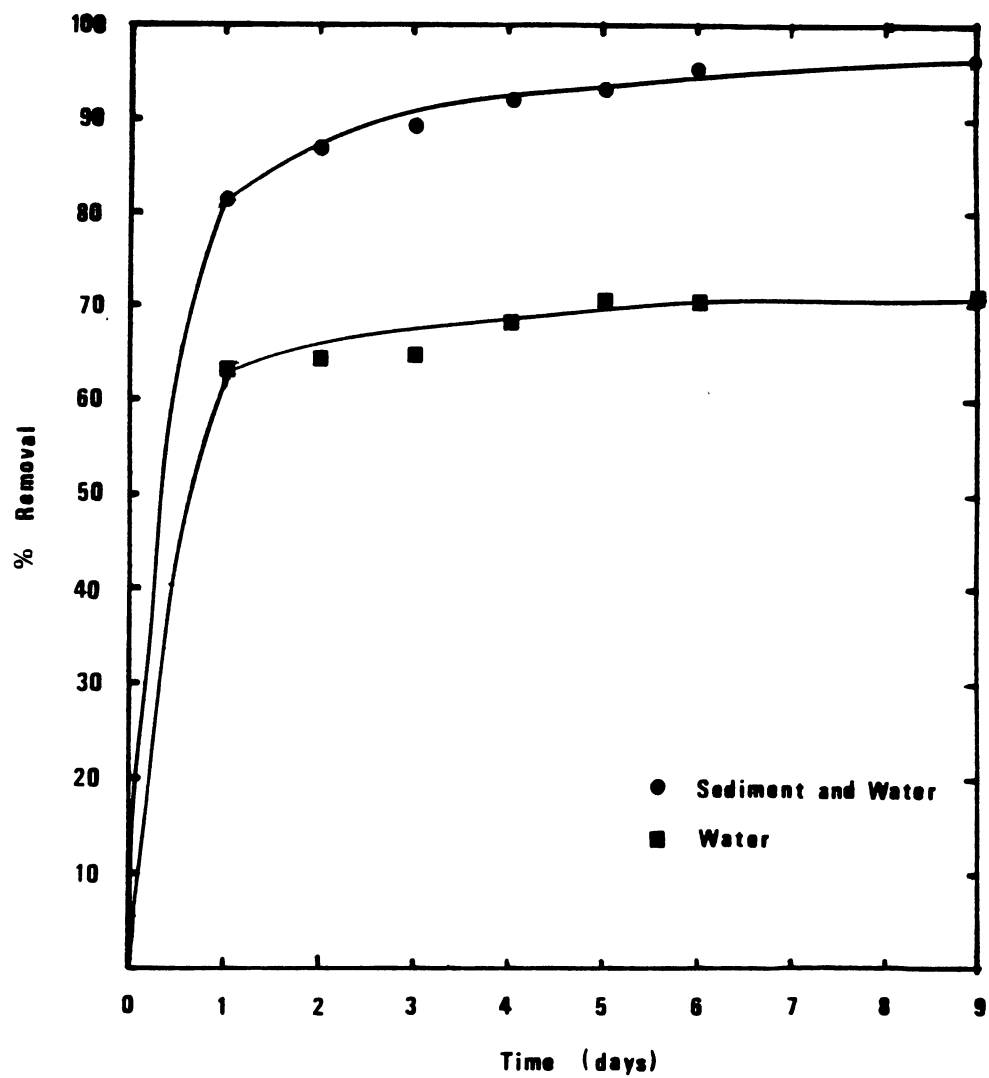it's higher alkalinity and slightly higher pH.

