Lawrence Livermore Laboratory

QUARTERLY PROGRESS REPORT

ON

CHEMICAL EFFLUENTS IN SURFACE WATERS FROM NUCLEAR POWER PLANTS

MASTER

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ABSTRACT

The objectives of this research project are three-fold:

- o To obtain data on the behavior of potentially toxic substances introduced into surface waters from nuclear power plants,
- o To determine the impact magnitude of these substances on representative and economically important aquatic species, and
- o To develop models with which to predict the partitioning of these substances among the abiotic aquatic compartments.

To fulfill these objectives in our investigation of copper, we are determining the copper partitioning in seawater, evaluating the toxicity of copper to representative marine organisms, and developing a mathematical model to predict copper partitioning.

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PARTITIONING OF COPPER

Partitioning of copper between the soluble and particulate phases was determined with water and sediment from Diablo Canyon and San Onofre Power Plants. As no further collections are planned for the Diablo Canyon Site, we made a concerted effort this past quarter to complete all analyses with material from this area. Collections at Diablo Canyon were made in June, August and October. The sampling in October was made during start up of circulation of water through the condenser system following an approximate 2-month shut down.

Distribution coefficients (K_d) were determined for bottom sediments and suspended particles (Table 1). For the bottom sediments, K_d values for intact sediments were lower than those for the $< 150 \mu$ fraction. Considerable variation in K_d values was found for the $< 150 \mu$ fractions of sediment samples collected at different times. For suspended particles, K_d values were larger than those for bottom sediments and were similar in value.

Concentrations of copper and organic matter were determined in samples of bottom sediments and suspended particles (Table 2). Concentrations of copper in the bottom sediments were about the same in all collections within the cove. In contrast, large difference in concentration were found in the samples of suspended particles. The changes in concentration in the samples collected at intervals following start up indicate that copper concentrations in the particulate material decrease rapidly to background levels within a few hours. Concentrations of organic matter were highest in August.

TABLE 1
DIABLO CANYON
⁶⁴Cu Distribution Coefficients

1977	Bottom Sediments		Suspended Particles	
	<u>Intact</u>	<u>Site^a</u>	<u><150μ</u>	
June	160; 170	1. 790; 930		20,000
		2. 1,300; 1,300		24,000
		3. 770; 820		31,000
		4. 760; 1,100		33,000
	Ave. 160	970		27,000
August	150; 160 ^b	5,400; 5,500		32,000
				40,000
				37,000
	Ave. 160	5,400		36,000
October	<u>Site^a</u>			
	1. 72; 94	12,000; 12,000		
	2. 190; 230	7,100; 8,000		
	3. 550; 570	25,000; 31,000		
	Ave. 280	16,000		48,000

^a Values obtained with sediment samples obtained at different collection sites within the discharge cove.

^b Values obtained with sediment composited from samples collected at 4 sites within the discharge cove.

TABLE 2
COPPER AND ORGANIC CARBON CONCENTRATIONS
IN DISCHARGE COVE PARTICULATE MATERIAL

1977		Bottom Sediments		Suspended Particles	
		Copper ($\mu\text{g/g}$)	Organic Carbon ($\mu\text{g/g}$)	Copper ($\mu\text{g/g}$)	Organic Carbon ($\mu\text{g/g}$)
June	C ^a	10.2	0.08	290.	0.16
	1. ^b	9.3			
	2.	6.6			
	3.	14.1			
	4.	9.3			
August	C	7.8	0.09	170.	0.49
October	C	12.3	NC ^c	4.4	0.26
	1.	11.9			
	2.	10.3			
	3.	12.6			
	<150 μ	17.4			
Start Up:					
T ^d	+ 5 min.			310.	--
T	+ 15 min.			68.	--
T	+ 30 min.			28.	--
T	+ 60 min.			12.	--
T	+ 210 min.			4.4	0.26

^aComposite sample.

^bValues obtained with sediment samples obtained at different collection sites within the discharge cove.

