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STUDIES ON THE ADSORPTION/ DESORPTION AND MICROBIAL MOBILIZATION OF CONTAMINANTS FROM SEDIMENTS IN CORPS OF ENGINEERS RESERVOIR PROJECTS

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13. ABSTRACT (Maximum 200 words)

Laboratory studies were conducted to meet three recommendations developed in a previous technical report on sediment-water interactions and contaminants in Corps of Engineers reservoir projects (Technical Report E-89-2).

Each of three aspects of sediment-water interaction are addressed in a separate part of the report. These investigations include examination of the effects of adsorption kinetics, oxidation status of suspended sediments in the water column, and sediment concentration on interactions of trace metals with suspended sediment; examination of the effects of low sediment concentrations in the water column on loading kinetics, desorption kinetics, the distribution coefficient, and sequential desorption of low levels of an organic contaminant; and description of an investigation conducted to determine whether copper flux from reservoir sediments is enhanced in proportion to the microbial release of dissolved organic matter from sediment deposits.

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Contaminant	Microorganism	Sediment-water
Desorption	Organic matter	

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13. ABSTRACT (Concluded).

The results are summarized and considered in terms of the analytical and predictive techniques needed to describe the movement of sediment-associated contaminants in reservoirs.

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PREFACE

The work reported herein was conducted as part of the Water Quality Research Program (WQRP), Work Unit 32513, "Sediment-Water Interactions and Contaminant Processes in Reservoirs." The WQRP is sponsored by the Headquarters, US Army Corps of Engineers (HQUSACE), and is assigned to the US Army Engineer Waterways Experiment Station (WES) under the purview of the Environmental Laboratory (EL). Funding was provided under Department of the Army Appropriation No. 96X3121, General Investigation. The WQRP is managed under the Environmental Resources Research and Assistance Programs (ERRAP), Mr. J. L. Decell, Manager. Mr. Robert C. Gunkel was Assistant Manager, ERRAP, for the WQRP. Technical Monitors during this study were Mr. David Buelow, Mr. James Gottesman, and Dr. John Bushman, HQUSACE.

The study was conducted and the report prepared by Dr. Douglas Gunnison, Mr. Thomas C. Sturgis, and Dr. James M. Brannon of the Aquatic Processes and Effects Group (APEG), and Dr. Judith C. Pennington of the Contaminant Mobility and Regulatory Criteria Group (CMRCG), Environmental Research and Simulation Division (ERSD), EL. Dr. Aaron L. Mills, Mr. Michael Lehman, and Dr. Linda K. Blum of the Department of Environmental Sciences, University of Virginia, Charlottesville, VA, conducted the work on the effect of microbial formation of dissolved organic matter on mobilization of copper from reservoir sediments.

The study was conducted under the direct supervision of Dr. Thomas L. Hart, APEG, and under the general supervision of Mr. Donald L. Robey, Chief, ERSD, and Dr. John Harrison, Chief, EL. Technical reviews of the report were provided by Dr. Robert Gaugush, APEG, and Dr. Carlos Ruiz, Water Quality Modeling Group, EL. The report was edited by Ms. Jessica Ruff of the WES Information Technology Laboratory.

COL Larry B. Fulton, EN, was Commander and Director of WES Dr. Robert W. Whalin was Technical Director.

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CONTENTS

STUDIES ON THE ADSORPTION/DESORPTION AND MICROBIAL MOBILIZATION OF CONTAMINANTS FROM SEDIMENTS IN CORPS OF ENGINEERS RESERVOIR PROJECTS

PART I: INTRODUCTION

1. Recent information on processes linked to contaminant interactions with sediment and water was examined by Gunnison et al. (1989). These investigators examined (a) contaminant behavior at the sediment-water interface; (b) sorption of organic contaminants and metals by suspended sediment; (c) methods for assessing contaminant releases from sediment to water; (d) the importance of equilibrium and nonequilibrium processes; and (e) the influence of microorganisms on contaminant levels in sediment and water.

2. Gunnison et al. (1989) concluded that much information was available in the scientific literature on processes of contaminant interactions with sediment and water. However, the analytical and predictive methodologies needed to assess the influence of contaminated sediments in Corps of Engineers (CE) reservoir projects required considerable developmental work to make them suitable for use by CE field offices. In addition, the development of analytical and predictive techniques could not proceed until the factors influencing contaminant interactions with sediment and water are understood and the experimental procedures for measuring these interactions have been established. They finally concluded that the primary challenge to managing problems resulting from the presence of contaminants in CE reservoirs is the inability to quantify contaminant movement within the project.

3. Based on their investigation, Gunnison et al. (1989) recommended that research be carried out to determine: (a) adsorption/desorption rates for contaminants of concern, (b) the impact of sediment concentration on equilibrium distribution coefficients and adsorption/desorption kinetics, and (c) the effect of microbial transformation reactions on the mobilization of contaminants of concern.

4. Investigations were undertaken to develop methodologies to address these recommendations. Each of these investigations is presented as a separate part of this report. Part II examines the effects of adsorption kinetics, oxidation status of suspended sediment in the water column, and sediment concentration on interactions of trace metals with suspended sediment. Part III examines the effects of low sediment concentrations in the

water column on loading kinetics, desorption kinetics, the distribution coefficient (K_d), and sequential desorption of low levels of an organic contaminant. Part IV describes an investigation conducted to determine whether copper flux from reservoir sediments is enhanced in proportion to the microbial release of dissolved organic matter from sediment deposits. In Part V, the results presented in Parts II-IV are summarized and considered in terms of the analytical and predictive techniques needed to describe the movement of sediment-associated contaminants in reservoirs. The conclusions developed from this consideration are then used to formulate the next steps for the development of these analytical and predictive techniques.

PART II: EFFECTS OF ADSORPTION KINETICS, WATER COLUMN OXIDATION
STATUS, AND SEDIMENT CONCENTRATION ON INTERACTIONS BETWEEN
SUSPENDED SEDIMENT AND TRACE METALS

Purpose and Scope

5.   Although methods have been used to describe contaminant distribution
between suspended sediment and water in natural aquatic systems, all are vari-
ations of either equilibrium or nonequilibrium approaches (Gunnison et al.
1989). The selected methods must allow comparison of residence time of sedi-
ment particles in the water column with the time required for contaminant
adsorption/desorption processes. This study focused on adsorption kinetics,
oxidation status of the aquatic environment, and sediment concentration
effects upon adsorption. These are key factors that must be understood before
trace metal-sediment interactions can be adequately described.

6.   This study had two objectives:

a.   To examine adsorption kinetics for copper (Cu) and cadmium (Cd)
at various sediment concentrations.

b.   To determine the effects of anaerobic and aerobic conditions on
Cd and Cu adsorption at various sediment concentrations.

Materials and Methods

7.   Sediments used in this study were collected from Green River Lake,
Kentucky, and Mark Twain Lake, Missouri, by the US Army Engineer Districts,
Louisville and St. Louis, respectively. Green River Lake is operated pri-
marily for flood control in the upper Green River watershed. However, the
lake and surrounding land also provide opportunities for outdoor recreational
activities, including fishing, hunting, and trapping. Green River Lake is
situated in a section of central Kentucky known as the Highland Rim. Mark
Twain Lake is located on the Salt River in Missouri and is also used for rec-
reational activities, including fishing and boating. Selected chemical and
physical characteristics of sediments from these lakes are presented in
Tables 1 and 2, respectively.

8.   Copper and cadmium were selected for use in this study because of
their importance as trace metals and their potentially toxic nature in the
environment. Sediments from Green River and Mark Twain Lakes were selected
based on results of a survey conducted by the WES (Gunnison et al. 1989),

which showed that these lakes had potential water quality problems. Copper and cadmium concentrations in these sediments are given in Table 1.

Aerobic testing

9. Batch studies to assess adsorption and desorption under aerobic conditions were conducted in 70.5-ℓ cylindrical Plexiglas settling columns (Palermo, Montgomery, and Poindexter 1978) (Figure 1). These experiments were conducted in a controlled-environment chamber, where the temperature was regulated at $20° \pm 0.5°$ C. Sediment concentrations of 50, 500, and 5,000 mg/ℓ were tested in quadruplicate for each sediment. During aerobic testing, the desired sediment concentration was added to each column, which already contained 60.6 ℓ of deionized water. The sediment was maintained in suspension by continually bubbling air through the base of the column.

10. To initiate the adsorption experiment, solutions of Cd and Cu were added to each sediment concentration to give a final concentration of 500 μg/ℓ of metal in each column, and aeration was begun. Aliquots of sediment suspension were then removed from each column at intervals of 0, 0.5, 1, 2, 8, 24, 48, and 120 hr. The particulate and aqueous phases were separated by centrifugation at 9,000 rpm (12,000 × g) for 30 min, followed by passage through a 0.45-μm membrane filter. Aqueous samples were preserved by acidification with Ultrex nitric acid to pH 2 and stored at $4°$ C. Water samples were analyzed for Cd and Cu using a Perkin-Elmer Model 503 atomic adsorption spectrophotometer.

11. The desorption experiment was initiated with three concentrations of unamended fresh sediment (50, 500, and 5,000 mg/ℓ). The desired sediment concentration was added to the water in the columns and aerated. Aliquots of the sediment suspension were removed at 0, 7, and 14 days, centrifuged at 9,000 rpm for 30 min, filtered through 0.45-μm pore size membrane filters, preserved by acidification with Ultrex nitric acid to pH 2, and then stored at $4°$ C until analyzed for Cd and Cu.

Anaerobic testing

12. Batch studies to assess the effect of anaerobic conditions on adsorption and desorption of Cd and Cu were carried out using 250-ml airtight centrifuge bottles. Incubations were conducted in a controlled-environment chamber where the temperature was regulated at $20° \pm 0.5°$ C. Sediment concentrations of 50, 500, and 5,000 mg/ℓ were investigated in quadruplicate. The amount of sediment needed to obtain the desired sediment concentration was added to each centrifuge bottle, followed by 200 ml of nitrogen-purged

deionized water. All transfers of anaerobic sediments were conducted in a glove box under a nitrogen atmosphere. The centrifuge bottles were then capped and mechanically shaken at 120 excursions per minute to maintain the sediment in suspension. All filtering and sample handling procedures were conducted under a nitrogen atmosphere.

13. Adsorption testing was conducted with 500 μg/ℓ of Cd and Cu as described for aerobic testing, except that all operations were conducted under a nitrogen atmosphere. Desorption studies were conducted with unamended sediment at sediment concentrations of 50, 500, and 5,000 mg/ℓ for 14 days. The centrifuge bottles were removed from the shaker at 0, 7, and 14 days for determination of Cd and Cu concentrations in the aqueous phase. Samples were prepared and stored as described for aerobic testing except that sample preparation was conducted under a nitrogen atmosphere.

Results

Adsorption under aerobic
and anaerobic conditions

14. <u>Green River Lake sediment.</u> Cadmium and copper adsorption in Green River Lake sediment is affected by changes in sediment concentration under aerobic conditions (Figures 2 and 3). Copper adsorption was greater than Cd adsorption for all sediment concentrations. The Cd and Cu adsorption decreased as sediment concentrations decreased, in the order 5,000 mg/ℓ > 500 mg/ℓ > 50 mg/ℓ.

15. During the early phases of anaerobic testing, different sediment concentrations resulted in differing concentrations of Cu and Cd in the water (Figures 4 and 5). However, as anaerobic incubation time increased, the differences due to sediment concentration narrowed and were virtually nonexistent for Cd after 8 hr and for Cu after 120 hr.

16. Initial adsorption of added Cu and Cd was rapid under both aerobic and anaerobic conditions and was virtually complete under aerobic conditions within the first 2 hr. Even under aerobic conditions, the concentrations of Cu and Cd gradually increased as contact (adsorption) time increased for some treatments.

17. <u>Mark Twain Lake sediment.</u> Results of adsorption studies under aerobic and anaerobic conditions were similar in Green River Lake and in the Mark Twain sediments (Figures 6-9). The concentration of sediment in

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suspension affected the magnitude of Cd and Cu adsorption under aerobic conditions, with concentration adsorbed under aerobic conditions decreasing in the order 5,000 mg/ℓ > 500 mg/ℓ > 5C mg/ℓ. Under anaerobic conditions, no substantial difference between any of the sediment concentrations was found in 120 hr of sediment-water contact. Adsorption kinetics observed in this study under both aerobic and anaerobic conditions can be divided into two stages: (a) initial rapid adsorption and (b) slow approach to steady state. Steady state was achieved more rapidly under aerobic than under anaerobic conditions. In general, rapid adsorption under aerobic conditions was complete within 2 hr, while further changes were not evident until 24 to 48 hr.

Desorption under aerobic
and anaerobic conditions

18. Cadmium and copper concentrations in water in contact with Green River and Mark Twain sediments were not affected by sediment concentrations or the oxidation status of the sediment-water suspension (Tables 3-6). Desorption of Cu and Cd initially present in the sediment was minor.