Figure 3.  Percent Zinc Removed vs. Time for Lake Carl
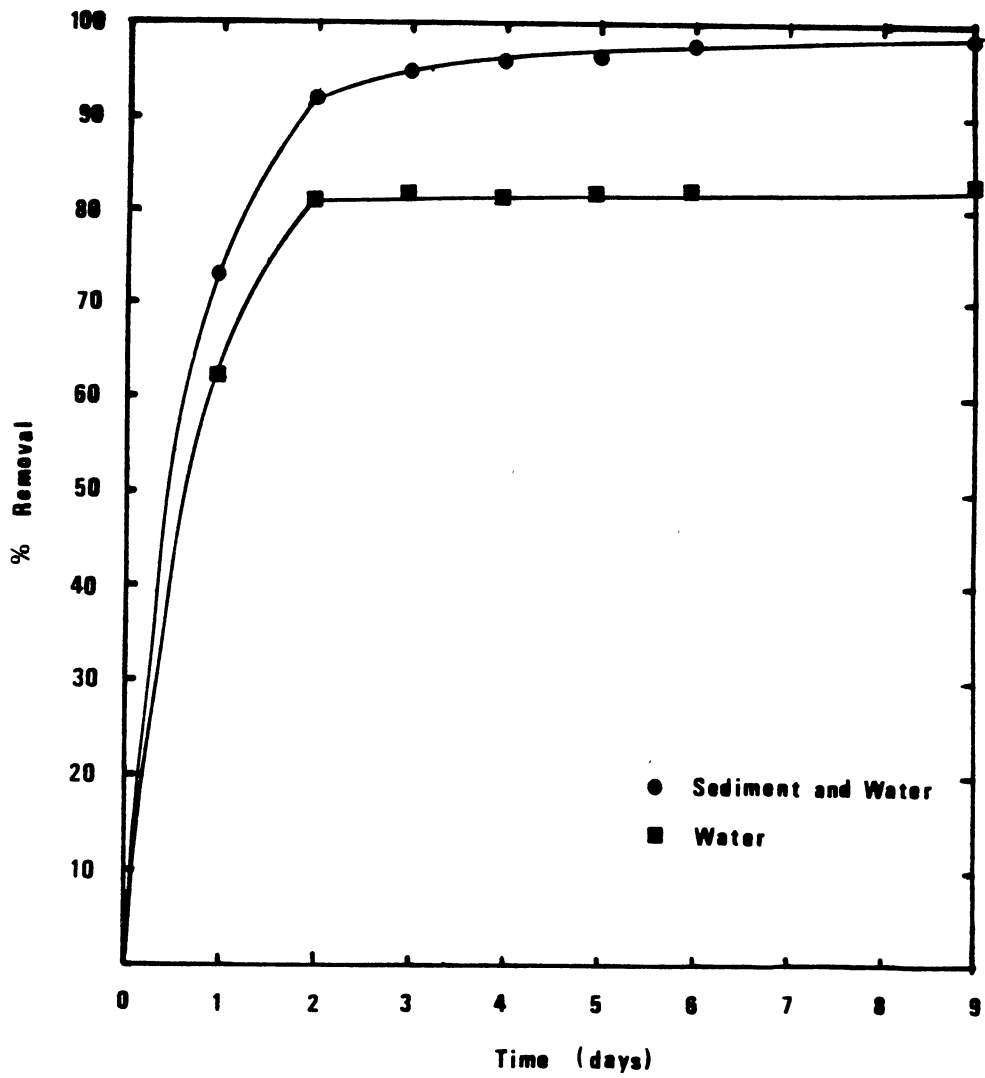Blackwell