^cAnalysis not completed.

^dTime Zero

The kinetics of binding of copper to suspended particles and bottom sediments was evaluated using tracer techniques. To determine the rate of binding to the $<150 \mu$ fraction of bottom sediments, known quantities of sediment were added to seawater that had been spiked with high specific activity ^{64}Cu . The samples were filtered serially at specified times to determine the partitioning of the copper. The partitioning between the soluble and particulate phases was followed in seawater with and without the addition of 2 mg yellow stuff (naturally occurring dissolved organic material). The presence of the additional organic material reduced the affinity of copper to the particulate material (Figure 1).

The kinetics of binding of copper to suspended particles was determined also. The percent bound and the rate of binding of copper to particles differed for samples collected at different times (Figure 2).

The concentrations of total copper in seawater that had not been circulated through the cooling system were relatively low (Table 3). The highest concentration ($2\mu\text{g/liter}$) was found in June.

Increased leaching of copper from the cooling system was seen immediately after water circulation was initiated in October. Although titanium was used to replace the copper-nickel tubing in the main system at Diablo Canyon, there is still copper in part of the auxiliary pumping system. Our first sample taken about 5 minutes after the flow of water was initiated contained about $28\mu\text{g}$ copper/liter. Copper levels dropped rapidly and, after 3 1/2 hours, little difference could be seen between the intake and discharge waters.

The partitioning of copper between the soluble and particulate phases in uncirculated water differed greatly with time. In June and August the copper was about equally distributed between the soluble and particulate phases whereas in October it was more than 90% in the soluble phase (Table 3).

TABLE 3
DIABLO CANYON
WATER CONCENTRATIONS
($\mu\text{g/liter}$)

<u>1977</u>	<u>Pumps</u>		<u>Soluble</u>	<u>Particles</u>	<u>Total</u>
June	Off		1.0	1.3	2.3
August	Off		0.3	0.3	0.6
October	On	In ^a	0.7	0.03	0.7
Discharge ^b					
		T ^c + 5 Min.	26.0	1.9	27.9
		T + 15 Min.	1.7	0.13	1.8
		T + 30 Min.	1.7	0.09	1.8
		T + 60 Min.	1.4	0.04	1.4
		T + 210 Min.	0.6	0.03	0.6

^aSample collected from intake cove

^bSample collected from discharge cove

^cTime zero

TOXICITY OF COPPER

GIANT KELP

The sensitivity of Macrocystis pyrifera gametophytes to copper is being tested currently in a flow-through system. we decided to initiate this procedure when polarographic analysis of the bioassay water in the static system indicated that at low concentrations of copper in the water (<50 µg/liter) the copper chloride added to the water quickly became bound. The rapid formation of this complex may have rendered the copper unavailable to the gametophytes.

ADULT OYSTERS

Rates of accumulation of ^{64}Cu by adult oysters were measured in seawater containing concentrations of either approximately 1, 800, or 24 µg copper/liter. The accumulation rates of ^{64}Cu in the oyster soft tissues decreased with increasing concentrations of copper in the water (Figure 3). The average as well as the maximum amounts of ^{64}Cu increased linearly for the first 10 h at all three exposure concentrations. The average rate of accumulation in the oysters at the control concentration was 390, at 800 µg copper/liter was 260, and at 2400 µg copper/liter was 60 pCi/g wet weight-h; the maximum rates at all three concentrations were about 1.7 times the average rates. Since the initial specific activity of the water was known, calculations of the accumulation rates of stable copper were possible. The rates of accumulation of a representative 50 g wet weight oyster in µg copper/liter were 0.25 in the control, 32 at 800 µg copper/liter and 23 at 2400 µg copper/liter.

Copper concentrations were determined in oysters in the test system. Oysters maintained at increased levels of copper in the water contained more copper than those in control groups (Table 4). However, the increases were not linear with concentrations in the water; the highest levels were found in the oysters in water containing 230 µg copper/liter. The quantities of copper contained in oysters held in seawater with copper concentrations greater than 230 µg/liter did not differ significantly from each other.

