NUREG/CR-3132
UCRL-53047

Concentration and Distribution of Copper in Effluents from the H.B. Robinson Steam Electric Plant

F. L. Harrison, D. J. Bishop, D. W. Rice, Jr., and J. P. Knezovich

Prepared for
U.S. Nuclear Regulatory Commission

Lawrence
Livermore
National
Laboratory

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability of responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights.

Availability of Reference Materials Cited in NRC Publications

Most documents cited in NRC publications will be available from one of the following sources:

1. The NRC Public Document Room, 1717 H Street, N.W.
   Washington, DC 20555
2. The NRC/GPO Sales Program, U.S. Nuclear Regulatory Commission,
   Washington, DC 20555
3. The National Technical Information Service, Springfield, VA 22161

Although the listing that follows represents the majority of documents cited in NRC publications, it is not intended to be exhaustive.

Referenced documents available for inspection and copying for a fee from the NRC Public Document Room include NRC correspondence and internal NRC memoranda; NRC Office of Inspection and Enforcement bulletins, circulars, information notices, inspection and investigation notices; Licensee Event Reports; vendor reports and correspondence; Commission papers; and applicant and licensee documents and correspondence.

The following documents in the NUREG series are available for purchase from the NRC/GPO Sales Program: formal NRC staff and contractor reports, NRC-sponsored conference proceedings, and NRC booklets and brochures. Also available are Regulatory Guides, NRC regulations in the *Code of Federal Regulations*, and *Nuclear Regulatory Commission Issuances*.

Documents available from the National Technical Information Service include NUREG series reports and technical reports prepared by other federal agencies and reports prepared by the Atomic Energy Commission, forerunner agency to the Nuclear Regulatory Commission.

Documents available from public and special technical libraries include all open literature items, such as books, journal and periodical articles, and transactions. *Federal Register* notices, federal and state legislation, and congressional reports can usually be obtained from these libraries.

Documents such as theses, dissertations, foreign reports and translations, and non-NRC conference proceedings are available for purchase from the organization sponsoring the publication cited.

Single copies of NRC draft reports are available free upon written request to the Division of Technical Information and Document Control, U.S. Nuclear Regulatory Commission, Washington, DC 20555.

Copies of industry codes and standards used in a substantive manner in the NRC regulatory process are maintained at the NRC Library, 7920 Norfolk Avenue, Bethesda, Maryland, and are available there for reference use by the public. Codes and standards are usually copyrighted and may be purchased from the originating organization or, if they are American National Standards, from the American National Standards Institute, 1430 Broadway, New York, NY 10018.

GPO Printed copy price $3.75

NUREG/CR-3132
UCRL-53047
RE

Concentration and Distribution of Copper in Effluents from the H.B. Robinson Steam Electric Plant

Manuscript Completed: January 1983
Date Published: August 1983

Prepared by
F. L. Harrison, D. J. Bishop, D. W. Rice, Jr., and J. P. Knezovich

Lawrence Livermore National Laboratory
7000 East Avenue
Livermore, CA 94550

Prepared for
Division of Health, Siting and Waste Management
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555
NRC FIN No. A-0119

ABSTRACT

Water and bedload sediments were sampled at the intake and discharge areas of the H.B. Robinson Steam Electric Plant and at a control area upstream of the plant in November 1979 and May and July 1980. Water samples were analyzed for total, for soluble and particulate, and for labile and bound copper; sediments were analyzed for total copper. During the July field survey, samples were taken at three additional sites downstream of the plant.

Total copper concentrations in water samples from the discharge area were always higher than in those from the intake. Concentrations of copper in discharge waters ranged from 33 to 79 μg/L, whereas those in intake waters ranged from 27 to 58 μg/L. The concentration of copper in the water in the control area upstream from the power station ranged from 3.1 to 5.8 μg/L; this was significantly lower than that in the discharge and intake areas. Downstream water also contained less copper, with a low concentration of 12 μg/L and a high of 22 μg/L. The percent of copper in the particulate fraction was 20% in November, 30% in May, and about 40% in the July sampling period. In most samples, copper in the soluble fraction appeared equally as labile and bound. The concentration of dissolved organic carbon in the water samples from the impoundment area showed little variation with time; the values range from 3.8 to 5.7 mg C/L. The organic carbon in the particulate fraction was ≤1 mg C/L.

Determination of molecular size distribution of the copper and iron species by ultrafiltration of discharge and control waters indicated that the largest concentration of copper appeared in the >10,000, <100,000 molecular weight fraction both in untreated and UV-oxidized water. However, very little copper was found in the >1,000, <10,000 fraction after UV exposure for 6 h. The largest concentration of iron shifted from the >10,000, <100,000 fraction to the >100,000 fraction following UV treatment.

Analysis of water for anions and 24 elements showed little change in concentration between intake and discharge waters of the same collection period. However, the control waters upstream were significantly lower in concentrations of copper, zinc, and calcium.

Copper concentrations in intact bedload sediments of the intake area ranged from 4.4 to 260 μg/g dry weight; those in the discharge area ranged from 6.1 to 72 μg/g. Copper in the upstream sediments was very low, ≤3.7 μg/g. Higher concentrations appeared in the <62-μm fractions than in intact sediments. Copper distribution coefficients of intact bedload sediments in the intake and discharge areas ranged from 300 to 21,000.

CONTENTS

Abstract . . . iii
List of Tables . . . vi
Preface . . . vii
Executive Summary . . . 1
  Techniques . . . 1
  Findings . . . 1
  Conclusions . . . 2
  Recommendations . . . 2
Introduction . . . 3
Site Characteristics . . . 3
Materials and Methods . . . 5
  Sample Collection and Processing . . . 5
    Water and Suspended Particles . . . 5
    Bedload Sediments . . . 6
  Reagents . . . 7
  Copper Analyses . . . 8
    Water . . . 8
    Suspended Particles . . . 9
    Bedload Sediments . . . 10
  Apparent Complexing Capacity . . . 10
  Ultrafiltration . . . 10
  Organic Carbon Analyses . . . 12
  Distribution Coefficients . . . 12
    Suspended Particles . . . 12
    Bedload Sediments . . . 13
Results and Discussion . . . 13
  Water Column . . . 13
    Soluble and Particulate Copper Concentrations . . . 13
    Copper Sorption Rates . . . 15
    Copper Speciation . . . 15
    Apparent Complexing Capacity . . . 16
    Copper in Molecular Weight Fractions . . . 16
  Bedload Sediments . . . 22
    Copper Concentrations . . . 22
    Distribution Coefficients . . . 24
    Particle Size Distribution, Carbon Content, and Mineral Composition . . . 24
References . . . 29
Appendix A. Procedure for Cleaning Sample Containers . . . 33
  Containers of < 10 µg Cu/L Samples . . . 33
  Containers of > 10 µg Cu/L Samples . . . 33

LIST OF TABLES

1. Analyses performed and volumes and numbers of samples collected from study sites at the H.B. Robinson Steam Electric Plant 6
2. Temperature, pH, and conductivity of water collected at the H.B. Robinson Steam Electric Plant 7
3. Copper concentrations (μg/L) in water collected at the H.B. Robinson Steam Electric Plant 14
4. Characteristics of suspended particles in water collected at the H.B. Robinson Steam Electric Plant 15
5. Dissolved (DOC), particulate (POC), and total (TOC) organic carbon (mg C/L) in water collected at the H.B. Robinson Steam Electric Plant 17
6. Percentages of ^{64}Cu, ^{59}Fe, and dissolved organic carbon (DOC) in different molecular weight fractions of ultrafiltered water from the H.B. Robinson Steam Electric Plant assuming unavailability of copper sorbed on walls and membranes 18
7. Percentages of ^{64}Cu, ^{59}Fe, and dissolved organic carbon (DOC) in different molecular weight fractions of ultrafiltered water from the H.B. Robinson Steam Electric Plant assuming availability of all copper recovered 19
8. Percentages of ^{64}Cu and ^{59}Fe recovered in the dissolved (filtrate plus the solution remaining in the ultrafiltration cell) and sorbed (to the walls and membrane) fractions of the ultrafiltered water 20
9. Chemical species of copper 21
10. Concentrations of soluble elements (μg/L) in water collected at the H.B. Robinson Steam Electric Plant 23
11. Concentrations of anions (μg/L) in water collected near the H.B. Robinson Steam Electric Plant 24
12. Copper concentrations in bedload sediments (μg/g dry weight) collected at the H.B. Robinson Steam Electric Plant 25
13. Characteristics of sediments collected at the H.B. Robinson Steam Electric Plant 26
14. Distribution coefficients for bedload sediments collected at the H.B. Robinson Steam Electric Plant 27
15. Particle size distribution, organic carbon, calcium carbonate, and mineral content of intact bedload sediments collected from the H.B. Robinson Steam Electric Plant, July 1980 28

PREFACE

This study is part of a larger research project that has three purposes: (1) to study the behavior of potentially toxic substances introduced to surface waters from nuclear power stations; (2) to determine the magnitude of the impact of these substances on representative, economically important species; and (3) to develop models to predict the behavior and the impact of these substances. The initial thrust of the research was to investigate the impact of corrosion products from cooling systems, in particular, copper. Copper is of special interest because it is toxic to aquatic organisms.

We wish to thank the scientific staff of the Carolina Power and Light Company (CP&L) for their excellent cooperation and advice. Special thanks go to Dave Herlong from CP&L for his assistance in the collection of samples. The authors also thank Jack Dawson and Jacqueline Lam from Lawrence Livermore National Laboratory for their assistance in sample analysis.

CONCENTRATION AND DISTRIBUTION OF COPPER IN EFFLUENTS FROM THE H.B. ROBINSON STEAM ELECTRIC PLANT

EXECUTIVE SUMMARY

Field studies were performed at the H.B. Robinson Steam Electric Plant to obtain a better understanding of the fate of copper corrosion products released from cooling systems to the impoundment. Data on copper are important for an assessment of its rate of dispersion in ecosystems, rates of interaction with other pollutants, final distribution, and toxic effects on biota.

Copper concentrations were obtained for the soluble and particulate fractions of water samples and in bedload sediments collected in control, discharge, and intake areas during November 1979 and May and July 1980; additional samples from the July 1980 collection period were obtained from three downstream locations and were analyzed for copper concentrations. In addition, copper distribution coefficients (K_ds) of particles suspended in the water column and present in the bedload sediments were determined.

TECHNIQUES

Several analytical techniques were used to identify the forms and quantities of copper present in the water. Total soluble and particulate copper were determined after separating the fractions by filtering the water through membranes with 0.4-μm pores. Labile copper in the soluble fraction was measured by an ion exchange technique and by differential pulse, anodic stripping voltammetry (DP ASV). Ultrafiltration indicated the molecular weight distribution of the copper and iron species and the effect of dissolved organic matter on distribution.

