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QUARTERLY PROGRESS REPORT
ON
CHEMICAL EFFLUENTS IN SURFACE WATERS FROM NUCLEAR POWER PLANTS

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JULY 28, 1977

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Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

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QUARTERLY PROGRESS REPORT
ON
CHEMICAL EFFLUENTS IN SURFACE WATERS FROM NUCLEAR POWER PLANTS

Research Order No. 60-76-144

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July 28, 1977

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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.
- 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 freshwater and seawater, evaluating the toxicity of copper to representative marine organisms, and developing a mathematical model to predict copper partitioning.

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I. Partitioning of Copper:

Partitioning of copper between the water and particulate phases was determined for water and particles collected at three coastal power plants. Three collections have been made to date at San Onofre Nuclear Power Plants (4/5/77, 5/5/77, 7/21/77), one at Diablo Canyon Nuclear Power Plant (6/7/77) and one at Morro Bay Fossil Fuel Power Plant (6/16/77). Distribution coefficients determined with bottom sediments from the outfall area at San Onofre were lower than those from Diablo Canyon (Table 1). Data are available currently for only the first two collections at San Onofre.

⁶⁴Cu Distribution Coefficients

for Bottom Sediments

<u>Power Plant</u>	<u>Date</u>	<u>Site</u>	<u>Sediments</u>	
			<u>Intact</u>	<u><150 μ</u>
San Onofre	4/5/77	Outfall	58;60 ¹	260;280
		Control ²	260;280	1700;3000
	5/5/77	Outfall	300;320	340;340
		Control	240;300	350;380
Diablo Canyon	6/7/77	Outfall ³	_____	a)790;930
				b)1300;1300
				c)770;820
				d)760;1100

¹ Replicates of same sample

² 22,000 ft south of outfall

³ Collection made at 4 different areas

Distribution coefficients for suspended particles were determined for collections made at the Morro Bay as well as at the San Onofre and Diablo Canyon Plants. We were given the opportunity to participate in a field trip at Morro Bay with the research staff of Pacific Gas and Electric Company. The purpose was to determine the concentrations of metals in the discharge water contributed by the Cu/Ni cooling system. Distribution coefficients for suspended particles were higher than those for bottom sediments (Table 2).

⁶⁴Cu Distribution Coefficients
for Suspended Particles

<u>Power Plant</u>	<u>Date</u>	<u>Site</u>	<u>Suspended Particles</u>	
			<u>Kd</u>	<u>mg/l</u>
San Onofre*	5/5/77	Outfall	1,020;1,030	14.5
Diablo Canyon**	6/7/77	Intake	20,800 ± 4600	4.2
Morro Bay**	6/16/77	Discharge	84,300 ± 3800	3.5
		Intake	79,400 ± 3400	3.2
		Offshore	40,800 ± 4900	3.4

* Analysis performed 1-week after collection on samples that had been stored at 4°C.

** Analysis performed same day as collection on samples that had been stored at 4°C.

Copper concentrations in some of the compartments in the water were determined for the samples collected at the different power plants. Concentrations of inorganic copper were higher in the discharge than in the intake and offshore water (Table 3).

Table 3
Concentrations of Copper in Water
Samples from Coastal Power Plants

Power Plant	Site	<u>Inorganic</u>	Concentrations <u>Organic*</u>	g/liter <u>Particulate</u>
San Onofre:				
4/5/77	Outfall	0.42	---	---
5/5/77	Outfall	0.12	---	0.69
Diablo Canyon:				
6/7/77	Intake	0.13	---	1.06
Morro Bay:				
6/16/77	Offshore	0.19	0.15	0.30
	Intake	0.17	0.14	0.35
	Discharge	0.84	0.27	1.84

* Values based on ^{64}Cu recoveries. Analyses in progress.

Effects of different chelators on distribution coefficients were determined for bottom sediments (<150 fraction) from Diablo Canyon. K_d values differed with the chelator and particle type (Table 4).

Effect of Chelators on K_d

Diablo Canyon <150 μ		
<u>Chelator</u> ¹	<u>Particle Type</u>	<u>K_d</u>
None	Suspended Bottom	6400;7300 ² 1300;1400
EDTA	Suspended Bottom	2200;2400 1600;1600
Glycine	Suspended Bottom	32,500;38,500 20,000;21,000
Citrate	Suspended Bottom	4,800;5,400 19,400;20,000
Yellow Stuff	Suspended Bottom	4,100;2,000 -----

¹ Chelator concentrations were $1 \times 10^{-5} M$.

² Replicates of some samples.

II. Toxicity of Copper

A. Giant kelp:

The first series of experiments on Macrocystis pyrifera tested the effects of copper exposure from the spore through the mature gametophyte stage. The spore stage lasts from one to two days, after which time the plant has grown into a multicellular gametophyte. The mean growth of copper-spiked cultures is statistically different at the 0.05 level after three weeks, for concentration greater than or equal to 50 ppb. The results of these experiments were presented in greater detail in an earlier program report.

The second series of experiments tested the effects of continuous exposure to copper on one, two and five week old gametophytes. Results showed that the growth of one-week old gametophytes is inhibited 10% after one weeks' 30% after two weeks' and 40% after four weeks exposure to 50 ppb copper. At a concentration of 100 ppb, growth is inhibited 28% after one weeks', 40% after two weeks' and 65% after 5 weeks' exposure to 100 ppb. copper. Five week old gametophytes show a 10% growth inhibition after one weeks' and a 20% inhibition after two weeks' exposure to 100 ppb copper.

