Overview Aquatic Life Risk Assessment

Copper-Contaminated Sediments at

National City Marine Terminal

Prepared by

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3.1 EXECUTIVE SUMMARY

This section of the report presents a review of available information pertinent to assessing the hazards (risks) that the copper ore concentrate in the National City Marine Terminal (NCMT)-area sediments represents to the designated beneficial uses of San Diego Bay. The objective of this risk assessment is 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 the designated beneficial uses of San Diego Bay.

Elevated concentrations of copper have been found in the sediments throughout San Diego Bay since before Paco Terminal's copper ore concentrate transfer operations began at the NCMT. The concentrations of copper in the sediments near the NCMT prior to the use of the terminal for transfer of copper ore concentrate were substantially higher than the concentrations of copper that would be expected without input from anthropogenic (man-related) sources. The copper currently present in the NCMT-area sediments was likely derived from a variety of activities in addition to the transfer of copper ore concentrate, including the use of toxic forms of copper as anti-fouling agents on ship hulls, and street runoff.

The greatly elevated concentrations of copper in the sediments near the pierface of the NCMT (as high as 58,000 mg/kg dry wt. measured during the present study) are of potential concern since some forms of copper in aquatic systems are toxic to aquatic life. However, there is a wide variety of well-known chemical reactions that occur with copper in aquatic sediments that convert copper to forms that are not toxic to aquatic life. Nine different types of test organisms (considering 14 response characteristics) have been used to evaluate the toxicity of sediments from areas near the NCMT that contain elevated concentrations of copper. Those organisms were shrimp, flat fish, sea urchin eggs and embryos, clams, worms, two different types of amphipods (small sediment-dwelling organisms), fish larvae, and oyster embryos/larvae. The test organisms and procedures used are standard, sensitive tests of the type prescribed by the US EPA and the US Army Corps of Engineers (as well as others) to evaluate the potential impacts on aquatic life of contaminants associated with sediments. Embryos of the Pacific oyster, reported by the US EPA to be one of the two most sensitive organisms/stages to copper in salt water, were among the organisms used for toxicity tests in the present investigation.

It was found that eight of the nine organism types tested (including the Pacific oyster embryos) exhibited no toxicity response to the copper-contaminated sediments under the standardized laboratory toxicity test conditions. The one organism that exhibited a toxicity response, *Rhepoxynius abronius* (one of the two types of amphipods tested), exhibited a toxicity response independent of the copper concentration in the sediment. That organism is known to exhibit toxicity responses to a variety of ill-defined physical and chemical conditions. In this investigation, the toxicity response manifested by that organism in response to laboratory exposure to the "reference" site sediments (low copper concentration) was as great as that manifested in response to laboratory exposure to the sediments containing elevated concentrations of copper. Thus, the toxicity response of that organism was likely due to physical factors or to chemical factors other than copper.

Studies of the numbers and types of organisms present in the sediments in the vicinity of the NCMT have shown that differences and similarities between numbers, types, and diversity of organisms in that area are not related to the amount of copper present in the sediments.

In previous studies it was found that concentrations of copper in the watercolumn above NCMT-area sediments containing elevated concentrations of copper were higher than the California water quality objective currently applicable to San Diego Bay. Similar situations were found in other parts of San Diego Bay even prior to the copper ore concentrate transfer operations at the NCMT. In its studies to establish the water quality criterion for copper (recently adopted as the water quality objective by the state Water Resources Control Board), the US EPA found that the embryos of a particular mussel, *Mytilus edulis*, were the most acutely sensitive to copper of the marine organisms it evaluated. That species of mussel presently occurs naturally in the vicinity of NCMT in an area in which the sediments contain some of the highest concentrations of copper. This indicates that the concentrations of copper reported in the watercolumn near the NCMT sediments, if still present, are not available/toxic to those organisms.

The concentrations of copper in mussels planted in the vicinity of the NCMT as part of the state of California Mussel Watch program and in mussels collected from the piers and sediments near the terminal area, while elevated, were not significantly different from the concentrations in tissues of mussels taken from other parts of San Diego Bay. Based on the current information on the toxicity of copper to humans, the levels of copper in the mussels in the NCMT area would not be expected to represent a threat to public health.

While it would be expected that the copper from the copper ore concentrate that is in the NCMT-area sediments would be non-toxic because of its chemical make-up, it is interesting to note that the copper in the sediments from a variety of other areas in San Diego Bay has also been found to be non-toxic to a variety of marine organisms, even though the origin of that copper is likely to have been predominantly the highly toxic anti-foulants applied to boat hulls. Thus it is apparent that, in accordance with the chemistry of copper, even copper introduced into the water of San Diego Bay in highly toxic forms undergoes chemicals reactions in the sediments that lead to its detoxification.

It is concluded that the 1,000 mg Cu/kg remediation objective for the sediments in the vicinity of the NCMT established by the Water Quality Control Board, San Diego Region is highly protective of aquatic life and other designated beneficial uses of San Diego Bay. Further, it is likely that a remediation objective considerably above that concentration could be established and still protect the designated beneficial uses of the Bay. This results from the fact that the form of copper in the copper ore concentrate (cupric iron sulfide) is highly insoluble in anoxic (oxygen-free) sediments such as those beneath the thin oxidized layer at the sediment surface in the vicinity of the NCMT, and the fact that there is a variety of precipitation, complexation, and sorption reactions that cause copper to be converted to non-toxic forms in both anoxic and oxic (oxygen-containing) waters, rendering the copper unavailable and non-toxic to aquatic life in the San Diego Bay sediments and water. Based on the results of toxicity testing, it is concluded that those sediments could be considered for disposal at a designated dredged sediment disposal site off the coast of southern California.

The Department of Health Services (DHS) classifies wastes, soils, and sediments that contain concentrations of copper greater than 2,500 mg/kg wet wt. (approximately 4,000 mg/kg dry wt.) as "hazardous waste." Such a classification could be imposed on the NCMT-area sediments and thereby preclude the open-water disposal of those sediments. However, the approach used to develop the limiting concentration of 2,500 mg/kg wet wt. was based on approaches for solid waste management that do not properly consider the behavior or impacts of these copper-contaminated sediments when disposed in marine waters at an offshore, marine, designated dredged sediment disposal site. Therefore that DHS limit is not appropriate for assessing whether copper-contaminated sediments dredged from near the NCMT may be suitable for disposal at a designated ocean disposal site.

3.2 INTRODUCTION

Under ideal circumstances, an aquatic life risk assessment is a selective, sequential testing and evaluation of the aquatic chemistry - chemical fate and transport - of the contaminants of concern, and their aquatic toxicology - impact, in a tiered framework of increasing sophistication and specificity. It is designed to yield an assessment of the adverse impacts that the given situation has on designated beneficial uses of the water. It can be used to determine the degree of contaminant control needed to protect designated beneficial uses of the waterbody, and to evaluate the improvement in water quality - beneficial uses - that could be achieved as a result of implementing various contaminant control approaches.

Given the nature of this project, the risk assessment conducted for it is based in a synthesis evaluation of the information generated from previous studies augmented by the results of the present investigation of the sediment, water, and organism characteristics in the National City Marine Terminal (NCMT) area. As discussed in other sections of this report, there has been a number of limited-scope studies conducted over the past decade that provide information pertinent to assessing the water quality significance of the copper ore in the sediments near the NCMT. However, in order to evaluate whether attaining the level of removal of copper-contaminated sediment specified in the WQCB-SD "Clean-up and Abatement Order no. 85-91 Addendum no. 6" (the Order) would provide for protection of the designated beneficial uses of San Diego Bay, there was need for additional information to determine the current distribution of copper in the sediments near the NCMT and the impacts that that copper could be having at this time on the aquatic life resources of San Diego Bay. Given the time limitations and the objectives of the risk assessment, a limited-scope series of additional studies was carried out to augment the data base from previous studies, for the risk assessment.

3.3 DEFINITION OF BENEFICIAL USES AND SCOPE OF EVALUATION

The Order specified the aim of providing protection of the designated beneficial uses of San Diego

Bay. In its "California Enclosed Bays and Estuaries Plan - Water Quality Control Plan for Enclosed Bays and Estuaries of California," the state Water Resources Control Board (WRCB, 1991) referred to regional Basin Plans for definitions of beneficial uses of particular waters. According to the Basin Plan for San Diego Bay, "Comprehensive Water Quality Control Plan Report, San Diego Basin, Region 9" (WRCB and WQCB-SD, 1974), what are termed "existing beneficial uses" are present beneficial uses determined by an inventory of water uses in the region. According to WRCB and WQCB-SD (1974), the existing beneficial uses of San Diego Bay are as follows:

- industrial service supply - includes uses which do not depend primarily on water quality such as mining, cooling water supply, hydraulic conveyance, gravel washing, fire protection and oil well repressurization
- navigation - includes commercial and naval shipping
- water contact recreation - includes all recreational uses involving actual body contact with water, such as swimming, wading, waterskiing, skin diving, surfing, sport fishing, uses in therapeutic spas, and other uses where ingestion of water is reasonably possible
- non-contact water recreation - recreational uses which involve the presence of water but do not require contact with water, such as picnicking, sunbathing, hiking, beachcombing, camping, pleasure boating, tidepool and marine life study, hunting and aesthetic enjoyment in conjunction with the above activities as well as sightseeing
- ocean commercial and sport fishing - the commercial collection of various types of fish and shellfish, including those taken for bait purposes, and sport fishing in ocean, bays, estuaries and similar non-freshwater areas
- saline water habitat - provides an inland saline water habitat for aquatic and wildlife resources
- preservation of rare and endangered species - provides an aquatic habitat necessary, at least in part, for the survival of certain species established as being rare and endangered species. This designation is included for all coastal waters in this Region to provide for the reestablishment of the habitat of the brown pelican which is reportedly becoming well-established once again in the San Diego Region.
- marine habitat - provides for the preservation of the marine ecosystem including the propagation and sustenance of fish, shellfish, marine mammals, waterfowl and vegetation such as kelp
- fish migration - provides a migration route and temporary aquatic environment for anadromous and other fish species

- shellfish harvesting - the collection of shellfish such as clams, oysters, abalone, shrimp, crab and lobster for either commercial or sport purposes.

The WRCB and WQCB-SD (1974) also addressed "potential beneficial uses" of the waters of the San Diego Basin, uses that they indicated would probably develop prior to the year 2000 through the implementation of any of the alternative water quality control plans discussed in that document. However, no additional, "potential" beneficial uses were identified for San Diego Bay.

The primary use of San Diego Bay in the area of the NCMT is navigation; the presence of copper in the sediments poses no threat to that use. However, in light of the designated beneficial uses of San Diego Bay overall, the concern about the copper ore concentrate-contaminated sediments focuses on their potential toxicity to aquatic life, and their effect on the numbers and types of organisms in the sediments and on the accumulation of copper from the sediments into aquatic organisms to render them unsuitable for use as food. These are the areas of focus in this hazard/risk assessment. Protection of these uses of the Bay should provide protection for all of the other designated beneficial uses of the Bay.

The scope of this risk assessment has necessarily been limited to evaluating the evidence for the ability of the remediation approach outlined in the "Clean-up and Abatement Order no. 85-91 Addendum no. 6" (the Order) to protect the designated beneficial uses of San Diego Bay. That remediation approach would involve the removal of those sediments in the area of the NCMT used by Paco Terminals, Inc. (Paco) that now contain in excess of 1,000 mg Cu/kg sediment dry wt. Since previous studies in the area of the NCMT showed that there was no toxicity to sensitive aquatic organisms in toxicity tests of copper-contaminated sediments from that region, that the numbers and types of infaunal (sediment-dwelling) organisms appeared to be unrelated to the copper concentration in the sediments, and that there did not appear to be excessive bioaccumulation of copper in aquatic organisms in the region, there were significant questions about the need to remove any or all of the copper-contaminated sediments from the NCMT area in order to protect beneficial uses of San Diego Bay. As discussed below, the basis for the development of the remediation goal of 1,000 mg Cu/kg dry wt. was somewhat arbitrary and had limited technical foundation. Those findings and issues notwithstanding, the studies that would be needed to address the technical aspects of those issues were beyond the scope of this project. Instead, the focus was on whether designated beneficial uses of the Bay would be protected after removal of sediments containing more than 1,000 mg Cu/kg dry wt.

3.4 AQUATIC CHEMISTRY COMPONENT OF RISK ASSESSMENT

3.4.1Principles of Aquatic Chemistry of Sediment-Associated Copper

As discussed by Lee and Jones (1983) as well as the US EPA (1985) and others, chemical contaminants exist in aquatic systems in a variety of forms, only some of which are available to adversely affect aquatic life and related beneficial uses. In assessing the potential risk that a contaminant represents to aquatic life-related beneficial uses of a water, it is important to focus on those forms that are available. These points are addressed in some detail in this section of this report and are illustrated with the results of selected works related to the copper situation in San Diego Bay.

The importance of understanding that many forms of copper are unavailable to affect aquatic life is echoed throughout the technical literature. For example, Tessier and Campbell (1987) concluded from their study of the partitioning of trace heavy metals in sediments, *"... the total concentrations of a metal in sediments provides little indication of the potential interactions of the sediments with the abiotic* [non-living] *and biotic* [living] *components..."* They noted the complexity of heavy metal/sediment association, pointing out that heavy metals in sediments can be associated with clay surfaces, clay structural matrices, fumic acids, surfaces of iron and manganese hydrous oxides, detrital as well as freshly precipitated carbonates, nodules, detrital organic matter of terrestrial and aquatic origin, and crystalline and amorphous sulfides. The complexity of the chemistry of heavy metals in sediments makes their significance to aquatic life difficult to ascertain by chemical means.