Suspended particles and bedload sediments were dissolved in acid and copper quantified by atomic absorption spectrophotometry. Copper K_ds were determined by radiolabeling techniques.

FINDINGS

Total copper concentrations in water from the intake area ranged from 27 μg/L in July 1980 to 58 μg/L in November 1979; copper in the discharge water was also lowest in July at 33 μg/L and highest in November at 79 μg/L. Copper concentrations in water from upstream (control) and downstream sites were always lower than those from intake and discharge areas within the impoundment. Control water had copper concentrations ranging from 3.1 to 5.8 μg/L, and downstream water ranged from 12 to 22 μg/L. Water from the July collection had the highest percentage of copper in the particulate fraction in comparison with the May and November collections. Labile and bound copper in the soluble fraction were approximately equal in most samples. The range of concentration of dissolved organic carbon in intake and discharge waters was small, from 3.8 to 5.7 mg C/L.

Determination of molecular size distribution of the copper and iron species by ultrafiltration of the soluble fraction of the discharge water from all three collection periods revealed the highest concentration of copper in the >10,000, <100,000 molecular weight fraction (MWF). This same MWF had a high percentage of copper after UV oxidation for 6 h, although the percentage in the >1,000, <10,000 MWF decreased significantly, if not entirely. Iron was also present in highest percentage in the >10,000, <100,000 MWF in untreated water, but >90% of the iron was found in the >100,000 MWF following UV treatment. The percentages of copper in the various MWFs following UV oxidation of water from H.B. Robinson differed somewhat from those of earlier studies in marine and estuarine waters, possibly because of the differences in salt content, but more likely because of the lower pH of H.B. Robinson water.

Intact bedload sediments from the discharge area contained copper ranging from 6.1 to 72 µg/g dry weight; copper in sediments from the intake areas ranged from 4.4 to 260 µg/g. Higher concentrations appeared in the <62-µm fraction than in intact sediments. Copper K_ds of intact bedload sediments from discharge and intake areas ranged from a low of 300 in November 1979 to a high of 21,000 in May 1980.

CONCLUSIONS

Total copper concentrations in influent and effluent waters collected at H.B. Robinson were in the range reported to be toxic to sensitive organisms such as some species of primary producers and early life stages of some species of higher trophic-level organisms. Because a high percentage of copper in water from both intake and discharge areas was in the labile form (33 to 45%), biota in the impoundment should be monitored on a regular basis for possible adverse effects. Downstream water analyses showed that the copper was diluted, so the impact of such effluents would be limited to the impoundment area.

Ultrafiltration of H.B. Robinson water into MWFs demonstrated the presence of copper predominantly in the intermediate MWFs from >1,000 to <100,000 and iron predominantly in the >10,000, <100,000 MWFs. In water that was UV oxidized, a low percentage of copper was present in the >1,000, <10,000 MWF and of iron in the >10,000, <100,000 MWF. These data indicate that the two metals behave differently in the presence and absence of organic ligands.

The concentration of copper in the bedload sediments from both intake and discharge areas showed significant increases in May and July 1980 compared with November 1979. This increase in copper may indicate a buildup of copper in the sediment with time.

RECOMMENDATIONS

The physicochemical forms of copper in the H.B. Robinson water appear to be different from those at other freshwater sites. Additional data are needed to establish whether the copper partitioning and binding behavior was attributable to the lower pH of the water system and/or to differences in the kinds and quantities of organic ligands present.

The partitioning between the soluble and particulate forms of copper as well as the nature of the physicochemical forms may affect its availability to the biota. Therefore, it is important to further study the effects of environmental factors and seasonal variations on the speciation, sedimentation, and bioavailability of copper in the ecosystem.

INTRODUCTION

The siting of nuclear power stations adjacent to freshwater ecosystems has been a common practice because of the need for cooling water. However, the use of these waters has not only added waste heat to the ecosystem, but also corrosion products from the heat exchangers. The impact on local ecosystems from power station waste waters is dependent on the quantities of corrosion products released and their physical and chemical forms (Ref. 1).

Copper alloys are frequently used in cooling systems because of their favorable heat exchange and antifouling properties. Previous investigations of the effect and distribution of copper corrosion products in effluents from power stations have been conducted (Refs. 2-7). Copper corrosion products were implicated in the abalone kill that occurred in the discharge cove of the Pacific Gas and Electric Company, Diablo Canyon Nuclear Power Station before the copper-nickel tubing in the cooling system was replaced by titanium tubing (Ref. 8). However, our investigations of the concentration and physicochemical forms of copper in the intake and discharge areas of the Diablo Canyon and San Onofre Nuclear Power Stations in California and of the Surry and Salem stations in the East indicate that we can expect little or no impact from the release of copper when the stations are operating normally and no chemicals are added to the cooling water (Refs. 4-6).

The present investigation was initiated to determine the impact of the use of copper alloys in cooling systems of nuclear power stations situated on cooling lakes. The H.B. Robinson Steam Electric Plant was selected for study because there is some recirculation of the discharge waters, and the station has a long history of operation.

SITE CHARACTERISTICS

The H.B. Robinson Steam Electric Plant is located near Florence, South Carolina, and is operated by the Carolina Power and Light Company (CP&L). The power station consists of two units. Unit 1 has a gross capacity of 185 MW and is coal fired. Unit 2 has a gross capacity of 700 MW and is nuclear. Condensers of both units are cooled with water drawn from and returned to the H.B. Robinson impoundment. When the field survey was conducted, the tubing in the condensers of both Units 1 and 2 was constructed of 70-30 copper-zinc alloy. During March 1982, the old tubing was removed and replaced with stainless steel tubing.

The Robinson impoundment is on Black Creek, a tributary of the Pee Dee River (Fig. 1). Black Creek is a typical blackwater stream exhibiting a combination of low pH (3.9 to 6.7) and darkly colored water that results from the leaching of organic material from the swampy headwater drainage.

Sample collections were made in November 1979 and in May and July 1980. Samples were collected from two sites each in the intake zone, the discharge zone, and a control site upstream of the plant. During the July 1980 collection, three additional sites (referred to here as I, II, and III) downstream of the impoundment were also sampled. The power station was operating normally during all collections.

Figure 1. Location of Units 1 and 2 of the H.B. Robinson Steam Electric Plant near Florence, South Carolina.

MATERIALS AND METHODS

SAMPLE COLLECTION AND PROCESSING

Water and Suspended Particles

During all samplings at the H.B. Robinson Steam Electric Plant, we used the following water and suspended-particle collection procedures. Filtered water was collected through an all-plastic peristaltic pump at about 50 mL/min. The water sample intake was covered with a 150-μm (pore size) nylon screen. Water samples were filtered *in situ* through a 0.4-μm (pore size), Nuclepore 293-mm (diam) membrane filter and collected into meticulously cleaned (ultraclean) polypropylene 8-L carboys (see Appendix A). A separate filter was used for filtering the water collected in each carboy. Filtration was stopped when the flow from the filter was <10 mL/min. The filter carrier was then purged of water and the filter removed and placed in an ultraclean vial. The volume of water that passed through each filter was recorded. A 1-L aliquot of filtered water was removed at the collection site from each carboy and acidified to pH 1 with HCl to reduce sorption of copper to the walls of the container.

Unfiltered water samples were collected in two ways. Water samples used to determine the copper distribution coefficients (K_ds) of suspended particles were pumped directly into ultraclean 1-L bottles. Unfiltered water samples for the analysis of organic carbon were collected in precombusted (450°C), 1-L glass-stoppered bottles by submersing them to a depth of about 0.5 m until they were filled. Triplicate 10-mL aliquots of the water were placed in precombusted glass vials for analysis of total organic carbon (TOC). From the remainder of this unfiltered water sample, two aliquots of different sizes were then filtered in triplicate through precombusted glass-fiber filters. Each loaded filter was placed into a precombusted glass vial and sealed with aluminum foil for subsequent particulate organic carbon (POC) analysis. Aliquots of the pooled filtrate were also placed into precombusted vials for subsequent dissolved organic carbon (DOC) analysis. The TOC, DOC, and POC samples were frozen as soon as possible. The analyses performed and the kind, number, and volume of samples collected from the water column at the study sites are summarized in Table 1.

Because of the difficulty of establishing differences among stations when copper concentrations are only a few micrograms per liter, extreme care was taken to keep the equipment free from contamination. Before use, the plastic water-sampling pickup tubing, the peristaltic pump chambers, and the polyvinylchloride filter carrier were acid washed and rinsed with doubly (glass-) distilled water (DDW). The containers used to transport and collect samples were cleaned carefully (see Appendix A) and transported in plastic bags. After collection, all samples were immediately sealed in the field, enclosed in plastic bags, and shipped in crushed ice to the Lawrence Livermore National Laboratory (LLNL). Samples were received at LLNL 12 to 24 h after collection.

Intake water samples were collected 3 to 4 m offshore near the entrance to the cooling system; discharge water from near the mouth of the discharge canal; and control water from Black Creek, upstream of the plant (Fig. 1). The water was sampled 30 to 60 cm below the surface during collections at all three sites. The temperature, pH, and conductivity of the water were measured (Table 2).

Table 1. Analyses performed and volumes and numbers of samples collected from study sites at the H.B. Robinson Steam Electric Plant.

Analysis	Volume of replicate (L)	Replicates	
		Intake	Discharge
	Filtered water		
Total copper (acidified)	1	4	4
Labile copper	8	3	3
Ultrafiltration	8	2	2
Dissolved organic carbon	0.01	3	3
Dissolved organic carbon	0.005	3	3
	Unfiltered water		
Total organic carbon	0.01	3	3
Copper distribution coefficient	1	3	15
	Nuclepore filters		
Weight of suspended particles	--	4	4
Copper concentration of suspended particles	--	4	4
	Glass-fiber filters		
Particulate organic carbon	--	6	6

Bedload Sediments

During all field surveys, we collected bedload sediments from intake and discharge areas and from the control area. In each sampling area, collections were made at each of two or three sites. A stainless-steel ponar dredge or plastic coring device was used to remove approximately 1 kg of sediment from the top 6 to 10 cm of the bedload. The samples were immediately placed into plastic bags, purged of any air, and tightly sealed. All samples were held at ambient temperature, and Eh and pH were measured within 4 to 6 h of collection in a glove bag filled with nitrogen. The dredged sediment samples were homogenized by kneading, a small incision was made in the bag, and the Eh and pH measurements were made. For all collections, one aliquot of sediment homogenized by kneading in a plastic bag was treated as an intact sample; a second aliquot was filtered through a 62-μm (pore size) Nitex screen to separate the fine-grain component. The <62-μm sediment fraction was washed through the screen using filtered water from the collection site.