Discussion

19. Adsorption kinetics for Cd and Cu were biphasic, consisting of rapid initial adsorption followed by a slower approach to steady state. Most changes in solution concentration (percent of steady-state values) occurred within the first few hours following addition of the soluble metals to sediment-water suspensions. Three mass transfer steps establish the equilibrium kinetics: diffusion to the sediment, sorption by external surfaces of sediment, and movement into and sorption or bonding to internal surfaces of sediments (micropores and gels) (Podoll and Mabey 1987).

20. Diffusion of the chemical to the sediment and sorption onto external surfaces occur very quickly in turbulent or well-mixed aquatic systems. However, sorption to internal surfaces is probably kinetically controlled by diffusion within the pore structure of the sediment (Karickhoff 1980, Freeman and Cheung 1981). The half-life of the slow sorption process is about an order of magnitude longer (several hours) than that of sorption onto external surfaces for a well-mixed system (Karickhoff 1980). Therefore, the initial rapid adsorption observed in this study is postulated to be due to surface adsorption, while the slower phase, which many times resulted in an

increase in Cu or Cd concentration, may be ascribed to physical, chemical, and/or biological processes.

21. The reason for the increase in concentration of solution Cu and Cd observed for some sediment concentrations (50 mg/ℓ) under both anaerobic and aerobic conditions is unclear. Instead of further sorption of added Cu and Cd, release of Cu and Cd originally present in the sediment appears likely.

22. Sediment concentration strongly affected the magnitude of Cd and Cu sorption in the aerobic treatments. As sediment concentration increased, the amount of Cd and Cu sorbed also increased. Increased sediment concentration resulted in an increase in sorption sites because of the greater mass and surface area/unit of mass or volume of sediment in a given volume of solution. Particle size fraction may also influence adsorption (Singh 1971, Salim and Cooksey 1981, Podoll and Mabey 1987, Honeyman and Santschi 1988). For example, sand has a lower sediment-water partition coefficient (K_p) than silt due to the lower specific surface area and lower organic carbon content of sand. Mark Twain and Green River sediments demonstrated similar adsorption capacities for Cd and Cu, even though the Green River sediment had significantly higher silt and total organic carbon content.

23. Many other factors have the potential to influence adsorption capacity, including, for example, silt and clay composition and quantity of oxyhydroxide compounds present in the sediment. The reasons for the lack of differences between these sediments should be explored. Mark Twain and Green River sediments did show a stronger affinity for Cu than for Cd, possibly because of the stronger binding capacity of organic matter for Cu compared to Cd (Plavsic 1987).

24. Initial adsorption kinetics of Cd and Cu were similar under anaerobic and aerobic conditions. Therefore, the factors controlling adsorption of these metals were probably not influenced initially by the oxidation-reduction status of the sediments. However, as incubation time increased, marked differences between Cu and Cd distribution in the aerobic and anaerobic sediment-water mixtures were observed, perhaps due to formation of sulfides or carbonates under increasingly anaerobic conditions. The adsorption/desorption behavior of metals under anaerobic conditions may also have differed markedly from behavior under aerobic conditions because of precipitation.

PART III: EFFECTS OF LOW SEDIMENT CONCENTRATIONS IN THE WATER COLUMN
ON LOADING KINETICS, DESORPTION KINETICS, DISTRIBUTION COEFFICIENT,
AND SEQUENTIAL DESORPTION OF LOW LEVELS OF AN ORGANIC CONTAMINANT

Purpose and Scope

25. Quantifying contaminants within a project is a multifaceted problem
that involves all aspects of sediment-water interactions. For example, an
inverse relationship between the concentration of adsorbing solids and parti-
tion coefficients* has been demonstrated for several organic contaminants,
e.g., DDT, heptachlor, lindane, kepone, and polychlorinated biphenyls (PCBs)
(O'Connor and Connolly 1980; Horzempa and Di Toro 1983; Voice, Rice, and Weber
1983; Weber et al. 1983). Therefore, this research has focused on analytical
methodologies for assessing contaminant interactions with sediment and water.

26. Specific objectives were as follows:

a. To determine the rate of adsorption and desorption of PCBs in
   sediments over a range of relatively low sediment
   concentrations.

b. To measure partitioning coefficients for PCBs over a range of
   low sediment concentrations.

c. To quantify solution PCB concentrations following adsorption
   and desorption.

Materials and Methods

Adsorption kinetics

27. Sediments from Green River and Mark Twain reservoirs were adsorbed
for 0.5, 1.0, 2.0, and 24.0 hr and 7 and 30 days with a PCB. Treatment was
accomplished by evenly coating the inside surface of 25-ml glass centrifuge
tubes with a methanol solution of the compound and allowing the methanol to
evaporate to dryness. It had previously been shown that little or no PCB
remains sorbed on the walls of the tube after shaking with a sediment suspen-
sion (Brannon et al. 1989). Water and sediment were added to each of four
replicates for each time, and the mixture was allowed to shake on a

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* Since the distribution coefficient and the partition coefficient are
  essentially the same, for this report the decision was made to use K_d to
  represent the partitioning coefficient.

reciprocating box shaker (280 excursions per minute) until the appropriate adsorption times had passed.

28.   Treatment concentration was 10 μg [G-^{3}H]2,2',3,5,5',6-hexachloro-biphenyl (PCB 151) per gram of sediment on an oven-dried weight basis (ODW). The [^{3}H]PCB had a specific activity of 196 milliCuries per millimole and a purity of 97 percent as determined by gas liquid chromatography. Sediment concentration was 500 mg (ODW) per liter. After shaking, tubes were centrifuged at 7,400 RCF (12,000 rpm) for 1 hr at 20° C. One milliliter of the solution was counted in 20 ml of Aquasol Universal Liquid Scintillation Cocktail (Biotechnology Systems, DuPont, Boston, MA) for 10 min three times using a Beckman LS100 Liquid Scintillation Counter (LSC) (Beckman Instruments, Inc., Fullerton, CA). Solution concentration of PCB was plotted against time to generate an adsorption kinetics curve.

Desorption kinetics

29.   Desorption kinetics were determined by adsorbing 10 μg PCB per gram of sediment for 24 hr as described above for adsorption kinetics. Adsorption solution was replaced by distilled deionized water, and all tests were returned to the shaker for the following desorption times: 1, 2, 3, 6, and 24 hr and 7 and 30 days. Solution phase was assayed as described above, and desorption curves were plotted. Desorption kinetics were determined for Green River and Mark Twain Lakes sediments in four replicates.

Effects of sediment
concentration on desorption

30.   Effects of different sediment and PCB concentrations on desorption were determined by adsorbing five concentrations of PCB onto three concentrations of sediment for 24 hr, removing the adsorption solution, and desorbing for 24 hr. Sediment concentrations were 250, 500, and 5,000 mg/ℓ. The PCB concentrations were 1, 5, 10, 15, and 20 μ/g. Only Green River Lake sediment was tested.

Sequential desorption

31.   Two sediments and two PCB concentrations were desorbed through seven sequences. Sediment concentrations were 500 and 5,000 mg/ℓ, and PCB concentrations were 10 and 20 μg/g.

Results and Discussion

Kinetics

32. Results of adsorption kinetic tests (Figure 10) indicated that adsorption of PCB to sediments was virtually complete within 2 hr for Green River and Mark Twain Lake sediments. The rapid attainment of steady-state conditions by PCB in this study agrees with findings of previous kinetics studies (Environmental Laboratory 1987, Myers and Brannon 1988, Palermo et al. 1989), which showed that 24 hr was sufficient to attain steady-state conditions in leachate from dredged material for hydrophobic organic contaminants such as PCBs. These results indicate that even for short particle residence times, an equilibrium approach can be used for describing interactions between suspended sediments and PCBs. Very little PCB was desorbed from either sediment over time (Figure 11). These results indicate that long-term desorption of hydrophobic organics from sediment to water will not appreciably impact test results. Therefore, the equilibrium assumption should hold for desorption as well as for adsorption tests, and shorter testing times can be used.

Effects of sediment concentration

33. The PCB desorption was low at low sediment concentrations, regardless of PCB concentration in test sediments (Figure 12). However, at the highest sediment concentration (5,000 mg/ℓ), PCB desorption increased with PCB concentration in the sediment. This result at the highest sediment concentration agrees with results reported in the literature for partitioning of hydrophobic organic contaminants such as PCBs (O'Connor and Connolly 1980; Di Toro et al. 1982; Voice, Rice, and Weber 1983; Gschwend and Wu 1985).

34. At 20 μg PCB/g of sediment, K_d decreased with increasing sediment concentration in the order 250 = 500 > 5,000 μg sediment/ℓ. The value of K_d was 3.11 × 10^6, 2.41 × 10^6, 0.43 × 10^6, respectively. The inverse relationship between K_d and sediment concentration is consistent with results of others for hydrophobic organic contaminants (O'Connor and Connolly 1980; Horzempa and Di Toro 1983; Voice, Rice, and Weber 1983; Weber et al. 1983). Therefore, sediment concentration must be taken into consideration when implementing sorption tests.

35. Sequential desorption failed to remove PCBs from sediments after the first cycle. These results indicate that the PCB is tightly bound to the sediment; therefore, the environmental fate of sediment-laden PCB will be determined to the greatest extent by the fate of the sediment.

36. Both adsorption and desorption of PCB 151 to sediments occurred rapidly, permitting the use of a relatively short testing period of 2 hr. An inverse relationship between K_d and sediment concentration, which is typical for hydrophobic organic contaminants, was demonstrated for PCB 151 at 5,000 μg sediment per liter. This result necessitates careful attention to sediment concentration when implementing partitioning studies. Desorption was extremely limited. At low sediment concentrations, partition coefficients (K_d's) were of the magnitude 10^6. Therefore, the environmental fate of PCB 151 will be dictated by the transport fate of the sediment to which it is tightly adsorbed.

PART IV: EFFECTS OF MICROBIAL FORMATION OF DISSOLVED ORGANIC MATTER
ON MOBILIZATION OF COPPER FROM RESERVOIR SEDIMENTS

Purpose and Scope

37. It is presently unknown whether mobilization of copper (or other heavy metals) through interactions with dissolved organic matter represents a significant mechanism for metal translocation from contaminated sediments to the water column. The objective of this investigation was to determine whether copper flux from impoundment sediments is enhanced in proportion to the decomposition of particulate organic matter and release of dissolved organic matter at the sediment-water interface.

Materials and Methods

Flux chambers

38. Flux chambers were constructed from 25.4-cm-diam polyvinyl chloride pipe (Figure 13). The height of each chamber was 10 cm, yielding a chamber volume of approximately 4 ℓ when placed on the sediment surface. A sampling port was provided by gluing the screw-top portion of a polyethylene centrifuge tube into a 2.5-cm hole. A stirring paddle was included to mix the chamber contents prior to sampling.

Preparation of particulate organic carbon

39. Particulate organic carbon (POC) was added to the chambers in the form of a dried phytoplankton culture or as ground oak leaves (*Quercus albus*). The phytoplankton culture was obtained by enhancing the growth of a mixed indigenous population in local pond water by the addition of nutrients (nitrogen and phosphorus) and light in a laboratory aquarium. The culture consisted of nearly equal portions of green algae and cyanobacteria, but no effort was made to identify the organisms or to quantify the relative abundance of individual members of the assemblage. The culture was harvested by centrifuging the suspension in 250-ml polypropylene bottles for 20 min at 7,000 $\times$ g, air-drying the remaining pellet, pulverizing it with mortar and pestle, and then freezing the preparation until reconstitution on the day of the experiment. This was accomplished by adding 1 g of freeze-dried phytoplankton (or oak leaves) to 10 ml of distilled water.

40. For the experiment in which oak leaves were used as a source of POC, dry brown leaves were collected from the forest floor and ground to form a coarse powder. The dry powder was then reconstituted as described for the algal material.

Field procedures

41. Depending on the specific experiment, three chambers were placed on the bottom of one of two reservoirs. The first was Pace Pond, a small impoundment on the Robert S. Pace farm in Fluvanna County, VA. The pond is managed by the Department of Environmental Sciences of the University of Virginia and has a surface area of approximately 3 ha, with a maximum depth of about 4 m near the dam. Alternatively, chambers were placed in the Contrary Creek arm of Lake Anna, Virginia, in about 1.5 m of water by scuba divers. In both locations, particulate organic matter was added to two of the three chambers, and a period of 0.5 hr was allowed for these amendments to settle in the chamber. At this point, 50-ml samples of water were withdrawn from the chambers to determine initial conditions. The control chambers received no amendments.