Particulate (insoluble) forms of copper, such as result from precipitation reactions and sorption (attachment of dissolved copper onto sediment particle surfaces), are essentially unavailable to be toxic to or accumulate within aquatic organisms. While the ionic copper aquo-species is generally considered available, not all other soluble forms of copper are available-toxic to aquatic life. Soluble copper can react with organics and inorganics to form soluble chemical complexes that are not toxic to aquatic life. As discussed below, both the insoluble and the non-toxic soluble forms of copper reduce the impact that the total concentration of copper has on aquatic organisms.

Waldichuk (1985), Senior Scientist at the West Vancouver Laboratory of the Canada Department of

Fisheries and Oceans, discussed the importance of focusing contaminant control programs on forms of contaminants that are available to aquatic organisms. In particular, his review addressed his agency's experience in the examination of the water quality impacts of copper mine tailings-ore in marine waters. Waldichuk (1985) discussed at length many of the various mechanisms noted in the present authors' review by which copper and other heavy metals are detoxified - made unavailable - in saltwater systems. He discussed the variability in the solubility of metals in inorganic matrices and that the physical and chemical treatment to which an ore is subjected can alter the extent of leaching of metals when the copper ore tailing are discharged into seawater. He used as an example the differences in availability of heavy metals in tailings from a zinc/lead mine on the westcentral coast of Greenland when discharged into seawater and in tailings from a copper mine that are discharged to Rupert Inlet on the west coast of Vancouver Island, reported by Waldichuk and Buchanan (1980). It was reported that while the mine tailings discharged through the Rupert Inlet on the west coast of Vancouver Island showed little availability to aquatic organisms, this was not the case for zinc/lead tailings discharged off the coast of Greenland. Those findings point to the importance of conducting site-specific investigations to determine whether or not the materials of concern are available in the receiving waters.

Windom *et al.* (1982) studied the uptake (accumulation) of metals by a marine polychaete (worm), *Capitella capitata*, as it is influenced by the metal content and "nutritional status" (i.e., nitrogen content) of the organic detritus that that organism uses for food. They found that the nitrogen content of the detritus influenced the accumulation of metals in the organism. They also reported an influence of the heavy metal content of the detrital food source on the accumulation of metals, although their data did not indicate a positive correlation between the detrital copper concentration and the amount of copper accumulated in those organisms in their test conditions. Those results point to the complexity of the factors controlling uptake of heavy metals from particulates in aquatic systems; factors not related to contaminants, such as the nitrogen content of the detritus particles used as food, appear to exert some influence on the uptake of heavy metals from the particles by certain aquatic organisms.

Elderfield (1981), and Elderfield *et al.* (1981a,b) examined the behavior of various heavy metals, including copper, in interstitial waters from Narragansett Bay, RI sediments. Elderfield (1981) reported that on the order of 80% of the dissolved copper (separated by centrifugation followed by filtration through a 0.4 μ pore-size filter) in the interstitial waters of the anoxic sediments of

Narragansett Bay were complexed with natural dissolved organic matter or associated with colloidal organic matter. He also reported that insoluble sulfide was a major factor controlling the availability of copper in the interstitial waters and that it caused the copper concentration in the interstitial waters to be very low. It may thus be concluded that the interstitial water copper was significantly complexed by or bound to organics that would affect the availability of copper to be toxic to aquatic life. Elderfield *et al.* (1981a) reported that the fluxes of copper and several other heavy metals from the anoxic sediments to the interstitial water were extremely low due to the formation of metal sulfides. They further suggested that there is a small net flux of sulfide-forming metals, including copper, into anoxic sediments. Elderfield *et al.* (1981b) reported that the concentrations of copper in the interstitial water were controlled by highly insoluble copper sulfides; the copper concentrations in the interstitial water decreased with increasing depth in the sediments and became undetectable within a few cm of the sediment-seawater interface. The concentrations of copper found in the interstitial waters of the sediment that they studied were less than about 1 µg/L.

Loring (1981, 1982) investigated the factors controlling the accumulation and availability of copper and other heavy metals in sediments from the Bay of Fundy and other eastern Canadian estuarine and coastal areas. Loring (1981) noted that no one chemical extractant for sediment has been shown to accurately predict the bioavailability of any element in sediment, and that any assessment of impact of sediment-associated heavy metals must take into account the availability of the forms present. He concluded that copper was associated to a limited extent with calcareous (carbonate) fractions of the sediment. In sediments containing sulfide, copper as well as several other heavy metals were present primarily precipitated as a sulfide and not available to biota.

Much of the work on the speciation and the toxicity of copper in aquatic systems has been done in freshwater environments. While the chemistry-speciation of copper in fresh and salt water are controlled by the same reactions, characteristics of salt water, such as its comparatively greater carbonate content and ionic strength, tend to make a given amount of copper less toxic in saltwater than in fresh water. Pagenkopf *et al.* (1974) discussed the various copper carbonate and hydroxide complexes and their respective toxicities to fathead minnows and rainbow trout. They noted that the uncomplexed soluble copper (II) aquo species was the most toxic form of copper.

Andrew *et al.* (1977) investigated the acute (72-hr) toxicity of inorganic copper complexes to *Daphnia magna* (a small "water flea") in soft Lake Superior water. They found that based on calculated species composition of the test waters, the Cu^{2+} (ionic, aquo species of copper) and $Cu(OH)_n$ (hydroxide complex) forms caused toxicity, while soluble $CuCO_3$ (copper carbonate) and other complexes such as those with phosphate were non-toxic. Toxicity was found to be independent of the concentrations of dissolved copper and of total copper in the presence of complexing agents.

Stiff (1971) reported on the presence of copper complexes in freshwater systems and noted that in addition to forming complexes with carbonate and hydroxide, copper readily complexes with cyanide, amino acids, polypeptides, and humic substances. He concluded that the copper in the variety of freshwater systems he studied was primarily associated with the suspended solids or existed as soluble copper complexes. The concentrations of free copper ion were very low compared to the total copper concentrations of those waters.

Dodge and Theis (1979) discussed various forms of soluble copper that exist in aquatic systems and their availability to freshwater aquatic life. They conducted laboratory studies of the uptake (i.e., accumulation) of various species of copper from solution by the freshwater midge larvae (*Chironomus tentans*). They found that while copper was taken up from solutions in which the dominant copper species was the free cupric ion or a copper-hydroxy complex, no uptake was found when the copper was present as a complex with glycine (an amino acid) or NTA (nitrilotriacetate). Andrew *et al*. (1977) and Pagenkopf *et al*. (1974) also reported direct correlations between the cupric ion activity in a solution and the mortality of the freshwater *Daphnia magna*, and of fish (fathead minnow and rainbow trout), respectively in toxicity tests.

Meador (1991) investigated the bioavailability of copper as a function of pH and dissolved organic carbon in fresh water. He found that both factors were important in controlling the amount of ionic copper in solution and the toxicity of the copper to *Daphnia magna*. The copper was less available (less toxic) at higher pH's, as would be expected owing to the formation of less toxic copper complexes with hydroxyl species. At the pH's found in seawater, much of the copper in solution would be expected to be present as copper-hydroxyl complexes. Meador (1991) also noted that dissolved organic carbon complexed with ionic copper to form copper complexes; copper in water with higher dissolved organic carbon content was less toxic than the same amount of copper in water with lower concentrations of dissolved organic carbon.

On behalf of the International Copper Research Association, Lewis (1989) prepared a review of the literature published in 1986-1987 on various aspects of copper in the environment. The International Copper Research Association published similar literature reviews in 1973, 1978, and 1984. The 1989 literature review was much more comprehensive than the earlier reviews and covered essentially all aspects of the biological significance of copper in terrestrial and aquatic environments. Of importance to this project is the listing of information from the literature on the concentrations of various chemical forms of copper and their biological significance in aquatic organisms and in fresh and marine waters. Those literature reviews may be consulted for additional information and references.

It is evident from the literature that sediment-associated copper, especially a sediment-associated copper sulfide ore, would not be expected to be available to cause toxicity to or accumulation in aquatic organisms, especially in marine environments. It would also be expected that substantial portions of soluble copper in a watercolumn or in the interstitial waters of a sediment would exist as soluble complexes that are non-toxic to aquatic life, again especially in marine waters.

3.4.2Characteristics of Copper Ore Concentrate in NCMT-Area Sediments

The copper ore concentrate transferred at the NCMT was composed of finely divided cupric ferrous sulfide ($CuFeS_2$), with 85% of the particles being less than 100 μ in diameter; the material reportedly contained up to 30% copper (Lester, 1991). According to the Merck Index (1983), cupric ferrous sulfide (chalcopyrite) has a density of 4.1 to 4.3 which makes it considerably denser than normal marine sediment particles. As discussed by Morse *et al.* (1987), the chemistry of metal sulfides in sediments is highly complex and not fully understood. However it is known that in anoxic (oxygen-free) environments cupric ferrous sulfide is one of the most stable, insoluble forms of copper. Therefore, in the anoxic sediments of San Diego Bay, the copper in the copper ore concentrate would be expected to be stable, highly insoluble, and thus largely unavailable to affect aquatic life. When in contact with dissolved oxygen, such as would be found at the surface of the sediments or in the watercolumn, this mineral could be slowly oxidized and solubilized. However, in oxic (oxygen-containing) environments copper can be readily removed from solution through a variety of precipitation reactions; copper also tends to strongly sorb onto sediment particles. Lindsay (1979) reported that sorption of copper can lower the concentrations of soluble copper almost to the same degree as the precipitation of copper as a sulfide. Precipitated and sorbed species of copper are largely unavailable to aquatic life.

3.4.3Copper in NCMT-Area Sediments

3.4.3.1Concentrations of Copper

There has been a number of studies on the characteristics of the sediment in San Diego Bay and the NCMT area in particular, that provide data pertinent to assessing the water quality significance of the elevated concentrations of copper in those sediments. An overview discussion of the results of those studies and a presentation of the data generated during the current study are presented elsewhere in this report. A summary of key information from that work pertinent to conducting the risk assessment for the NCMT-area sediments is presented below. Figure 3-1 shows the locations of sampling areas mentioned below as discussed in the literature cited.

Zirino (1990) reported that in 1972 J. Mathewson found that copper concentrations in sediments in the Bay ranged from 24 mg/kg dry wt. near its mouth to 892 mg/kg dry wt. near the US Navy Pier at 32nd Street (about 0.3 mi north of the NCMT). According to Delaney (1985), in April 1979 concentrations of copper in sediments 240 to 720 ft offshore of the NCMT ranged from 92 to 178 mg/kg dry wt. According to the California Department of Health Services (DHS, 1984), Conner and Shacklette (1975) reported that the mean concentration of copper naturally occurring in soils of the western US is 21 mg/kg dry wt. Table 7-1 in this report shows that in 1979, sediments near the Navy Pier 13 just north of the NCMT contained more than 300 mg Cu/kg. Thus even prior to the copper ore concentrate transfer operations at the NCMT that began in 1979, concentrations of copper present in sediments of San Diego Bay, including the NCMT area, were above those that would be expected without anthropogenic sources of copper.

In 1984 NOAA began its National Status and Trends Program for Marine Environmental Quality to define the geographic distribution of contaminant concentrations in sediments and marine organism tissue. Five sites in the San Diego Bay area were included in those data bases (Figure 3-2). The data bases for that compilation of information included the "Benthic Surveillance Project" (providing data for 1984-1986) and the "Mussel Watch Project" (providing data for 1986-1989). Samples from each of three separate stations (which themselves consisted of a composite of three separate samples of the uppermost 1 or 3 cm of sediment) within a "site" were collected at each sampling; the sampling stations were within 1 km of one another. The NOAA (1991) data for the region near the NCMT are presented in Figure 3-2. They show that the concentrations of copper in San Diego Bay sediments ranged from tens to hundreds of mg Cu/kg dry wt.

The vertical and horizontal distributions of copper in the sediments near the NCMT in 1989 and at present are shown in this report in Tables 7-5 and 7-7. At this time, the sediments in the area in which the highest concentrations have been found (Transect 5 near the pierface) contain as much as 58,269 mg Cu/kg dry wt; that concentration was found 2 to 3 ft beneath the sediment surface. From the comparison of the most recent data with that collected in 1989 (Table 7-7), there is some evidence that the copper ore concentrate-contaminated sediments are moving deeper into the sediments. This would be expected based on the specific gravity of the ore particles compared with that of the typical particles in the sediment. Because of the reducing conditions deeper in the sediments, that movement would further decrease the availability of the copper in those sediments to aquatic life.

3.4.3.2 Sources of Copper in the NCMT-Area Sediments

In assessing the water quality significance of copper in the NCMT-area sediments, it is important to consider all of the potentially significant sources of the copper in those sediments and their relative availability to adversely affect water quality in the Bay. As discussed earlier, the sediments from many areas of San Diego Bay, including the NCMT area, have contained elevated concentrations of copper compared with sediments in many other bays, estuaries, and coastal marine waters in the US, since before the copper ore concentrate transfer activities began at the NCMT. Thus, the copper ore concentrate is not the only source of the copper in the sediments near the NCMT. Copper has been, and continues to be, used in the San Diego Bay area in anti-foulant paints. According to sources cited by WESTEC (1985), on the order of 50 metric tons of copper in copper-based anti-foulant paints are applied annually to the hulls of ships in boatyards in San Diego Bay. The specific purpose of the application of such anti-foulants is to kill and repel aquatic life. The anti-foulant paint is designed to gradually release copper in forms toxic to aquatic life. Thus paint chips and scrapings that enter the water and that reach the sediments would be expected to release available forms of copper. Copper has been used as an anti-fouling agent at electric generating stations in the San Diego Bay area as well.