Table 2. Temperature, pH, and conductivity of water collected at the H.B. Robinson Steam Electric Plant.

Collection date	Collection site	Temperature (°C)	pH	Conductivity ($\mu\Omega$ cm^{-1})
November 1979	Intake	20.6	5.6	--
	Discharge	30	5.7	--
	Control	--	4.7	--
May 1980	Intake	25.5	5.5	60
	Discharge	33	5.4	70
	Control	23	5.2	
July 1980	Intake	32	5.7	40
	Discharge	40	5.6	40
	Control	24.5	5.3	25
	Downstream			
	I	33	5.3	39
	II	32	4.8	60
	III	33	6.7	160

The <62-µm sediment fractions in wash water and intact sediment were held at 4°C and shipped to LLNL. On arrival, the samples of <62-µm sediment fractions in wash water were centrifuged at 90,000 x g for 20 min. The wash water was decanted from the sediment, and the fine sediments were mixed well with a porcelain spatula before analysis. Intact sediment samples collected for sediment characterization were dried at 100°C for 48 h. Samples were stored in glass containers until they were shipped to Dr. D. S. Gorsline at the University of Southern California for analysis of particle size distribution and of total carbon and $CaCO_3$ content. Particle size was determined using a settling tube apparatus. Organic material in the sediment was determined on a Leco Carbon Analyzer in which total carbon and $CaCO_3$ are measured and the organic carbon constituent is then calculated by the difference.

Mineral composition was determined by x-ray diffraction by Dr. Alan Colville at California State University at Los Angeles.

REAGENTS

J. T. Baker Ultrex-grade nitric, perchloric, and hydrochloric acids were used throughout, except as indicated. The DDW water was passed through a column of Chelex-100 resin before it was used as a solvent for all reagents and standards. All reagents were of analytical grade or higher purity. Polypropylene and Teflon labware was used.

COPPER ANALYSES

Water

Total soluble copper was determined by direct injection of a filtered, acidified water sample into a model HGA 2100 graphite furnace attached to a model 303 Perkin Elmer Atomic Absorption Spectrophotometer (AAS) and by differential pulse, anodic stripping voltammetry (DP ASV) (Ref. 9). On the AAS, sample copper concentrations were determined by the method of additions. Four 40-mL aliquots were spiked with copper to yield copper concentrations of 0.002, 0.004, 0.006, and 0.008 µg Cu/mL in addition to the original copper concentration in the sample; one 40-mL aliquot received no copper spike. The sample injection volume was 50 µL. A least-squares linear regression analysis was performed on the resulting data. The total copper originally present in the sample was obtained by dividing the y-intercept value by the slope of the regression line.

With DP ASV, copper is reduced at a potential more positive than the reduction potential (vs Ag/AgCl reference cell) and concentrated onto a mercury electrode. The amalgamated copper is measured by anodically stripping the copper from the mercury electrode by applying a potential gradient and measuring the current produced as the system reaches the oxidation potential of copper. The anodic stripping current i is proportional to the equilibrium concentration of the kinetically labile metal, $i = k_c (M^{n+})$, where k_c is an empirical constant whose value depends on the electrode geometry and surface area; cell geometry; stirring efficiency in the cell; length of preelectrolysis; scan rate of the linear stripping potential; and diffusion coefficient of copper, both in solution and in mercury (Ref. 10). A Princeton Applied Research 374 polarographic analyzer with a Hewlett-Packard microprocessor and X-Y recorder was used. The electrode system consisted of an Ag/AgCl reference electrode, a platinum counter electrode, and a hanging mercury-drop working electrode. Prepurified N_2 was used to purge samples of dissolved oxygen. All measurements were made at room temperature (20 ± 2°C). Analyses were performed in Teflon cups that had been washed with nitric acid and rinsed with purified water.

Labile copper was measured using Chelex-100 ion-exchange resin and by polarographic analysis. The Riley and Taylor method was used to determine the amount of copper bound to the Chelex-100 ion-exchange resin (Ref. 11). The filtered water samples were processed immediately upon arrival at LLNL. No alteration was made in the pH of the water. Each 8-L carboy was fitted with tubing to permit the water to be gravity fed into a 2-cm-diam borosilicate glass column packed with 5 cm of Chelex-100 resin in the ammonium form (Fig. 2). The rate of flow of water through the column did not exceed 5 mL/min; flow rate was adjusted by altering the height of the water sample carboy. After the water sample passed through the column, the column was eluted with two 10-mL aliquots of $2\underline{N}$ HNO_3 to collect the species of copper bound to the resin. After use, the filtered-water sample carboys were rinsed thoroughly with 50 mL of $2\underline{N}$ HNO_3. This acid rinse removed copper adsorbed on the carboy walls. Copper recovered in the acid rinses was considered to be part of the labile component.

Eluants from the columns and the acid rinses of the carboys were analyzed by direct aspiration into the flame of the AAS or by direct injection into a graphite furnace attachment to the AAS. All standards were prepared in $2\underline{N}$ HNO_3.

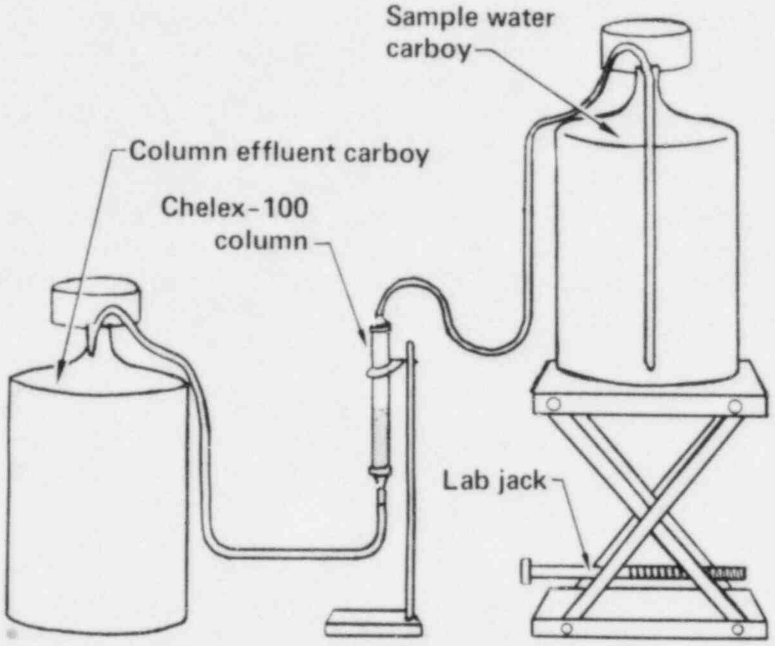

Figure 2. Gravity-fed system used to pass filtered water sample through Chelex-100 resin.

Because the levels of copper in the water were low, special care was taken in the preparation of the Chelex-100 resin and the columns (Ref. 4). The resin was washed carefully, converted to the ammonium form, and packed into a column in a laminar-flow clean hood using talc-free gloves. Average copper values for the Chelex-100 column blanks were subtracted from those of the samples.

Copper in the column blanks was low; the eluant contained 2.8 ± 0.6 x 10^{3} µg Cu/mL. This was usually <2% of the total copper in the sample eluant.

Labile copper concentrations were determined also by DP ASV. Either 5 or 10 mL of water were added to a cup and then the sample was purged with N_2 for 10 min, deposited for 6 min at -0.6 V, and then scanned from -0.6 to 0 V or 0.1 V at 10 mV/s. A medium mercury-drop size was used, and the sensitivity was 1 µA full scale. Supporting electrolyte for the analyses was provided by the addition of 100 µL of 1M $NaClO_4$. Subsequent to the analysis for labile copper, each sample was acidified with 50 to 150 µL of perchloric acid to dissociate the copper ligands, digested for up to 2 wk, and then analyzed for total copper.

Suspended Particles

The wet and dry weights of particulate material collected on the Nuclepore filters was determined and analyzed for copper. The filters were placed in clean platinum crucibles for drying, ashing, and digesting. The filters were dried at 100°C for

48 h; then the dry weights were recorded. The filters were then placed in a muffle furnace, the temperature was raised from 100 to 450°C at 50°C/h, and the samples were ashed for 48 h at 450°C. Each filter was digested with 10 mL of analytic-grade, concentrated HCl and 10 mL of analytic-grade HF. After the samples were evaporated to dryness at about 200°C, 10 mL of analytic-grade HNO_3 were added and the samples again evaporated to dryness. The samples were then dissolved in 2<u>N</u> HNO_3, transferred to 25-mL volumetric flasks, brought to volume, and analyzed on the AAS. Copper concentrations were corrected for the amount of copper in filters and reagent blanks. Filters plus reagent blanks averaged 3.2 μg copper per digestion. This was usually less than 0.5% of the total copper recovered from the suspended particles on the filter. Suspended particulate dry weights were also corrected for filter-blank dry weights. Because it was noted that filter dry-weight blanks vary with different filter lots, care was taken to keep track of the lots used.

Bedload Sediments

Total copper in the intact sediments and <62-μm sediment fractions was determined after acid digestion. Sediments were dried at 100°C for 48 h and then powdered using a porcelain mortar and pestle. Triplicate aliquots of sediment samples of about 0.25 g were weighed in platinum crucibles and ashed at 450°C for 48 h. Total copper in the sediments was determined by the same acid-digestion procedure described for the suspended particles. Copper concentrations in the sediments were corrected for the amount of copper in the reagent blanks. The blanks averaged 0.3 ± 0.1 μg copper per digestion. This was usually less than 2% of the total copper recovered in sediments. Our procedures were verified by analyzing National Bureau of Standards (NBS) orchard leaves on three separate occasions. Our analyses averaged 12.2 ± 1 μg Cu/g dry weight. The NBS analysis yielded 12 ± 1 μg Cu/g dry weight.

APPARENT COMPLEXING CAPACITY

The apparent complexing capacity (ACC) was determined using the polarographic method of Chau et al. (Ref. 12). Either 5- or 10-mL samples of filtered water were aliquoted into cups and then spiked with quantities of copper that would result in concentrations of added copper ranging from 1 to 100 μg/L. The spiked samples were equilibrated 15 to 18 h at 10°C; then a labile copper analysis was performed on each sample. The area of the copper peak on each voltammogram was determined and plotted on the Y-axis versus concentration of added Cu^{2+}. The complexing capacity of the sample corresponds to the copper concentration intercepted on the abscissa.