42. Samples (50-ml) were withdrawn from the chambers at intervals of 0, 1.5, 28, 52, 98, 147, and 672 hr. At the time of sampling, chamber contents were gently mixed with the stirring paddle. Samples were then withdrawn from the chambers using a 60-ml acid-washed syringe tipped with a 5-in.-long rubber tube. Samples were transferred to 100-ml acid-washed, high-density polyethylene bottles. Oxygen status of the chambers at the time of sampling was measured by inserting a YSI Model 54A polarographic oxygen probe (YSI Instruments, Yellow Springs, OH) into the sampling port of each chamber. The probe was connected to a meter, and the electrode meter combination was calibrated at each sampling time against a Winkler titration for dissolved oxygen in 60-ml BOD bottles (American Public Health Association 1989). All glassware, plastic ware, and syringes contacting the water samples were acid washed. Samples were preserved by acidification and stored at 4° C prior to analysis.

43. Subsamples were prepared for analysis of dissolved organic carbon (DOC) and dissolved copper by filtering aliquots through an acid-washed (0.5 percent HNO_3) 0.2-μm pore size membrane filter into acid-washed 20-ml glass liquid scintillation vials; these were subsequently acidified to pH < 2. The remaining sample was acidified by addition of concentrated HNO_3 (0.3 ml/ 100 ml sample) for analysis of total copper by atomic absorption spectroscopy or ion chromatography.

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Analytical methods

44. The DOC analysis was performed by the ultraviolet-assisted persulfate oxidation method using a Dohrman Model 18 Total Organic Carbon Analyzer. Dissolved organic carbon is reported in units of milligrams per liter (equivalent to parts per million) referenced to a potassium hydrogen phthalate standard.

45. Ion chromatographic analysis for copper was performed using a Dionex 2000I ion chromatograph with a CS-5 cation separator column and a CG-2 guard column connected in series. Eluent consisted of 25 mM sodium acetate, 3 mM PDCA, and 25 mM acetic acid. Detection was by colorimetric reaction with 0.2 mM PAR reagent in 1 M acetic acid buffered by 3M NH_4OH. Absorbance of the colored complex was measured at 520 nm.

46. Atomic absorption spectroscopy (AAS) was performed on acidified filtered samples using a Thermo Jarrel Smith Hieftje 22 AAS with a copper hollow cathode lamp, a bandwidth of 1 nm, and an air-acetylene fuel source with absorbance measured at 324.7 nm. Copper concentrations were expressed as micromoles of copper per liter.

47. The pH and redox potential of the chamber water was evaluated immediately following sampling (in the field) using a Ross Model 81-55 combination pH electrode and an Orion Model 96-78 combination redox (Eh) electrode. Sampling and analysis procedures consistent with US Geological Survey guidelines were observed. Redox potentials were corrected relative to the standard hydrogen electrode.

48. Preconcentration of samples for copper analysis was carried out by freezing an acidified (HNO_3 to pH <2) sample of filtered (0.2-μm pore diameter for dissolved copper) or unfiltered (for total copper) water, then lyophilizing the sample to remove the water. Samples were then reconstituted in one tenth the original volume using concentrated HNO_3.

Results

Comparison of ion chromatography and AAS for copper determination

49. The methods originally proposed for copper speciation were inadequate for the ambient levels encountered. Atomic absorption spectroscopy (atomization mode) can effectively distinguish between total and dissolved (<0.2-μm pore diameter filter) fractions to about 0.1 μm copper, a level at or

near the upper levels of copper present in many surface water samples. However, submicromolar concentrations are well below the working threshold of the cupric-ion-selective electrodes on the market. In addition, other ions, including iron and chloride, often interfere with the operation of these electrodes. As a result, ion chromatography (IC) was chosen to determine all three copper fractions (total, dissolved, and free ion).

50. The sensitivity of IC far exceeded that of AAS, with reliable measurement of standards to 1 nM copper (although interferences in environmental samples would complicate measurements at this level). Since work was conducted in the micromolar range, sensitivity limitation with the IC determination was not a problem. Measurements of total and dissolved copper in samples using IC were made on the basis of particle size fractionation prior to acidification and gave reliable, repeatable results.

51. Reports of the use of IC methods for determination of copper levels in environmental samples were not found during searches of the literature. However, measuring the free cupric ion concentration alone was of concern. Since treating the sample by acidification would alter the speciation of copper, biological activity in these samples was allowed to continue until analysis. More importantly, due to the nature of the ion separator columns and eluent (regardless of eluent or sample pH), many of the copper complexes were broken during passage of the sample through the column. This resulted in an overlap between the measured cupric ion and dissolved (including complexed) fractions that was deemed unsatisfactory. The amount of overlap could not be determined. This depends on the relative values of undetermined complexation constants of the organic ligands present in the natural sample in competition with latex in the column and chelator in the eluent for the cupric ion. Evidence for this behavior was obtained through numerous trials involving the addition of various amounts of strong chelating agents, such as EDTA and citric acid, to both environmental samples and prepared standards and running these aliquots through the machine at various pHs.

52. Copper analysis (excluding free ion) proceeded on the IC with adjustments in eluent strength made initially to spread the distance between the neighboring ferric and cupric peaks. Subsequently, addition of ascorbic acid reduced the iron present in the conflicting ferric peak, allowing appropriate separation between the cupric and the more distinct ferrous peak.

53. A major problem with the IC analysis arose when samples from the enclosure experiments were analyzed. Initial samples from the chambers

responded well to the analysis. However, when samples taken some time after POC input were analyzed on the IC, a large amount of iron was present. This swamped the column and rendered it unusable until reconditioned. Dilution of the sample to reduce the overall iron concentration resulted in acceptable levels of iron, but dropped the copper levels below the detection limit. Methods to remove iron interference, such as iron precipitation, would almost certainly result in loss of detectable copper as well. This would be unacceptable, because the loss would be unquantifiable and would probably reduce the copper concentration to a level too small for reliable determination.

54. Lyophilization of diluted acidified samples proved to be a reasonable method for concentrating copper to a level appropriate for analysis by AAS. A comparison of standard solutions (Table 7) indicates the recovery of total copper by this method. Recovery of standards was always slightly greater than 100 percent and was linear over the range examined (r^2 = 0.99). Standard spikes were added to aliquots of experimental samples to determine an appropriate recovery for each experimental system.

Field experiments

55. Three experimental runs were made in the field during fall 1989. Field trials were carried out in Pace Pond. Concentrations of total Cu in the water column were usually in the range of 1 to 3 μM. Sediment concentrations were approximately 1,000 μM Cu/g dry sediment. Initial runs were conducted to establish operating conditions and eliminate problems with the experimental manipulations, and not all parameters were measured each time. Despite the lack of complete data for these runs, some interesting relationships were observed between microbial DOC production and Cu mobilization.

56. Run 1. In the first run, only copper concentrations were measured. Initial values for total Cu were in the range typically seen in Pace Pond water (Table 8). In the treated chambers, the Cu concentration rose during the first half hour of incubation, but after 24 hr of incubation, the amount of Cu in the treated chambers was higher than the original in one chamber and lower than the original in the other. The Cu concentration in the unamended chamber rose slightly during the 24-hr period. Only one value could be obtained after the 26-day incubation period; this exceeded the initial value, but was not vastly different from the 24-hr level.

57. Run 2. The second run was begun 1 October 1989. Copper levels increased in all three chambers during the first 28 hr of incubation (Table 9). In each of the POC-amended chambers, the Cu level at least doubled

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during the first 1.5 hr of incubation, but did not change appreciably in the unamended chamber. After 28 hr of incubation, the Cu level in the unamended chambers was approximately 0.83 μM, but at that time, the concentration in the unamended chamber had reached 0.67 μM. The analytical technique used for this run was ion chromatography. For all points after 28 hr, the concentration of iron decreased drastically, and the chromatographic peak for Cu could no longer be read. For those points, AAS was used to obtain an estimate of the copper concentration. During the first 98 hr, total copper in the water inside the amended chambers exceeded that of the unamended chamber. After the 98-hr sampling, the copper concentration in the amended chambers decreased. In the unamended chamber, the total copper concentration in the water increased in the latter two sampling periods.

58. Oxygen concentrations in the chambers decreased from the initial ambient level of 93 μM to about 10 μM in the first 28 hr (Table 10). The speed of oxygen depletion was demonstrated by the drop in concentration observed in all chambers during the first 1.5 hr of incubation. Except for two unexplained points, when oxygen concentration measurements yielded values of about 45 μM, the low dissolved oxygen persisted throughout the incubation. The DOC levels obtained were equivocal, and no large differences were observed between treated and untreated chambers (Table 11).

59. Run 3. The persistent interference by iron forced a change in the analytical procedures by the time Run 3 was attempted. To eliminate the iron interference, all Cu values from the third run were obtained using AAS. No preconcentration was used at this time. The total copper concentration in the water increased in all the chambers, but the rate of increase was much greater in the amended chambers as opposed to the unamended chambers (Table 12). Dissolved oxygen decreases in this run were more pronounced in POC-amended chambers than in unamended units (Table 13). The DOC levels increased with time in all units, but larger increases were observed in the POC-amended units (Table 14).

Microcosm experiment

60. During the winter of 1989-90, a microcosm experiment was run in an 80-ℓ laboratory aquarium partially filled with sediment from the Contrary Creek arm of Lake Anna. The sediment was overlain with lake water. Small flux chambers were prepared by removing the bottoms from 250-ml brown polyethylene, narrow-mouth bottles and placing the tops of the bottles on the sediment surface, isolating a section of that interface. Water samples were

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collected through the tops of the bottles. Measurements were taken in a manner similar to those for the field runs of the previous fall. Three chambers were amended with POC to a level similar to that of the field chambers (250 mg preparation per liter of water in the chamber).

61. Oxygen disappeared rapidly from the amended chambers, but never completely disappeared from the control chambers (Table 15). The measured Eh dropped in all small experimental chambers compared to the ambient readings in the aquarium, but the data did not indicate any major differences or trends. (Note that Eh measurements in undefined systems are not very reliable.)

62. The pH in the aquarium and chambers increased from 5.6 to 6.7 over the course of the experiment. This is not unexpected, since the portion of Lake Anna from which the sediments were collected is known to form ions responsible for high levels of alkalinity; these are then transferred to the water column (Mills, Bell, and Herlihy 989).

63. Dissolved organic carbon increased in both the amended and unamended chambers (Figure 14). In the amended chambers, the increase was rapid during the first 30 hr. A decrease in DOC concentration was noted at Day 3, followed by a rise to a relatively steady level of 11 to 12 mg DOC/ℓ during the rest of the incubation. This pattern of rapid rise, decrease, and subsequent rerise has been noted in a number of other situations in which organic matter is added to a sediment.* The DOC level in the unamended chambers rose to a stable level that was lower than that in the amended chambers, but a later increase to about 8 mg DOC/ℓ was observed in the unamended chambers.

64. Copper from both the amended and unamended chambers was fractionated into total and dissolved copper, based on passage through a 0.2-μm pore size filter. In the chambers with no POC added, the dissolved copper approximated the total copper, except for the peak in total copper at about Day 5 (Figure 15). A similar effect was observed with the amended chambers except that the dissolved copper level was less than the total copper during the initial rise in DOC (Figure 16). The exact form of the total copper not accounted for by the dissolved fraction is unknown.

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* L. K. Blum and A. L. Mills. 1986. "Evaluation of the Literature on the Role of Microorganisms in Production of Dissolved Organic Matter and Mobilization of Contaminants in Dissolved Organic Form from Flooded Soils and Sediments," prepared for US Army Engineer Waterways Experiment Station, Vicksburg, MS.

65. In a concurrent experiment, a set of chambers in an aquarium received the ground oak leaf preparation. In that study, a very different pattern of copper behavior was observed as compared with the phytoplankton amendment (only copper data are available). In the unamended treatments, the dissolved fraction accounted for nearly all the copper, and the amount of material decreased monotonically after the first 3 days (Figure 17). (Note the lack of a large peak as was observed in the unamended chambers of the phytoplankton-amendment experiment.) In the amended chambers, the copper also decreased during the incubation, but the proportion of dissolved copper decreased more rapidly, and dissolved copper disappeared after 1 week. This observation suggests that the origin of the organic matter may be important in determining the ultimate mobilization of copper from the sediment.

Discussion

66. Results from studies at Pace Pond and the aquarium studies were inconclusive relative to the role of microbial production of DOM in the mobilization of copper from reservoir sediments. However, some important relationships were evident. In most cases, copper levels increased during the first few hours after initiating incubation. In general, this coincided with an increase in the concentration of DOC in the chambers (Figure 18). When the total copper concentrations (Figure 18) were regressed against the DOC concentrations, a regression line with an r^2 value of 0.76 was obtained, suggesting a relationship between DOC and copper mobility.

