

Evaluation of the Water Quality Significance of Copper in San Diego Bay Sediments

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Sediments in many harbors and waterways contain elevated concentrations of copper. In addition to its being derived from point source discharges and non-point source discharge/runoff (e.g., from auto brake shoes), copper in aquatic sediments near harbor and marina terminal areas comes from its use as an antifoulant on boat hulls. In some locations, such as the National City Marine Terminal (NCMT) area of San Diego Bay, spills of copper ore during ship-to-shore transfer has also contributed copper to the sediments. Copper concentrations in sediments of open areas of San Diego Bay are on the order of tens to hundreds of mg Cu/kg dry wt., while in marina and other commercial areas concentrations are higher, on the order of several hundred mg Cu/kg or more. Some sediments in the NCMT area contain as much as 50,000 mg Cu/kg dry wt. derived primarily from the spillage of chalcopyrite (CuFeS_4) ore concentrate during shore-to-ship transfer operations in the early to mid-1980's. Some of that spillage of copper ore concentrate was determined by the local regulatory agency to have been in violation of the NPDES permit. The NCMT terminal operators, affected mining companies, and the Port of San Diego were ordered to "remediate" the NCMT-area copper-contaminated sediments. In order to establish a "clean-up" objective for the copper, the regulatory agency required that an aquatic life/human health/environmental hazard assessment of the copper-contaminated NCMT-area sediments be conducted. This paper summarizes the studies that were conducted to evaluate the water quality significance of the copper-contaminated sediments in the NCMT area of San Diego Bay.

An aquatic life/human health hazard assessment is the development and integrated use of information on the aquatic and human toxicology and aqueous environmental chemistry in a tiered decision matrix to evaluate the expected exposure (concentrations of available forms/contaminant availability, and duration of exposure) relative to that which could cause adverse impacts on beneficial uses of the water/sediment. In this case, the assessment involved the determination of the availability of the copper in the sediment to cause toxicity to aquatic life, adverse impacts to terrestrial animals or people who use aquatic organisms for food, or other adverse impacts on recreation and other beneficial uses of the waters of the area. The approach used by the authors in conducting the hazard assessment was to establish a plausible worst-case scenario screening testing/evaluation program to determine if copper in the NCMT-area sediments, independent of source, was likely adverse to the designated beneficial uses of San Diego Bay which had been specified to be industrial service supply, navigation, contact recreation, non-contact recreation, ocean commercial and sport fishing, saline water habitat,

preservation of rare and endangered species, marine habitat, fish migration, and shellfish harvesting. In addition to the critical review of the previous NCMT-area studies, and the literature in general as well as pertaining to similar situations at other locations, a series of sediment screening toxicity tests was used to confirm results of the previous NCMT-area studies.

It was found that the copper ore concentrate-contaminated sediments, with whatever other contaminants were also present in them, were not sufficiently toxic/available to adversely affect aquatic life and therefore to adversely affect higher organisms, including man. This finding was based on the aquatic chemistry and toxicology of the copper ore concentrate in the sediment and water, assessments of aquatic life toxicity of the sediments, determinations of bioaccumulation of copper in organism tissue, and the nature and abundance of aquatic life in the area. The key findings included the following.

- Toxicity tests on NCMT-area sediments showed no toxicity to the nine types of sensitive organisms tested, including embryos of Pacific Oyster, reported by the US EPA to be one of the most sensitive organisms/stages to copper in salt water. Not only was the chalcopyrite in the sediment non-toxic, but also none of the other forms of copper or other contaminants in the NCMT-area sediments tested was toxic.
- *Mytilus edulis* occur naturally in an area of the NCMT in which the sediments contain some of the highest concentrations of copper reported. The US EPA found that embryos of *Mytilus edulis* are the most acutely sensitive to copper of the marine organisms it evaluated. It was the sensitivity of *Mytilus edulis* that formed the basis for the US EPA water quality criterion for copper, which in turned served as the basis for the water quality objective (standard) for San Diego Bay waters.
- The bioaccumulation of copper in mussels taken near the NCMT was not different from that in mussels from other areas of the San Diego Bay.
- Based on the expected aqueous environmental chemistry of copper in San Diego Bay water and sediments, the copper ore concentrate in the NCMT area sediments would not be expected to be in toxic/available forms in sufficient amounts to be adverse to aquatic life.