ULTRAFILTRATION

Two 2-L aliquots of filtered water that had been stored at 4°C since collection (24 to 48 h) were spiked with ^{64}Cu, allowed to equilibrate a minimum of 12 h, and then subjected to ultrafiltration (Fig. 3). After the 12-h equilibrium period, the ^{64}Cu serves as an effective tracer for the different species of stable copper present in the water at the time of analysis.

One of the 2-L aliquots was photooxidized with UV light to reduce the concentration of dissolved organic matter. The UV treatment destroys most effectively those molecules that strongly absorb UV irradiation. Two drops of 35%

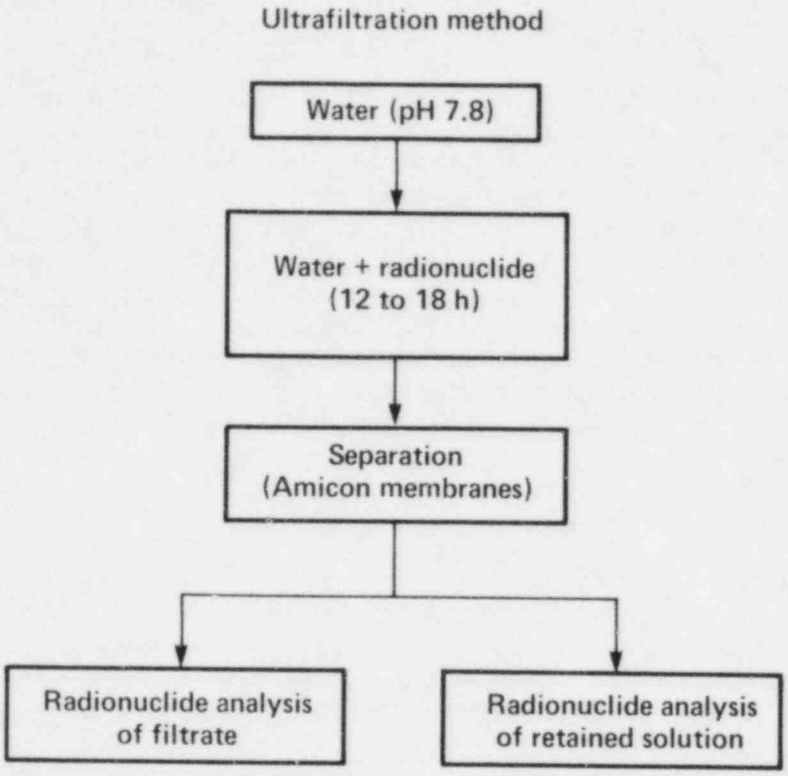

Figure 3. Ultrafiltration procedure flow diagram.

H_2O_2 were added to each 100 mL of water to accelerate the oxidation. The reaction rate was also increased by the higher temperature that occurs during irradiation (60°C). Care was taken in the UV irradiation step to avoid contaminating the samples. The quartz irradiation tubes were rinsed with 0.1N HCl and then with DDW before use. To determine the loss of copper to the walls, aliquots taken before and after irradiation were counted for ^{64}Cu; in all samples, the ^{64}Cu concentrations were lower after irradiation.

Ultrafiltration was performed with standard model 402 cells, which contained magnetic stirrers (Amicon Corporation, Lexington, MA). Membranes used for the experiment were the XM-100A, UM-10, and UM-2 types (Amicon Corporation Diaflo). These membranes are made of complex, noncellulosic hydrous gels of inert polymers, which allow for retention of molecules above a specified molecular weight. The nominal molecular weight retentions of the membranes used in this test are as follows: XM-100A, 100,000; UM-10, 10,000; and UM-2, 1,000. The retention is related to the shape, as well as the size, of the molecules. For elongated molecules, the molecular weight cutoff is larger than the nominal one. Some leaching of organic matter, resulting mostly from the glycerin protective coating applied by the manufacturer, occurs when these membranes are first used.

All membranes were pretreated to reduce organic material and metal contamination. Under positive N_2 pressure, 50 mL of 0.1N HCl and 2 L of DDW were passed through the membranes sequentially. This procedure was adopted after monitoring the filtrates on a spectrophotometer at 200 nm and analyzing the filtrate for soluble organic carbon; the treatment resulted in adequate reduction of potentially interfering substances.

Each ultrafiltration experiment was initiated by transferring 270 mL of the ^{64}Cu-spiked water to an ultrafiltration cell. The water was stirred for 3 min, three 10-mL aliquots were removed for counting, the remaining 240 mL was subjected to positive N_2 pressure and constant stirring until 120 mL of filtrate was collected, and then the cell was vented. The filtrate was sampled serially to monitor the changes in ^{64}Cu concentration; a 10-mL sample was taken from each of the first, second, and third 40-mL aliquots of the filtrate. The retentate was sampled only after venting. The filters were removed and placed in vials for counting. The cell assembly was rinsed well with 50 mL of 0.1$\underline{N}$ HCl, and a 10-mL aliquot of this acid wash was counted. Recovery of the ^{64}Cu present in the initial test solution was calculated from the ^{64}Cu concentrations in the different fractions.

ORGANIC CARBON ANALYSES

Analyses for organic carbon were performed on unfiltered water samples as well as the soluble and particulate fractions of water that had been filtered through precombusted glass equipment. The filter and filtrate were analyzed for POC and DOC, respectively, with an Oceanography International Carbon Analyzer by the standard persulfate oxidation method (Ref. 13). Unfiltered water was analyzed for TOC.

DISTRIBUTION COEFFICIENTS

Suspended Particles

Copper K_ds of particles in the unfiltered water were determined. Each 1-L bottle containing water was spiked with ^{64}Cu within a few hours of arrival at LLNL. The bottles were placed in a water bath at 12 to 14°C and shaken continuously before filtration. The times between the addition of the ^{64}Cu spike and filtration were generally 0, 0.25, 0.5, 0.75, 1, 4, 8, 12, 16, and 24 h.

The entire sample of water was filtered through a 0.45-μm (pore size) Millipore filter. After filtration, the bottle and the filtration apparatus were rinsed with 25 mL of 0.1$\underline{N}$ HCl to remove sorbed ^{64}Cu. Activities of ^{64}Cu were determined in the unfiltered water, in duplicate samples of the filtrate, in the material on the filter, and in the acid wash. Recovery of the added radionuclide was generally >95%.

In preliminary experiments, the sample of water was filtered through two membranes. The first membrane contained activity from ^{64}Cu on particles and ^{64}Cu sorbed on the membrane; the second membrane contained only sorbed ^{64}Cu. The difference between the two represents the activity associated with the particles. The quantities sorbed were extremely small compared with those associated with the particles. The use of two filters was therefore discontinued in later samples, and no correction was made for ^{64}Cu sorbed by the membrane. All samples were counted in a gamma well counter and corrected for background counts and decay to the zero time of the experiment.

The K_ds were calculated from the data and the following relationship:

$$K_d = \frac{fs}{(1 - fs)} \times \frac{V}{W} , \qquad (1)$$

where

fs = fraction of ^{64}Cu on filter,
$(1 - fs)$ = fraction of ^{64}Cu in filtrate,
V = weight of water (g), and
W = dry weight of particles (g).

The K_d as defined is dimensionless, and greater sorption of ^{64}Cu to the particulate fraction results in higher K_ds.

Bedload Sediments

The K_ds of bedload sediments were determined by weighing about 0.75 g of sediment directly into acid-washed, 6-oz polyethylene bottles and adding 100 mL of filtered water that was spiked with tracer quantities of ^{64}Cu. The bottles were placed in a water bath at 12 to 14°C and shaken continuously for approximately 24 h. The samples were processed by procedures similar to those used for suspended particle samples. Duplicate samples were analyzed.

RESULTS AND DISCUSSION

WATER COLUMN

Soluble and Particulate Copper Concentrations

Total copper concentrations in the discharge waters differed greatly during the three sampling periods; the range was 32.6 to 79.3 µg Cu/L (Table 3). The highest concentration we observed was in November 1979. However, the maximum concentration that was present in discharge waters and the total range that occurred may have been considerably greater than we observed. In the routine analysis of discharge waters conducted by CP&L, total copper concentrations of >150 µg/L were documented approximately 15 times during 1981 (Ref. 14).

Concentrations in the intake and discharge waters were about an order of magnitude higher than in those from the control site. The differences between intake and discharge waters were not constant and the largest was detected in November 1979. Samples collected downstream from the power station were lower than those from the intake and discharge zones but higher than those from the control area. The first downstream site was at the second bridge below the H.B. Robinson Dam, the second at the Prestwood Dam, and the third about 2 mi below the Prestwood Dam.

The partitioning of copper between the soluble and particulate fractions of the water was highly variable. The particulate fraction was about 20% of the total copper in water collected from both the intake and discharge sites in November 1979, about 30% in that collected in May 1980, and about 40% in that collected in

Table 3. Copper concentrations (μg/L) in water collected at the H.B. Robinson Steam Electric Plant.

Collection date	Collection site	Total	Fraction			
				Soluble		
			Particulate	Labile[a]	Bound	Total
Nov. 1979	Intake	57.8	11.5	26.4	19.9	46.3
	Discharge	79.3	18.6	33.9	26.8	60.7
	Control	3.1	0.5	1.5	1.1	2.6
May 1980	Intake	33.9	10.4	12.3	11.2	23.5
	Discharge	48.1	12.8	18	17.3	35.3
	Control	5.8	0.7	0.3	4.8	5.1
July 1980	Intake	27.4	11.5	9.1	6.8	15.9
	Discharge	32.6	14.7	13	4.9	17.9
	Control	3.1	0.3	0.6	2.2	2.8
	Downstream					
	I	22.4	8.3	--	--	14.1
	II	11.7	4.6	--	--	7.1
	III	16.8	9.7	--	--	7.1

[a] Chelex-100-labile copper.

July 1980. The control water had low percentages of particles; values ranged from 10 to 16%. Except in downstream sample III collected in July 1980, the percentage of copper was larger in the soluble than in the particulate fraction of the water; the range was from 55 to 88%.

Characterization of suspended particles in the water column showed that the variations in copper concentrations in the particulate fraction resulted from differences both in the quantities of the particles and in the amount of copper associated with the particles (Table 4). Large differences were also observed in K_ds and POC.

Total copper concentrations in freshwater has been determined for a number of sites (Ref. 15). Concentrations of copper observed in samples of discharge water from the H.B. Robinson site were higher than most of those from other power stations. The higher concentrations may be attributable to the low pH of the water. High total concentrations were reported also in drainage from a copper mine near Lake George in Uganda (Ref. 16). However, in this body of water the pH ranged between 8 and 10.