67. The results of the microcosm work also suggest a relationship between DOC and copper. Figure 19 depicts the concentrations of DOC in the phytoplankton-amended chambers of the microcosms plotted against total copper levels achieved over time. Both variables generally increased over the first day of incubation; however, after 72 hr, the copper disappeared from the water, while DOC levels remained high. The high sulfate levels in the water of Lake Anna (approximately 0.5 mM) (Mills, Bell, and Herlihy 1989) and the high rates of sulfate reduction suggest that the copper was precipitated as insoluble sulfide.

68. Although much of the data indicate an unquantified relationship between DOC production and copper mobilization, other data suggest that copper mobilization, while related to microbial activity, may not be directly linked to DOC. The decrease in total copper in the microcosms observed while the DOC

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remained high suggests that the copper may not have been complexed with the DOC. This is further supported by the frequent failure of the peak in mobilized copper to coincide with the peak in DOC concentration (Figures 14-16). One possible explanation for the observation of a lag between the copper and the DOC peaks may be the time required for DOC to diffuse into and then out of the sediments.

69. There is also evidence suggesting that a direct DOC effect may not have been responsible for the observed copper mobilization. The peaks in copper concentration were for total, not dissolved, copper. The measured DOC passed a $0.2\text{-}\mu m$ micropore filter, while the peak copper concentrations (in the microcosm study) consisted of material that did not pass this filter. Another observation is that the oak leaves did not produce the same mobilization of copper as the phytoplankton preparation. This may have occurred if the dried brown oak leaves did not provide sufficient usable carbon/energy supply for the microbes to generate significant levels of DOC. The chambers went anaerobic (as did unamended chambers), but no analysis of DOC was done. Alternatively, any DOC released from the oak leaves was likely very different from the phytoplankton DOC, and the compounds produced from the oak leaves may not have been good complexing agents for copper.

70. The results presented in this work do not negate the possibility of Eh effects, although copper loss from the water after several days of incubation would not be expected. Also, during the period that copper levels were decreasing, the platinum electrode potential remained relatively constant. However, in the past it has been demonstrated that the presence of mixed organic couples may influence the Eh, in spite of extensive changes in inorganic chemistry of aquatic systems (Brannon et al. 1978, 1983). The microcosm study is presently being repeated with radiation-sterilized sediment and water to determine if active populations of microorganisms are required for mobilization. Microcosms are also being amended with fulvic acids to determine if this material can enhance copper mobility in the presence and absence of active microorganisms.

71. While the results obtained are equivocal, they do suggest that microbial activity is related to the release of copper from sediments. However, this does not appear to be responsible for release of a large amount of copper in the reservoirs examined. These results also indicate a need for further field evaluations and controlled laboratory studies to obtain

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conclusive information about the microbial role in copper mobilization and the specific mechanisms of mobilization.

PART V: SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

72. Contaminants may enter the reservoir sorbed to sediments or in solution from which they may quickly become associated with sediment. Therefore, an understanding of several factors is necessary to accurately describe the fate of a given contaminant in a reservoir system: (a) whether the contaminant remains with the sediment or is desorbed, resulting in negative impacts on reservoir water quality, and (b) what effects the reservoir environment has on major factors responsible for the desorption and/or mobilization of contaminants. Additional factors potentially affecting contaminant fates are sediment suspension and concentration, particle size and composition, aerobic versus anaerobic conditions, organic matter, and sediment transport and deposition.

73. The Cd and Cu adsorption/desorption study showed that adsorption kinetics for both metals were biphasic, having a rapid phase that was essentially complete within 2 hr and a slower phase that resulted in higher metal concentrations in solution with increased time of contact. In addition, increased sediment concentrations resulted in increased sorption of these metals as a result of the increased number of sorption sites available. Particle size and sediment organic matter content were ineffective determinants of the adsorption capacities. In like manner, the oxidation-reduction status of the water column apparently had no effect in controlling adsorption kinetics; however, sulfide formation may have influenced the removal of these metals from solution.

74. Both adsorption and desorption of PCB 151 occurred rapidly, but an inverse relationship was found between K_d and sediment concentration. PCB adsorption/desorption was extremely limited at low sediment levels, but increased at higher sediment concentration. Following adsorption, PCB 151 becomes tightly bound to sediment, as indicated by the failure to remove additional PCB from sediment after the first desorption cycle. Therefore, long-term desorption will probably not significantly alter initial observations. If results can be extrapolated to reservoir conditions, the fate of PCBs strongly bound to sediments will be determined by the transport of the sediments, rather than by desorption.

75. For low to medium sediment concentrations (50 to 500 mg/ℓ), the adsorption/desorption effects for Cd and Cu and for PCB 151 were highly dependent on sediment concentration. An equilibrium approach to prediction of

sediment-water interactions for metal adsorption may be possible for areas where particle residence time in the water column is greater than 1 to 2 hr. For areas with shorter particle residence times, a kinetic approach for adsorption may be more appropriate. The results from the PCB 151 work suggest that an equilibrium approach is suitable for describing interactions between suspended sediments and PCBs, regardless of the residence time for suspended sediment.

76. Microbial production of dissolved organic matter was not conclusively shown to affect copper mobilization from reservoir sediments. It was apparent, however, that copper mobilization occurred immediately upon addition of organic matter. Complexation with organic matter was not established as the responsible mechanism, but no other process accounting for the observed mobilization was evident. The oxidation-reduction status of the water column was unrelated to the loss of copper from the water column under conditions favoring a role for DOC in copper mobilization; however, sulfide or carbonate formation may have been responsible for copper removal from solution.

77. Microbial formation of dissolved organic matter should not be considered a significant source of soluble copper to the water column, because water column concentrations of Cu were low and could not be strongly correlated with formation of dissolved organic matter. For this reason, future work to develop analytical and predictive techniques to describe the fate of contaminants in reservoirs should emphasize descriptions of physical and chemical processes occurring between contaminants, sediments, and water. Further, because most contaminants are associated with fine sediment particles and organic matter that are likely to remain suspended in the reservoir water column for extended periods, equilibrium approaches will be developed to describe the fate and mobility of metals and organic contaminants. Future investigations will focus on the environmental interactions of contaminants in suspended and bottom sediments.

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Table 1

Comparison of Chemical Characteristics of Green River Lake and Mark Twain Lake Sediments

| Constituent | Concentration of Constituent, mg/kg | |
	Green River Lake Sediment	Mark Twain Lake Sediment
Cd	0.4500	1.1100
Cu	5.6000	9.8000
Pb	18.4000	10.3000
Hg	<0.1000	0.2670
Fe	8,340.000	9,650.0000
Mn	222.0000	376.0000
TOC	26,158.0000	12,047.0000

Table 2

Comparison of Physical Characteristics of Green River Lake and Mark Twain Lake Sediments

| Constituent | Concentration of Constituent, percent | |
	Green River Lake Sediment	Mark Twain Lake Sediment
Sand	10.0	45.0
Silt	75.0	37.5
Clay	15.0	17.5
Organic matter	5.7	3.7

Table 3

Desorption of Cu and Cd from Green River Lake Sediment Under Anaerobic Conditions

Time days	Desorption at Sediment Concentration, mg/ℓ					
	50 mg/ℓ		500 mg/ℓ		5,000 mg/ℓ	
	Cd	Cu	Cd	Cu	Cd	Cu
0	0.00010 ± 0.0007	0.0010 ± 0.001	0.00010 ± 0.00005	0.0001 ± 0.0002	0.00005 ± 0.0000	0.001 ± 0.00
7	0.00005 ± 0.0000	0.0010 ± 0.001	0.00010 ± 0.00003	0.0001 ± 0.0003	0.00005 ± 0.0000	0.002 ± 0.00
14	0.00005 ± 0.0000	0.0005 ± 0.000	0.00005 ± 0.00000	0.0001 ± 0.0003	0.00030 ± 0.0003	0.003 ± 0.00

Table 4

Desorption of Cu and Cd from Green River Lake Sediment Under Aerobic Conditions

Time days	Desorption at Sediment Concentration, mg/ℓ					
	50 mg/ℓ		500 mg/ℓ		5,000 mg/ℓ	
	Cd	Cu	Cd	Cu	Cd	Cu
0	0.067 ± 0.03	0.04 ± 0.01	0.0002 ± 0.00009	0.001 ± 0.00	0.00005 ± 0.00	0.001 ± 0.00
7	0.067 ± 0.02	0.10 ± 0.08	0.0002 ± 0.00010	0.001 ± 0.00	0.00010 ± 0.00	0.001 ± 0.00
14	0.063 ± 0.02	0.11 ± 0.10	0.0003 ± 0.00020	0.001 ± 0.00	0.00010 ± 0.00	0.001 ± 0.00

Table 5

Desorption of Cu and Cd from Mark Twain Lake Sediment Under Anaerobic Conditions

Time days	Desorption at Sediment Concentration, mg/ℓ					
	50 mg/ℓ		500 mg/ℓ		5,000 mg/ℓ	
	Cd	Cu	Cd	Cu	Cd	Cu
0	0.00030 ± 0.0001	0.0005 ± 0.0000	0.0002 ± 0.00010	0.00005 ± 0.0000	0.0002 ± 0.00002	0.002 ± 0.000
7	0.00005 ± 0.0000	0.0005 ± 0.0000	0.0001 ± 0.00005	0.00005 ± 0.0000	0.0001 ± 0.00002	0.001 ± 0.000
14	0.00020 ± 0.0001	0.0006 ± 0.0001	0.0001 ± 0.00005	0.00005 ± 0.0000	0.0002 ± 0.00010	0.002 ± 0.000

Table 6

Desorption of Cu and Cd from Mark Twain Lake Sediment Under Anaerobic Conditions

Time days	Desorption at Sediment Concentration, mg/ℓ					
	50 mg/ℓ		500 mg/ℓ		5,000 mg/ℓ	
	Cd	Cu	Cd	Cu	Cd	Cu
0	0.002 ± 0.0030	0.0004 ± 0.0001	0.0003 ± 0.0001	0.004 ± 0.001	0.00030 ± 0.0002	0.004 ± 0.00
7	0.001 ± 0.0005	0.0200 ± 0.0070	0.0005 ± 0.0002	0.005 ± 0.003	0.00020 ± 0.0001	0.005 ± 0.00
14	0.004 ± 0.0004	0.0100 ± 0.0014	0.0002 ± 0.0001	0.004 ± 0.001	0.00005 ± 0.0000	0.004 ± 0.00

Table 7

Recovery of Copper from Standard Solutions upon Lyophilization and

Reconstitution in Concentrated HNO_3

Original Concentration	Expected Final Concentration	Observed Final Concentration	Percentage Recovered
0.33	3.33	3.88	117
1.00	10.00	10.48	105
5.00	50.00	51.53	103

Notes: The regression of observed versus expected values was
Observed = 1.0228 (Expected) + 0.371 . All concentrations are
expressed as micromoles per liter.

Table 8

Copper Concentrations Obtained from Flux Chambers During the

First Preliminary Run (Begun 5 September 1989)

Time hr	Copper Concentration, μM		
	Chamber 1 (With POC)	Chamber 2 (With POC)	Control Chamber (No Added POC)
0	4.32	0.81	1.03
0.5	10.81	1.08	--
24	1.08	1.62	1.57
624	--	--	1.49

Notes: Dissolved oxygen concentration at T_0 was approximately 250 μM and
at T_{624} was approximately 40 μM.
Values are given for each of two chambers amended with POC and for
one unamended chamber. Dashed line entry indicates that no data
were available.

Table 9

Total Copper Concentrations Obtained from Flux Chambers During

the Second Preliminary Run (Begun 1 October 1989)

Time hr	Copper Concentration, μM		
	Chamber 1 (With POC)	Chamber 2 (With POC)	Control Chamber (No Added POC)
0	0.37	0.6	0.32
1.5	0.77	1.68	0.37
28	0.81	0.84	0.67
52	0.12*	0.30*	0.07*
98	2.31*	2.81*	0.12*
147	1.19*	1.47*	1.78*
672	0.10*	0.98*	2.54*

Note: Values are given for each of two chambers amended with POC and for
the unamended chamber.
* Copper peaks on IC were "overwhelmed" by released iron. (Data from
AAS analysis with no preconcentration.)

Table 10

Dissolved Oxygen Concentrations Obtained from Flux Chambers During
the Second Preliminary Run (Begun 1 October 1989)

Time hr	Oxygen Concentration, μM		
	Chamber 1 (With POC)	Chamber 2 (With POC)	Control Chamber (No Added POC)
0	93	93	93
1.5	25	68	71
28	9.3	9.4	15
52	9.3	12	6.3
98	6.3	9.4	43
147	--	--	--
672	46	6.2	9.4

Notes: Values are given for each of two chambers amended with POC and for the unamended chamber. Dashed line entry indicates that no data were available.
Ambient dissolved oxygen concentrations in the surface and bottom waters were 188 and 94 μM, respectively.