Another source of copper that is of potential significance in the Bay sediments is urban runoff. WESTEC (1985) cited estimates of copper input to the Southern California Bight from stormwater runoff in 1972-1973 of 42 metric tons/year. It would be expected that the concentrations of soluble and total copper would increase in San Diego Bay near storm sewer inputs after runoff events. Pitt and Field (1990) summarized the US EPA National Urban Runoff Program urban stormwater drainage data and reported that the median concentration of total copper in stormwater drainage from large US cities was 35 μg/L. As discussed below, that level is about 10 times the water quality objective for San Diego Bay. According to their data, the concentration of copper in apparently soluble forms exceeded 10 μg/L in some urban stormwater drainage. Therefore for a period after a rainfall runoff event, the concentrations of total and soluble copper would likely exceed the water quality objective due to runoff from streets. Eventually some of total copper would settle or precipitate and become part of the sediments, and some would be diluted in the Bay waters. Lee and Jones (1990a) discussed an approach that should be used to determine the potential water quality impacts of heavy metals such as copper and other constituents in urban stormwater drainage on the beneficial uses of waters receiving such drainage. The approach advocated is similar to that used in the present study, i.e., conducting a hazard/risk assessment to determine the fate and toxicity of the constituents in the receiving waters.

Concentrations of copper in coastal bays and estuaries in several locations in the US (including San Francisco Bay and New York Harbor) are being found to exceed US EPA water quality criteria (see Lee and Jones, 1991). One significant source of that copper has been found to be domestic wastewater discharged to bays or estuaries. The copper in domestic wastewater can be derived from water utilities' using copper in water supply reservoirs to control algal growth as well as from the corrosion of copper pipe used in the water distribution system, especially in homes. The copper added to the reservoir is carried through the city and becomes part of its wastewaters. While domestic wastewaters are not now being discharged into San Diego Bay, at one time they were. It is possible that some of the elevated copper in the San Diego Bay sediments was derived from its use as an algicide in water supply reservoirs.

In summary, while the substantially elevated concentrations of copper in the immediate area of the NCMT was likely largely derived from the copper ore concentrate transfer activities at that terminal, there are other sources of copper that also contribute to the total copper concentration in those sediments. The forms of copper contributed from at least some of those other sources, in particular anti-foulants, are expected to be considerably more available to aquatic organisms than the copper from the copper ore concentrate. Thus, while the copper ore concentrate-derived copper would contribute substantially to the total concentration of copper in the sediment, the concentrations of copper in the interstitial water and in the watercolumn in the vicinity of the NCMT, and the accumulation of copper in mussels, could be influenced or controlled by the more readily available, other sources of copper in the sediments. As discussed subsequently in this section, studies on the concentrations and availability of copper have been conducted in parts of San Diego Bay in which copper has been derived from such other sources.

3.4.3.3 Implications of Acid Volatile Sulfides for the Availability of Copper in NCMT-Area Sediments

As discussed earlier, it has been known for many years that if sulfides, either crystalline or amorphous forms, are present in aquatic sediments, they control the solubility of many sediment-associated heavy metals, including copper, through metal precipitation reactions. Copper sulfide is one of the most insoluble of the metal sulfides. The importance of sulfide in controlling the toxicity of heavy metals in aquatic sediments has led to the US EPA's current efforts to try to develop sediment quality criteria for heavy metals based on normalization of the heavy metal concentrations in the sediment by the concentrations of so-called "acid volatile sulfides" in the sediments.

"Acid volatile sulfides" comprise a group of amorphous (non-crystalline) sulfides and polysulfides that occur in sediments that do not contain dissolved oxygen. In many aquatic sediments, bacterial utilization of organic matter derived from natural as well as anthropogenic sources depletes the dissolved oxygen in the sediment. In the absence of dissolved oxygen, sulfate in sediments is reduced to sulfide. The sulfides, in turn, interact with heavy metals to form highly insoluble metal sulfides. Those reactions are discussed by Morse *et al*. (1987). It has been found (e.g., see DiToro *et al*., 1990) that when the molar sum of the so-called acid volatile sulfides exceeds the molar sum of the non-iron heavy metals in the sediment, the heavy metals in the sediment are not available, and hence are not toxic, to aquatic life. This finding is to be expected based on the chemistry of heavy metal sulfides in sediments.

At the US EPA "Contaminated Sediment Assessment Methods Workshop" held in May 1991, several US EPA representatives and their contractors discussed their current work on the use of acid volatile sulfides in the estimation of the availability of heavy metals in sediments. Their work on this topic includes the development of a standardized analytical procedure for the determination of acid volatile sulfides in sediment (US EPA, 1991a). The measurement of amorphous sulfides in sediments is operationally defined; the amount of sulfide measured depends on the analytical procedure used and the forms in which the sulfide exists in the particular sediment.

The procedure being proposed by the US EPA does not measure all of the forms of precipitated sulfides that can occur in sediments and hold copper or other heavy metals unavailable to aquatic life. For example, it appears that the US EPA procedure would not measure the sulfide associated with the copper ore concentrate of concern at the NCMT site since the US EPA procedure specifies use of HCl for the liberation of sulfides from the sediments; according to the Merck Index (1983) chalcopyrite (cupric ferrous sulfide) is not soluble in HCl. Thus, the sulfide associated with that material would not be released for measurement in the analysis. It should be noted that chalcopyrite is not an amorphous sulfide targeted by the US EPA procedure, but rather is a crystalline heavy metal sulfide typically associated with some copper ore bodies. Nevertheless, Morse *et al.* (1987) indicated that there is some evidence for the formation of this cupric ferrous sulfide in aquatic sediments, and copper associated with crystalline sulfides are not available-toxic. Further, in addition to chalcopyrite, there is a number of other highly insoluble copper sulfide species that can limit the solubility and therefore the toxicity of copper associated with sediments and yet are not measured by the US EPA procedure.

Since no sulfide measurements had been made in previous studies of the sediments in the NCMT area, samples were collected for this determination in the current study (Table 7-8). Comparison of those data with the copper concentrations in sediments from the same areas shows that the molar concentrations of copper exceeded those of acid volatile sulfides by a factor of 10 to 10,000. Superficially this might lead someone to conclude that the copper in those sediments would be toxic to aquatic life. However, it is important to understand that the principal form of copper in the NCMT area is copper iron sulfide (chalcopyrite). While the analytical method used for copper determination employed a sufficiently strong acid to dissolve the copper from the chalcopyrite, as discussed above the analytical method for sulfide does not release the sulfide from that mineral. Thus, the amount of copper is disproportionately higher than the sulfide. It may therefore be concluded that the acid volatile sulfide normalization procedure for copper in sediments that contain copper in the form of chalcopyrite is not reliable for estimating the potential availability of the copper.

3.4.4Copper in the Watercolumn

3.4.4.1 Concentrations of Copper

One of the issues of concern in evaluating the risk that the copper in the sediment near the NCMT represents to beneficial uses of San Diego Bay is the possibility that the solid phase contributes sufficient copper to the overlying waters to adversely affect aquatic life. WESTEC (1986a) reported the concentrations of copper in the water near the NCMT, 1 and 2 m above the sediment surface at high and low tides in an area where the sediment copper concentration was elevated (19,800 mg Cu/kg dry wt.). They found that the total copper concentrations in those waters were 3 to 33 µg Cu/L; they also reported that the "soluble" copper concentrations were between <2 and 8 µg Cu/L. The interpretation and implications of these results are discussed subsequently in this section of this report.

Anderson *et al.* (1991) reported on a series of toxicity tests to determine the toxicity of copper (in the form of copper chloride) to sperm, embryos, and larvae of topsmelt (*Atherinops affinis*); the response parameters measured were fertilization, embryo development, and larval survival, respectively. The EC50 for the chronic bioassays ranged from 24 to about 190 µg Cu/L; NOEC (no observed effects concentration) values ranged from 32 to 123 µg/L. The LC50 values for the larval survival tests ranged from 212 to 288 µg Cu/L; the NOEC values ranged from 90 to 160 µg/L. The form of copper tested is known to be highly available. Those results indicate that the copper concentrations measured in the watercolumn near the NCMT terminal, even if totally available, would not be adverse to the reproduction of topsmelt since the concentrations found were typically below those that have been found by Anderson *et al.* to cause no chronic toxicity impacts.

Krett (1979) reported on a study directed toward evaluating the impact of copper in San Diego Bay waters on phytoplankton in the Bay. The three sampling stations were the US Navy Pier 6 located about halfway down the east side of the Bay at the 32nd Street Naval Shipyard; the Shelter Island Fishing Pier on the southeast (bayward) side of Shelter Island, a station reportedly close to the main

Bay channel and with good tidal flushing; and a docking facility on the northwest side of Shelter Island (Shelter Island Yacht Basin). Samples were collected of the upper 1 m of water monthly at those stations between July 1978 and early June 1989 (prior to the copper ore concentrate transfer operations at the NCMT); in addition, at three different times during the sampling year, six samples were collected during a four-day period. Krett reported that a total of 31 samples of the upper one meter of the water was collected at the Shelter Island stations during her study.

Krett's samples were analyzed for various fractions of copper by anodic stripping voltammetry (ASV). The copper measured in unfiltered samples at ambient water pH was termed "soluble-uncomplexed" (soluble) copper; copper measured in unfiltered samples adjusted to pH 2 was said to approximate total copper; and copper in filtered samples adjusted to pH 2 was said to approximate the colloidal plus soluble copper. The concentrations of copper associated with the suspended particulates were also measured. The procedures used do not yield a fraction of copper that was interpretable in terms of its potential biological significance; the problems associated with using chemical speciation of that type to draw conclusions about the available copper have already been discussed in this section. The concentrations of what Krett called "soluble" and "total" copper are discussed below.

The total copper concentrations in the surface water at the Navy Pier ranged from about 2.1 to 22.6 µg/L with a mean of 6.7 µg/L. The mean soluble copper at the Navy Pier was 3.1 µg/L. The total copper in the waters from the southeast (channel) side of Shelter Island ranged from 0.7 to 4.0 µg/L with a mean of 2.2 µg/L. The mean soluble copper at that location was 1.0 µg/L. The Shelter Island Yacht Basin samples contained total copper concentrations ranging from 1.7 to 19.1 µg/L with a mean of 8.2 µg/L. The soluble copper at that location was 3.4 µg/L. Those results indicate that approximately 50% of the copper present in the samples from those locations was "soluble," i.e., the copper in unfiltered samples analyzed at ambient pH using ASV was about half that measured in unfiltered samples acidified to pH 2. Based on the known use of copper as an anti-foulant on boat hulls, it would be expected and was found that the Shelter Island Yacht Basin samples had the highest concentrations of copper; the concentrations at the Navy Pier were somewhat lower, and the concentrations from the Shelter Island Pier significantly lower. The total copper present in the Shelter Island Yacht Basin and Navy Pier waters exceeded the water quality objective adopted by the State Water Resources Control Board in April 1991 of 2.9 µg/L.

Krett (1979) attempted to assess the potential impact of copper on phytoplankton by adding known amounts of copper sulfate (available copper) to samples of the Bay water taken from each of the stations. The primary productivity as measured by carbon 14 uptake was assessed over a four-hour period. While differences in C-14 uptake were noted among the samples, that approach is not reliable for assessing the impact of contaminants on phytoplankton populations. It is well-known that in order to properly assess the impact of copper on phytoplankton, it would be necessary to examine the change in primary productivity over about a two-week period (Plumb and Lee, 1979). While the four-hour incubation used by Krett may show short-term "impacts," that incubation period is inadequate to reliably assess the actual longer-term impacts in that systems. It is the authors' (Lee and Jones') opinion based on examining the impacts of heavy metals and other contaminants on phytoplankton that it would be very unlikely that copper at a few μg/L would be significantly toxic to planktonic algae in San Diego Bay waters.

Johnston (1989) conducted a study of the Shelter Island Yacht Basin (Yacht Basin) in San Diego Bay for the purpose of assessing the potential biological significance of copper and organotin compounds in the water to the composition of organism communities that attach to structures in that area of the Bay. His study included four sampling stations, three within the Shelter Island Yacht Basin and one outside the Basin, in the Bay at the NOSC Pier 159. Water samples were collected as a function of tide, from the 0.5-m depth at those stations during the period June 17 through September 16, 1986, during the period December 16, 1986 through January 23, 1987, and on September 13, 1987. Concentrations of total copper were measured, as were the concentrations of copper that responded to the anodic stripping voltammetric analysis of unfiltered, acidified (pH 1.8) samples (ASV-copper); more than 100 chemical analyses of those two types of copper were performed. The copper measured by anodic stripping analysis of a filtered, acidified sample is somewhat closer to the biologically available copper than the total copper. However, the samples were not filtered in that study; the acidification of the sample prior to analysis by anodic stripping causes the release and hence measurement of forms of copper that are not available, such as copper complexes and copper associated with particulates.

The mean concentration of ASV-copper outside the Shelter Island Yacht Basin was 2.6 μg/L, while the mean concentrations of ASV-copper in the samples from within the Yacht Basin ranged from 7.1 to 11 μg/L. Concentrations of total copper in the samples collected outside the Yacht Basin averaged 5.1 μg/L while the average total copper concentrations from the stations within the Yacht Basin ranged from 6.5 to 11.8 μg/L. Some samples from within the Yacht Basin contained concentrations of total copper and of ASV-copper on the order of 12 to 15 µg/L, with some as high as 24 µg/L. About 50% of the average total copper in the samples from the more open-water site was ASV-copper, while the ASV-copper represented 70 to nearly 100% of the total copper in the samples from within the Yacht Basin. As expected, samples collected at high tide contained lower concentrations of copper due to the diluting effect of the incoming tidal waters. A comparison can be made of the concentrations of copper measured by ASV on unfiltered, pH-adjusted samples (pH 1.8 to 2) in the Shelter Island Yacht Basin area by Krett in 1979 and those measured by Johnston eight to nine years later. The concentrations of copper measured with that procedure in 1979 ranged from 1.7 to 19.1 µg Cu/L (average: 8.2 µg Cu/L); concentrations in the same general area in 1986-1987 ranged from 4.9 to 23.9 µg Cu/L (average: 11.1 µg Cu/L). While superficially it might appear that there was an increase in the concentration of copper between the two sampling periods, examination of the data shows that the variability about the mean concentrations is such that the two means are not statistically significantly different.