Large variations in partitioning of copper between soluble and particulate fractions have also been determined at other sites (Ref. 15). Differences may result from the primary physicochemical form of the copper discharged, from reactions occurring under the variable conditions that are present in the environment, or from changes in hydrology and sedimentation. Important environmental variables

Table 4. Characteristics of suspended particles in water collected at the H.B. Robinson Steam Electric Plant.

Collection date	Collection site	K_d	Copper (µg/g dry)	Suspended particles (mg/L)	POC[a] (mg/L)
Nov. 1979	Intake	29,300	2,700	4.1	0.5
	Discharge	19,400	2,600	6.7	0.6
	Control	15,900	131	4.8	0.2
May 1980	Intake	2,300	1,300	8.1	0.9
	Discharge	4,400	1,500	8.9	1.1
	Control	3,700	50	15.8	0.4
July 1980	Intake	37,200	1,300	9.5	0.9
	Discharge	25,400	1,280	11.7	0.8
	Control	10,200	15	17.1	0.7
	Downstream				
	I	8,000	549	15.1	1.4
	II	20,200	375	12.4	0.5
	III	16,100	310	31.1	3.2

[a] Particulate organic carbon.

include salinity, pH, Eh, and concentrations of other metals; important processes include coagulation, coprecipitation, and sorption.

Copper Sorption Rates

The rate of sorption of radiolabeled copper with the particulate phase of unfiltered water collected from the discharge area was generally rapid; equilibrium occurred within the first 15 min after the ^{64}Cu was added.

Copper Speciation

The distribution of copper between labile and bound forms in the soluble fraction of water collected at H.B. Robinson differed greatly (Table 3). At the three collection sites, both the absolute amounts in the labile and bound fractions and the percentages differed with sampling time. The percentages of labile copper in the soluble fraction of the intake water samples were similar, averaging about 55%. The percentages of labile copper in discharge water samples ranged from 51 to 73%. The highest percentage was observed in July and may possibly have been due to the high water temperature in the impoundment during the summer months (Ref. 17).

Labile copper concentrations determined using Chelex 100 differed from those determined by DP ASV. The two methods are reported to quantify different species of labile copper (Ref. 18). The Chelex-100 labile copper is the fraction that binds to Chelex-100 ion exchange resin at pH 7.8, and the DP ASV labile copper is the fraction that is available for deposit onto, and stripping from, a hanging mercury-drop electrode at pH 7.8. We had some difficulty in determining labile copper by DP ASV. We attributed this to poisoning of the electrode by the high concentrations of dissolved organic material that was present in the waters. This organic material was quite refractory; we found that it was necessary to digest the DP ASV samples at pH 1 for as long as two weeks to obtain total soluble copper values that agreed with those determined by AAS.

Apparent Complexing Capacity

All samples of the intake and discharge waters analyzed by DP ASV showed DP ASV-labile copper. This indicates that there were insufficient ligands in the appropriate chemical form to bind all the copper. An indication of the variation in the availability of copper-binding ligands can be obtained by comparing the quantities of bound copper in the water samples. Values of bound copper in the discharge waters were not the same as those in the intake waters; the values from both sites ranged from 4.9 to 27 µg Cu/L.

Concentrations of organic carbon in the waters from the three collection sites were determined (Table 5). Concentrations of DOC ranged between 3.8 and 6.4 mg C/L and showed no relationship with bound copper (compare Table 3 and 5). However, some correlation is apparent between DOC concentration and total copper in water samples from the three sites.

The measurement of complexing capacity of waters has been reviewed recently (Ref. 19). The methods used to determine complexing capacity include solubilization (Refs. 20-24), biological response (Refs. 25-27), voltammetry (Refs. 4, 5, 18, 21, 28-37), ion exchange (Ref. 38), and selective ion electrodes (Refs. 39, 40). The values obtained for complexing capacity range from 32,000 µg Cu/L for an oil field brine (Ref. 20) to 1 µg Cu/L for pristine waters off the coast of California (Ref. 4). In general, the complexing capacities of marine waters are lower than those for estuaries and freshwater ecosystems.

High and variable values for ACC were determined for both estuarine water and freshwaters (Refs. 5, 15). These contrast with the low values observed at Diablo Canyon and San Onofre Nuclear Power Stations. However, it is expected that higher concentrations of humic and fulvic acids would be present in freshwater and estuarine water than in marine water because of the runoff from the land and the high productivity of many freshwater and estuarine ecosystems.

Copper in Molecular Weight Fractions

In the filtered water samples collected from the discharge zone of the power station, the percentage of copper in each of four MWFs (<1,000; >1,000, <10,000; >10,000, <100,000; and >100,000) differed with time and site. Because of the uncertain availability of ultrafiltration for the ^{64}Cu-tagged copper that was sorbed on the walls and membrane of the ultrafiltration chamber, the percentage in each MWF was calculated in two ways: (1) by assuming that the available ^{64}Cu-tagged copper was only that in the filtrate and in the solution remaining in the chamber (retentate), and (2) by assuming that the available copper was that which was recovered from all parts of the ultrafiltration system. Table 6 shows the results from the ultrafiltration of the water samples, assuming unavailability of copper sorbed on the walls and membrane. In contrast, Table 7 shows the results based on

Table 5. Dissolved (DOC), particulate (POC), and total (TOC) organic carbon (mg C/L) in water collected at the H.B. Robinson Steam Electric Plant.

Collection date	Collection site	DOC	POC	TOC
Nov. 1979	Intake	4.9	0.5	5.4
	Discharge	4.9	0.6	5.5
	Control	6.4	0.2	6.6
May 1980	Intake	5.7	0.9	6.6
	Discharge	4.6	1.1	5.6
	Control	6.2	0.4	6.6
July 1980	Intake	4.2	0.9	5.1
	Discharge	3.8	0.8	4.6
	Control	4.9	0.7	5.6
	Downstream			
	I	2.7	1.4	4.1
	II	3.3	0.5	3.8
	III	8.6	3.2	11.8

the assumption of availability of all the copper recovered. A comparison of the data in Tables 6 and 7 shows that the agreement is better for the untreated than for the UV-treated water. This is expected because more copper is sorbed after the organic matter is destroyed by UV treatment (Table 8).

The largest fraction of ^{64}Cu-tagged copper in the untreated samples was in the >10,000, <100,000 MWF. In waters treated with UV light for 6 h, the percentage of the copper increased in the <1,000 and >10,000, <100,000 MWFs and decreased in the >1,000, <10,000 and >100,000 MWFs. In May and July 1980, the samples were spiked with ^{59}Fe as well as ^{64}Cu. The distribution of the ^{59}Fe before and after treatment with UV differed from that of the ^{64}Cu. However, more than 48% of both ^{64}Cu and ^{59}Fe was present in the >10,000, ≤100,000 fraction in all of the non-UV-treated waters that were collected. For ^{59}Fe, almost all activity was associated with the >100,000 MWF after UV treatment.

The DOC in the untreated waters was not present in the four MWFs in the same percentages as that of copper and iron and differed greatly with sampling time. The sample collected from the discharge area in July had a much larger percentage of DOC in the <1000 MWF. Analysis for DOC after UV treatment indicated that most of the DOC was not destroyed. Similar results were observed in water collected from the Surry Nuclear Power Station in October 1978 (Ref. 5). These data indicate the presence of small organic molecules that do not absorb UV light and consequently are not degraded by the 6-h exposure.

Recovery of ^{64}Cu added to the water samples initially ranged between 95 and 104%; the mean is 99 ± 4 in the untreated water and 94 ± 5 for the UV-treated water. The final distribution of the ^{64}Cu spike added to each water sample

Table 6. Percentages of ^{64}Cu, ^{59}Fe, and dissolved organic carbon (DOC) in different molecular weight fractions of ultrafiltered water from the H.B. Robinson Steam Electric Plant assuming unavailability of copper sorbed on walls and membranes.

Collection date and location	Analysis	UV treatment (h)	Molecular weight fraction			
			<1,000	>1,000, <10,000	>10,000, <100,000	>100,000
Nov. 1979 (Discharge)	^{64}Cu	0	12	15	65	8
		6	24	2	70	4
	DOC	0	0	29	53	18
		6	0	0	0	0
May 1980 (Discharge)	^{64}Cu	0	12	26	48	14
		6	22	1	69	8
	^{59}Fe	0	4	6	64	26
		6	2	0	2	96
	DOC	0	15	2	19	64
		6	0	0	0	0
July 1980 (Discharge)	^{64}Cu	0	13	24	51	12
		6	41	0	59	0
	^{59}Fe	0	1	3	54	42
		6	1	0	0	99
	DOC	0	43	21	9	27
		6	97	3	0	0
July 1980 (Control)	^{64}Cu	0	10	12	69	9
		6	20	6	74	0
	^{59}Fe	0	2	2	55	41
		6	1	0	3	96

differed with the water and treatment (Table 8). The percent of the ^{64}Cu in the dissolved fraction (filtrate and retentate) of untreated water for all sampling periods was 93 ± 4, and that of UV-treated water was 92 ± 8. The amount of ^{64}Cu in the dissolved and sorbed fractions underwent little change after UV treatment. The pH of all H.B. Robinson water samples used in ultrafiltration ranged between 5 and 6.2. A negligible pH change of ≤ 0.1 pH units occurred after UV oxidation for 6 h, unlike observations by Laxen and Harrison (Ref. 41). The percent of ^{64}Cu sorbed onto the filters was 3.5 for untreated water and 2.9 for UV-treated water. The acid wash of the walls recovered 3.2% ^{64}Cu in untreated water and 4.7% in UV-treated water. The ^{59}Fe behaved more typically like ^{64}Cu from previous

Table 7. Percentages of ^{64}Cu, ^{59}Fe, and dissolved organic carbon (DOC) in different molecular weight fractions of ultrafiltered water from the H.B. Robinson Steam Electric Plant assuming availability of all copper recovered.

Collection date and location	Analysis	UV treatment (h)	Molecular weight fraction			
			< 1,000	> 1,000, < 10,000	> 10,000, < 100,000	> 100,000
Nov. 1979 (Discharge)	^{64}Cu	0	11	14	61	7.8
		6	23	2.5	67	3.8
	DOC	0	0	29	53	17
		6	0	0	0	0
May 1980 (Discharge)	^{64}Cu	0	11	25	46	14
		6	21	0.4	66	8.2
	^{59}Fe	0	3.3	5.1	59	24
		6	0.9	0	1.3	52
	DOC	0	15	1.6	19	64
		6	0	0	0	0
July 1980 (Discharge)	^{64}Cu	0	11	21	45	11
		6	34	0	50	0
	^{59}Fe	0	0.8	2.8	46	36
		6	1	0	0	68
	DOC	0	43	21	9.6	27
		6	97	2.6	0	0
July 1980 (Control)	^{64}Cu	0	9.4	11	64	9.2
		6	18	5.9	69	0
	^{59}Fe	0	2	1.6	50	37
		6	1.1	0	1.8	57

tests at Salem and Surry after UV oxidation (Ref. 5). The percent of ^{59}Fe sorbed or trapped on the membrane filter was 7.8 in untreated water and rose to 38 after UV oxidation. This increase indicates the presence of large inorganic iron complexes that occur after the organic matter is destroyed. The acid wash recovery of ^{59}Fe remained low following UV treatment.