Table 11

Dissolved Organic Carbon Obtained from Flux Chambers During
the Second Preliminary Run (Begun 1 October 1989)

Time hr	Dissolved Organic Carbon, μM		
	Chamber 1 (With POC)	Chamber 2 (With POC)	Control Chamber (No Added POC)
0	--	--	--
1.5	--	--	--
28	--	--	--
52	--	--	--
98	--	--	--
147	25	27	27
672	7.8	7.8	6.9

Notes: Values are given for each of two chambers amended with POC and for the unamended chamber. Dashed line entry indicates that no data were available.

Table 12

Total Copper Concentrations Obtained from Flux Chambers During the

Third Preliminary Run (Begun 28 October 1989)

Time hr	Copper Concentrations, μM		
	Chamber 1 (With POC)	Chamber 2 (With POC)	Control Chamber (No Added POC)
0	2.22	0.19	0.10
20	2.00	2.63	0.46
190	--	5.93	1.51

Notes: Values are given for each of two chambers amended with POC and for the unamended chamber. Dashed line entry indicates that no data were available.

Table 13

Dissolved Oxygen Concentrations Obtained from Flux Chambers During

the Third Preliminary Run (Begun 28 October 1989)

Time hr	Oxygen Concentration, μM		
	Chamber 1 (With POC)	Chamber 2 (With POC)	Control Chamber (No Added POC)
0	263	263	263
20	6.3	15	43
190	--	9.4	--

Notes: Values are given for each of two chambers amended with POC and for the unamended chamber. Dashed line entry indicates that no data were available.
Ambient dissolved oxygen levels in the surface and bottom water were 325 and 262.5 μM, respectively.

Table 14

Dissolved Organic Carbon Concentrations Obtained from Flux Chambers
During the Third Preliminary Run (Begun 28 October 1989)

Time	Dissolved Organic Carbon, μM		
hr	Chamber 1 (With POC)	Chamber 2 (With POC)	Control Chamber (No Added POC)
0	10	8.0	10
20	13	17	11
190	--	38	25

Note: Values are given for each of two chambers amended with POC and for the unamended chamber. Dashed line entry indicates that no data were available.

Table 15

Dissolved Oxygen Concentration in the Aquarium (Ambient)
and the Unamended and Amended Chambers

Time		Dissolved Oxygen Level, mg/ℓ		
Hours	Days	Ambient	Unamended	Amended
0	0	5.9	5.9	5.9
5	0.2	5.9	5.6	5.5
30	1.25	5.8	3.8	0.5
72	3.0	5.1	2.1	0.7
129	5.4	5.3	1.0	0.0
232	9.7	5.6	0.8	0.0
331	13.8	5.9	1.0	0.0
403	16.8	5.2	1.9	0.0