FIGURE 3

TABLE 4

AVERAGE COPPER CONCENTRATIONS^a IN OYSTERS

Copper in bioassay water ($\mu\text{g/ml}$)		Whole body	Gills	Digestive gland and stomach	Remainder of body
0.001 (control)	$\mu\text{g/g}$ total	19.4 1,790.	65.0 426.	42.0 131.	15.3 1,230.
0.23	$\mu\text{g/g}$ total	221. 11,400.	368. 1,530.	382. 1,250.	195. 8,650.
0.44	$\mu\text{g/g}$ total μg	73.8 3,380.	95.2 404.	90.9 237.	70.8 2,740.
0.51	$\mu\text{g/g}$ total μg	68.4 3,510.	99.9 515.	85.7 251.	63.3 2,750.
0.76	$\mu\text{g/g}$ total μg	57.6 2,310.	111. 404.	50.8 126.	53.3 1,870.
1.3	$\mu\text{g/g}$ total μg	49.6 2,770.	112. 592.	66.2 164.	42.4 1,990.

^aFractional standard deviation (standard deviation/mean) generally ranged between 0.2 and 0.4 for the concentrations expressed in $\mu\text{g/g}$ and ranged between 0.4 and 0.6 for the total amounts.

Early Stages of Oysters

The effect of organic chelators on the toxic response to copper was tested on early life history stages of oysters. The decrease in sensitivity to added copper was related to the stability constant of the organic ligand (Table 6).

Early Stages of Abalone

Evaluation of the effects of copper on early life history stages of abalone is being performed in cooperation with the research staff of the Monterey Abalone Farm, Monterey, Calif. Experiments with the very young stages were postponed due to a current shortage of good breeding stock. However, data from some preliminary experiments with juveniles indicate that a significant decrease in growth occurs in animals held in water containing about 15 μg copper/liter.

Adult Herring

Experiments to determine the sensitivity of adult herring to copper and the concentrations of copper in the bioassay water have been completed. In progress are copper analyses of the experimental animals.

Adult Anchovy

The toxic response of adult anchovies to copper has been defined and analyses of the bioassay water have been completed. In progress are copper analyses of the experimental animals.

Model Development

The first phase of model development has been completed and a draft of the report will be submitted to NRC in the very near future.

OYSTER EMBRYOS

TABLE 5

EFFECT OF ORGANIC CHELATORS ON MORTALITY^a

% Mortality

<u>Copper</u> <u>(μg/l)</u>	<u>Control</u>	<u>Oxalic Acid</u>	<u>Glycine</u>	<u>Citrate</u>	<u>Yellow Substance</u>	<u>EDTA</u>
0	3.9	4.3	3.1	4.3	5.4	2.4
10	28.5	13.4	4.9	4.9	2.3	3.6
20	96.9	97.2	95.6	89.9	10.8	1.4
40	99.2	- -	- -	- -	91.2	2.3
60	100	- -	- -	- -	97.2	2.4
100	100	- -	- -	- -	100	84.7

^aConcentration of all chelators was 1×10^{-6} M except for yellow stuff;
2 mg of yellow stuff was added per liter of seawater.

PUBLICATIONS

1. F. L. Harrison and D. W. Rice, Jr. "Copper Sensitivity of Adult Pacific Oysters". Presented at the Symposium on Energy and Environmental Stress in Aquatic Ecosystems, Nov. 2-4, 1977, Augusta, Georgia.
2. D. W. Rice, Jr, and F. L. Harrison. "The Sensitivity of Adult, Larval and Embryonic Stages of the Northern Anchovy, Engraulis mordax, to Copper," Presented at the California Cooperative Fisheries Investigation (Cal. Co. F. I) Conference, La Jolla, California Nov. 1-3, 1977.