It was concluded that there was no need to remove the copper ore concentrate-contaminated sediment from the NCMT area of San Diego Bay in order to protect the designated beneficial uses of the Bay.

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### **Remediation Objective of 1000 mg/kg Technical Considerations**

"Technical" Basis:

- Equilibrium Partitioning Approach with
- WESTEC Estimates of Interstitial Water Concentration of "Soluble" Copper

Basis Not Technically Valid

- Procedures Used by WESTEC to Separate "Soluble" Copper Component of Interstitial Water Overestimate "Soluble" Fraction
- Filtration Method Can Allow Passage of Appreciable Amounts of Particulate, Non-Toxic Forms of Copper and Inclusion in Measurements of "Soluble" Copper
- Equilibrium Partitioning Approach Not Demonstrated to Be Applicable to Heavy Metals, Such as Copper, in This Type of Sediment
- Based on Chemistry of Copper, Approach Would Not Be Expected to Be Appropriate for Copper in San Diego Bay Sediment
- Water Quality Criterion and Objective Values Not Appropriate for Judging Significance of Interstitial Water Copper
- Sensitivity and Significance of Organisms
- Dissolved Oxygen
- Relationship between Interstitial Water Copper and Sediment Copper Not Highly Significant (best  $r^2=0.35$ )
- Some Soluble Species of Copper Are Not Available-Toxic

**NCMT Pacific Oyster Larvae Toxicity Test Results  
Compared with California Water Quality Objective**

| <b>Sample Station</b> | <b>Sediment Copper (mg/kg dry wt)</b> | <b>Copper in Replicate 1</b> | <b>Elutriate Replicate 2</b> | <b>% Elutriate LC50</b> | <b>% Elutriate NOEC</b> |
|-----------------------|---------------------------------------|------------------------------|------------------------------|-------------------------|-------------------------|
| 5/0-1                 | 18,333                                | 24                           | 52                           | >100                    | >100                    |
| 5/0-2                 | 16,235                                | 6                            | 13                           | >100                    | 100                     |
| 1/80-1                | 1,372                                 | 2                            | 6                            | >100                    | >100                    |
| 1/80-2                | 1,174                                 | <2                           | 5                            | >100                    | >100                    |
| 6/160-1               | 151                                   | <2                           | 2                            | >100                    |                         |
| 6/160-2               | 122                                   | <2                           | <2                           | >100                    |                         |

Dilution Water: <2 µg Cu/L

Station Identification: Transect/Distance from Pierface-Replicate  
48-hr Exposure

California Water Quality Objective:

1-hr Average Not to Exceed 2.9 µg Cu/L

**California Water Quality Objective  
Equivalent to US EPA Water Quality Criterion**

US EPA Criterion: Concentration That Would Not Cause Lethality to Embryo of Mussel, *Mytilus edulis*, Would Not Cause Chronic Toxicity

*Mytilus edulis* Live Naturally in NCMT Area, and Were Harvested as Part of Study from Area at NCMT Pierface at Which Highest Concentrations of Sediment-Associated Copper in Area Have Been Found

**KEY**

|                 |             |             |
|-----------------|-------------|-------------|
| No. Individuals | 2 - 9       | 4 - 11      |
| S-W Diversity   | 0.22 - 0.54 | 0.22 - 0.6  |
| No. Species     | 2 - 4       | 2 - 4       |
| No. Individuals | 28 - 83     | 149 - 905   |
| S-W Diversity   | 0.21 - 0.68 | 0.01 - 0.08 |
| No. Species     | 4 - 8       | 2 - 8       |

From WESTEC (1986)

**Location of Station Groups  
Identified by Dendrogram Analysis**

Risk Assessment

Selective, Sequential Testing and Evaluation of

- **Aquatic Chemistry** (Chemical Nature, Fate and Transport) of Contaminant(s) of Concern, and
- Their **Aquatic Toxicology** (Impact) in a
- Tiered Framework of Increasing Sophistication of Specificity

Yield Assessment of

- Adverse Impacts That the Given Situation Has on Designated Beneficial Uses
- Degree of Contaminant Control Needed to Protect Designated Beneficial Uses

- Evaluate Improvement in Water Quality That Could Be Achieved as a Result of Implementing Various Contaminant Control Approaches

**Chemical Contaminants Exist in Aquatic Systems in a Variety of Forms, Only Some of Which Are Toxic-Available to Adversely Affect Aquatic Life**

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**Risk Assessment Study  
Approach**