Figure 4.  Percent Zinc Removed vs. Time for Sooner Lake
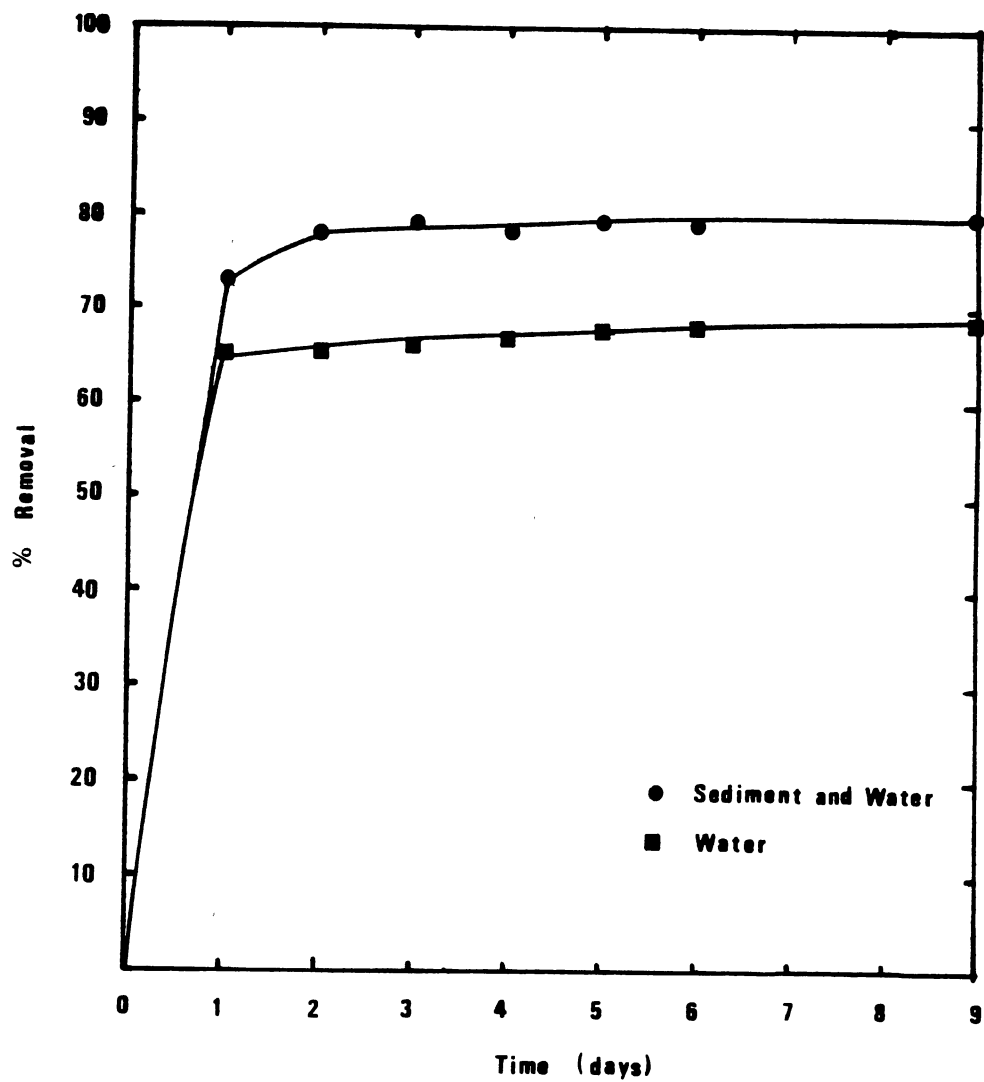
Figure 5.   Percent Zinc Removed vs. Time for the Arkansas
            River
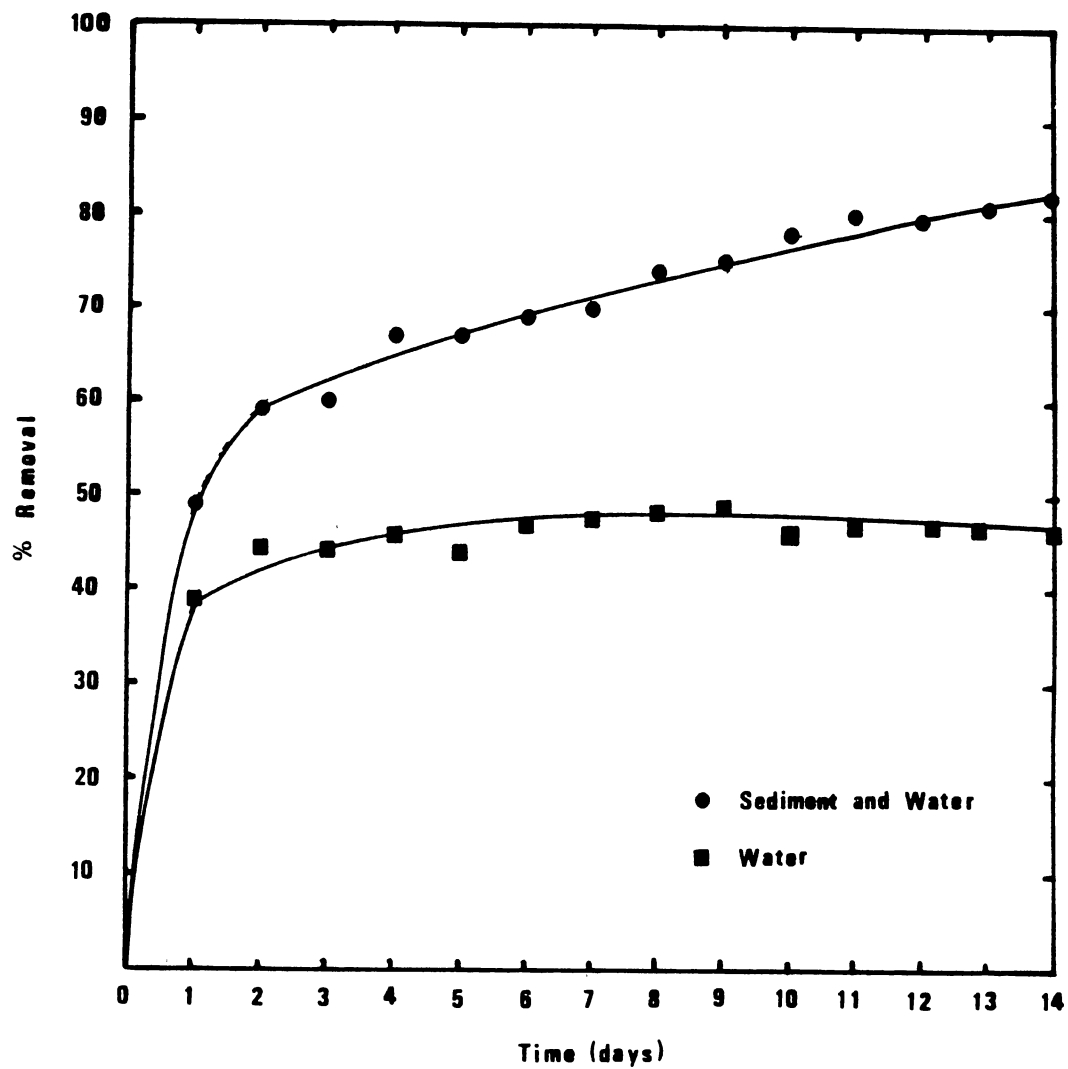
Figure 6.  Percent Cadmium Removed vs. Time for Lake Carl