Notes: Ambient values are from a single measurement, unamended values are the means of duplicate chambers, and amended values are the means of triplicate chambers.
Coefficients of variation were usually 10 percent or less of the reported mean value.
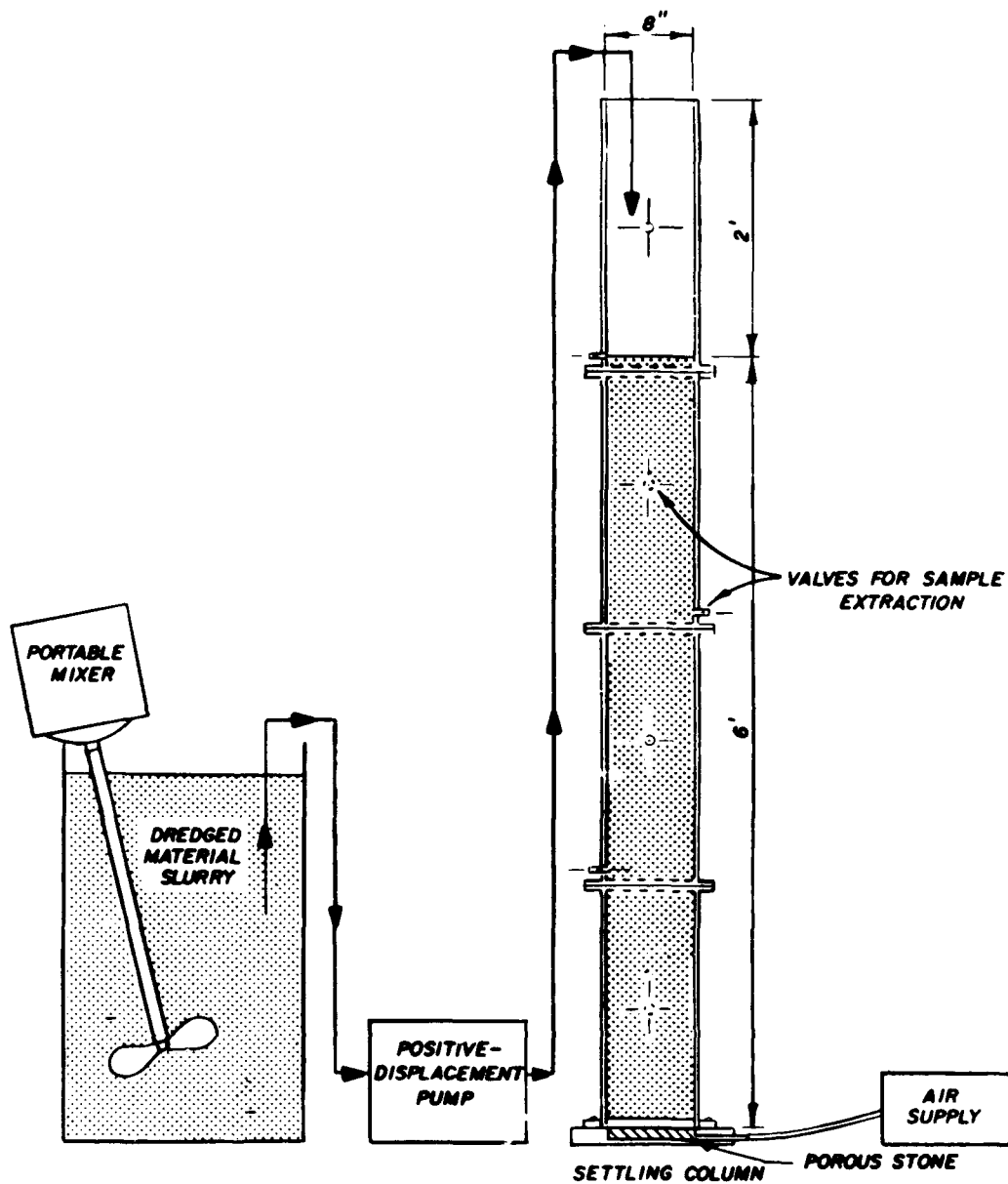
Figure 1. Plexiglas settling columns. (Also shown are the mixed slurry
and positive displacement pump used to load sediment into the column.)
To maintain the sediment in suspension, a continuous supply of air is
provided to the settling column through the porous stone at the bottom
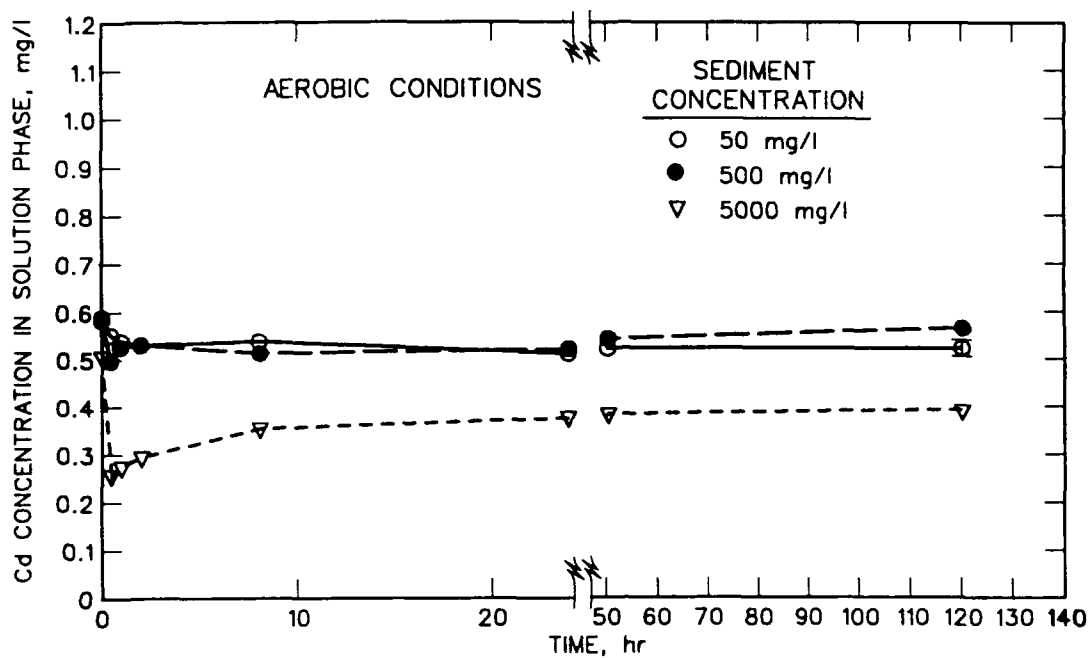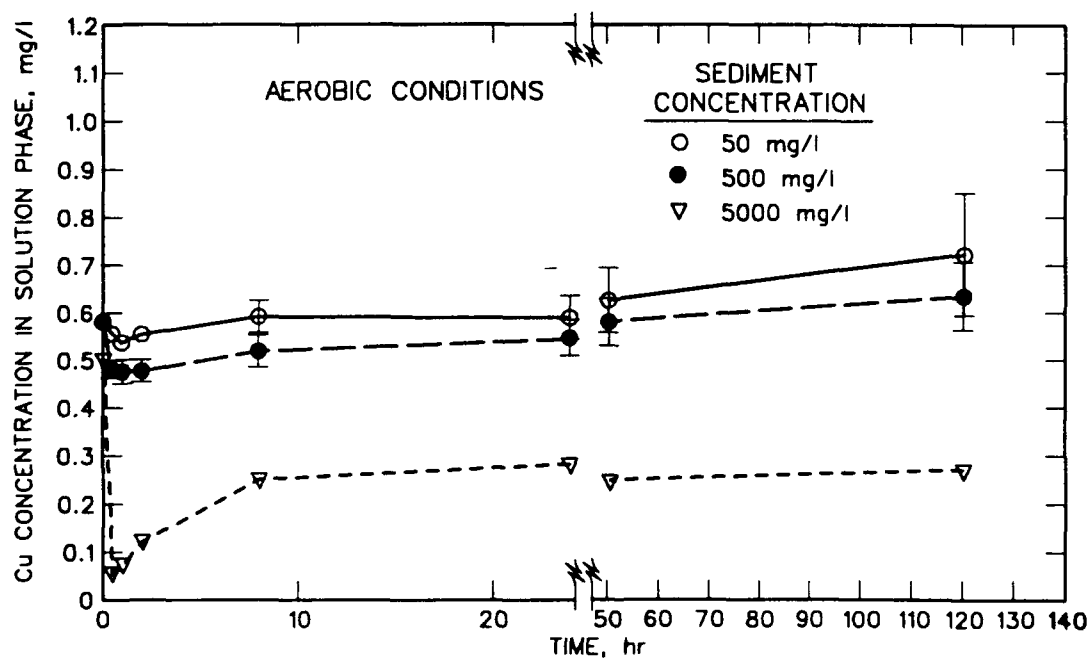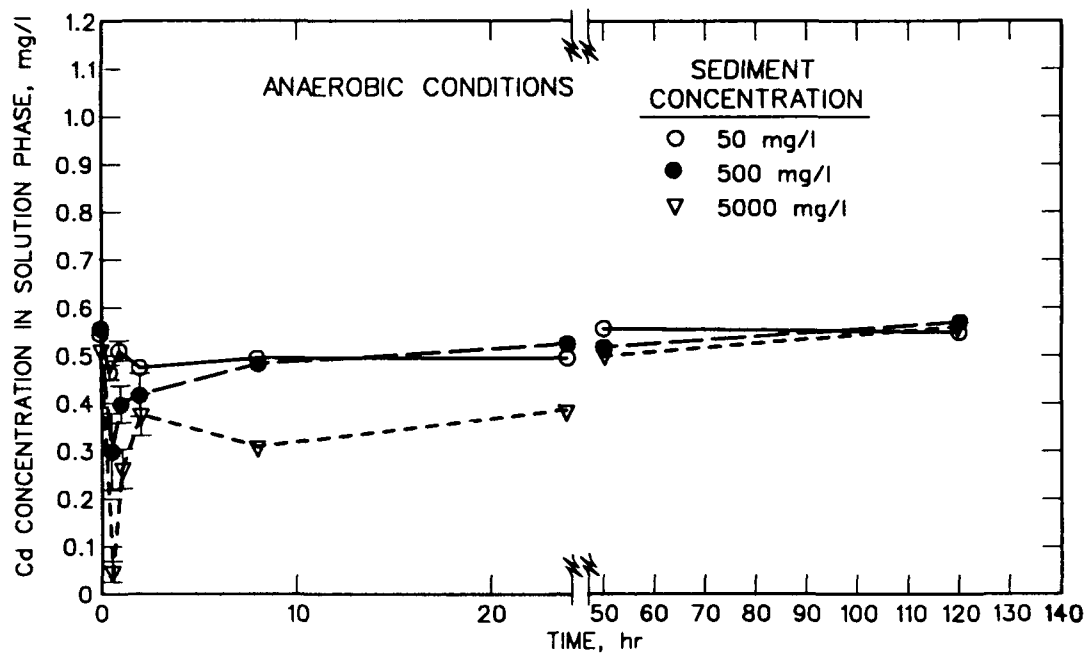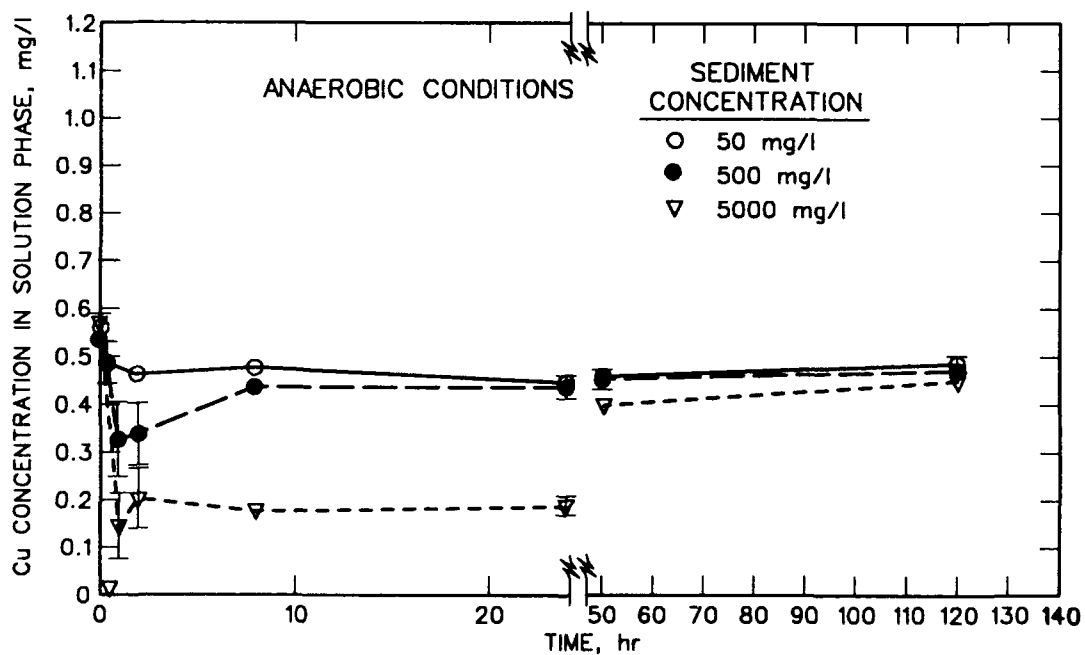(after Palermo, Montgomery, and Poindexter 1978)
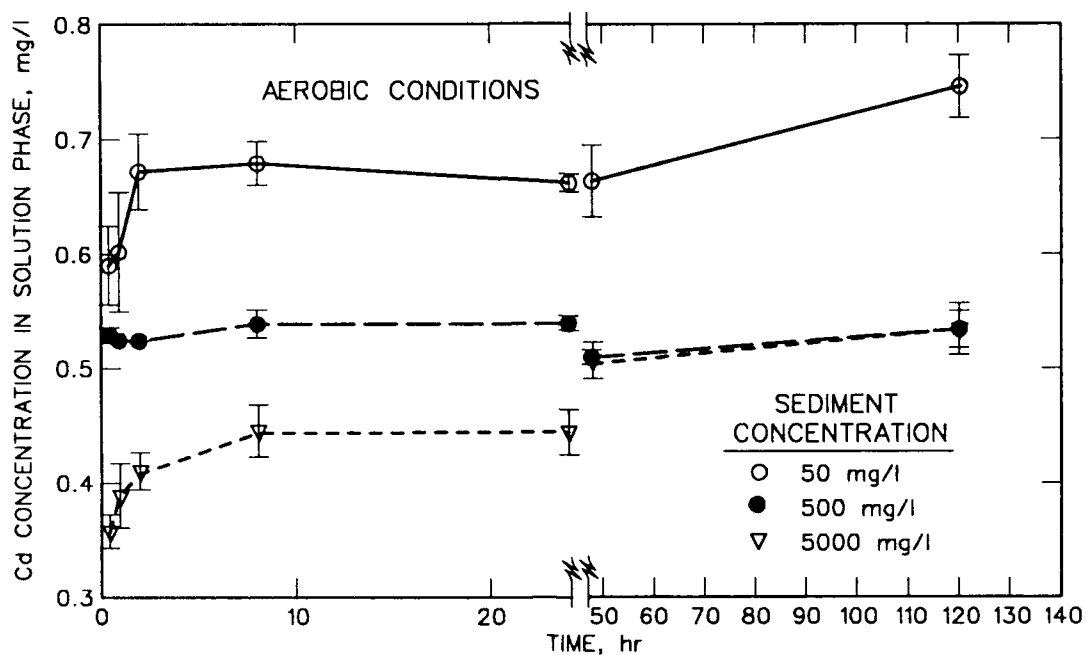
Figure 2. Effect of Green River Lake sediment concentration
on adsorption and equilibrium kinetics of Cd under aerobic
conditions
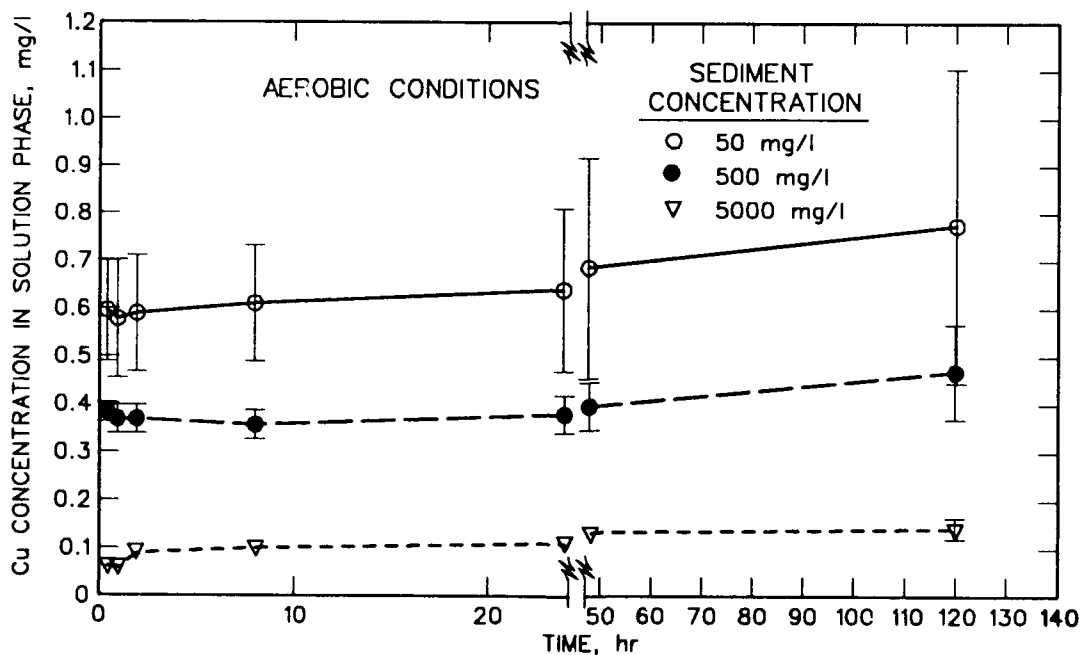
Figure 3. Effect of Green River Lake sediment concentration
on adsorption and equilibrium kinetics of Cu under aerobic
conditions
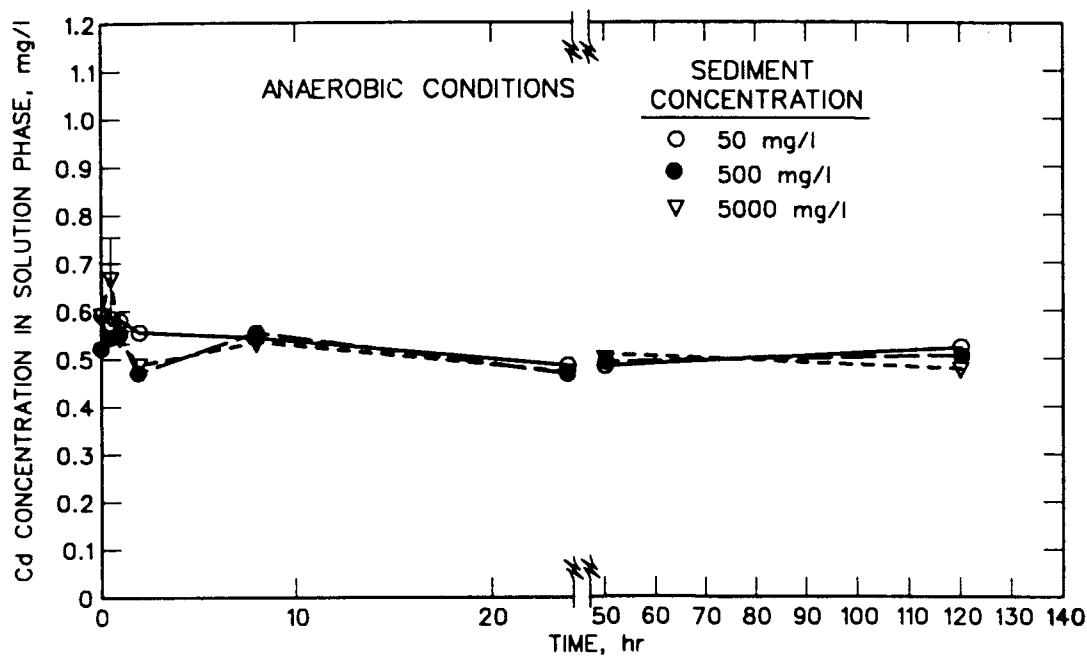
Figure 4. Effect of Green River Lake sediment concentration on adsorption and equilibrium kinetics of Cd under anaerobic conditions
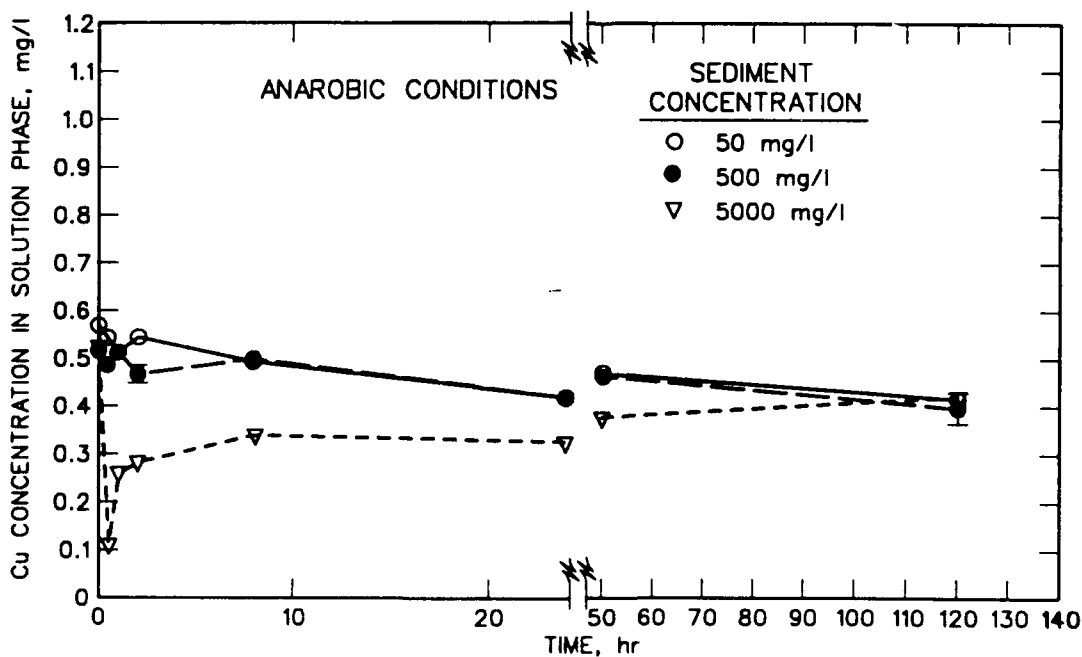
Figure 5. Effect of Green River Lake sediment concentration on adsorption and equilibrium kinetics of Cu under anaerobic conditions