Synthesis Evaluation of

- Information Generated from Previous Studies, Augmented by

Results of Summer 1991 Investigation

Objectives:

- To Evaluate Whether Attaining the Water Quality Control Board Order no. 85-91 Remediation Objective of 1,000 mg Cu/kg dry wt. Would Be Protective of Beneficial Uses of San Diego Bay
  - Examine Existing and New Information for Implications for Impact on Beneficial Uses of San Diego Bay from Higher Remediation Objective
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**Summary of Results of Lee & Jones  
Risk Assessment Study**

Findings:

- NCMT-Area Sediments Contain Copper to 50,000 mg Cu/kg dry wt. (at 2-3 ft deep)
- Toxicity Tests with NCMT-Area Sediments Containing 18,000 mg Cu/kg dry wt. Did Not Adversely Affect Sensitive Test Organisms
- Overall, 9 Different Types of Organisms Tested
- Considered 14 Response Parameters
- Shrimp, Flat Fish, Sea Urchin Eggs & Embryos, Clams, Worms, 2 Types of Amphipods, Fish Larvae, Pacific Oyster Embryos/Larvae
- Embryos of Pacific Oyster Reported by US EPA to Be One of the Most Sensitive Organisms/Stages to Copper in Salt Water
- *Mytilus edulis* (mussel) Occurs Naturally in Area of NCMT in Which Sediments Contain Some of Highest Concentrations of Copper Reported
- US EPA Found That Embryos of *Mytilus edulis* Were the Most Acutely Sensitive to Copper of the Marine Organisms It Evaluated
- Sensitivity of *Mytilus edulis* Basis for US EPA Water Quality Criterion for Copper

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*"Although Quite Limited, the Benthic Community Found near the Paco Terminal Pier Provides Evidence That Some Bivalvia Mollusks (sic - Bivalve Molluscs), Like Clams, Mussels, Have Become Established on Sediment Which Is ... Quite High in Copper Ore." "These Adult and Juvenile Forms of Mussels in an Area Where They Would Have Had a (sic - to) Settle Out of the Water Column. So It Did Provide Information That This Wasn't Severely Toxic. Otherwise These Very Sensitive Stages of These Organisms (sic - Organisms) Wouldn't Have Been Able to Settle Out and Live and Mature into Adult Forms."*

Deposition of Greg Peters  
July 24, 1991

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**Summary Testimony of  
G. Fred Lee, Ph.D. and R. Anne Jones, Ph.D.  
G. Fred Lee & Associates  
El Macero, CA**

Dr. G. Fred Lee and Dr. R. Anne Jones (Lee and Jones) were contracted by the Port of San Diego through Woodward-Clyde Consultants (WCC) to conduct a water quality risk assessment for the copper ore concentrate present in the sediments near the National City Marine Terminal (NCMT)

The Lee and Jones report of the results of the risk assessment were submitted by WCC to Port and to San Diego Regional Board last August.

**Objectives**

- Investigate Whether Copper Ore-Contaminated Sediments near NCMT Is Adversely Affecting Beneficial Uses of San Diego Bay
- Evaluate Whether Attaining the Water Quality Control Board Order No. 85-91 Remediation Objective of 1,000 mg Cu/kg dry wt. Would Be Protective of Beneficial Uses of San Diego Bay
- Examine Existing and New Information for Implications for Impact on Beneficial Uses of San Diego Bay from Higher Remediation Objective

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**Conclusions**

Based on the aquatic chemistry and toxicology of copper, the copper in the NCMT-area sediments that was derived from copper core concentrate is expected to have been and now be informs largely unavailable to adversely affect water quality.

Whatever the specific forms of copper, and whatever other chemical contaminants may exist in the NCMT-area sediments, and whatever the forms and concentrations of copper in interstitial water:

- the broad spectrum of toxicity tests conducted showed that the sediments did not adversely affect test organisms;
- mussels known to be highly sensitive to copper exist naturally in the NCMT-area sediments highly contaminated with copper ore concentrate;
- work of WESTEC on the benthic organism community composition, numbers, and diversity in the NCMT area has shown that the differences and similarities between organism assemblages in that area are not related to the amount of copper in the sediments.

No technical justification for the selection of the 1,000 mg Cu/kg dry wt. remediation objective.

No discernible water quality significance of potential spreading of NCMT-area sediment into Bay

The technical information available indicates that a clean-up objective on the order of 15,000 to 20,000 mg Cu/kg dry wt for the NCMT-area sediment could potentially be justified; it is possible that further study could also justify an even higher objective.