Based on data provided by Kenis *et al*. (1978) and Johnston (1989), Zirino (1990) reported that the dissolved copper concentrations in San Diego Bay water ranged from about 2 µg/L in the main body of the Bay to about 12 µg/L at the head of the Bay near the Shelter Island Yacht Basin. Zirino (1990) also indicated that the concentrations of dissolved copper in Commercial Basin and in some other areas may be much higher.

Therefore, the range of dissolved copper concentrations found by WESTEC (1986a) are in accord with what has been found in other parts of the Bay.

3.4.4.2 Water Quality Criteria and Objectives for Copper

The US EPA water quality criterion for copper in marine waters is a one-hour average not to exceed 2.9 µg Cu/L (US EPA, 1985). According to Hansen (1991), the US EPA is not currently working toward revision of that criterion, even though it is well-established that for many waters its current criterion value is unnecessarily restrictive for the protection of aquatic life-related beneficial uses. In its "Enclosed Bays and Estuaries Plan," the California Water Resources Control Board adopted the US EPA copper criterion as the state water quality objective for the protection of marine organisms in its enclosed bays and estuaries from impacts of copper (WRCB, 1991). The state of California objectives for the protection of organisms in open marine waters ("Ocean Plan") are a six-month median concentration of 3 µg Cu/L, a daily maximum concentration of 12 µg Cu/L, and an instantaneous maximum concentration of 30 µg Cu/L (WRCB, 1990). While the basic numeric values for the water quality objectives for copper in the Enclosed Bays and Estuaries Plan (2.9 µg Cu/L) and the Ocean Plan (3 µg Cu/L) are essentially the same, the Ocean Plan allows excursions to concentrations 10-times that basic objective. This difference in the excursions allowed in the two Plans reflects the high degree of uncertainty that exists in developing the water quality objectives. While San Diego Bay is included under the Enclosed Bays and Estuaries Plan rather than the Ocean Plan, it is important to understand that the water quality objectives in both Plans are designed to protect the same types of marine organisms.

If it is assumed that the concentrations of copper measured in the watercolumn by WESTEC (1986a) are representative of conditions that exist in the NCMT area today, the concentrations of copper in the watercolumn exceed currently applicable water quality objectives. However, as discussed below, this should not lead to the conclusion that the beneficial uses of San Diego Bay have been or will be adversely affected by copper from the copper ore concentrate.

It is well-known that as implemented today, US EPA water quality criteria and state water quality objectives equivalent to those criteria are, in general, overly restrictive in protecting aquatic life-related designated beneficial uses. This is especially true for copper. There are several issues that need to be considered in the evaluation of the potential impact that an exceedance of the water quality objective for copper means for aquatic life-related designated beneficial uses. Of particular import is the fact that the US EPA water quality criteria, and therefore the state water quality objectives, are based on worst-case or near-worst-case assumptions. First, in the laboratory studies used to establish the criteria values, efforts were made to present the contaminant tested to the organisms in 100% available forms; the objectives, however, are applied to total concentrations of contaminants irrespective of availability. As discussed earlier and additionally below, copper (as well as many other contaminants) exists in aquatic systems in a variety of forms, only some of which are available to affect aquatic life. Thus, the concentration of total copper in a water is an unreliable measure of the potential for the copper present to adversely affect aquatic life.

Second, the criteria/objectives are based on the assumption that an organism receives a chronic (extended-duration) exposure to the chemical. It is well-known that even though the copper criterion and objective are listed as "one-hour average maximum" levels, organisms can be exposed to concentrations higher than the objective for periods of time considerably greater than one hour without adverse impact. In a system such as San Diego Bay, the exposure duration of watercolumn organisms to sediment-associated contaminants would be expected to be considerably shorter than the chronic exposure duration. Storms, ship traffic, unusual tides, etc. can stir sediments into the watercolumn for short periods of time; the sediments then settle again. Soluble contaminants that could be released during that time would be expected to be rapidly diluted.

The US EPA criterion and the state of California water quality objective are applied to the total copper concentration present in the water as measured after strong acid digestion of the water to solubilize particulate forms and break-down copper complexes. However, it is widely recognized that particulate and some complexed forms of copper are non-toxic. The US EPA (1985) recognized that its criterion value applied to total concentrations of copper would be overly restrictive. Today, the US EPA is exploring a policy of application of its criteria to ambient-water-soluble forms of heavy metals (Delos, 1990). Lee and Jones (1990b) recommended that the state Water Resources Control Board apply its objectives to ambient-water-soluble forms of heavy metals because that approach would more properly consider the toxic-available forms of those contaminants.

The overly restrictive nature of the water quality objective for copper in marine waters is also recognized by the San Francisco Bay Water Quality Control Board; at this time that Regional Board is conducting a quarter-million-dollar study to develop a water quality objective for copper in San Francisco Bay waters that is more appropriate than that developed by the State Board. The justification for that effort is that total copper concentrations in San Francisco Bay waters exceed the water quality objective yet the waters have been found to be non-toxic to sensitive forms of aquatic life. It may therefore be concluded that the water quality objective applicable to San Diego Bay (one-hour average concentration not to exceed 2.9 μg Cu/L) is more restrictive than needed for the protection of beneficial uses and that concentrations of copper in the San Diego Bay waters, and for that matter its interstitial waters, can exceed this amount without significant adverse impacts on beneficial uses.

3.4.4.3 Significance of Copper Concentrations in Watercolumn at the NCMT

It is clear that it is inappropriate to compare the water quality objective for copper to the total concentration of copper in the watercolumn at the NCMT in the assessment of potential adverse impacts of copper. Because the truly soluble forms of copper more closely estimate available forms, the authors further evaluated the concentrations reported by WESTEC (1986a) for "soluble" copper in the watercolumn near the NCMT. The "soluble" copper was defined in that study as the copper that passed through a 0.45 µ pore-size membrane filter. While that approach is often used to separate chemical forms that are called "soluble," it is well-known that in many situations appreciable amounts of particulate matter can pass through such a filter and be included in the amount of the constituent quantified as "soluble." As noted above, particulate forms of many contaminants, including copper, are typically not toxic. Therefore, the measurements of "soluble" copper in the NCMT-area water by WESTEC (1986a) likely overestimated the amount of copper in true solution and available to cause toxicity to aquatic life. Even if the WESTEC (1986a) data were representative of the truly soluble concentrations of copper in the NCMT area, it would be unlikely that that exceedance of the objective would result in an adverse impact on the beneficial uses of San Diego Bay because of the likely presence of soluble copper complexes of the type discussed above. As discussed above, copper reacts with organics and some inorganics to form soluble complexes that are non-toxic.

According to US EPA (1985), the embryos of the blue mussel (*Mytilus edulis*) were the most sensitive organism/stage to copper of all the saltwater species for which acute toxicity data were available and considered in the development of its marine water quality criterion. The "mean acute value" reported for that organism was 5.8 µg Cu/L. The US EPA reasoned that the concentration that would not cause lethality (acute toxicity) to the that mussel's embryo stage (critical life stage) would not cause chronic toxicity. It was thus on the basis of that toxicity to *Mytilus edulis* embryos that the "final chronic value" (criterion value) of 2.9 µg Cu/L was developed. *Mytilus edulis* live naturally in the NCMT area and in fact were harvested as part of the present study from an area at the pierface of the NCMT at which the highest concentrations of sediment-associated copper in the area have been found. It is therefore apparent that whatever the concentration of available forms of copper in the watercolumn, it is not sufficient to prevent the existence of that organism. According to Bayne's (1976) review of the ecology and physiology of marine mussels, some mussels including *Mytilus edulis* can live for a decade or more. Thus, while *Mytilus edulis* individuals present today in the NCMT area could have established themselves there prior to the copper ore transfer operations, it appears likely that they are continuing to establish there at this time and that therefore the concentrations of whatever the forms of copper (and other contaminants) that exist in the watercolumn near the NCMT are not sufficient to preclude the survival and development of larval forms of that organism.

In the study conducted by Johnston (1989) discussed earlier, all of the water samples from within the Yacht Basin that were analyzed contained concentrations of total copper and ASV-copper in excess of the water quality objective for those waters of 2.9 μg/L. The total copper concentrations in all but one sample collected outside the entrance to the Yacht Basin exceeded the water quality objective; the ASV-copper in more than half of the samples from that location also exceeded water quality objective. However, as discussed subsequently, Johnston (1989) also found that a wide variety of organisms, including larval (more sensitive) life stages, colonized existing structures as well as artificial substrates in those areas.

3.4.5Copper in NCMT-Area Interstitial Water and Its Role in the Development of the Remediation Objective

Interstitial water is the water between the particles that make up bedded (settled) sediments. One of the several approaches that are being explored as bases for establishing the acceptable levels of contaminants in sediments is the "equilibrium partitioning" approach which is based on a comparison between interstitial water concentration of soluble forms of a contaminant and the corresponding water quality objective-criterion. In the application of this approach, if the concentration of the soluble forms of the contaminant measured or estimated in the interstitial water exceeds the water quality objective for watercolumn organisms, the contaminant is deemed to be present in the sediment at an excessive concentration and therefore responsible for altering the numbers and types of organisms in the sediment (US EPA, 1991b). The US EPA (1991b) is attempting to use that approach to develop "sediment quality criteria" for some non-polar organic chemicals.

In the WESTEC (1986a,b; 1987) studies, copper concentration was measured in interstitial waters from sediments from the NCMT area; those data are plotted as a function of copper concentration in the sediment in Figure 2-14** of this report. WESTEC reported concentrations of "soluble" copper in interstitial water ranging from <2 to 480 μg Cu/L in areas of the NCMT where sediments were reported to contain total copper between about 13,000 and 23,900 mg Cu/kg dry wt. As discussed above, the current US EPA water quality criterion for copper as well as the applicable water quality objective for San Diego Bay (Enclosed Bays and Estuaries Plan objective) is a one-hour average maximum of 2.9 µg Cu/L.

According to Peters (1987, 1991), WQCB-SD used the equilibrium partitioning approach and the WESTEC estimates of interstitial water concentration of "soluble" copper in its development of the remediation objective of 1,000 mg Cu/kg dry wt. for the NCMT-area sediments. This produces several areas of significant technical concern. First, the equilibrium partitioning approach has not been demonstrated to be applicable to heavy metals, such as copper. In fact, there is a variety of reasons related to the chemistry of copper why that approach would not be appropriate for copper or other heavy metals. The basic assumption of that approach is that all forms of the contaminant in solution in the interstitial water are in equilibrium with all solid phases of the contaminant in the sediment. Therefore, it is assumed that all of the solid phases of that contaminant are in equilibrium with each other. For heavy metals such as copper, this condition is almost never achieved. Therefore, there can be large concentrations of some solid-phase contaminants, such as copper ore, that are not contributing to the soluble copper found in the interstitial waters. Thus the use of interstitial water concentrations for evaluating the need to "remediate" sediment-associated contaminants such as copper-ore could render inappropriate conclusions.

Second, the issues of the validity of using the water quality criterion and objective values as bases for judging what constitutes an "excessive" concentration of copper for the protection of aquatic life-related beneficial uses of a water were addressed in a previous portion of this section of the report. There, it was noted that significant exceedances of objective concentrations can occur without adverse impacts on beneficial uses of the water. This situation reflects the highly conservative approach used in the development of water quality criteria and objectives by federal and state agencies.

Third, even if the equilibrium partitioning approach were applicable to copper ore concentrate-contaminated sediment, the authors' review of the procedures used by WESTEC to separate the "soluble" copper component from the interstitial water revealed that the reported concentrations for soluble copper in the interstitial water were likely higher than the levels that actually occurred. WESTEC (1986a,b; 1987) filtered the water drawn from within the sediments or drained from the sediment, through a 0.45 u pore-size filter to separate the "soluble" copper from "non-soluble" forms of copper. While that approach is often used to separate chemical forms that are "soluble," it is well-known that in many situations appreciable amounts of particulate matter can pass through such a filter and be included in the amount of the constituent quantified as "soluble" (e.g., see Lee and Jones, 1983). That approach can thus result in the inclusion of non-soluble forms of copper that are not available to affect aquatic organisms, in the "soluble" copper determination. This is especially true when the concentration of total copper in the sediments is high. It has been the experience of the authors (Lee and Jones) that when properly conducted, centrifugation can be reliably used for this separation. Ankley (1991) indicated to the authors that the US EPA has also found that the filtration procedure is not reliable for separating the soluble component of interstitial water. According to him, the US EPA will soon release a "Toxicity Investigation Evaluation" (TIE) procedure for contaminants in sediments that will prescribe centrifugation for separating the soluble from the non-soluble forms of contaminants in interstitial waters.

Fourth, as discussed previously, there are soluble species of copper that are not available to adversely affect aquatic life. Thus, even a properly determined soluble copper concentration could overestimate the amount of available copper. Since the reported concentrations for "soluble" copper in the NCMT-area interstitial water likely included some non-soluble forms as well as non-available soluble forms, the remediation objective selected (1,000 mg Cu/kg dry wt.) is likely to be more conservative (lower) than intended.