            Blackwell
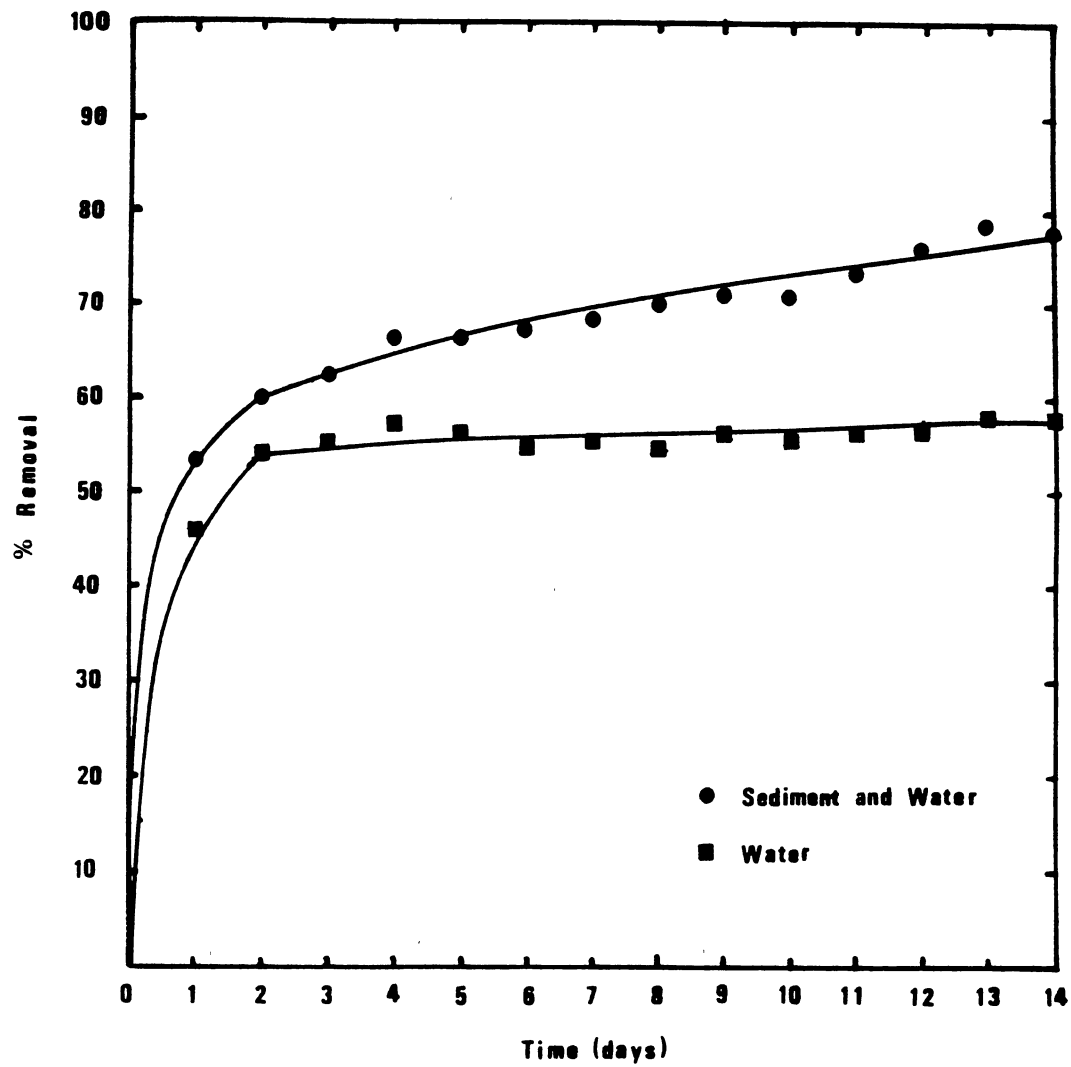
Figure 7.   Percent Cadmium Removed vs. Time for Sooner Lake
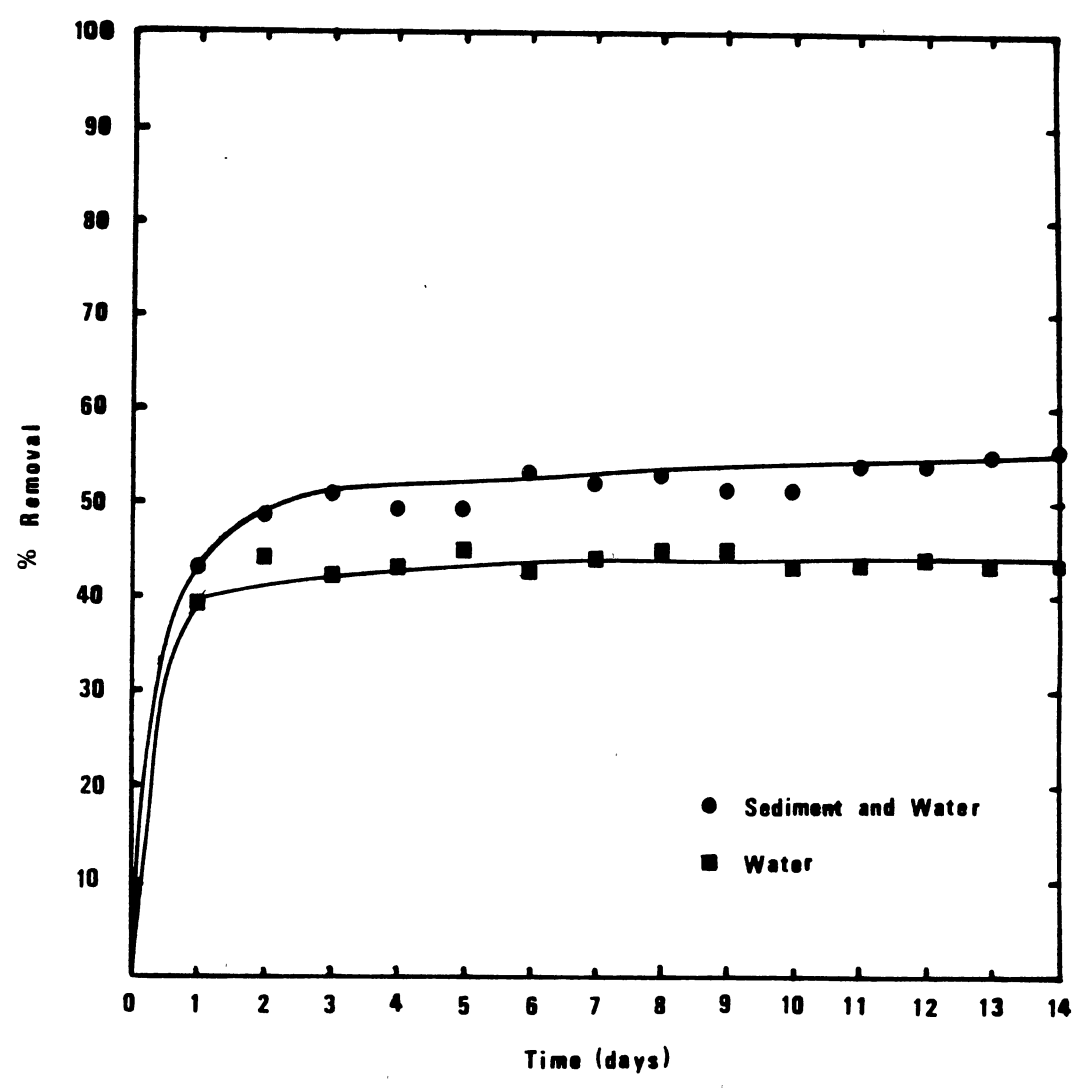
Figure 8.  Percent Cadmium Removed vs. Time for the
Arkansas River