Figure 6.   Effect of Mark Twain Lake sediment concentration
on adsorption and equilibrium kinetics of Cd under aerobic
conditions

Figure 7.   Effect of Mark Twain Lake sediment concentration
on adsorption and equilibrium kinetics of Cu under aerobic
conditions

Figure 8. Effect of Mark Twain Lake sediment concentration
on adsorption and equilibrium kinetics of Cd under anaerobic
conditions

Figure 9. Effect of Mark Twain Lake sediment concentration
on adsorption and equilibrium kinetics of Cu under anaerobic
conditions
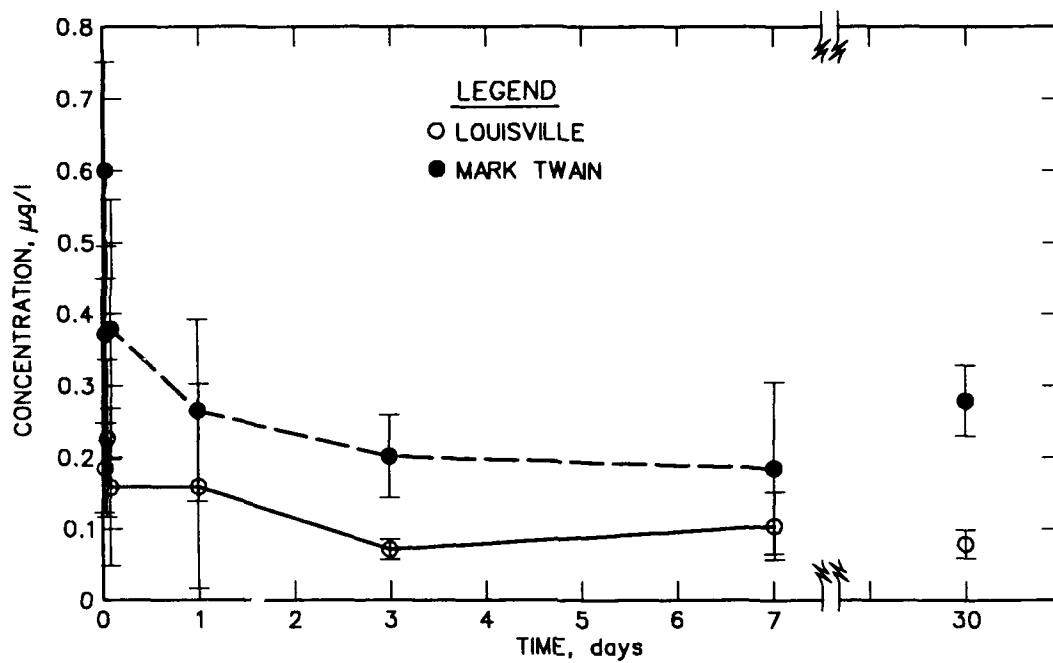
Figure 10. Kinetic curve for adsorption of PCB 151 to
Green River and Mark Twain Lakes sediment
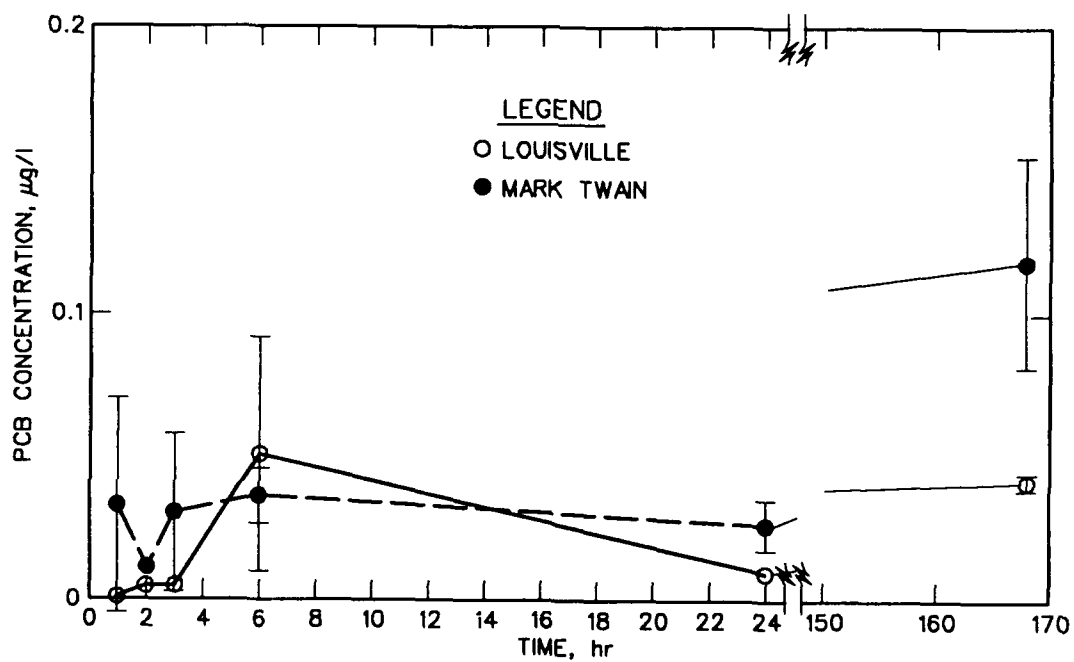
Figure 11. Kinetic curve for desorption of PCB 151 from
Green River and Mark Twain Lakes sediment

LOUISVILLE SEDIMENT
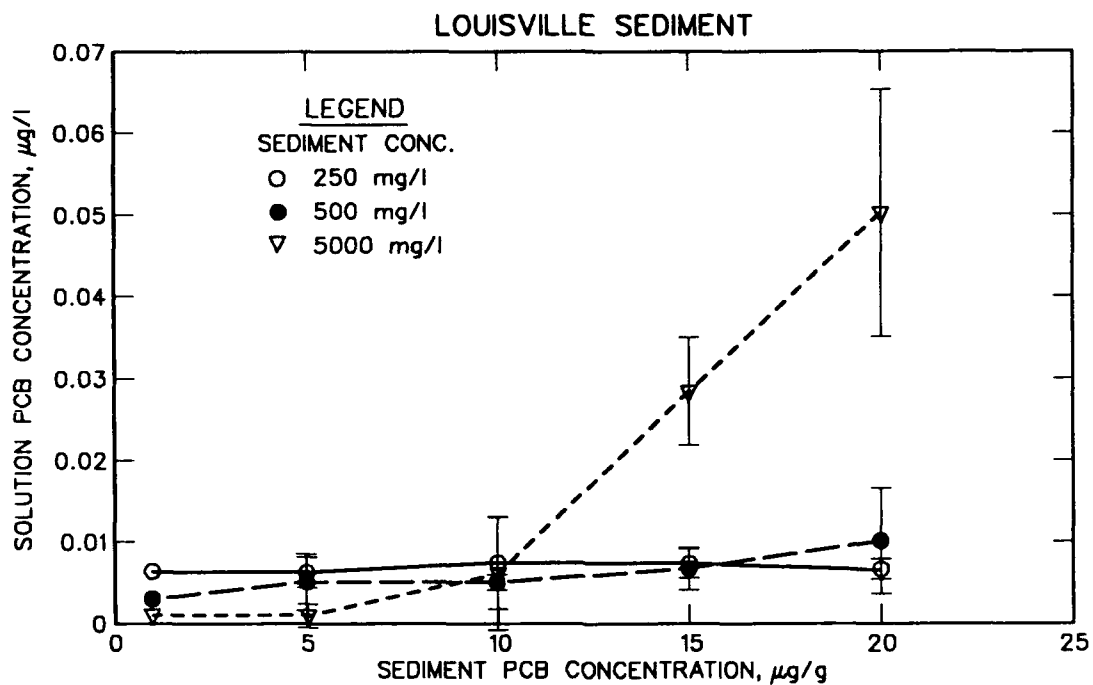
Figure 12. Desorption isotherms for PCB 151 in Green River Lake sediment
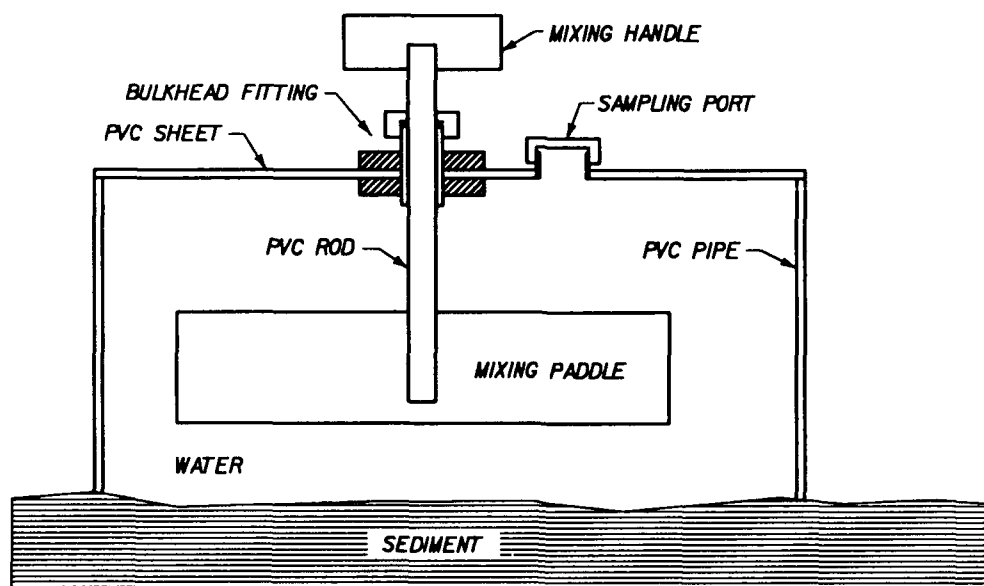
Figure 13. Flux chambers used to determine mobilization of copper from sediments
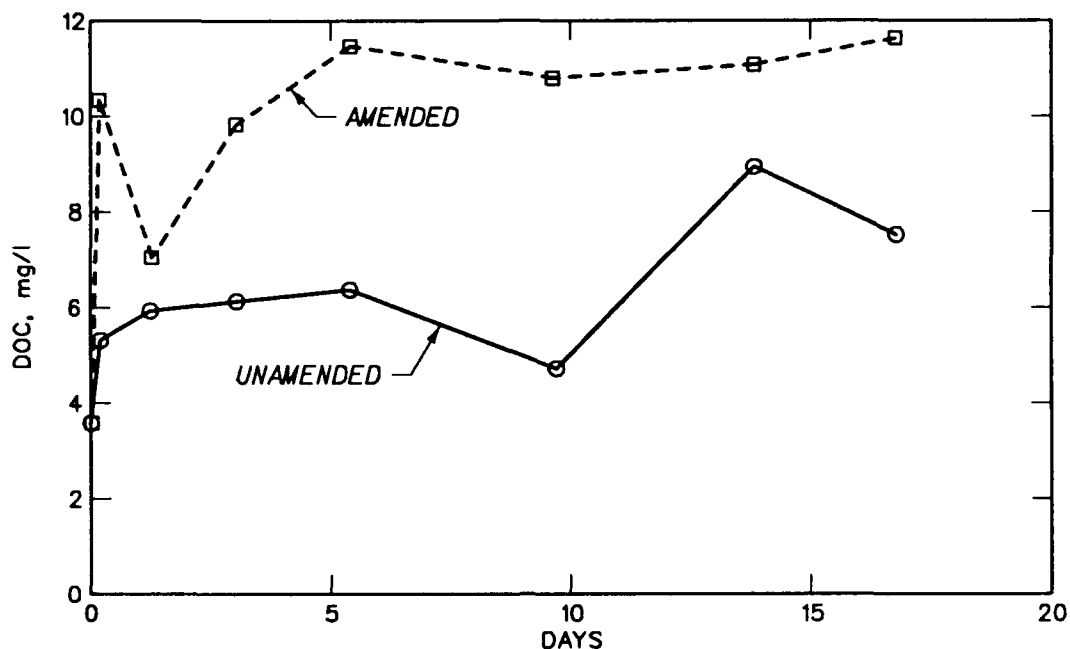
Figure 14. DOC concentration in amended and unamended
chambers in the microcosm (aquarium) study. Data points
are averages of results from two chambers for the
unamended and three chambers for the amended treatments.
Coefficients of variation for each point were usually
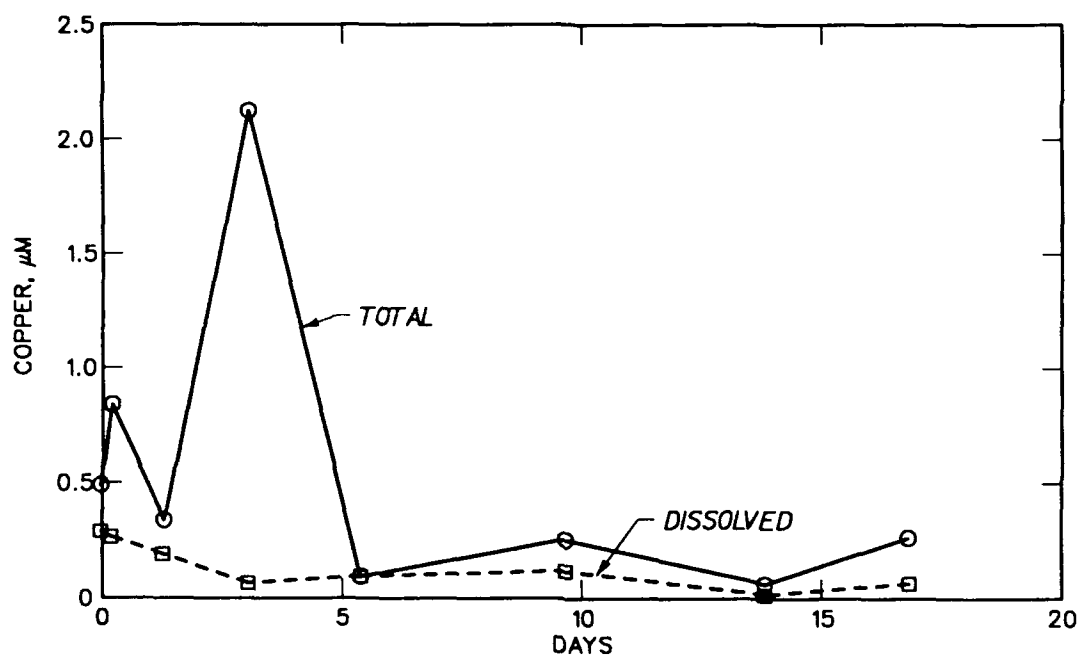about 30 percent of the mean value
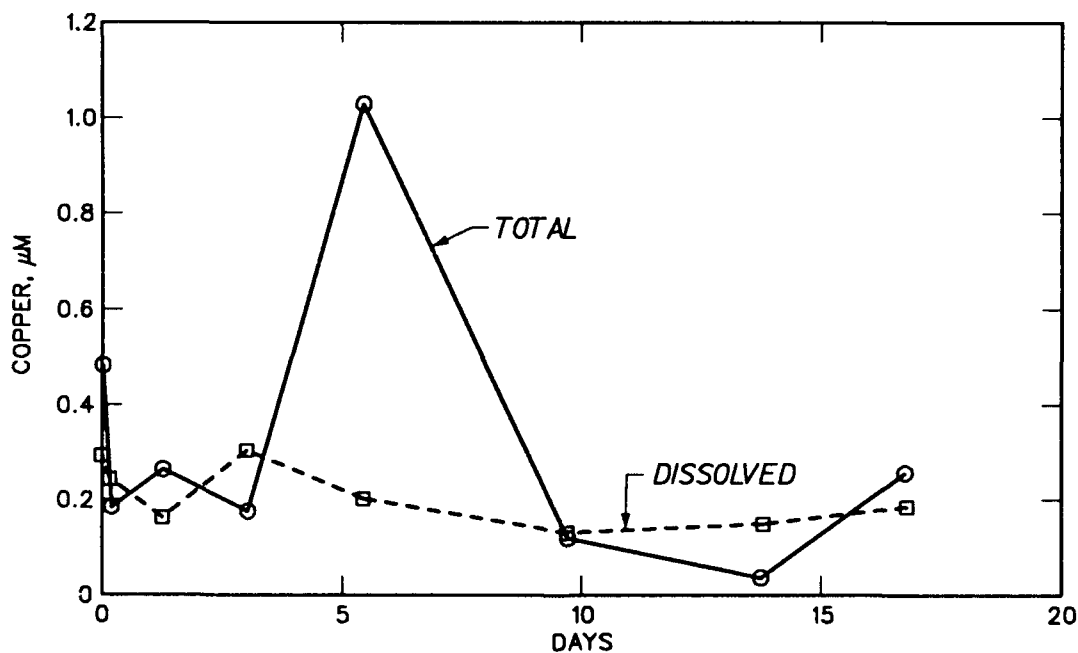
Figure 15. Total and dissolved copper in unamended
chambers in the microcosm study. Coefficients of
variation were about 30 percent of the reported mean
value for the two chambers. Dissolved copper was
determined as that portion of the copper sample in
solution passing a 0.2-μm pore diameter filter