It is well established that copper may exist in a number of chemical and physical forms. In Table 9, the chemical forms are related to molecular size. One reaction that may occur is the formation of colloids; these are generally greater than 100,000 in molecular weight. Another reaction is the sorption of one metal to

Table 8. Percentages of ^{64}Cu and ^{59}Fe recovered in the dissolved (filtrate plus the solution remaining in the ultrafiltration cell) and sorbed (to the walls and membrane) fractions of the ultrafiltered water.

Collection date and location	Analysis	UV treatment (h)	Dissolved fraction	Sorbed fraction	
				Membrane	Wall
Nov. 1979 (Discharge)	^{64}Cu	0	95	3	2
		6	96	2	2
May 1980 (Discharge)	^{64}Cu	0	96	3	1
		6	96	2	2
	^{59}Fe	0	92	6	2
		6	54	45	1
July 1980 (Discharge)	^{64}Cu	0	89	4	7
		6	84	5	11
	^{59}Fe	0	86	11	3
		6	69	29	2
July 1980 (Control)	^{64}Cu	0	94	4	2
		6	94	2	4
	^{59}Fe	0	91	6	3
		6	60	39	1

colloids of other metals. In this study, we found that UV treatment resulted in an increase of ^{59}Fe but not of ^{64}Cu in the >100,000 MWF. This reaction of copper was different from that observed in water from other power stations (Refs. 4, 5, 15). The behavior of the ^{64}Cu-tagged copper at H.B. Robinson may be related to the lower pH of the water. It does not appear to be related to the operation of the power station because in water from the control site collected in July 1980, the behavior of ^{64}Cu and ^{59}Fe before and after UV treatment was similar to that observed in water from the discharge area collected in May and July 1980. That is, the percentage of ^{59}Fe in the >100,000 MWF increased greatly, whereas the percentage of ^{64}Cu remained greatest in the >10,000, <100,000 MWF.

The fraction of ^{59}Fe sorbed on the membrane increased following UV treatment. Increases in this fraction indicate changes in physicochemical forms of the iron when the organic matter, which contains important binding sites, has been removed. The increase in sorbed fraction is most likely a result of large inorganic complexes that may be retained in the pores of the membrane.

Most researchers agree that organic ligands form complexes and chelates with copper that affect transport and availability in natural waters (Refs. 43-45). Two mechanisms by which organic compounds can solubilize metals are (1) by forming

Table 9. Chemical species of copper.[a]

	Filterable						
	Free metal ions	Inorganic ion pairs, inorganic complexes	Organic complexes, chelates	Metal species bound to high molecular-weight organic material	Metal species in the form of highly dispersed colloids	Metal species sorbed on colloids	Precipitates, organic particles, remains of living organisms
	Cu^{2+} (aq.)	$Cu_2(OH)_2^{2+}$ $CuCO_3$	Cu-SR[b] Cu-OOCR	Cu-lipids Cu-humic-acid polymers Gelbstoffe Cu-polysaccharides	$Cu(OH)_n$-$Me(OH)_n$	$Cu(OH)_n$, $CuCO_3$, CuS, etc. on clays	--
Ultrafiltration diameter range:	←	12 Å	15 Å	52 Å		1,000 Å	--
Molecular weight:		< 1,000	> 1,000, < 10,000	> 10,000, < 100,000	> 100,000	--	--

[a] Modified from Stumm and Brauner (Ref. 42).

[b] R = organic ligand.

metal-ligand complexes with sorption characteristics different from those of the free-metal ion, or (2) by solubilizing the iron and manganese oxides and thus releasing sorbed trace metals (Ref. 45). Humic substances form an important group of dissolved organic material, which includes refractory organic molecules that constitute approximately 90% of the dissolved organic material in seawater.

Humic substances are classified by solubility and references are usually to two classes: humic acid, which is soluble in base and insoluble in acid, and fulvic acid, which is soluble in both base and acid. The molecules consist of long carbon chains; complex aromatic structures (Ref. 46); and oxygen, nitrogen, sulphur, and phosphorus functional groups such as the aromatic amine (-N:) and carboxylate (-CO^-) groups. Humic substances may scavenge copper ions and thus play a major role in its physicochemical transformation.

Several researchers have investigated the MWFs of aquatic humus by ultrafiltration (Refs. 47, 48). Allen studied some of the ecological implications of dissolved organic matter after fractionating lake water into molecular weight compartments (Ref. 49). Giesy and Briese have extensively studied various metal associations of naturally occurring, aquatic organic fractions (Ref. 48). Smith determined the copper complexation capacities of various MWFs of dissolved organic matter in estuarine waters by a combination of ultrafiltration and anodic stripping voltammetry techniques (Ref. 30). Laxen and Harrison studied the concentration and size distribution of different species of copper in effluent from sewage disposal plants using filtration, anodic stripping voltammetry, and Chelex-100 ion exchange resin; they concluded that interactions with organics are important in copper speciation patterns (Ref. 41).

The source and nature of the organic matter associated with the copper are as yet unresolved. Organic compounds may be excreted by aquatic organisms, may arise from the decomposition of dead organisms, or may be introduced in freshwater runoff. Foster and Morris suggest that concentrations of organic-bound copper in seawater result at least partially from active marine production of organic matter (Ref. 50).

The variation of DOC in water samples from Salem and Surry was small (2.2 to 5.1 mg C/L) compared with the variation in ACC (4 to 60 μg Cu/L). More data are required before sources of seasonal variation can be identified.

We determined the concentrations of some elements as well as anions in the soluble fraction of water collected in May and July 1980 (Tables 10 and 11). Chloride and sulfate were the predominant anions. Only copper, zinc, and calcium were consistently higher in the intake and discharge areas than in the control area.

BEDLOAD SEDIMENTS

Copper Concentrations

Copper concentrations in intact bedload sediments from the intake and discharge areas were considerably higher than those from the control area (Table 12). Some of the highest concentrations were determined in sediment from the intake area. In all of the samples collected, the copper concentrations in the <62-μm fractions were generally higher than those in the intact sediments.

Table 10. Concentrations of soluble elements (µg/L) in water collected at the H.B. Robinson Steam Electric Plant.

Element	May 1980			July 1980					
	Intake	Discharge	Control	Intake	Discharge	Control	Downstream		
							I	II	III
Al	99	92	81	<16	24	74	27	61	139
As	<40	<40	<40	<100	<100	<100	<100	<100	<100
B	8	8	9[a]	<12	<12	<12	12	<12	45
Cd	<1	<1	<1	<3	<3	<3	<3	<3	<3
Co	<4	<4	<4	<6	<6	<6	<6	<6	<6
Cu	24	32	2	20	21	<2	9	17	9
Fe	96	58	54	66	63	120	97	46	206
Li	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	1	3
Mn	25	23	18	11	11	11	9	20	36
Mo	<10	<10	<10	<11	<11	<11	<11	<11	<11
Ni	<1	2[a]	3[a]	<14	<14	<14	<14	<14	<14
P	<130	<130	<130	<82	<82	<82	<82	<82	<82
Pb	<20	<20	<20	<22	<22	<22	<22	<22	<22
Se	<70	<70	<70	<60	<60	<60	<60	<60	<60
Si	1,000	1,100	890	1,200	1,300	2,000	830	1,500	1,300
Sr	9[a]	6[a]	5[a]	6	7	<3	9	11	21
Ti	<1	<1	<1	<1	<1	<1	<1	<1	<1
V	<3	<3	<3	<2	<2	<2	<2	<2	3
Zn	19	19	11	28	52	<6	20	20	65
Ca	6,000	7,900	650	1,500	1,600	530	1,400	1,100	2,900
K	490	490	440	380	410	250	670	440	1,100
Mg	550	490	410	450	430	330	670	510	740
Na	1,700	1,700	1,500	1,600	1,600	1,200	3,500	2,000	13,000

[a] Fractional standard deviation = 0.25.

Large differences with sampling time were found in the copper concentrations in interstitial waters; the highest concentrations were observed in July. These differences may be related to oxidizing and reducing states of the sediments. The characteristics of the sediments differed with sampling site; differences were observed in the color, Eh, and pH of the sediments (Table 13).

Considerable controversary exists about the application of Eh measurements. It is usually accepted that Eh is an index of oxidizing or reducing conditions but cannot be used to demonstrate the presence or absence of oxygen (Ref. 51). It is apparent from the measurements taken that both oxidizing and reducing conditions were present. However, it is not known whether these are the function of the biological consumption of oxygen or the amount of soluble iron and microbial-generated hydrogen sulfide. Regardless of the cause of the change in potential, it can be expected that the physicochemical form of the copper will differ under oxidizing and reducing conditions.

Table 11. Concentrations of anions (µg/L) in water collected near the H.B. Robinson Steam Electric Plant.

Ion	May 1980			July 1980		
	Intake	Discharge	Control	Intake	Discharge	Control
F^{-1}	∿70	∿50	∿50	50	150	100
Cl^{-1}	2000	1800	1730	2300	2400	1800
NO_2^{-1}	ND[a]	ND	ND	ND	ND	ND
PO_4^{-3}	ND	ND	ND	ND	ND	ND
Br^{-1}	ND	ND	ND	ND	ND	ND
NO_3^{-1}	ND	ND	ND	ND	430	220
SO_4^{-2}	3200	4000	1200	4000	7900	1400

[a] Not detected.

Distribution Coefficients

The copper K_ds of intact bedload sediments collected from the different sites in the intake, discharge, and control areas differed with area and sampling time (Table 14). The K_ds were usually higher in the <62-µm fraction than in intact sediments. Considerable heterogeneity of K_ds was found at all sampling areas.

The iron K_ds of the bedload sediments were also determined. The K_ds for iron were always higher than those for copper (Table 14).

Information on copper K_ds is limited to that which we obtained at other power stations. The K_ds of intact sediments from the discharge area of the San Onofre Nuclear Power Station ranged from 50 to 400 and those from Diablo Canyon from 50 to 570 (Ref. 6). These are much lower values than the 3,800 to 48,000 determined for intact sediments from the discharge area at Surry and the 250 to 33,000 for the comparable area at Salem.