TABLE III

WATER QUALITY ANALYSIS

| Test (mg/l) | LCB | SL | ARK |
|---|---|---|---|
| Alkalinity $(C_aCO_3)$ | 126.0 | 144.0 | 106.0 |
| pH | 7.6 | 7.95 | 7.55 |
| Total Dissolved Solids | 432.0 | 1044.0 | 432.0 |
| Phosphates | 1.1 | 1.5 | 1.3 |
| Nitrates | 1.8 | 3.7 | 1.0 |
| Sulfates | 10.0 | 150.0 | 37.0 |
| Silica | 1.5 | 9.5 | 0.37 |
| Chlorides | 30.5 | 312.5 | 100.0 |
| Calcium | 49.1 | 81.2 | 74.2 |
| Magnesium | 48.0 | 38.1 | 33.2 |
| Cadmium | 0.14 | 0.12 | 0.17 |
| Zinc | 0.05 | 0.07 | 0.03 |

With respect to the combined systems, the Lake Carl Blackwell unit (Figure 6) removed the most cadmium whereas the Sooner Lake system was responsible for removing the most zinc (Figure 4). However. the removal of zinc by the Sooner Lake and Lake Carl Blackwell systems was very close. The Arkansas River combined systems (Figures 5 and 8) removed the lowest quantity of both metals. Table IV shows the initial and final concentrations and the percent removed for each metal for each system. The amount of metal removed by the sediment in the presence of the natural water was determined by subtracting the quantity removed by the water from the amount of metal removed in the combined systems. The majority of the metal removed in all of the combined systems could be attributed to precipitation.

The removal attributed to the sediments is substantially lower than that observed in the sediment-distilled water systems (Figures I and 2). There are several possible reasons for this. The first of which is that the sediments in the combined systems had to compete for zinc and cadmium with the precipitating and complexing components of the aqueous phase. This competition was not significantly present in the systems where distilled water was used as the aqueous phase. Secondly, the precipitates formed covered the sediments and prevented sediment-soluble metal contact which would limit adsorption. All systems, however, were uniformly covered by precipitate. Therefore, any masking of the sediment by the precipitate was approximately the same for all systems.

The effect of pH on the uptake or release of the metal from the sediments was studied by reducing the pH to below 3 for each of the metal systems and increasing the pH to above 10 in duplicate systems. The initial pH values were in the range between 6.0-8.0. All systems

TABLE IV

AEROBIC

|  | Cadmium | | | Zinc | | |
|---|---|---|---|---|---|---|
|  | Initial Conc. (mg/l) | Final Conc. (mg/l) | % Removed | Initial Conc. (mg/l) | Final Conc. (mg/l) | % Removed |
| LCB |  |  |  |  |  |  |
| Water and Sediment | 300 | 50 | 83 | 100 | 3 | 97 |
| Water | 300 | 150 | 50 | 100 | 29 | 71 |
| Sediment |  |  | 33 |  |  | 26 |
| SL |  |  |  |  |  |  |
| Water and Sediment | 300 | 70 | 77 | 100 | 2 | 98 |
| Water | 300 | 130 | 57 | 100 | 18 | 82 |
| Sediment |  |  | 20 |  |  | 16 |
| ARK |  |  |  |  |  |  |
| Water and Sediment | 300 | 135 | 55 | 100 | 20 | 80 |
| Water | 300 | 170 | 43 | 100 | 31 | 69 |
| Sediment |  |  | 12 |  |  | 11 |

were initially operated at the natural unaltered pH with a soluble metal

concentration of 100 mg/l. After equibilibrating for four days, the

soluble metal concentration was determined and the pH was altered. The

systems were then monitored for an uptake or release of the metals from

the sediments by analyzing for the soluble metal concentration.

Table V shows the results of altering the pH. Under acidic condi-

tions for both metals and for all systems, metals were released from

the sediments. Lake Carl Blackwell had the lowest percent recovery fol-

lowed by Sooner Lake and finally the Arkansas River in which all the

metal that was added was recovered. As the metal was released in the

systems an increase in pH was also noted for all systems. The amount

of metal released under acidic conditions for Lake Carl Blackwell, which

is primarily composed of clay and silt, was significantly less in the

zinc systems then in the cadmium systems. This can be correlated to

the results of Farrah and Pickering (24) who examined the effects of pH

on the amount of metal ion adsorbed by different clays. They found that

zinc was more strongly bound than cadmium to montmorillonite, illite and

kaolinite clays at low pH's (24). In the Sooner Lake systems, there was

not a very significant difference between the zinc and cadmium systems.