Figure 16. Total and dissolved copper in amended chambers in the microcosm study. Coefficients of variation were about 30 percent of the reported mean value for the three chambers. Dissolved copper was determined as that portion of the copper in solution passing a 0.2-μm pore diameter filter
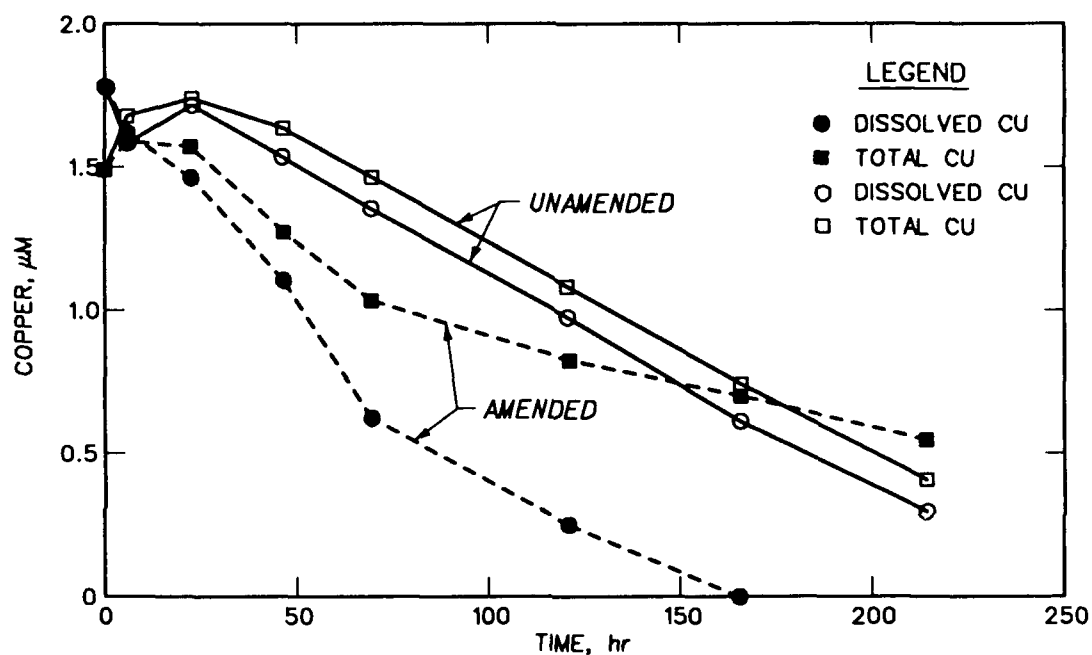
Figure 17. Total and dissolved copper in unamended
chambers and chambers in an aquarium that were amended
with ground oak leaves. Coefficients of variation
were about 30 percent of the reported mean value for
the chambers (three amended, two unamended). Dissolved
copper was determined as that portion of copper in solu-
tion passing a 0.2-μm pore diameter filter. Solid lines
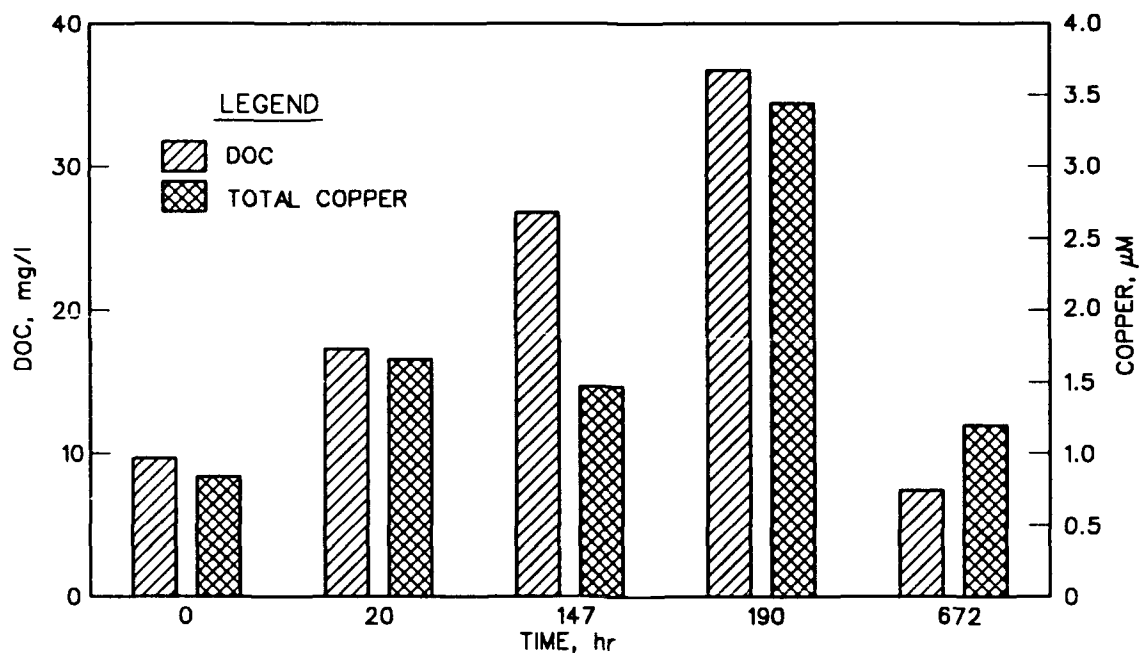are amended samples. Dotted lines are unamended
samples

Figure 18. Relation of DOC to total copper in the Pace Pond
runs. Data represent a composite of Runs 2 and 3 for which
paired data were available. Correlation of the two variables
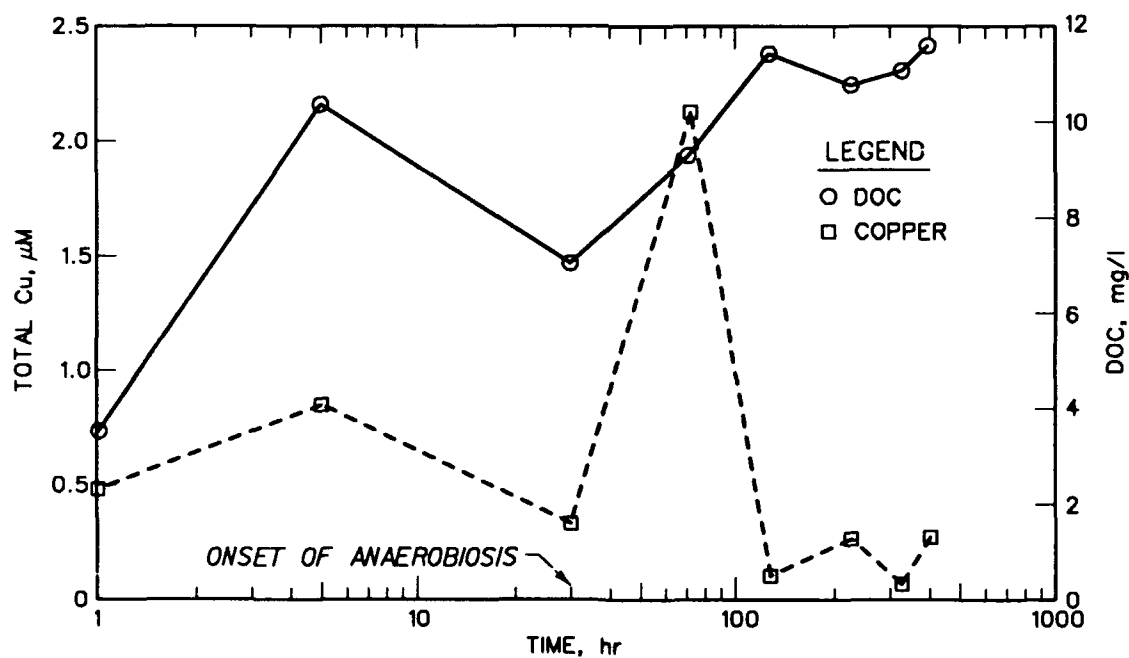yielded an r^2 of 0.76

Figure 19. Total copper and DOC concentrations in
phytoplankton-amended chambers in the microcosm
study. Note that time is presented on a logarithmic
scale to enhance the short sampling intervals near
the beginning of the study