DHS has established TTLC of 4,000 mg Cu/kg dry wt. for classification as "hazardous waste."

It is not technically defensible to apply DHS TTLC values to NCMT-area sediment for determination of need for or extent of remediation.

Establishment of an appropriate and acceptable clean-up level above 4,000 mg Cu/kg dry wt. (TTLC value) would likely require additional time in permitting, obtaining variance, and further testing.

Extensive review and testing has led to the conclusion that at present the copper in the NCMT-area sediments is not having an adverse impact on water quality; this would not be expected to change to a situation in which it would become adverse. Therefore, delay of whatever remediation may be decided upon would not be expected to adversely affect water quality.

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## **Water Quality Significance of Potential Spreading of Copper Ore Concentrate in San Diego Bay**

Evidence does not indicate substantial spreading.

Even if copper ore concentrate-contaminated sediment spreading occurred further into San Diego Bay, there would not likely be adverse impact on water quality

- Concern would be the oxidizing environment
- Oxidizing environment occurred during toxicity testing that showed no toxicity

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### **Bioaccumulation of Copper in NCMT-Area Organisms**

Concern: Accumulation of contaminant in an aquatic organism's flesh to levels that would adversely affect higher trophic-level organisms (primarily man and fish-eating birds) that consume the aquatic organism.

"Excessive" body burden determined by FDA Action Levels

No FDA Action Level, or other accepted, reliable guideline for assessing significance of copper

- Copper not particularly toxic to man
- NAS Food & Nutritional Board review (Ahmed, 1991) did not consider bioaccumulation of copper in seafood to be represent a potentially significant health hazard to humans

Summer 1991 study included analysis of 2 types of existing, naturally occurring mussels:

- *Mytilus edulis* ("watercolumn mussel") and
- *Musculista senhousia* ("benthic mussel")

collected from 2 locations:

- near pierface (17,000 mg Cu/kg dry wt.)
- WQCB-SC reference site (150-300 mg Cu/kg dry wt.)

*Little difference in body burdens in mussels from contaminated and reference areas.*

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## **Impact of Further Delay in Remediation of NCMT-Area Sediment**

Copper in NCMT-Area Sediments from Copper Ore Concentrate Expected to Have Been and Now Be in Forms Largely Unavailable to Affect Water Quality

- Expected Based on Aquatic Chemistry of Copper
- Substantiated through Toxicity Testing and Presence of Copper-Sensitive Mussels at Site

Chemical Processes That Occur in Sediment/Water Environment over Time Would Be Expected to

- Maintain the Copper in Unavailable Forms
- Reduce the Availability of More Available Forms

Therefore, Delay of Whatever Remediation May Be Decided Would Not Be Expected to Adversely Affect Water Quality

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## **Copper Ore Concentrate as Source of Copper**

**Copper Exists in a Variety of Chemical Forms, Only Some of Which Are Available-Toxic to Aquatic Life**

Copper Introduced into NCMT Area from Transfer of Copper Ore Concentrate:

*Finely Divided Ore - Cupric Ferrous Sulfide*

*Cupric Ferrous Sulfide as Would Exist in Sediments:*

*One of the Most Stable, Insoluble, and Thus Unavailable Forms of Copper*

*In Contrast with Other Forms of Copper Introduced into San Diego Bay*

*Copper-Based Anti-Fouling Paints Applied to Hulls of Ships; Used at Electric Generating Stations*

*Purpose for Application and Use Is to Kill and Repel Aquatic Life*

*Expected to Initially Have Greater Availability to Aquatic Life Than Copper in an Ore*

*Availability of Copper Derived from Other Sources May Be Significantly Different from That Derived from Copper Ore Concentrate*

**Remediation Objective >1,000 mg Cu/kg  
Consistent with Objectives of Ocean Plan  
and Enclosed Bays and Estuaries Plan**

Intent of Ocean Plan Objectives:

"to ensure the reasonable protection of beneficial uses and the prevention of nuisance."

Intent of Enclosed Bays and Estuaries Plan Objectives:

"to ensure the reasonable protection of beneficial uses and the prevention of nuisance."