The amount of metal released under acidic conditions may be related to

the grain size and possibly organic carbon content, in which those sedi-

ments higher in clay and organics release less metal than sandy soils

low in organic matter.

When the pH was raised to above 10 with ammonium hydroxide, all

systems showed an increase in the amount of metal fixed as compared to

fixation at the natural sediments-water pH. The increase may have been

due to precipitation of the metal as the hydroxide species as well as

TABLE V

HNO$_3$ AND NH$_4$OH

| | HNO$_3$ | | | | | |
|---|---|---|---|---|---|---|
| | Cadmium (100 mg/l) | | | Zinc (100 mg/l) | | |
| | Soluble Conc (mg/l) After 4 Day Equil. | Final Conc (mg/l) After pH Altered | mg/l Released | Soluble Conc (mg/l) After 4 Day Equil. | Final Conc (mg/l) After pH Altered | mg/l Released |
| LCB | 1 | 44 | 43 | 0 | 20 | 20 |
| SL | 12 | 67 | 55 | 5 | 58 | 53 |
| ARK | 39 | 100 | 61 | 37 | 100 | 63 |
| | NH$_4$OH | | | | | |
| | Cadmium (100 mg/l) | | | Zinc (100 mg/l) | | |
| | Soluble Conc (mg/l) After 4 Day Equil. | Final Conc (mg/l) After pH Altered | mg/l Fixed | Soluble Conc (mg/l) After 4 Day Equil. | Final Conc (mg/l) After pH Altered | mg/l Fixed |
| CB | 3 | 0 | 100 | 0 | 0 | 100 |
| SL | 12 | 0 | 100 | 8 | 0 | 100 |
| ARK | 32 | 0 | 100 | 37 | 0 | 100 |

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the increased affinity of the sediment for metals at higher pH's (7).

The effect of reducing the dissolved oxygen content on metal fixation or release was also investigated using natural sediment-water systems. The redox potential was reduced by bubbling nitrogen through systems that had been operated several weeks under aerobic conditions. The initial DO of the systems before the addition of nitrogen was 8.3. After bubbling nitrogen gas into the systems a final DO of less than 1.0 was obtained.

Table VI shows the results of the studies conducted at low dissolved oxygen levels. For the cadmium Lake Carl Blackwell and Sooner Lake systems, additional metal was fixed as the DO concentration was lowered. Lake Carl Blackwell showed a decrease in the soluble metal concentration of 57 mg/l (20 %) and Sooner Lake showed a decrease of 16 mg/l (6%). The Arkansas River showed no change.

In the zinc systems, after a four day period of reducing the DO, a slight increase of soluble zinc in solution of 1 mg/l was noted for Lake Carl Blackwell and for Sooner Lake an increase of 5 mg/l was seen. The Arkansas River on the other hand showed no significant change.

Zinc and cadmium react differently to a change in redox potential. The solubility of zinc is affected by reducing conditions, whereas, according to Khalid et al. (38), redox potential may not be a major control mechanism for uptake and release of cadmium. However, the results of this study, gained by reducing the DO level, only show a significant change in the soluble metal concentration for cadmium. A possible explanation for this is that the sediments from Lake Carl Blackwell and Sooner Lake were not saturated with respect to cadmium and therefore, continued to fix the metal independently of the effects of a change in

TABLE VI

REDUCED DO

| | Cadmium (300 mg/l) | | | Zinc (100 mg/l) | | |
|---|---|---|---|---|---|---|
| | Initial Soluble Conc (mg/l) Before Reduction | Conc (mg/l) | % Change | Initial (mg/l) | Conc (mg/l) | % Change |
| LCB | 99 | 42 | -20 | .5 | 6 | +1 |
| SL | 88 | 72 | - 6 | 3 | 8 | +5 |
| ARK | 153 | 153 | 0 | 36 | 34 | -2 |

DO. It should also be noticed that although the DO was lowered in this study, anaerobic conditions were not achieved and therefore it may have been inappropriate to have expected zinc and cadmium to follow established patterns.

In summary, the adsorption of zinc and cadmium by the lake and river sediments was a function of composition and grain size. The finer fixtured soils composed of clay and silt with higher organic carbon fractions fixed more metal than the sandy river sediments low in organic matter. The aqueous chemistry of the waters overlying the sediments affected the solubility of both metals. Loss of zinc and cadmium from the aqueous phase could be particularly correlated with the alkalinity and pH of the water utilized. With respect to the effects of pH and dissolved oxygen concentration on metal uptake or release, it could be concluded that acidic conditions promoted the release of the metals whereas metal was fixed under alkaline conditions as the pH was increased. Sediments with a higher clay content retained more of the metal than those comprised primarily of sand as the pH was altered. The effects of lowering the DO concentration were not significant for zinc. However, the soluble concentration of cadmium decreased as the DO was lowered.

