Regulatory Issues Governing Establishment of Remediation Level for Copper in San Diego Bay Sediment

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Over a several-year period a decade ago, copper ore concentrate consisting primarily of chalcopyrite, was discharged into the National City Marine Terminal (NCMT) area of San Diego Bay. This caused the local regulatory agency to try to develop a clean-up objective for the remediation of those copper-contaminated sediments for the purpose of protecting the designated beneficial uses of Bay waters without significant, unnecessary expenditures for copper control.

Several different approaches were suggested for establishing the sediment copper clean-up objective. One approach was the attempted association of a sediment concentration with a "soluble" copper concentration in the interstitial water equivalent to the water quality standard (objective) applicable to the watercolumn. Samples of NCMT-area sediment were filtered through cloth and analyzed to derive what was described to be the "soluble" copper concentration in the interstitial water. The data obtained by that procedure showed that there was no relationship between the copper concentration in the sediment and what was described as the copper concentration in the interstitial water. However, by the discarding of selected data points (arbitrarily characterized as "outliers"), a "relationship" ($r^2 = 0.35$) appeared between concentrations of copper in the sediment and in what was described as interstitial water. Using that "relationship," the regulatory agency concluded that sediments containing more than 1,000 mg Cu/kg had interstitial water with copper in excess of the water quality objective (standard) for copper in the watercolumn. That approach was technically invalid for a number of reasons including the following. The sample handling and analytical procedures used to determine the interstitial water copper concentrations were unreliable. The separation procedure for sampling the interstitial water was unreliable; it would be expected to, and did, produce highly erratic data on the copper concentration in the "interstitial" waters. The data manipulation to exclude certain data points from consideration was arbitrary and highly biased in a effort to try to produce the appearance of a relationship between the total copper in the sediments and the concentration of copper in the interstitial water. Even with the data exclusions, the "relationship" was poor. Finally, the application of the water quality objective for copper in the watercolumn to what was described to be the interstitial water copper concentration is without technical justification or water quality significance.

Another approach was suggested by a local environmental activist group that tried to get the regulatory agencies to adopt a sediment clean-up of objective of 390 mg Cu/kg on the basis that that value had been selected sediments in Puget Sound near Seattle, WA. The 390 mg/kg value cited by that activist group was the "apparent effects threshold" (AET) value had been developed, albeit questionably, in the state of Washington for Puget Sound sediment. In other writings the authors discussed the technical inadequacies of the AET approach and values put forth in the state of Washington, and the reasons that they are not valid for establishing clean-up levels. Even if that AET value had been appropriate for Puget Sound, it should not be directly transposed to the San Diego Bay system. While the approach itself is unreliable, if California regulatory agencies were to have used the site-specific AET approach for the NCMT-area sediments, the clean-up objective that would result would be more than 18,000 mg Cu/kg. That is because the site-specific testing of those sediments (that would form the basis for the AET value) has shown that NCMT-area sediments containing as much as 18,000 mg Cu/kg (the highest concentrations tested) showed no impact on sensitive aquatic organisms, that organisms sensitive to copper have been found living associated with sediments containing copper above that level, and because the numbers and types of aquatic organisms in the copper-contaminated NCMT-area sediments were similar to those found outside of that area.

In separate matters, the state of California Department of Health Services had arbitrarily established that a soil that contained copper in excess of 4,000 mg/kg would be classified as a "hazardous waste." While that value is not applicable to aquatic sediments, it played an important political role in the establishment of the sediment copper clean-up objective recommended by the Regional Water Quality Control Board (RWQCB).

The water quality and public health hazard assessment study undertaken by the authors revealed clearly that the copper-contaminated sediments in the NCMT area were not causing significant adverse impacts on public health or beneficial uses of the Bay waters. That finding and the associated technical substantiation, however, was largely disregarded in the formulation of the sediment clean-up objective that was adopted by the State Water Resources Control Board (WRCB). For example, the WRCB staff chose to ignore the finding that neither the copper nor any of the other contaminants in the NCMT-area sediments caused toxicity to the nine different types of test organisms investigated (some of which were noted by the US EPA for their sensitivity to copper) in an attempt to impose a stricter copper clean-up objective than that which had been adopted by the RWQCB.

Because of the highly complex nature of aquatic sediments as chemical systems, a more effective regulatory system needs to be established if high-quality technical information is to be used in evaluating the water quality significance of chemical contaminants in aquatic sediments, and in formulating technically valid, cost-effective control programs. This paper summarizes approaches that are used in making those regulatory decisions and discusses their technical merits. It also discusses the difficulties that regulatory agencies and the public have in discerning technically reliable information from that which is unreliable, and in the proper use of technical information/approaches in regulatory actions for contaminated sediments.

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

Sample Station	**Sediment Copper** (mg/kg dry wt)	**Copper in** Replicate 1	**Elutriate** Replicate 2	% Elutriate LC50	% Elutriate NOEC
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

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

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

"Although Quite Limited, the Benthic Community Found near the Paco Terminal Pier Provides Evidence That Some Bivalvia Mollosks (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 Organisims (sic - Organisms) Wouldn't Have Been Able to Settle Out and Live and Mature into Adult Forms."*

Deposition of Greg Peters
July 24, 1991

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*

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 in 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.

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*

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.

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

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."

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

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.

Reference as: "Lee, G. F., and Jones-Lee, A., 'Regulatory Issues Governing Establishment of Remediation Level for Copper in San Diego Bay Sediment,' Division Environmental Chemistry, American Chemical Society meeting, extended abstract, Washington, DC, pp. 104-105, March (1994)."