Particle Size Distribution, Carbon Content, and Mineral Composition

Selected sediment samples were analyzed for particle size distribution, organic carbon, and calcium carbonate (Table 15). Sediment from the discharge area appeared to be high in organic carbon. The mineral composition was determined with a combination of microscope examination and x-ray diffraction. Quartz predominated in all samples, although the intake sediments contained some mica and some of the downstream sediments contained a small amount of steel-mill slag (gehlinite-akermainte).

Table 12. Copper concentrations in bedload sediments (μg/g dry weight) collected at the H.B. Robinson Steam Electric Plant.

Collection area	Component	Collection date and site					
		November 1979		May 1980		July 1980	
		Site 1	Site 2	Site 1	Site 2	Site 1	Site 2
Intake	Intact sediments	5.8	4.4	260	185	181	183
	Interstitial water	21	26	--	--	0.13[a]	
	<62-μm fraction	65[a]		252	180	314[a]	
Discharge	Intact sediments	34	6.1	33	46	72	68
	Interstitial water	2290	86	--	--	1.29[a]	
	<62-μm fraction	822[a]		105	112	575[a]	
Control	Intact sediments	3.7	1.3	0.9	0.9	0.6	0.5
	Interstitial water	71	38	--	--	0.14[a]	
	<62-μm fraction	27[a]		24	25	5[a]	
Downstream I	Intact sediments	145	--	--	--	11.6	--
	Interstitial water	--	--	--	--	--[b]	--
II	Intact sediments	162	--	--	--	5.4	--
	Interstitial water	--	--	--	--	0.16	--
III	Intact sediments	--	--	--	--	24	--
	Interstitial water	--	--	--	--	0.02	--

[a] Composite sample.

[b] Too sandy to collect interstitial water.

Table 13. Characteristics of sediments collected at the H.B. Robinson Steam Electric Plant.

Collection date	Collection area	Characteristics		
		Sites	Eh, pH	Comments
Nov. 1979	Intake	1,2	--	Light tan, sandy with white chalk inclusions
	Discharge	1	--	Brown, sandy
		2	--	Black, sandy with organic material present
	Control	1,2	--	Brown, sandy with organic material present
May 1980	Intake	1	Eh, -50; pH, 4.7	Tan, sandy
		2	Eh, -60; pH, 4.6	
	Discharge	1	Eh, +60; pH, 4	Gray, sandy with numerous black particles
		2	Eh, +65; pH 4	
	Control	1	Eh, +10; pH, 4.5	Gray, sandy with small amount of organic material
		2	Eh, +30; pH, 4.5	
July 1980	Intake	1	Eh, -210	Fine clay, gray-brown with light gray inclusions
		2	Eh, -110	
	Discharge	1	Eh, -160	Fine clay, ∿50% sand with small amount of organic material
		2	Eh, -80	
	Control	1	Eh, +60	Gray, sandy with ∿5% black organic material
		2	Eh, +50	
	Downstream	I	Eh, +10	Coarse sand, very hard packed
		II	Eh, -10	Sandy
		III	Eh, -260	Oily, sulphur smell

Table 14. Distribution coefficients for bedload sediments collected at the H.B. Robinson Steam Electric Plant.

Collection date	Collection site	Intake		Discharge		Control	
		Intact	<62 µm	Intact	<62 µm	Intact	<62 µm
				Copper			
Nov. 1979	1	810	2,000	400	8,900	3,900	8,200
	2	1,800	2,600	300	25,000	400	15,000
	3	800	1,000	300	12,000	600	8,400
May 1980	1	9,500	9,800	10,000	23,800	900	16,000
	2	12,000	11,000	21,000	54,000	400	8,100
July 1980	1	4,700	6,400	800	10,000	100	1,800
	2	4,200	7,500	600	12,000	80	3,700
				Iron			
May 1980	1	19,000	20,000	10,000	39,000	2,600	29,000
	2	19,000	21,000	44,000	83,000	1,300	26,000
July 1980	1	11,000	18,000	2,300	17,000	600	9,400
	2	11,000	13,000	1,700	21,000	410	19,000

Table 15. Particle size distribution, organic carbon, calcium carbonate, and mineral content of intact bedload sediments collected from the H.B. Robinson Steam Electric Plant, July 1980.

Collection site	Particle type (%)[a]			Organic carbon (%)[a]	Calcium carbonate (%)[a]	Mineral content[b]
	Gravel-sand	Silt	Clay			
Intake	24.2	65.1	10.7	3.9	negligible	quartz, mica
Discharge	93.7	6.3	--	25.6	0.62	quartz, muscoite
Control	96.7	3.3	--	0.9	negligible	quartz
Downstream						
I	98.8	1.2	--	1.5	0.12	quartz[c]
II	99.4	0.6	--	0.13	negligible	quartz
III	98	2	--	1.1	negligible	quartz

[a] Analyses performed by Dr. D. S. Gorsline, Department of Geological Sciences, University of Southern California, California.

[b] Analyses performed by Dr. A. Colville, Department of Geology, California State University at Los Angeles, California.

[c] Gehlinite-akermainte, possibly steel-mill slag.

REFERENCES

1. F. L. Harrison, "Effects of Copper Speciation on Aquatic Ecosystems," Carolina Power and Light, Electric Power Research Institute, Raleigh, NC, Mar. 23-24, 1982.

2. J. W. Warrick, S. G. Sharp, and S. J. Friedrick, "Chemical, Biological, and Corrosion Investigations Related to the Testing of the Diablo Canyon Unit 1 Cooling Water System," Pacific Gas and Electric Co., Department of Engineering Research, San Ramon, CA, report 7333, 1975, p. 129.

3. D. R. Young, T.-K. Jan, and T. C. Heesen, "Cycling of Trace Metal and Chlorinated Hydrocarbon Wastes in the South California Bight," pp. 481-496, in Estuarine Interactions. Fourth Biannual Estuarine Research Conference, Mt. Pocano, PA, Oct. 2-5, 1977, M. L. Wiley, Ed. (Academic Press, Inc., NY, 1978).

4. F. L. Harrison, D. J. Bishop, R. R. Emerson, and D. W. Rice, Jr., "Concentration and Speciation of Copper in Waters Collected Near the San Onofre and Diablo Canyon Nuclear Power Stations," Lawrence Livermore National Laboratory, U.S. Nuclear Regulatory Commission, Livermore, CA, NUREG CR/0750, UCRL-52706, 1980.

5. F. L. Harrison, D. J. Bishop, D. W. Rice, Jr., and J. P. Knezovich, "Copper in the Intake and Discharge Zones of the Surry and Salem Nuclear Power Stations," Lawrence Livermore National Laboratory, U.S. Nuclear Regulatory Commission, Livermore, CA, NUREG/CR-2965, UCRL-53325, 1983.

6. R. R. Emerson and F. L. Harrison, "Copper Distribution in Abiotic Compartments of Aquatic Ecosystems Near the Diablo Canyon and San Onofre Nuclear Power Stations," Lawrence Livermore National Laboratory, U.S. Nuclear Regulatory Commission, Livermore, CA, NUREG/CR-1090, UCRL-52555, 1981.

7. D. G. Waslenchuk, "The Concentration, Reactivity, and Fate of Copper, Nickel, and Zinc Associated with a Cooling Water Plume in Estuarine Waters," Environmental Pollution (Series B) 3, 271-287 (1982).

8. M. D. Stephenson, M. Martin, and J. H. Martin, "Copper Toxicity Experiments in Relation to Abalone Deaths Observed in a Power Plant's Cooling Waters," California Fish and Game 63(2), 95-100 (1977).

9. T. M. Florence and G. E. Batley , "Determination of the Chemical Forms of Trace Metals in Natural Waters, with Special Reference to Copper, Lead, Cadmium, and Zinc," Talanta 23, 151-158 (1977).

10. S. F. Sugai and M. L. Healy, "Voltammetric Studies of the Organic Association of Copper and Lead in Two Canadian Inlets," Marine Chemistry 6, 291-308 (1978).

11. J. P. Riley and D. Taylor, "Chelating Resins for the Concentration of Trace Elements from Sea Water and Their Analytical Use in Conjunction with Atomic Absorption Spectrophotometry," Analytica Chimica Acta 40, 479-487 (1968).

12. Y. K. Chau, R. Gachter, and L. S. Chan, "Determination of the Apparent Complexing Capacity of Lake Waters," Journal of the Fisheries Research Board of Canada 31, 1515 (1974).

13. J. D. H. Strickland and T. R. Parsons, A Practical Handbook of Seawater Analysis, Fisheries Research Board of Canada, Ottowa, Canada, 1962.

14. B. J. Ward, Carolina Power and Light Company, New Hill, NC, letter to F. L. Harrison, LLNL, Subject: manuscript review, dated April 5, 1983.

15. F. L. Harrison, D. J. Bishop, D. W. Rice, Jr., and J. P. Knezovich, "Concentration and Distribution of Copper in Effluents from Three Freshwater Nuclear Power Stations," Lawrence Livermore National Laboratory, U.S. Nuclear Regulatory Commission, Livermore, CA, NUREG/CR-3358, UCRL-53482, in press.

16. F. W. B. Bugenyi, "Copper Ion Distribution in the Surface Waters of Lakes George and Idd Amin," Hydrobiologia 64, 9-15 (1979).

17. Carolina Power and Light Co., "H.B. Robinson Steam Electric Plant 1976-78 Environmental Monitoring Program Results," Carolina Power and Light Co., Florence, SC, 1979, vol. 1.

18. P. Figura and B. McDuffie, "Determination of Labilities of Soluble Trace Metal Species in Environmental Samples by Anodic Stripping Voltammetry and Chelex Columns and Batch Methods," Analytical Chemistry 52, 1433-1439 (1980).

19. T. A. Neubecker and H. E. Allen, "The Measurement of Complexation Capacity and Conditional Stability Constants for Ligands in Natural Waters," Water Research 17, 1-14 (1983).

20. R. Kunkel and S. E. Manahan, "Atomic Absorption Analysis of Strong Heavy Metal Chelating Agents in Water and Waste Water," Analytical Chemistry 45, 1465-1468 (1973).

21. P. G. C. Campbell, M. Bisson, R. Gagne, and A. Tessier, "Critical Evaluation of the Copper (II) Solubilization Method for the Determination of the Complexation Capacity of Natural Waters," Analytical Chemistry 49, 2358-2363 (1977).