CHAPTER V

CONCLUSION

The effects of increasing levels of cadmium and zinc upon the aquatic environment depends upon the characteristics of the natural water, sediments, and the biota. This study has shown, in dealing with the sediments and natural waters from Lake Carl Blackwell, Sooner Lake, and the Arkansas River, that the different characteristics and conditions all act together in influencing the fate of the metal.

The sediments and natural waters of all of the sources studied were capable of removing significant quantities of cadmium and zinc from solution. Fixation of the metals by the sediments or precipitation of the metals from the aqueous phase are important mechanisms in controlling the surface water quality. However, these mechanisms do not provide a permanent sink for the metals. As shown in this study, a decrease in pH, which can occur as the result of eutrophic conditions, acid rainfall, or the discharge of acidic wastes into a surface water, can result in a significant resolubilization of both metals studied.

It becomes obvious that once a metal enters an aquatic system, its fate is controlled by many factors. The variety of factors and environmental conditions controlling the behavior of the metals illustrates the difficulty encountered in trying to alleviate the threat of heavy metal pollution of a aquatic system. In situ restoration plans are seldom totally effective and are very expensive. The best approach to solving

this environmental contamination problem would be to limit the discharge of metals to the atmosphere or surface waters.

## Recommendations

The recommendations are:

1.  Use different metals to determine the aquatic systems capability of heavy metals in general.

2.  Work with lower levels of cadmium and zinc to determine algal capability of removing these metals at concentrations that are not toxic.

3.  Use larger aquatic models to reduce interference by precipitate layer.

4.  Determine clay minerology and its effect on sediment fixation of cadmium and zinc.

5.  Analyze the waters and sediments for iron and manganese to determine their effect on the uptake of cadmium and zinc by the systems.

REFERENCES

1. The Clean Water Act Showing Changes Made by the 1977 Amendments. Serial No. 95-12, Washington: U.S. Government Printing Office, 1977.

2. Wedephol, K. H., "Zinc--Abundance in Natural Waters and in the Atmoshere." Handbook of Geochemistry. Wedepohl, K. H. (Ed.), Berlin, Heidelberg, New York: Springer (1972).

3. Boyle, E. A., Sclater, F. R., and Edmond, J. M., "The Marine Chemistry of Cadmium." Nature (London), 263, 42, (1976).

4. Durum, W. H., Hem, J. D., and Heidel, S. G., "Reconnaissance of Selected Minor Elements in Surface Waters of the United States.' U.S. Geol. Surv. Circ., 643, 49, (1971).

5. Wentsel, R. S. and Berry, J. W., "Cadmium and Lead Levels in Palestine Lake, Palestine, Indiana." Proc. Indiana Acad. Sci. 481, 84, (1974).

6. Funck, W. H. et al. An Integrated Study on the Impact of Metallic Trace Element Pollution in the Coer D'Alene-Spokane Rivers-Lake Drainage Systems. Washington State Univer./Univ. of Idaho, August, 1975.

7. Forstner U. and Wittmann, G. T. W. Metal Pollution in the Aquatic Environment. Springer-Verlag, 2nd Ed., Berlin, Heidelberg, New York, (1981).

8. Truit, R. E. and Weber, J. H., "Cooper (II) and Cadmium (II) Binding Abilities of some New Hampshire Freshwaters Determined by Dialysis Titration." Environmental Science and Technology, 1204, 15, (1981).

9. Huang, C. P., Elliott, H. A., and Ashmead, R. M., "Interfacial Reactions and the Fate of Heavy Metals in Soil-Water Systems." Journal of the Water Pollution Control Federation, 745, 49, (1977).

10. Hem, J. D., "Chemistry and Occurrence of Cadmium and Zinc in Surface Waters and Groundwater." Water Resources Research, 661, 8, (1972).

11. Wiley, J. O. and Nelson, P. O., "Cadmium Adsorption by Aerobic Lake Sediments." Journal of Environmental Engineering, 226, 110, (1984).

12. Leckie, J. O. and James, R. O., "Control Mechanisms for Trace Metals in Natural Waters." Rubin, A. J. (Ed.), Aqueous--Environmental Chemistry of Metals. Ann Arbor Science Publ., Ann Arbor, Mich. pp. 1-76, (1975).

13. Jenne, E. A., "Controls on Mn, Fe, Co, Ni, Cu, and Zn Concentrations in Soils and Water." Trace Inorganics in Water. American Chemical Society, Advances in Chemistry Series 73, Wash. D.C., pp. 337-387, (1968).

14. Chau, Y. K., Lum-Shue-Chan, K., "Determination of Labile and Strongly Bound Metals in Lake Water." Water Research, 383, 8, (1974).

15. Davis, J. A. and Leckie, J. O., "Effect of Adsorbed Complexing Ligands on Trace Metal Uptake by Hydrous Oxides." Environmental Science and Technology, 1309, 12, (1978).

16. Mantoura, R. F. C., Dickson, A., and Riley, J. P., "The Complexation of Metals with Humic Materials in Natural Waters," Estuarine Coastal Mar. Sci., 193, 6, (1978).

17. Nriagu, J. O. and Coker, R. D., "Trace Metals in Humic and Fulvic Acids from Lake Ontario Sediments." Environmental Science and Technology, 443, 14, (1980).

18. Reid, J. D. and McDuffie, B., "Sorption of Trace Cadmium on Clay Minerals and River Sediments: Effects of pH and Cd (II) Concentrations in a Synthetic River Water Medium." Water, Air, and Soil Pollution, 375, 15, (1981).