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**Aquatic Life Risk Assessment  
Copper-Contaminated Sediments near  
National City Marine Terminal**

*G. Fred Lee, Ph.D. and R. Anne Jones, Ph.D.*

Areas of Expertise:

- Aquatic Biology/Toxicology
- Aquatic Chemistry
- Environmental Engineering
- Public Health
- 30/15 yrs. Experience Evaluating the Significance of Chemical Contaminants in Sediments

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***Tentative Addendum No. 7***

*Assumes "violation" of numeric water quality objective for copper caused by NCMT-area sediment*

- *There is no evidence that copper from the copper ore concentrate now associated with the NCMT-area sediments is, in fact, contributing to so-called violations of the objective for copper.*
- *Concentrations in watercolumn near NCMT before Paco operations were about the same as they were in 1986.*
- *Concentrations in watercolumn near NCMT consistent with concentrations found at other locations in San Diego Bay*

*Assumes "violation" of numeric water quality objective in NCMT area impairing beneficial uses - sport and commercial fisheries*

- *Numeric objective based on available forms of chemical; applied to total concentration*
- *NCMT-area sediment-associated copper unavailable to adversely affect aquatic life; demonstrated through toxicity tests, assemblages of organisms, existence of sensitive mussels in NCMT-area with elevated concentration of copper in sediment*

*Assumes that clean-up objective for NCMT-area sediments of 4,000 or 6,000 mg Cu/kg dry wt. would not protect beneficial uses of San Diego Bay*

- *After extensive study and review, no demonstrated adverse impact currently occurring due to existing copper ore contamination of NCMT-area sediments*

*Used inappropriate data and statistical manipulations to try to show relationship between copper concentrations in sediment and interstitial water*

- *Procedures to separate "soluble" copper component of interstitial overestimated soluble fraction; judged unreliable in US EPA review (Ankley et al., 1991)*
- *Regression between copper concentration in sediment and in associated interstitial water unreliable*
- *Inappropriate elimination of data points*
- *Regression  $r^2 = 0.14$  or  $0.35$*
- *Cupric ferrous sulfide highly insoluble; stable in anoxic sediments*

*Assumes equilibrium partitioning approach provides valid assessments and is applicable to copper*

- *Based on environmental chemistry of copper - cannot assume equilibrium*
- *Acid volatile sulfide normalization not appropriate especially for this system due to analytical considerations*

*Assumes numeric water quality objectives are applicable to interstitial water*

- *US EPA finding: "Further research is required to extend existing knowledge of pore water's suitability for evaluating sediment toxicity."*
- *Other considerations exert control over impacts of contaminants in interstitial water on aquatic life - D.O., organism defenses (e.g., tubes)*

*Assumes concentrations of copper in elutriate can estimate concentrations of copper in watercolumn and interstitial water*

- *Elutriate tests not developed for estimating composition of interstitial water. US EPA also published conclusion that elutriates cannot be used for that purpose.*
- *Elutriate concentrations not applicable to watercolumn concentrations because they do not consider site-specific dilution.*

*It draws the unjustifiable and undocumented conclusion that a copper clean-up objective of 4,000 mg Cu/kg dry wt. would not comply with the Bays and Estuaries Plan requirement to protect beneficial uses of the Bay.*

- *The technical information available and presented in the risk assessment and testimony of the Port indicates that a clean-up objective of more than 4,000 mg Cu/kg dry wt. would protect the beneficial uses of the Bay in accord with the Bays and Estuaries Plan as well as State Water Resources Control Board Resolution No. 68-16, 'Statement of Policy with Respect to Maintaining High Quality of Waters in California,' and the U.S. Environmental Protection Agency's Antidegradation Policy.*

*It draws unjustifiable and undocumented conclusions about the relationship between the copper ore concentrate in the sediment and the concentration of copper in the overlying water in the NCMT area, and contends that a clean-up objective of 1,000 mg Cu/kg dry wt. is needed in order to meet the numeric water quality objective.*

- *From the information available there is no relationship expected for found between the concentrations of copper in the NCMT-area sediments and the concentrations in the watercolumn overlying those sediments.*
- *There is no justification to claim that removal sediment containing more than 1,000 mg Cu/kg dry wt. is needed in order to protect beneficial uses of the waters of the Bay or that such removal will have any influence on the concentrations of copper in the watercolumn.*

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Reference as: "Jones-Lee, A., and Lee, G. F., 'Evaluation of the Water Quality Significance of Copper in San Diego Bay Sediments,' Division Environmental Chemistry, American Chemical Society meeting, extended abstract, Washington, DC, pp. 107-108, March (1994)."