3.5 AQUATIC TOXICOLOGY COMPONENT OF RISK ASSESSMENT

3.5.1 Toxicity

3.5.1.1 Toxicity Associated with NCMT-Area Sediments

Since available forms of chemicals cannot typically be determined by chemical analysis, in order to evaluate the potential impact of chemical contaminants on aquatic life aquatic organisms need to be exposed to the forms and concentrations of the chemicals of concern. Such exposure is typically provided through standard toxicity tests (bioassays) using reliable, sensitive test organisms. The exposure that an organism receives in a toxicity test is typically more severe than the organism would receive in the field (see discussion by Lee and Jones, 1983).

Toxicity tests have been conducted on NCMT-area sediments using nine different, standard test organism types, considering 14 response parameters including both acute and chronic impacts, with the specific goal of evaluating the potential impact on aquatic organisms of the copper-contaminated sediments. Three species were tested during the present study considering sediments having concentrations of copper as great as 18,750 mg Cu/kg dry wt.; the remainder had been tested by WESTEC (1988) considering sediments having copper concentrations as high as 6,067 mg Cu/kg dry wt. (see Table 2-2, 2-3, 2-5, 2-7, and 2-9). Table 3-1 summarizes the types of organisms and NCMT-area sediments on which toxicity tests have been conducted and the general findings from each. As indicated in that table, of the nine sensitive organism types tested considering 14 response parameters, only one test type/response resulted in adverse impacts under the laboratory conditions, the survival of the amphipods *Rhepoxynius abronius*. The mortality of those test organisms was independent of copper concentration in the sediment. Tests with sediments containing 122 mg Cu/kg dry wt. showed as much mortality as tests with sediments from the NCMT pierface that contained more than 18,000 mg Cu/kg dry wt., and those with sediments containing 1,174 and 1,372 mg Cu/kg dry wt. While the survival of the *Rhepoxynius* in all NCMT area sediments tested was statistically lower than that in the control test on sediments from Yaquina Bay, OR, the survival of that amphipod in sediments from the NCMT areas of greater contamination was not statistically different from that in sediments 160 ft from the pierface (containing 122 and 151 mg Cu/kg dry wt.).

The reburial behavior of the surviving test *Rhepoxynius abronius* exposed to the NCMT-area sediments was not significantly different from the control test on sediments from Yaquina Bay. The NCMT area sediments were not toxic to the other amphipod tested, *Grandidierella japonica*. For the reasons discussed below, the response of *Rhepoxynius abronius* in the present investigation needs to be interpreted with caution; the results obtained cannot be assumed to indicate that this organism is the "most sensitive" of those tested.

3.5.1.1.1 Concentration of Copper in Elutriates. At the completion of the elutriate test bioassays conducted with the oyster embryos/larvae, the undiluted elutriate (100% elutriate) from each of the sediments tested was retained for copper analysis. The samples were preserved with nitric acid, and filtered through a 0.45 µ pore-size membrane filter prior to analysis. The concentrations of copper measured thus included the soluble copper as well as particulate forms that dissolved due to the low pH condition used for sample preservation. The procedure used was similar to that recommended by the State Water Resources Control Board for implementation of the water quality objective for copper.

The concentrations of total copper in the sediments elutriated and the concentrations of copper in the 100% elutriate to which the embryos/larvae of the Pacific oyster were exposed are presented in Table 3-2. The sediments from the NCMT pierface at Transect 5 contained 16,000 to 18,000 mg Cu/kg dry wt. The 100% elutriates of those sediments contained 6 to 52 µg Cu/L. The concentrations of copper in all of those elutriates exceeded the US EPA criterion and state water quality objective for copper of 2.9 µg/L. However, as discussed above, there was no toxicity to the test organisms (Pacific oyster embryos/larvae) exposed to those elutriates; the US EPA found that the Pacific oyster (embryos) were one of the two most sensitive organisms to copper in salt water. It is therefore evident that while some of the elutriates contained concentrations of copper in excess of the water quality objective for San Diego Bay waters, much of that copper was present in non-toxic forms. These data further substantiate the finding that copper released from the NCMT-area sediments that contain elevated concentrations of copper, is not toxic; concentrations of copper up to 16 times the water quality objective were not toxic to one of the most sensitive marine organisms in its most sensitive life stage.

3.5.1.2 *Rhepoxynius abronius* as a Toxicity Test Organism

There is concern about the use of *Rhepoxynius abronius* for sediment toxicity testing, especially in areas in which this organism does not occur naturally, such as San Diego Bay. In an effort to further examine the water quality implications of the apparent aberrant behavior of that test organism, the authors examined the results of toxicity tests with that organism on other sediments in San Diego Bay as well as at some other locations. This review revealed that there seems to be toxicity to that organism in tests of sediment from some areas of San Diego Bay independent of the concentrations of various known contaminants in the sediments.

In unpublished studies, the US EPA has used *Rhepoxynius* to examine the toxicity of San Diego Bay sediments at various locations (Swartz, 1991). While the data from those studies are not currently in a form that can be presented to others, Swartz (1991) indicated to the authors that he had taken samples of sediments in the vicinity of the NCMT and found that the toxicity of the sediments to that organism was independent of copper concentration in the sediments, as was found in the present study. According to Salazar (1991), Swartz also found no relationship between tributyltin concentrations in sediments and the toxicity response of *Rhepoxynius* exposed to those sediments in toxicity tests. The finding of no relationship between the concentrations of potentially toxic chemical contaminants and the response of that organism has also been noted by a number of other investigators who have used *Rhepoxynius abronius* as a test organism for sediment in San Diego Bay. It is important to point out that *Rhepoxynius abronius* is not a native organism in San Diego Bay and that there apparently is some factor(s) that causes a toxicity response to that organism that is not related to any known or suspected contaminants of potential concern in the Bay sediments.

According to DeWitt *et al*. (1988), *Rhepoxynius abronius* shows a "toxic" response to the particle size of sediments, independent of the chemical content of the sediments; the survival of that organism in fine-grain sediments is lower than it is in coarse-grain sediments. The sediments in the vicinity of the NCMT are fine-grain sediments. The response observed in the present study, however, is greater than the response that DeWitt *et al*. (1988) found in their study to be attributable to grain size. It is not possible at this time to rule-out the influence of undefined or unknown physical factors or unknown contaminants in causing some or all of the toxicity response of *Rhepoxynius* in the present study.

Rhepoxynius is considered to be highly sensitive to certain types of chemicals. However, the authors have observed that there are common contaminants (such as ammonia) in sediments that are highly toxic to many types of organisms, but to which *Rhepoxynius* is highly insensitive.

In 1989, Kinnetic Laboratories, Inc. investigated the toxicity of sediments from an area of Commercial Basin in San Diego Bay to *Rhepoxynius abronius* (Kinnetic Laboratories, Inc., 1990). They found that the toxicity to *Rhepoxynius* was uniform throughout their study area, including their reference area in the middle of Commercial Basin. They noted that there was no relationship between the toxicity observed and the concentrations of contaminants, including copper, in the sediments. The results of Kinnetic's studies are similar to those of the present study that showed some unexplainable toxicity to this organism. Work of ERC (1989) discussed subsequently also showed toxicity to *Rhepoxynius* that was unrelated to copper concentration in the sediment in the 40 to 300 mg Cu/kg range.

The problems with toxicity to *Rhepoxynius abronius* in "reference" areas in San Diego Bay are known to those laboratories that have attempted to use that organism for testing San Diego Bay sediments. Kline (1991) indicated that he has observed unexplainable toxicity to that organism associated with tests exposures to sediments from several locations in the Bay. He reported, however, that sediment samples collected several miles offshore of San Diego Bay do not cause a toxicity response to *Rhepoxynius*.

There are other indications that the results of toxicity tests on *Rhepoxynius abronius* are considered differently than the results of tests on other species. Until recently in order for a response in a toxicity test for dredged sediment evaluation to be considered different from the response of the reference, there had to be at least a 10% difference between the response to the test condition and the response to the reference sediment. The 1991 "Green Book" (US EPA and US COE, 1991) for evaluation of the appropriateness of ocean disposal of contaminated dredged sediments recognized that the variability (background "noise") in sediment toxicity tests on the kinds of organisms it allowed for testing was such that the minimum response difference between test conditions and the reference should be raised; it was raised to 20%. Now, according to Wright (1991), the US EPA and Corps of Engineers in the Seattle, WA area have recently raised the response difference further for tests on *Rhepoxynius abronius*, to 30% above that of the reference site impacts. This 30% difference is only allowed for *Rhepoxynius* and reflects its response to unknown factors in laboratory toxicity tests. It is evident that while *Rhepoxynius abronius* is a standard test organism allowed by both the US EPA and the Corps of Engineers for toxicity testing of sediments, there is a variety of factors, some of which are unknown, that affect the response of this organism under test conditions.

Ordinarily, important characteristics of a good toxicity test organism include a consistent response to toxicants and a relative insensitivity to factors other than toxicants such as other characteristics of the matrix being tested, handling in the laboratory, etc. It is important to have a clear understanding of chemicals and conditions that cause toxicity responses for any test organism so the results can be properly interpreted in a regulatory framework.

Thus it may be concluded that given the state of understanding of the factors affecting the response of *Rhepoxynius abronius* in sediment toxicity tests as currently designed, tests with that organism should not be a deciding factor in the management of contaminated sediments. There can be little doubt that these highly sensitive organisms will have a valuable role to play in regulating contaminant concentrations in aquatic systems, water, and sediments. However, at this time, because of the unknown factors that cause a toxicity response to that organism, it should be used for regulatory purposes only with great caution. It should only be used in conjunction with tests on a variety of other sensitive organism, such as have been included in the present evaluation. When that organism's response is different from that of all the other sensitive organisms, it cannot be assumed to represent a "more sensitive" organism for the particular contaminant or matrix of concern.

It is the authors' conclusion that based on the information available, the toxicity response of *Rhepoxynius abronius* in tests of sediments near the NCMT should not influence decisions on the remediation objective for the copper ore concentrate-contaminated sediments. The preponderance of evidence from the eight other test organisms, the infaunal populations discussed subsequently, and the presence of native *Mytilus edulis* in the "contaminated" areas near the NCMT, coupled with the response of *Rhepoxynius* to unknown factors and factors not related to the presence of known contaminants, causes the authors to conclude that the copper ore in the vicinity of the NCMT is not causing toxicity to aquatic life in the sediments or water of San Diego Bay.

3.5.1.3 Toxicity of Sediments in Other Areas of San Diego Bay

Lockheed Ocean Science Laboratories (Lockheed, 1983) conducted a study of the sediments in the vicinity of Southwest Marine Inc. (Yard #4) to determine their suitability for ocean disposal after dredging. Two different locations within the Southwest Marine area were investigated; one contained 910 mg/kg copper and the other, 2,000 mg/kg copper. The reference sediment used in those studies contained 790 mg/kg copper. Toxicity tests were performed on those sediments using a mysid *(Acanthomysis sculpta)*, a mollusc *(Macoma nasuta)*, and a polychaete *(Neanthes arenaceodentata)* in the US EPA and US COE standard dredged sediment 10-day, solid phase testing procedure. The 10-day toxicity tests for the controls, reference sediment, and the two study site sediments showed no toxicity to any of the three types of test organisms. The toxicity tests on standard liquid/suspended particulate phase derived from the same sediments using a copepod *(Acartia tonsa)*, a mysid *(Acanthomysis sculpta)*, and a flat fish (sand dab) *(Citharichthys stigmaeus)*, showed no toxicity. Therefore, as with other studies, very high levels of copper in sediments at locations other than the NCMT area have been found to be non-toxic to a variety of standard, sensitive test organisms.

ERC (1989) conducted sediment bioassays on four sediment samples from the area of Continental Maritime of San Diego at Pier 6 in San Diego Bay. A group of standard bioassay organisms, including *Rhepoxynius abronius*, was tested in standard US EPA and COE dredged sediment toxicity tests. The sediments tested contained a wide variety of organic and inorganic contaminants; the copper concentrations in the four test samples ranged from 40 to 283 mg/kg. The copper concentrations in the sea water above the sediments was 0.3 µg/L. None of the suspended particulate phase tests showed toxicity to *Acanthomysis sculpta* (mysid shrimp). Suspended particulate phase tests with sediments from Site 1 on the north nearshore area of Pier 6 resulted in toxicity to *Citharichthys stigmaeus* (sand dab - flat fish); those with sediments from the other three sites showed no toxicity to that organism. Suspended particulate phase tests with sediments from Sites 1 and 4 showed toxicity to larval *Crassostrea gigas* (oyster), while those with sediments from Sites 2 and 3 showed no toxicity to that organism. There was no toxicity to mysid shrimp, *Nephtys caecoides* (polychaete worm), or *Macoma nasuta* (clam) in solid phase tests with sediments from any of the four sites. Solid phase tests with sediments from Sites 1 and 4, however, resulted in toxicity to *Rhepoxynius abronius*. The cause of the toxicity to *Rhepoxynius* was not determined. However, the toxicity found in this suite of tests does not appear to have been related to copper since the sediment at Site 4 had the lowest concentration of copper of the four sites studied (40 mg/kg), while the sediment from Site 1 had the highest concentration of copper (283 mg/kg).