22. J. F. Elder, K. E. Osborn, and C. R. Goldman, "Iron Transport in a Lake Tahoe Tributary and Its Potential Influence Upon Phytoplankton Growth," Water Research 10, 783-788 (1976).

23. R. A. Kerr and J. G. Quinn, "Chemical Comparison of Dissolved Organic Matter Isolated from Different Oceanic Environments," Marine Chemistry 8, 217-229 (1980).

24. Y. Avnimelech and A. Raveh, "Decomposition of Chelate Leached from Waste Disposal Sites," Journal of Environmental Quality 11, 69-72 (1982).

25. E. W. Davey, M. J. Morgan, and S. J. Erickson, "A Biological Measurement of the Copper Complexation Capacity of Seawater," Limnology and Oceanography 18, 993-997 (1973).

26. R. Gachter, J. S. Davis, and A. Mares, "Regulation of Copper Availability to Phytoplankton by Macromolecules in Lake Waters," Environmental Science and Technology 12, 1416-1421 (1978).

27. P. A. Gillespie and R. F. Vaccaro, "A Bacterial Bioassay for Measuring the Copper Chelation Capacity of Seawater," Limnology and Oceanography 23, 543-548 (1978).

28. Y. K. Chau, "Complexing Capacity of Natural Water--Its Significance and Measurement," Journal of Chromatographic Science 11, 579 (1973).

29. T. A. O'Shea and K. H. Mancy, "Characterization of Trace Metal Organic Interactions by Anodic Stripping Voltammetry," Analytical Chemistry 48, 1603-1607 (1976).

30. R. G. Smith, "Evaluation of Combined Applications of Ultrafiltration and Complexation Capacity Techniques to Natural Waters," Analytical Chemistry 48, 74-76 (1976).

31. J. C. Duinker and C. J. M. Kramer, "An Experimental Study on the Speciation of Dissolved Zinc, Cadmium, Lead, and Copper in the River Rhine and North Sea Water by Differential Pulsed Anodic Stripping Voltammetry," Marine Chemistry 5, 207-228 (1977).

32. K. W. Hanck and J. W. Dillard, "Evaluation of Micromolar Compleximetric Titrations for the Determination of the Complexing Capacity of Natural Waters," Analytica Chimica Acta 89, 329-338 (1977).

33. M. S. Shuman and J. L. Cromer, "Copper Association with Aquatic Fulvic and Humic Acids: Estimation of Conditional Formation Constants with a Titrimetric Anodic Stripping Voltammetry Procedure," Environmental Science and Technology 13, 543-545 (1979).

34. C. M. G. Van den Berg, "Complexation of Copper in Natural Waters. Determination of Complexing Capacities and Conditional Stability Constants in Natural Waters by MnO_2, and the Implications for Phytoplankton Toxicity," Ph.D. Thesis, McMaster University, Hamilton, Ontario, Canada, 1979.

35. M. R. Hoffmann, E. C. Yost, S. J. Eisenreich, and W. J. Maier, "Characterization of Soluble and Colloid Phase Metal Complexes in River Water by Ultrafiltration. A Mass-Balance Approach," Environmental Science and Technology 15, 655-661 (1981).

36. B. T. Hart and S. H. R. Davies, "Copper Complexing Capacity of Waters in the Magelan Creek System, Northern Australia," Environmental Technology Letters 2, 205-214 (1981).

37. B. Lazar, A. Katz, and S. Ben-Yaakov, "Copper Complexing Capacity of Sea Water: A Critical Appraisal of the Direct Anodic Stripping Voltammetry," Marine Chemistry 10(3), 221-232 (1981).

38. C. M. G. Van den Berg and J. R. Kramer, "Determination of Complexing Capacities of Ligands in Natural Waters and Conditional Stability Constants of the Copper Complexes by Means of Manganese Dioxide," Analytica Chimica Acta 106, 113-120 (1979).

39. S. Ramamoorthy and D. J. Kushner, "Heavy Metal Binding Components of River Water," Journal of the Fisheries Research Board of Canada 32, 1755-1766 (1975).

40. J. P. Giesy, Jr., L. A. Briese, and G. J. Leversee, "Metal Binding Capacity of Selected Maine Surface Waters," Environmental Geology 2, 257-268 (1978).

41. D. P. H. Laxen and R. M. Harrison, "A Scheme for the Physico-Chemical Speciation of Trace Metals in Freshwater Samples," Science of the Total Environment 19, 59-82 (1981).

42. W. Stumm and P. A. Brauner, "Chemical Speciation," Chemical Oceanography 1, 173 (1975).

43. E. A. Jenne, "Controls on Mn, Fe, Co, Ni, Cu, and Zn Concentrations in Soils and Water: The Significant Role of Hydrous Mn and Fe Oxides," in Advances in Chemistry Series (American Chemical Society, Washington, DC, 1968), No. 73, pp. 337-386 .

44. M. A. Rashid and J. D. Leonard, "Modifications in the Solubility and Precipitation Behavior of Various Metals as a Result of Their Interaction with Sedimentary Humic Acid," Chemical Geology 11, 89 (1973).

45. R. D. Guy, C. L. Chahrabarti, and L. L. Schramm, "The Application of a Sample Chemical Model of Natural Waters to Metal Fixation in Particulate Matter," Canadian Journal of Chemistry 53, 661-669 (1975).

46. J. Cline, "Pathways and Interactions of Copper with Aquatic Sediments," Ph.D. Thesis, Michigan State University, East Lansing, Michigan, 1974.

47. E. T. Gjessing, "Gel and Ultra Membrane Filtration of Aquatic Humus: A Comparison of the Two Methods," Schweizerische Zeitschrift fuer Hydrologie 35, 286-294 (1973).

48. J. P. Giesy and L. A. Briese, "Metals Associated with Organic Carbon Extracted from Okefenokee Swamp Water," Chemical Geology 20, 109-120 (1977).

49. H. S. Allen, "Dissolved Organic Matter in Lakewater: Characteristics of Molecular Weight Size Fractions and Ecological Implications," Oikos 27, 64-70 (1976).

50. P. Foster and A. W. Morris, "The Seasonal Variation of Dissolved Ionic and Organically Associated Copper in the Menai Straits," Deep-Sea Research 18, 231-236 (1971).

51. J. A. Novitsky, I. R. Scott, and P. E. Kepkay, "Effects of Iron, Sulfur, and Microbial Activity on Aerobic to Anaerobic Transitions in Marine Sediments," Geomicrobiology Journal 2, 211-223 (1981).

JAS/adf

APPENDIX A. PROCEDURE FOR CLEANING SAMPLE CONTAINERS

CONTAINERS OF < 10 µg Cu/L SAMPLES

New polypropylene containers were filled with reagent-grade, concentrated HNO_3 and stored at room temperature for at least 7 d to leach out metal contaminants. The acid was then removed and the containers rinsed five times with doubly (glass-) distilled water (DDW) and filled with 0.05% Ultrex HNO_3 in DDW. After at least 4 d, the dilute acid was discarded and the containers were rinsed five times with DDW and then stored filled with DDW until use.

CONTAINERS OF > 10 µg Cu/L SAMPLES

New polypropylene containers were soaked for at least 2 d in a 2% MICRO bath. The containers were removed from the bath, rinsed five times with DDW, drained, and stored in sealed plastic bags until use.

NRC FORM 335
(7-77)

U.S. NUCLEAR REGULATORY COMMISSION

BIBLIOGRAPHIC DATA SHEET

1. REPORT NUMBER *(Assigned by DDC)*
NUREG/CR-3132
UCRL-53047

4. TITLE AND SUBTITLE *(Add Volume No., if appropriate)*
Concentration and Distribution of Copper in Effluents from the H. B. Robinson Steam Electric Plant

2. *(Leave blank)*

3. RECIPIENT'S ACCESSION NO.

7. AUTHOR(S)
F.L. Harrison, D.J. Bishop, D.W. Rice, Jr., and J.P. Knezovich

5. DATE REPORT COMPLETED

MONTH	YEAR
January	1983

9. PERFORMING ORGANIZATION NAME AND MAILING ADDRESS *(Include Zip Code)*
Lawrence Livermore National Laboratory
P.O. Box 5507, Mail Code L-453
Livermore, CA 94550

DATE REPORT ISSUED

MONTH	YEAR
August	1983

6. *(Leave blank)*

8. *(Leave blank)*

12. SPONSORING ORGANIZATION NAME AND MAILING ADDRESS *(Include Zip Code)*
Division of Health, Siting and Waste Management
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555

10. PROJECT/TASK/WORK UNIT NO.

11. CONTRACT NO.
A0119

13. TYPE OF REPORT
Topical

PERIOD COVERED *(Inclusive dates)*

15. SUPPLEMENTARY NOTES

14. *(Leave blank)*

16. ABSTRACT *(200 words or less)*

Water and bedload sediments were sampled at the intake and discharge areas of the H. B. Robinson Steam Electric Plant and at a control area upstream of the plant in November 1979 and May and July 1980. Total copper concentrations in discharge waters ranged from 33 to 79 µg/L, whereas those in intake waters ranged from 27 to 58 µg/L; copper in the water in the control area ranged from 3.1 to 5.8 µg/L. In most samples, copper in the soluble fraction appeared equally as labile and bound. The concentration of dissolved organic carbon in the water samples from the impoundment area showed little variation with time; the values range from 3.8 to 5.7 mg C/L. The organic carbon in the particulate fraction was ≤1 mg C/L. Determination of molecular size distribution of the copper species by ultrafiltration of discharge and control waters indicated that the largest concentration of copper appeared in the >10,000, <100,000 molecular weight fraction both in untreated and UV-oxidized water. Copper concentrations in intact bedload sediments of the intake area ranged from 4.4 to 260 µg/g dry weight; those in the discharge area ranged from 6.1 to 72 µg/g. Copper in the upstream sediments was very low, ≤3.7 µg/g. Higher concentrations appeared in the <62-µm fractions than in intact sediments. Copper distribution coefficients of intact bedload sediments in the intake and discharge areas ranged from 300 to 21,000.

17. KEY WORDS AND DOCUMENT ANALYSIS

17a. DESCRIPTORS

copper, copper speciation, nuclear power station, effluents, toxicity, sediments, corrosion products

17b. IDENTIFIERS/OPEN-ENDED TERMS

18. AVAILABILITY STATEMENT
UNLIMITED

19. SECURITY CLASS *(This report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES

22. PRICE
$

NRC FORM 335 (7-77)

UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20555

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300

120555078877 1 1ANIRE
US NRC
ADM-DIV OF TIDC
POLICY & PUB MGT BR-PDR NUREG
W-501
WASHINGTON DC 20555

NUREG/CR-3132

Effluents from the H.B. Robinson
Steam Electric Plant