19. Florence, T. M. and Batley, G. E., "Determination of Chemical Forms of Trace Metals in Natural Waters." Talanta, 151, 24, (1977).

20. Allen, H. E., Boolayangoor, C., and Noll, K. E., "Changes in Physiochemical Forms of Lead and Cadmium Added to Freshwater." Environment International, 337, 7, (1982).

21. Nriagu, J. O. (Ed.), Cadmium in the Environment Part I: Ecological Cycling. John Wiley & Sons, New York, (1980).

22. Nriagu, J. O. (Ed.), Zinc in the Environment Part I: Ecological Cycling. John Wiley & Sons, New York, (1980).

23. Tiller, K. G. and Hodgson, J. F., "The Specific Sorption of Cobalt and Zinc by Layer Silicates," Clays Clay Miner, 393, 9, (1962).

24. Farrah, H. and Pickering, W. F., "Influence of Clay-Solute Interactions on Aqueous Heavy Metal Ion Levels," Water, Air, and Soil Pollution, 189, 8, (1977).

25. McDuffie, B., El-Barbary, I., Hollod, G. J., and Tiberio, R. D., Trace Substances in Environmental Health-X, Univ. of Missouri, Columbia, 85, (1976).

26. Shuman, L. M., "The Effect of Soil Properties on Zinc Adsorption by Soils." Soil Sci. Amer. Proc., 454, 39, (1975).

27. Saeed, M. and Fox, R. L., "Relations Between Suspension pH and Zinc Solubility in Acid and Calcarous Soils." Soil Sci., 199, 124, (1977).

28. Dhillon, K. S., Sinha, M. K., and Randhawa, N. S., "Organo-Metallic Phosphates. V: Complexation of Zinc and Phosphorous by Humic Compounds," Plant Soil, 317, 43, (1975).

29. Tiller, K. G., "Silicic Acid and the Reaction of Zinc with Clays," Nature, 852, 214, (1967).

30. Hingston, F. J., Posner, A. M., and Quirk, J. P., "Anion Adsorption by Geothite and Gibbsite. I: The Role of the Proton in Determining Adsorption Envelopes." J. Soil Science, 177-192, 23, (1972).

31. Singh, S. S., "Sorption and Release of Cadmium in Some Canadian Soils," Canadian J. of Soil Science, 119, 59, (1979).

32. Levi-Minzi, R., Soldatini, G. F., and Riffaldi, R., "Cadmium Adsorption by Soils," J. of Soil Science, 10, 27, (1976).

33. Harding, J. P. and Whitton, B. A., "Zinc, Cadmium, and Lead in Water, Sediments, and Submerged Plants of the Derwent Resivoir, Northern England," Water Research, 307, 12, (1978).

34. Chubin, R. G. and Street, J. J., "Adsorption of Cadmium on Soil Constituants in the Presence of Complexing Ligands." J. of Environmental Quality, 225, 10, (1981).

35. Lion, L., Altman and Leckie, J. O., "Trace-Metal Adsorption Characteristics of Estuarine Particulate Matter: Evaluation of Contributions of Fe/Mn Oxide and Organic Surface Coatings," Environmental Science and Technology, 660, 16, (1982).

36. Luoma, S. N. and Bryan, G. W., "A Statistical Assessment of the Form of Trace Metals in Oxidized Estuarine Sediments Employing Chemical Extractants," Science of the Total Environment, 165, 17, (1981).

37. Benjamin, M. M. and Leckie, J. O., "Effects of Complexation by Cl, SO4, and S2O3 on Adsorption Behavior of Cd on Oxide Surfaces," Environmental Science and Technology, 162, 16, (1982).

38. Khallid, R. A., Gambrell, R. P., and Patrick, W. H., Jr., "Chemical Availability of Cadmium in Mississippi River Sediment." J. Environ. Quality, 523, 10, (1981).

39. Lu, C. S. and Chen, K. Y., "Migration of Trace Metals in Interfaces of Seawater and Polluted Surficial Sediments," Environmental Science and Technology, 174, 11, (1977).

40. Wong, P. T. S., Mayfield, C. l., and Chau, Y. K., "Cadmium Toxicity to Phytoplankton and Microorganisms," Nriagu, J. O. (Ed.), Cadmium in the Environment Part I, John Wiley and Sons, New York, (1980).

41. Bartlett, L. and Rabe, F. W., "Effects of Cu, Zn, and Cd on Selanastrum Capricornatum," Water Research, 179-183, 8, (1974).

42. Rachlin, J. W. and Farran, M., "Growth Response of the Green Algae Chlorella vulgaris to Selective Concentrations of Zinc," Water Research, 575, 8, (1974).

43. Bringmann, G. and Kuhn, R., "The Toxic Effects of Wastewater on Aquatic Bacteria, Algae, and Small Crustateans," Besundheits-Ing., 115, 80, (1959).

44. U.S. Envt. Protection Agency, "Qualaity Criteria for Water, Office of Water and Hazardous Materials," U.S. EPA, Washington, D.C., (1976).

45. Water Analysis Handbook, Hach Chemical Company, (1982).

46. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, 15th Edition: New York, (1980).

47. Huggins, Andrew K., "The Fate of Copper and Chromium in Aquatic Systems," M.S. Thesis, Oklahoma State University, (1981).

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