A number of studies has been conducted by the Water Quality Control Board, San Diego Region and by the Shelter Island Boatyard on the sediments near the Shelter Island Boatyard (SIB) in the Commercial Basin of San Diego Bay. SIB (1990) summarized previously collected data and provided additional data pertinent to this project, including data on total organic carbon (TOC), mercury, copper, various forms of butyltin, and sediment particle size. Toxicity of the sediments was also tested using *Rhepoxynius abronius*, and infaunal populations were determined. The copper concentrations in the sediments during the SIB (1990) studies ranged from 120 to 275 mg Cu/kg with a mean of 197 mg Cu/kg dry wt. Considering all data collected in that area excepting the central part of the Basin, the copper concentrations generally ranged from 150 to 350 mg Cu/kg; concentrations were 70 to 170 mg Cu/kg in the central part of the basin. Some nearshore sediments from an area north of the SIB contained copper in concentrations of 1,700 to >3,000 mg Cu/kg. Sediments collected by the Water Quality Control Board immediately offshore from the SIB had a mean copper concentration of 791 mg Cu/kg. It is evident that the sediments in the SIB area have elevated concentrations of copper and that some of the concentrations found approached those found in the copper ore-contaminated sediments near the NCMT. It should be noted, however, that the copper in the SIB area is likely to have been derived from its use in anti-foulants on boat hulls rather from the handling of copper ore concentrate. While the copper ore concentrate-derived copper would be expected to be highly unavailable to aquatic life, at least at the time the anti-foulant copper was on the boat hulls it was designed to be slowly available-toxic to aquatic life.

In the SIB (1990) studies, sediments from eleven locations in the SIB area were subjected to toxicity testing with *Rhepoxynius abronius*. The copper concentrations of those sediments ranged from 90 to 275 mg Cu/kg. None of those sediments caused toxicity (mortality) that was greater than that found in the reference sediments. One aspect of that study that should be noted is that the percent survival of *Rhepoxynius* in the reference sediment from the state of Oregon where those organisms are native, was on the order of 20% indicating that there was some factor that influenced the results of the tests on the reference sediments as well as on the tested sediments. However, the tests were valid and the toxicity in the tested sediments was no different from that of the reference sediments. Differences in the infaunal populations were noted in various locations in the SIB area. However, those differences were not related to toxicity responses as measured by the response of *Rhepoxynius*. The causes for the differences in organism assemblages in those sediments are unknown at this time, but they are apparently not related to the concentrations of copper in the sediments.

The Naval Ocean Systems Center (NOSC) released a report in April 1980 summarizing the results of sediment bioassays conducted for the NAVSTA San Diego dredging project (Salazar *et al*., 1980). That report presented the results of sediment analyses and toxicity tests conducted between March 1978 and January 1980 on sediments in the area of the 13 Navy piers extending for about 2 mi immediately north of the NCMT to Chollas Creek, and sediments on the north side of North Island in the north part of the Bay. The copper concentrations in sediment samples taken from those areas ranged from about 20 mg Cu/kg to more than 1,700 mg Cu/kg; many of the samples contained copper in the 200 to 500 mg Cu/kg concentration range. A variety of organisms, including copepods, mysid shrimp, clams, fish, and benthic polychaete worms, was used in toxicity tests on sediments from the pier areas; copper concentrations in the toxicity test sediments ranged from 80 to 995 mg Cu/kg with many of the values in the 200 to 300 mg Cu/kg range. While some of the sediments caused toxicity to some of the test organisms, in general most of the samples caused no toxicity; the toxicity that was found appeared to be unrelated to the concentration of copper in the sediment.

Chapman *et al*. (1979) reported on an investigation of a situation similar to that at NCMT. At their study site at Vancouver Wharves in Vancouver, B.C., copper ore became associated with sediments as a result of washdown and loading operations. The highest concentrations of copper found in the sediments were on the order of 14% (14,000 mg Cu/kg). Several laboratory acute toxicity tests, as well as *in situ* (caged-organism) field bioassays were conducted using water and sediments of the area. Those tests showed that the copper in the water and sediments had very low acute toxicity to aquatic life. Chapman *et al*. concluded that the discharge limit of 0.1 mg/L dissolved copper established by the regulatory agency for the discharge from this area was *"...considerably lower than the concentration that results in acute lethal or sublethal effects in salt water."* The conclusions from the Chapman *et al*. study were that the spillage of copper ore concentrate had resulted in elevated copper concentrations in the vicinity of the loading dock; that the elevated concentrations of total copper in sea water were not acutely toxic to coho salmon smolts or shore crabs; and that the copper ore concentrate tends to be less toxic in salt water than in fresh water. They also found that a healthy diverse community of organisms was living in the pilings near the loading dock, an area that had high concentrations of copper in the sediments.

In a follow-on study, Chapman *et al*. (1982) examined the bioaccumulation of copper in transplanted mussels, *Mytilus edulis*. They found that there was some bioaccumulation of copper in the mussels.

The copper concentrations in the tissue of un-purged mussels ranged from 11 to 335 mg/kg dry wt. Chapman *et al*. did not address the issue of whether or not the apparent bioaccumulation of copper in the mussels represented an adverse impact.

Hyland *et al*. (1988) investigated the potential water quality impacts resulting from the sinking of the freighter *Pac Baroness* that was carrying *"... 21,000 metric tons of a finely powdered copper concentrate of which approximately 71% was comprised of chalcopyrite..."* They found differences in the numbers and types of organisms present in the vicinity of the wreck compared to nearby areas. However, those differences appeared to have been related to impacts of the release of fuel oil from the sunken ship rather than to the copper concentrate.

In 1944 a World War II Liberty ship carrying a load of top-grade copper sank off Kittery, ME. Hansen (1991) indicated to the authors that that copper ore concentrate that is now associated with the sediments in that area is apparently not toxic to aquatic life there.

Salazar and Salazar (1991) summarized the results of toxicity tests conducted on San Diego Bay sediment during the 1980's as part of the Navy's dredging projects for various locations in the Bay. The study areas were principally on the west side of the Bay near its mouth, and at the Navy piers between Chollas Creek and the NCMT, specifically Fuel Pier, Med Moor A, Med Moor B, Mole Pier, Commercial Basin, Deperming Pier, Piers 1/2, 1, 2A, 2B, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and JK, Chollas Creek, Supply Pier, and Seawall. For each area, the chemical characteristics of the sediments, including copper concentrations, were reported as were the results of dredged sediment bioassays and bioaccumulation tests conducted in accord with US EPA and US COE dredged sediment evaluation procedures. Typically, particulate-phase tests were conducted with *Acanthomysis sculpta* (mysid), *Citharichthys stigmaeus* (flat fish), and *Acartia tonsa* (copepod). Solid-phase tests were conducted with *A. sculpta*, *Macoma nasuta* (clam), and *Neanthes arenaceodentata* (polychaete worm). The copper concentrations in the sediments ranged from about 20 to 250 mg/kg. There was no toxicity to any of those organisms in the toxicity tests conducted. It was concluded that there would be no significant adverse impacts associated with the disposal of sediments dredged from those areas at the US EPA designated marine disposal sites off the southern California coast. It may be concluded that the sediment-associated copper at those various sites was non-toxic to the test organisms under the conditions of the tests.

While it would be expected that the copper in the NCMT-area sediments would be non-toxic because of its chemical make-up, it is interesting to note that the copper in the sediments from a variety of other areas in San Diego Bay has also been found to be non-toxic to a variety of test organisms, even though the origin of that copper is likely to have been predominantly the highly toxic anti-foulants applied to boat hulls. Thus it is apparent that, in accordance with the chemistry of copper, even copper introduced into the water of San Diego Bay in highly toxic forms undergoes chemicals reactions in the sediments that lead to its detoxification.

3.5.1.4 San Diego Bay Report

Information is presented in the San Diego Bay 1989/1990 Report (SDIWQP, 1990) on the "ecological risks" associated with contaminants in San Diego Bay sediments. In the SDIWQP (1990) discussion of contaminants in sediment from a NOAA sampling site in South San Diego Bay, copper is listed as exceeding *"the median level (ER-M) associated with toxic effects as reviewed by Long and Morgan (1990; Figure 2)."* The "Figure 2" in SDIWQP (1990) shows that the concentration of copper in the South San Diego Bay sediment sampled was in the upper range of what the figure characterized as the "potentially toxic levels" ranging from "low toxicity" (70 mg Cu/kg) to "moderate toxicity" (390 mg Cu/kg) based on the work of Long and Morgan (1990). (It should be noted that the units of concentration in the SDIWQP Figure 2 are incorrect at least for copper; the levels of copper shown should be "ppm" rather than "ppb.") Those concentrations are typical of those found in San Diego Bay sediments even prior to the copper loading operations at the NCMT.

The SDIWQP (1990) discussion could be misinterpreted to mean that copper in those ranges of concentration has been found to be toxic to aquatic life. A casual review of the SDIWQP (1990) discussion of the concentrations of copper in South San Diego Bay could lead one to the mistaken conclusion that copper in San Diego Bay is having or would be expected to be having a toxic effect on aquatic life. This situation necessitates a discussion of the findings of Long and Morgan (1990) and the limitations on the use of their designations. While Long and Morgan (1990) carefully presented and qualified the results of their study, the present authors are finding that some individuals who cite their work do not properly use it or do not include the appropriate qualifications on the results. This, in turn, leads reviewers of the reviewers' work to misrepresent what Long and Morgan actually reported; this is of concern in the case of the SDIWQP (1990) report.

What Long and Morgan (1990) did was compile information on the concentrations of chemicals in sediments and the results of assessments of biological response to those sediments. Some of the "biological responses" included alterations in numbers and types - assemblages - of organisms, exceedances of arbitrarily established sediment classifications (such as AET classifications used in Puget Sound of Washington State), and results of toxicity tests on sediments containing a variety of contaminants. While the "toxic responses" were responses to the wide variety of contaminants that can be present in a sediment, and not necessarily a response to a specific contaminant, Long and Morgan (1990) assembled the information, by chemical, in tables of these "co-occurrences." Thus, independent of the cause of the biological response, the same degree of response was associated with the concentration of each individual chemical contaminant measured in the sediment. The tables of co-occurrence were not intended to, and cannot be used to, suggest cause-and-effect relationships between the concentration of an individual chemical and the "associated" toxic response. The information on the table of co-occurrence for each chemical was ordered from low concentration to high, and the lower 10-percentile and the 50-percentile computed for each. The Long and Morgan (1990) ER-L and ER-M values were the values for the 10-percentile and 50-percentile, respectively. While the lowest concentration on a table can indicate that, independent of the cause of the toxic response, no sediment that contained that given amount of a chemical has been found to cause a response, none of the values or percentiles can indicate that toxicity would be expected for a particular concentration of any chemical.

Those who are familiar with the effects of contaminants on aquatic life, including Long and Morgan, fully appreciate that the analysis made by Long and Morgan (1990) does not support the implications of the statements made by SDIWQP (1990) that the concentrations of contaminants, such as copper, listed by Long and Morgan are causing a toxic effect, and also understand that sediment concentration data cannot be translated into effects on aquatic life. For example, while Long and Morgan (1990) listed an organism impact to a Massachusetts Bay sediment that contained copper at 15 mg/kg, the fact is that there is virtually no possibility that copper at that level in those sediments was responsible for that response. Those particular sediments contain a wide variety of other contaminants that have a much higher probability of having caused the response than the copper levels.

One of the major difficulties with the Long and Morgan (1990) approach is that it enables individuals with a limited understanding of aquatic chemistry and the impacts of various forms of aquatic contaminants on aquatic life to obtain a numeric value for a particular contaminant with which to assert that that level of that contaminant at some location could be having an adverse impact on biological communities. However, a critical review of the Long and Morgan results - in light of what is known about the aquatic chemistry of various elements - can provide insight into whether copper in a particular sediment could be causing impacts on aquatic communities at the concentrations found. As discussed above, because of its very strong tendency to form insoluble, unavailable compounds and organic and inorganic complexes, copper should not be considered to be a significant suspect for causing biological responses in sediments that contain a wide variety of other contaminants. While Long and Morgan listed an ER-L for copper in sediments as 70 mg/kg and the median concentration (ER-M) of 390 mg/kg, it is highly likely that those numbers have no relationship to the actual toxicity of copper in sediments from which those data were derived. Copper in sediments at much higher concentrations is known not to cause toxicity responses. This was shown in the present study, for example, in which copper in concentrations of tens of thousands of mg/kg did not produce toxicity responses in eight different types of toxicity test organisms. As noted above, the precipitation and complexation reactions of copper associated with sediments and their interstitial waters provide a tremendously powerful detoxification mechanism that makes copper in many sediments inert or essentially inert.

It may therefore be concluded that great caution must be used in interpreting the statements made in the San Diego Bay report that copper in South San Diego Bay is present in concentrations that can possibly cause a toxic response.

3.5.2Bioaccumulation

The accumulation of chemical contaminants within aquatic organism tissue (bioaccumulation) is of concern because of the potential for the accumulated body burden to adversely affect higher trophic-level organisms, primarily man and fish-eating birds. At this time, the only reliable method for determining whether the accumulation of chemicals in aquatic organism tissue is "excessive" is to compare the body burden in edible flesh with Food and Drug Administration (FDA) Action Levels. The US EPA and other agencies are in the process of trying to develop other guidelines for interpreting the significance of chemical contaminants in aquatic organism tissue. At this time, there is no FDA Action Level or other accepted, reliable guideline for assessing the significance of copper in aquatic organism tissue.