The third series of experiments tested the effects of a one-week pulse exposure to copper. These experiments showed that cultures exposed to copper during the first week of the gametophyte stage exhibited initially depressed growth rates, as well as a reduction in the total amount of growth (total number of branches). Growth after two weeks in control medium was inhibited 30% for pulse-exposed concentrations greater than or equal to 50 ppb. After four weeks in control medium, however, differences in growth in the pulse-exposed cultures was not statistically significant when compared to controls.

B. Adult Oysters

The acute effects of copper on adult oysters have been defined and were reported in the last progress report. Copper analyses performed on the bioassay test water indicate that the copper was primarily in the inorganic rather than organic form. Soft tissues of oysters that were exposed to the different concentrations of copper are currently being analyzed for copper.

C. Larval oysters

Experiments are currently being performed to assess the sensitivity of developing eggs of Crassostrea gigas to copper. Adult oyster collected from commercial beds were conditioned in the laboratory in preparation for the induction of spawning. Fertilized eggs were placed in water containing different concentrations of copper and then the effects on development observed. Although we have followed development to the 72 hour stage, most of our tests were terminated after 48 hours; it appears that unless the development of the egg reaches the "D-hinge" stage by 48 hours, the larvae cannot survive. The results to date indicate that the early life history stages of the oysters are extremely sensitive to increased concentrations of copper. Increased mortality occurs at concentrations as low as 5 ppb (Table 5).

Table 5

Effect of Copper on Developing Embryos
of Crassostrea gigas
48-hour Toxicity Test

<u>Copper concentration</u>	<u>Percent mortality</u>
ppb	
100	Disintegrated by 24 hr.
80	Disintegrated by 36 hr.
40	100
20	100
10	45
5	18
control	5

D. Larval Abalone:

Experiments to be initiated.

E. 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 animal.

F. 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 animal.

III. Model Development

Mathematical modeling of the fate of copper in the marine environment is proceeding along two lines:

1. Development of the basic kinetics of copper interactions and partitioning for the dominant forms which are expected to exist following discharge of cooling waters, and
2. Imbedding the copper mass balance equations in an existing water quality model in order to simulate the effect of environmental factors such as temperature, pH and suspended sediment on the equilibrium state of copper in its various forms.

Development of a complete set of the kinetic equation for the likely forms of copper (ionic, adsorbed, complexed, etc.) is an essential first step that requires a preliminary assessment based on laboratory work just being completed. At this juncture it appears that at least 4 forms of copper will comprise the model. They are:

1. copper in the ionic form,
2. copper complexed with organic ligands,
3. copper in/on inorganic colloidal particles ($< 0.45 \mu$), and
4. copper sorbed to suspended particles ($> 0.45 \mu$).

The fundamental mass balance equations will be of the form

$$\frac{\partial (cV)}{\partial t} = -A + D + V \frac{dc}{dt} \pm s \quad (1)$$

where

c = concentration

V = volume of control element (physical compartment)

s - sources or sinks of c

A = advective transport

D = diffusive transport

$\frac{dc}{dt}$ = local derivative of c defining all kinetic processes governing the fate of the constituent c .

The local derivative will likely be comprised of zero and first order terms, exhibiting the coupling of the various forms of c (copper). For example:

$$\frac{dc_1}{dt} = -\alpha_1 c_1 + \alpha_2 c_2 - \alpha_3 c_3 \pm \alpha_4 \quad (2)$$

where

$\alpha_1, \alpha_2, \alpha_3$ are kinetic reaction coefficients for copper forms $c_1, c_2,$ and $c_3,$ respectively, and α_4 represents a constant sink or source.

Similar equations would be written for each of the other forms.

It is acknowledged that "equilibrium" per se signifies $\frac{dc}{dt} = 0$ such that constant kinetic coefficients for a set of equations like (2) would specify the proportions of $c_1, c_2, c_3, \dots, c_n$ in the aquatic environment. However, it is more likely that $\alpha_1, \alpha_2, \alpha_3, \dots, \alpha_n$ are functions of exogenous environmental factors like temperature, pH, suspended sediment, etc. or that they depend in some instances on values of c , i.e., second order terms exist for the model. Excluding, for the present the latter possibility, it is at least clear for the practical case that temperature, for example, will vary with time and distance from the source.

In order to consider the effects of environmental variables such as temperature in the model it is essential that we describe changes brought about in both c 's and α 's by physical process, i.e., advection and diffusion. This is the reason for imbedding the kinetic (or "equilibrium") equations in a water quality model capable of describing effects of dilution and interactions with other environmental factors. Models for such processes, adaptable to realistic discharge situations like San Onofre and Diablo Canyon, are well developed and available for the purposes noted.

Proceeding along these lines we have adapted a two-dimensional finite element water quality model, RMA-4, to the problem at hand, i.e., the simulation of the fate of copper in various forms after discharge of power plant cooling waters to a coastal marine environment. The model is operational and is being modified (reprogrammed) to accomodate the appropriate equations for copper.

It is important to recognize that the fate of copper is not determined merely by the equilibria established under laboratory controlled conditions, but also by the dynamics of natural processes peculiar to the real situation, e.g., San Onofre discharge. Thus, even if equilibrium is reached in a few minutes in the lab, these few minutes in the prototype may well be sufficient for a substantial change in state, notwithstanding the fact that temperature and other factors influencing rate constants are also changing rapidly in time and space. In essence, the real system is dynamic and should be regarded as such.

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