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

Florence L. Harrison

April 8, 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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April 8, 1977

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

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.

I. Partitioning of Copper

II. Toxicity of Copper

A. Giant Kelp

B. Adult Oyster

C. Larval Oyster

D. Larval Abalone

E. Adult Herring

III. Model Development

I. Partitioning of Copper

We performed experiments with clay (illite) particles to determine the effect of stable copper concentrations on ^{64}Cu sorption rates and distribution coefficients. Seawater containing copper concentrations of 50, 500, and 1000 ng/ml (ppb) was spiked with ^{64}Cu and aliquoted to test containers. Illite particles previously equilibrated with seawater were dispersed to each test container, yielding a particulate concentration of 5 ug/ml (ppm). The fraction of ^{64}Cu sorbed was determined at intervals of 0.0, 0.17, 0.33, 0.50, 0.67, 0.83, 1.0, 6.0, 12, 24, and 36 h. Little change in the percentage of ^{64}Cu bound to the clay particulate was evident after the 12-h period (Fig. 1). A similar pattern of sorption was seen for the particles in the higher concentrations of copper.

A preliminary examination of the kinetics of the sorption reactions suggests that a minimum of two copper-illite sorption rates are involved. The initial sorption, primarily into a compartment representing about 50% of the total sorption, occurs within the first 10 min. The $T_{1/2}$ of ^{64}Cu in the second compartment is approximately 3 h. The distribution coefficients for ^{64}Cu appear to be independent of the stable copper concentration (see Table 1).

Table 1. Copper-64 distribution coefficients for illite in seawater.

Copper Concentration, ng/ml	Equilibrium Time, h	
	24	36
1 to 2 ^a	8100	8100
	8600	7700
50	7900	7500
	8200	6000
500	7300	7600
	7600	6500
1000	7300	6700
	8900	7800

Figure 1.

II. Toxicity to Copper

A. Giant Kelp

Several experiments have been performed to determine the effect of copper on the development of Macrocystis spores. A spore is considered to have undergone development if, after a 1-wk period, it has changed from a circular to an elongated or dumbbell-shaped structure, the latter indicating the beginning of the gametophyte stage.

For each concentration of copper tested, the number of dumbbell-shaped young gametophytes was counted and compared to that of the controls. The percent inhibition of development was calculated from

$$\% \text{ Inhibition} = \frac{\bar{X}_{ct} - \bar{X}_{Cu}}{\bar{X}_{ct}}$$

where $\bar{X}_{ct}$ is the average number of young gametophytes in the control culture after a 1-wk growth period and $\bar{X}_{Cu}$ is the average number of young gametophytes in the copper-loaded culture after a 1-wk growth period.

The results of two experiments with two different concentrations of spore inoculum show 95 to 100% inhibition of spore development at copper concentrations of 1,000, 2,500 and 5,000 ng/ml. At 500 ng/ml copper, the inhibition ranged from 65 to 100%. Results from five experiments with different spore inoculum concentrations yield an average of 50% inhibition of spore development at a 200-ng/ml copper concentration. Additional experiments of the effects of lower copper concentrations indicate that the toxic responses of the spores are more variable and less dramatic. However, visible effects on the culture can be seen at copper concentrations as low as 25 ng/ml.

B. Adult Oysters

Experiments on the sensitivity of adult oysters to copper were conducted with a flow-through bioassay system. As mentioned in last quarter's progress report, the time vs concentration mortality response of oysters differed from that of other organisms because oysters can exclude copper-containing water from their mantle cavity by tightly closing their shells. However, because of this, reproducible results were obtained only after we began taking five or six observations per day at regular intervals and recording data on the open vs closed status of the individual oysters' shells.

For the final analysis of the data, the duration of exposure of each oyster was corrected for the differences between the time the animal first opened its shell and the time it was introduced into the copper-loaded water. Data were also corrected by a factor accounting for the ratio of the number of shell-open to shell-closed observations. In Fig 2, we present the mortality curves for adult oysters, corrected for both these factors.

Preliminary analysis of the oyster mortality data yields an LC 50₄₈ of 0.7 µg/ml and an LC 50₉₆ of 0.5 µg/ml with an estimated incipient LC 50 of 0.2 µg/ml.

ACUTE MORTALITY CURVES

Adult Oysters (Pooled data from tests III and IV) copper conc. $\mu\text{g/ml}$

Figure 2.

C. Larval Oysters

A population of adult oysters is currently being conditioned in preparation for induction of spawning.

D. Larval Abalone

Experiments to be initiated at a latter date.

E. Adult Herring*

Experiments evaluating the sensitivity of adult herring to copper were conducted using a recirculating, closed-bioassay system with 16 fish/200 gal seawater. The herring proved to be relatively resistant to copper. We only observed mortalities at copper concentrations greater than 0.2 $\mu\text{g/ml}$ (Fig. 3).

Results of the water analysis reveal that the copper was present in the ionic form; little organically complexed copper was found. A preliminary statistical analysis of the data gave the following values for median lethal times (LT 50) and median lethal concentrations (LC 50):

LT 50 _{2.4 $\mu\text{g/ml}$}	= 5 h	LC 50 ₄₈	= 0.45 $\mu\text{g/ml}$
LT 50 _{1.2 $\mu\text{g/ml}$}	= 9 h	LC 50 ₉₆	= 0.22 $\mu\text{g/ml}$
LT 50 _{0.8 $\mu\text{g/ml}$}	= 19 h		

From these values, we approximate the incipient lethal concentration to be 0.19 $\mu\text{g/lm}$.

*

Research funded by the U.S. Energy Research & Development Administration. Results are included for comparison to other aquatic organisms.

III. Model Development

From January 1 to April 1, 1977, we completed the initial assessment of available thermodynamic models of chemical reactions. Because of the absence of real-world applicability, none of these models was suitable for our needs. The principal drawbacks were the inability of the models to describe reactions at steady-state or equilibrium conditions and the lack of relevant model parameters for copper partitioning and chemistry.

Hence, we decided to abandon the theoretical model approach for the time being and to concentrate on an empirical approach using experimental data generated in our laboratory. Coefficients derived from these data will be incorporated into a series of equations simulating copper reactions and partitioning in seawater. Because of the extreme complexity of marine chemistry, these simulations are limited to reactions occurring within the water column. Continuing efforts will be made to use theoretical models and to verify their results with field and laboratory data. All experimentally investigated compartments that exhibit adequate statistical reliability will be included in such models.

A discussion of our review and evaluation of thermodynamic models as well as a list and description of selected copper reactions addressed in our selected model will be included in next quarter's report.

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