One of the reasons that the FDA has not developed Action Levels for copper is that copper is not particularly toxic to man. A recent review of seafood safety by the Food and Nutritional Board of the Institute of Medicine of the National Academy of Sciences (Ahmed, 1991a) presented an extensive discussion of the current information on the toxicity of chemical contaminants in seafood to man. Copper was not considered in that review since its bioaccumulation in seafood is not considered significant (Ahmed, 1991b). The San Diego County Department of Health Services (SDC-DHS, 1988) stated in a discussion of the significance to humans of copper in food, *"...it is generally felt that humans are able to satisfactorily regulate the body burden of copper provided there is not impairment of normal metabolic pathways..."*

As part of the California State Mussel Watch Program, the Water Resources Control Board (WRCB, 1988) stated,

> *"The National Academy of Sciences has set recommended maximum concentrations of toxic substances in animal tissue"*

and provided a reference to the 1973 "Blue Book" (NAS and NAE, 1973). WRCB (1988) stated that it used what it called the "NAS guidelines" in its interpretation of the significance of the concentrations of certain chemicals in mussel tissue. The senior author of this section of this report (Lee) was a peer-reviewer for the National Academies of Science and Engineering committee that developed the "Blue Book" of water quality criteria. He is highly familiar with the development of the information included in the "Blue Book." While the issue of bioaccumulation of certain chemical contaminants was discussed in the "Blue Book" and some concentration values were noted, those values did not then, and do not now, have the status of being "guidelines," much less being "recommended maximum concentrations of toxic substances in animal tissue." The concentration values included in the "Blue Book" were not and are not recognized as "guidelines" or "recommended maximum concentrations of toxic substances" by the National Academies of Science and Engineering.

The Water Resources Control Board State Mussel Watch Program also cited "Median International Standards for Trace Elements in Freshwater Fish and Marine Shellfish" (WRCB, 1988). Those so-called standards were reported to have been based on a compilation of values used in other countries. The so-called "Median Standard" for copper was reported to be 20 mg/kg wet wt. Great caution should be exercised in the use of that value to make any judgement about the significance of the bioaccumulation of copper in aquatic life. It has been the authors' experience that some other countries and international agencies do not follow the same rigorous approach that is followed in the US to establish critical concentrations of contaminants in tissue. Since that "standard" has been in existence for many years and since it has not been adopted by the US, it appears that there may be significant questions about the reliability of that value and its applicability to judging the significance of the presence of copper in aquatic life tissue.

The Water Resources Control Board State Mussel Watch Program used a statistical treatment of the data obtained from studies over the past 10 years of the accumulation of various constituents in transplanted, caged mussels, to define an EDL ("elevated data level") at various percentiles for data collected through the program. While that approach has some utility for identifying areas in which various contaminants accumulated in transplanted, caged mussels, exceeding a certain percentile developed in that survey framework should not be considered to have any particular meaning in terms of potential problems of or risks associated with accumulation of the contaminants in the transplanted or native organisms.

In summary, according to the information available, copper in aquatic organisms is not considered to represent a potentially significant health hazard to humans. Further, there is no reliable way to judge the significance of any particular body burden of copper in aquatic life tissue. Therefore, a risk assessment for copper in aquatic sediments should focus on the impact of the copper on the aquatic life in the vicinity of the sediments containing the copper.

Several investigations have been made into the body burdens of chemicals in mussels in San Diego Bay. Native mussels (*Mytilus edulis*) were collected from three locations at the NOAA Mussel Watch site near Harbor Island in San Diego Bay, each year between 1986 and 1988 for chemical analysis of body burden (NOAA, 1989). Concentrations of copper in those mussels ranged from 12 to 31 mg/kg dry wt. without pattern over time. Zirino (1990) reported, apparently based on NOAA Mussel Watch data, that the concentrations of copper in mussels taken from San Diego Bay was among the highest of the US bays and harbors similarly studied. During the state of California Mussel Watch (SMW) program, mussels (*Mytilus californianus*) were transplanted in cages to various locations for periods of 2 to 4 months, retrieved, and analyzed for a variety of constituents. These organisms were not purged prior to analysis. In some years between 1982 and 1989 sites near the

NCMT were used for transplanted mussel evaluation. Copper concentrations in mussels held near Navy Pier 13 contained 21 to 33 mg/kg dry wt. At the NCMT sites in 1982, and 1984-1989, concentrations of copper in transplanted, caged mussels ranged from 20 to 88 mg/kg dry wt.; there was no pattern in concentration over time. The one analysis made of transplanted, caged mussels at the Sweetwater Marsh location yielded a copper concentration of 35 mg/kg dry wt. Considering all SMW sites in San Diego Bay concentrations of copper in transplanted, caged mussels were as high as 137 mg Cu/kg dry wt.

The present study included the analysis of duplicate samplings of two types of existing, naturally occurring mussels, *Mytilus edulis*, a "watercolumn mussel," and *Musculista senhousia*, a "benthic mussel," collected from two locations in the vicinity of the NCMT. One of those locations was near the pierface where the sediments contained an estimated 17,000 mg Cu/kg dry wt.; the other was the WQCB-SD reference site where the sediments contained 150 to 300 mg Cu/kg dry wt. As shown in Table *, the concentrations of copper in replicate samplings of *Mytilus edulis* from the pierface area were 22.1 and 24.7 mg/kg dry wt, and in those from the reference site were 21.3 and 21.6 mg/kg dry wt. The concentrations of copper in *Musculista senhousia* from the pierface area were 72 and 78.9 mg/kg dry wt, and in those from the reference site were 48.9 and 65.6 mg/kg dry wt. While the concentration of copper in the benthic mussels (*Musculista senhousia*) were measurably higher than those in the watercolumn mussel (*Mytilus edulis*), there was little difference between the concentrations in either type of mussel living in association with sediments containing elevated concentrations of copper and those living in association with the reference site sediments. The results of the mussel tissue analysis obtained in the present study are in keeping with those from the NOAA and State Mussel Watch programs.

3.5.3Community Diversity

It is clear from the discussion presented in Section *, the previous work done by WESTEC (1986a) on the benthic organism community composition, numbers, and diversity at the NCMT area has shown that differences and similarities between organism assemblages in that area are not related to the amount of copper present in the sediments. These findings are consistent with the lack of toxicity of the sediments in the NCMT area to a variety of test organisms.

Johnston (1989) attempted to assess the impact of the copper and organotin concentrations in the waters at each of his four sampling stations in the Shelter Island Yacht Basin area to the ability of what he termed "fouling organism communities" to colonize. In addition to measuring various forms of copper as discussed earlier in this section, that investigator placed plexiglass sheets in the water for the purpose of providing surfaces for organism colonization, and left them in place for 3- to 9-wk periods. While differences were found among the colonizations found at the various sampling locations that associated to some extent with the copper and organotin concentrations, no cause-and-effect relationship can or should be associated with those data. A wide variety of factors influence the colonization of plexiglass plates besides the concentrations of those two toxicants. A far more-comprehensive study would have to be conducted to determine whether copper and/or organotin were causing the differences in the "fouling communities" that developed on the plexiglass sheets at each station.

In addition to examining the organisms that colonized the plexiglass plates, Johnston (1989) identified organisms that were present on existing piling and docks in the Shelter Island Yacht Basin. Organisms found on the plates and/or structures included various forms of algae including red and brown; various types of sponges; sea anemones; various types of round and flat worms; snails; limpets; common bay mussels including juvenile forms, and the mussel reportedly especially sensitive to copper, *Mytilus edulis*; oysters; barnacles; isopods; amphipods; crabs; various types of bryozoans ("moss animals"); and tunicates. It is interesting to note that even though the concentrations of copper were above the water quality objective for the samples collected within the Yacht Basin, there was appreciable colonization of the plexiglass sheet substrates as well as of the existing structures. Since as would be expected, Johnston (1989) noted that colonization was largely by larval forms of the organisms, the concentrations of copper that exceeded the water quality objective of 2.9 µg/L were not sufficient to be toxic to the larval and other forms of organisms that colonized the plexiglass sheets and existing structures. While this indicates that the water quality objective for copper may be overly restrictive, the numbers and types of organisms colonizing the plexiglass plates and other structures might have been significantly different if the copper, organotin, and other factors adverse to aquatic organisms were not present in the waters of the Yacht Basin. In accord with state of California regulations, if it were found that the presence of contaminants caused differences in organism assemblages, those differences would have to be interpreted in terms of whether or not they represent an impairment of the designated beneficial uses of San Diego Bay.

While the Johnston (1989) studies were not conducted at the NCMT, the results of that work point to other sources of copper and provide some information on the concentrations of some forms of copper in other areas of the Bay.

3.6POTENTIAL IMPACTS OF DREDGING AND DREDGED SEDIMENT DISPOSAL ON AQUATIC LIFE

Some express concern that dredging of sediments may cause adverse impacts on aquatic life at the dredging site by causing the release of chemical contaminants. This potential problem was investigated in the studies reported by the authors (Jones and Lee, 1978; Lee and Jones, 1987). They found that at the several sites they investigated, no water quality impacts could be found other than a short-term increase in turbidity in the vicinity of the dredging operations. Those short-term increases in turbidity were insignificant compared to the increases that occur in many waterways associated with ship traffic and storms that mix bedded sediments into the watercolumn. While the total concentrations of some contaminants associated with the dredging-induced turbidity increased to levels above US EPA criteria or state water quality standards (objectives), such increases did not impair beneficial uses of the waters because they were associated with particulates and unavailable to affect water quality. Contrary to statements that are sometimes made, the resuspension of sediments does not necessarily release contaminants from the sediments in sufficient concentrations to be adverse to aquatic life in the region of dredging. The US EPA and Corps of Engineers have determined that water quality impacts at a dredging site are *"de minimus"* and hence are not of concern. As discussed by Jones and Lee (1978), associated with the suspension of sediments in the watercolumn is the oxidation of ferrous iron in the sediments to ferric iron by the dissolved oxygen in the watercolumn; the ferric iron rapidly precipitates as ferric hydroxide. It is well-known that ferric hydroxide is a highly efficient scavenger for essentially all trace contaminants except ammonia; the contaminants are incorporated into the ferric hydroxide precipitate. Such scavenging action converts the trace contaminants to particulate forms which are in general non-toxic to aquatic life.

There is little doubt that the concentrations of total copper would increase in the watercolumn in the vicinity of dredging operations in the NCMT area for a short period of time during the operations themselves. However, it is unlikely that the concentrations of toxic forms of copper would be increased sufficiently to be adverse to aquatic life in the watercolumn in the vicinity of the terminal or elsewhere. Turbidity curtains can be used to limit the spread of suspended particulate matter from the area of the dredging. Some chemical and biological testing should be done at the time of the initial phases of dredging to confirm that what has been found at other locations with respect to the lack of impact on water quality applies to that location as well.

3.7"HAZARDOUS WASTE" DESIGNATIONS AND THEIR SIGNIFICANCE IN THE MATTER OF NCMT-AREA SEDIMENTS

In 1984 the California Department of Health Services (DHS) adopted Title 22, Division 4, Chapter 30, Article 11 that established regulations governing the classification of wastes. Using somewhat arbitrary approaches, DHS developed Total Threshold Limiting Concentrations (TTLC) for various contaminants in solid wastes, soils, and sediments; exceedance of a TTLC would cause a material to be classified as a "hazardous waste." Of relevance to the present investigation is the fact that through that regulation, any soil, sediment, or waste that contains copper in excess of 2,500 mg/kg (wet weight) is classified by DHS as a "hazardous waste." DHS has also, however, established procedures whereby a variance from that classification can be obtained (Title 22, Division 4, Chapter 30, Article 4). As discussed elsewhere in this report, such a variance may be issued if the physical and chemical characteristics of the material render it an insignificant hazard to human health and safety, livestock, and wildlife.

Concern has been raised at the staff level of the Water Quality Control Board, San Diego Region about the sediments in the NCMT area that contain copper in concentrations above the DHS TTLC for copper of 2,500 mg/kg (wet weight) (approximately 4,000 mg/kg dry wt.). The fact that some of those sediments exceed the TTLC could be an impediment to adopting management approaches that are technically valid, cost-effective, and provide protection for human health, livestock, and wildlife. There are significant, legitimate concerns about classifying as "hazardous waste" materials that do not represent a significant hazard to public health, livestock, and wildlife. The costs associated with managing what are classified as "hazardous wastes" are significantly higher than those associated with managing materials classified as "non-hazardous;" the costs of the former can be 10 to 30-times higher than the latter. One of the most common methods of handling "hazardous wastes" is to place them in "hazardous waste" landfills. Perhaps more important than the cost consideration, however, is the fact that by placing non-hazardous materials misclassified as "hazardous" in "hazardous waste" landfills, the limited space available for managing truly hazardous materials is diminished. Because of this situation, it is appropriate to examine the basis for DHS's listing wastes, soils, and sediments that contain more than 2,500 mg Cu/kg wet wt. as "hazardous waste."

Associated with the development of Title 22, DHS published a "Statement of Reasons" (SOR) (DHS, 1984) that discussed the basis for its development of those regulations. The approach used by DHS for waste classification, the TTLC, was based on a determination of the concentrations of various contaminants, which if leached from the waste under certain management scenarios such as landfilling, would be considered to be "excessive." That determination was made through the development of "Soluble Threshold Limit Concentrations" (STLC) for a variety of contaminants. According to the DHS (1984 - page 89),

> *"...the STLC was based upon the potential for soluble substances from improperly disposed wastes to migrate via a surface or ground water to sensitive aquifer systems such as drinking water supplies or aquatic wildlife environments."*

DHS recognized that the leaching action of various types of waters may be different and that attenuation/dilution is an important factor to consider in assessing the potential impacts of a contaminant. DHS typically uses an attenuation factor of 100 to judge whether the amounts of contaminants leached from a waste are "excessive;" that is, it considers it protective to allow concentrations of contaminants in leachate that are 100-times a critical value such as a primary drinking water standard. It is the authors' (Lee and Jones') experience that that factor of 100 was established somewhat arbitrarily, based on what was thought to be the amount of attenuation that typically occurs for municipal landfill leachate-associated contaminants in the unsaturated and saturated parts of a groundwater aquifer system. It is well-known today, however, that use of the 100-fold attenuation factor incorporated by DHS and the US EPA in their hazardous waste classification procedures may result in a significant overestimation or underestimation of the hazard that a particular constituent in a solid waste represents to the quality of a groundwater for use for domestic water supply purposes. Irrespective of its appropriateness for groundwater systems, the attenuation factor of 100 has no technical validity for assessing the impacts of constituents released from wastes by leaching in surface water systems. There will be few situations where the application of the attenuation factor of 100 does not significantly overestimate the hazards to surface water quality associated with chemical contaminants that can be leached from soil, sediments, or wastes.

DHS typically uses the national primary drinking water standards multiplied by the attenuation factor (commonly a factor of 100) to establish the STLC for the leaching of constituents from wastes, soils, and sediments. However, copper is considered to be non-toxic in drinking water and therefore does not have a primary drinking water standard; the secondary drinking water standard-guideline is based only on aesthetic considerations. The approach taken by DHS to develop the STLC for copper incorporated the acute toxicity of copper to fish as measured by the 96-hr LC50 in a bioassay instead of a drinking water standard. The 96-hour LC50 is the concentration of a contaminant that kills half of the test organisms (e.g., fish) in a four-day period under standardized laboratory test conditions. With this approach the "attenuation factor" was used along with an "application factor" of 0.05 incorporated to relate the acute lethal toxicity as measured by the 96-hour LC50 to the chronic safe concentration of the constituent to aquatic life.

In its application of this approach to copper, however, DHS (1984) used an attenuation factor of 1,000 for copper, stating that copper is *"especially prone to immobilization in soils and insolubilization in water."* The factor of 1,000 was multiplied by the 96-hour LC50 for fathead minnows which was 0.5 mg Cu/L, and the application factor of 0.05. This yielded a DHS STLC of 25 mg Cu/kg (according to DHS, 1984) or 25 mg Cu/L (according to Title 22, Division 4, Chapter 30, Article 11) as the maximum concentration of copper that can be leached from a soil, sediment, or waste in the Waste Extraction Test (WET) and have the waste, soil, or sediment classified as "non-hazardous."

In the WET procedure, the soil, sediment, or waste is leached with a pH 5, citric acid-buffered solution. The conditions of the WET were designed to mimic, to some extent, the conditions that exist in municipal landfills. The test does not in any way mimic the conditions that are present in marine waters or sediments, which are typically well-buffered at about pH 8 and which also typically have a relatively low organic-metal complexing capacity compared to that of municipal landfill leachate. It is the experience of the authors (Lee and Jones), who have conducted extensive studies on the leaching of contaminants from various types of wastes and aquatic sediments (e.g., Lee and Jones, 1981), that the WET used by DHS for waste classification is inappropriate for use in assessing the amount of copper that could be leached in marine waters, such as those that occur in San Diego Bay or at a designated dredged sediment disposal site in the southern California coastal waters, such as disposal site LA-5 near San Diego Bay.

DHS (1984) stated, *"However, very few studies or data are available to aid in establishing a TTLC* *value. It is expected that the environmental behavior of toxic substances contained in particles will be very different from those that occur in solution. Utilization of even a rudimentary mathematical model to predict attenuation or mobility of particulate toxics from improperly disposed wastes is not valid."* Nevertheless, in order to develop the TTLC value for a contaminant in a waste, soil, or sediment, DHS applied an "uncertainty factor" of 100 to the STLC. Since the STLC for copper was established as 25 mg/kg, the TTLC was established as 2,500 mg Cu/kg wet wt.

Based on the authors' experience, the application of this approach to copper in marine sediments is arbitrary and does not reflect an understanding or proper consideration of the factors affecting the potential availability and impact of sediment-associated contaminants. It is technically unjustified to require that management decisions for NCMT-area copper-contaminated sediments be based on the 2,500 mg Cu/kg TTLC, such that sediments exceeding that concentration must be managed as a "hazardous waste" and cannot be disposed at a designated dredged material disposal site off the coast of California. In addition to the technical inadequacies of the approach used for establishing the TTLC, this conclusion was based on the fact that NCMT-area sediments that contain concentrations of copper considerably above the TTLC have been found to be non-toxic to eight different test organisms (considering 13 response characteristics) under conditions that would reliably assess whether the copper in those sediments would represent a significant threat to aquatic life at a dredged sediment disposal site.

It is therefore concluded that it would be appropriate and technically justified to seek a variance from the DHS Title 22 regulations that classify NCMT-area sediments containing greater than 2,500 mg Cu/kg wet wt. as a hazardous waste as provided for in Section 66310 of Title 22 (Division 4, Chapter 30) of the California Administrative Code.

3.8 DISPOSAL OF COPPER-CONTAMINATED NCMT-AREA SEDIMENTS AT AN OFFSHORE MARINE DESIGNATED DISPOSAL SITE

It could be argued from the technical information available on the impacts of the copper-contaminated sediments in the NCMT-area on beneficial uses of San Diego Bay that there is no need to "remediate" the copper-contaminated sediments near the NCMT. However, the politics of the situation appear to be such that "remediation" will have to be performed. It is therefore important to consider the various "remediation" options relative to their potential environmental and public health impacts. It is beyond the scope of this risk assessment to present a comprehensive review of the potential public health and environmental impacts associated with various alternatives for remediation of copper-contaminated sediments at the NCMT. However, a preliminary evaluation can be made of the environmental aspects of and regulations associated with one of the least expensive approaches for the remediation of those sediments, dredging with disposal at a designated offshore marine disposal site. As discussed elsewhere in this report, the cost of that approach is a factor of 5 to 10 less expensive than alternative approaches.

As discussed by US EPA and US COE (1991), Section 103 of Public Law 92-532 (the Marine Protection, Research, and Sanctuaries Act of 1972) regulating ocean disposal of dredged sediments

> *"prohibits dumping of certain constituents as other than trace contaminants unless they are rapidly rendered harmless. This is a key section of the regulations. TRACE CONTAMINANTS ARE NOT DEFINED IN TERMS OF NUMERICAL CHEMICAL LIMITS, BUT RATHER IN TERMS OF PERSISTENCE, TOXICITY, AND BIOACCUMULATION THAT WILL NOT CAUSE AN UNACCEPTABLE ADVERSE IMPACT AFTER DUMPING. This is expressed in regulatory language in paragraphs 227.6(b) and (c)* [of PL 92-532]."

Basically, the disposal of contaminated sediments may take place at designated marine disposal areas provided that it can be demonstrated that the chemical constituents of the sediments will not cause adverse impacts in the disposal area through their persistence, toxicity, or bioaccumulation.

In 1977 the US EPA and Corps of Engineers published a guidance manual for evaluating the suitability of a dredged sediment for ocean disposal in accord with the requirements of PL 92-532. That manual was recently replaced by the US EPA and US COE (1991) "Green Book" entitled, "Evaluation of Dredged Material Proposed for Ocean Disposal." The WESTEC studies discussed in this report were conducted in accordance with the 1977 guidance document, while the present study was conducted in accordance with US EPA and US COE (1991). As discussed above it has been found that the copper in the NCMT-area sediments is not toxic and does not bioaccumulate to excessive levels. It may, therefore, be preliminarily concluded that the remediation of the copper-contaminated sediments could potentially be accomplished through dredging and offshore disposal. Obviously, some additional studies would be needed to evaluate whether other constituents in those sediments could cause them to be judged unsuitable for disposal at a designated disposal site.

3.9 CONCLUSIONS

It may be concluded from the studies that have been conducted on the water quality significance of copper ore concentrate present in the sediments near the NCMT that the copper in those sediments is not, and would not be expected to become significantly available to affect aquatic life through toxicity, bioaccumulation in aquatic organism tissue, or altering the numbers and types of organisms present in San Diego Bay. It is apparent that the 1,000 mg Cu/kg dry wt. remediation objective established by the Water Quality Control Board San Diego Region would provide for protection of the designated beneficial uses of San Diego Bay. While not specifically studied in this investigation, it is preliminarily concluded that remediation objectives considerably greater than that level could be adopted for remediation and that the residual copper left in the sediments after such remediation would present little risk to the beneficial uses of San Diego Bay. It has been suggested that consideration be given to using the DHS Title 22 TTLC limit of 2,500 mg/kg wet wt. (approximately 4,000 mg/kg dry wt.) for an alternative remediation level. That TTLC value is not based on technical information pertinent to assessing the potential impacts of sediment-associated copper in a marine environment. The results of the toxicity tests conducted in this and previous studies indicate that application of that limitation in the management of the NCMT-area sediments in the marine environment is inappropriate and technically invalid.

It is suggested that because of the lack of toxicity and bioaccumulation associated with copper in the sediments in the vicinity of the NCMT, consideration should be given to pursuing a variance from the Title 22 TTLC for the NCMT-area copper-contaminated sediments and pursue ocean disposal at a designated disposal site of those sediments that are to be remediated (removed).

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Summary of Expertise and Experience
G. Fred Lee and R. Anne Jones

Presented below is a summary of the expertise and experience of Drs. G. Fred Lee and R. Anne Jones that is pertinent to their conduct of the risk assessment for the NCMT study.

G. Fred Lee is president of G. Fred Lee & Associates, a consulting firm specializing in water quality and solid and hazardous waste management, located in El Macero, CA. He has a Bachelor's degree in environmental sciences from San Jose State College, a Master of Science in Public Health degree with emphasis in the environmental sciences, from the University of North Carolina, and a Ph.D. degree in environmental engineering and environmental sciences with emphasis in aquatic chemistry, from Harvard University. For nearly 30 years Dr. Lee taught graduate-level environmental engineering and environmental sciences courses, and conducted more than $5 million of research in water quality and solid and hazardous waste management; he has published more than 450 professional papers and reports on this work. In 1989, he retired from university teaching and research and began to expand the part-time consulting that he had been doing while a university professor into a full-time endeavor. It was at that time that he and Dr. Anne Jones moved G. Fred Lee & Associates to El Macero, California.

R. Anne Jones is vice president of G. Fred Lee & Associates. She earned a BS degree in biology from Southern Methodist University, and MS and Ph.D. degrees in environmental sciences focusing on aquatic toxicology, aquatic biology, and aquatic chemistry, from the University of Texas at Dallas. She held university research and professorial positions for a period of 12 years; she taught graduate-level environmental engineering and environmental science courses and conducted research on various aspects of water quality and solid and hazardous waste management. She has published more than 175 papers and reports on her work.

Drs. G. Fred Lee and R. Anne Jones have high degrees of expertise and many years of experience in aquatic chemistry, aquatic biology, aquatic toxicology, and environmental engineering pertinent to evaluating the water quality significance of copper-contaminated sediments near the National City Marine Terminal. Dr. Lee has focused much of his 30-year professional career on developing and applying new technology for evaluating the water quality significance of contaminants in sediments. He and Dr. Jones have worked on this topic as a team since the mid-1970's.

Further information on the expertise and experience of Drs. Lee and Jones is provided in the summary resumes appended. Copies of papers and reports referenced in their resumes are available upon request.

Table 3-1. Summary of Toxicity Test Results
NCMT-Area Sediments

(WESTEC, 1988)

Organism Type	(Name)	Test endpoint	Response
shrimp	(Acanthomysis sculpta)	death	The 4-day survival in 100% elutriate from sediments containing 1520 and 6067 mg Cu/kg dry wt. was **not statistically different** from that in the control (no copper added) tests
flat fish	(Citharichthys stigmaeus)	death	The 4-day survival in 100% elutriate from sediments containing 1520 and 6067 mg Cu/kg dry wt. was **not statistically different** from that in the control (no copper added) tests
sea urchin	(Strongylocentrotus purpuratus)	fertilization	The percent of fertilization of eggs in 100% elutriate from sediments containing 1520 and 6067 mg Cu/kg dry wt. was **not statistically different** from that in the control (no copper added) tests
		development	The percent of the fertilized eggs that exhibited normal development in 100% elutriate from sediments containing 1520 and 6067 mg Cu/kg dry wt. was **not statistically different** from that in the control (no copper added) tests
clam	(Macoma nasuta)	death	The 10-day survival in sediments containing 1520 and 6067 mg Cu/kg dry wt. was **not statistically different** from that in the reference sediments
worm	(Neanthes arenaceodentata)	death	The 10-day survival in sediments containing 1520 and 6067 mg Cu/kg dry wt. was **not statistically different** from that in the reference sediments
amphipod	(Grandidierella japonica)	death	The 10-day survival in sediments containing 1520 and 6067 mg Cu/kg dry wt. was **not statistically different** from that in the reference sediments
		reburial	The organisms exposed for 10 days to sediments containing 1520 and 6067 mg Cu/kg dry wt. exhibited reburial behavior **not**

			statistically different from that exhibited by organisms exposed to the reference sediments

(This Study)

fish larvae	(Menidia beryllina)	death	The 7-day survival in 100% elutriate from sediments containing as much as 18,755 mg Cu/kg dry wt. was **not statistically different** from that in the reference site tests
		growth	The growth of test organisms in elutriate from sediments containing as much as 18,755 mg Cu/kg dry wt. was **not statistically different** from that found in tests with reference site sediments
oyster larvae	(Crassostrea gigas)	death	The survival of oyster larvae in elutriate from sediments containing as much as 18,333 mg Cu/kg dry wt. was **not statistically different** from that found in the control tests
		abnormalities	The incidence of larval abnormalities in oyster larvae after exposure to elutriates from sediments containing as much as 18,333 mg Cu/kg dry wt. was **not statistically different** than that found in the control (no copper added) tests
amphipod	(Rhepoxynius abronius)	death	Mortality statistically greater than the controls was found in tests of sediments from all sites evaluated, irrespective of copper concentration in the sediment. **Mortality from sediments containing 18,333 mg Cu/kg same as from sediments containing 122 mg Cu/kg.** The significance of this finding is discussed in this section.
		reburial	The reburial of surviving organisms exposed to 18,333 mg Cu/kg was **not statistically different** from that of those exposed to 122 mg Cu/kg or from that of control.