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Environmental Effects from In-Water Hull Cleaning of Ablative Copper Antifouling Coatings

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EXECUTIVE SUMMARY

OBJECTIVE

The primary goal of this field study was to objectively evaluate the magnitude of environmental effects attributable to in-water hull cleaning operations in a typical Navy harbor. San Diego Bay was selected for detailed analyses of vessels coated with copper-based antifouling paints. This evaluation can be used to support dicussions with environmental regulators, strengthen future compliance strategies, and provide a framework for future monitoring studies.

RESULTS

Six classes of naval surface vessels were surveyed during commercial hull cleaning operations in San Diego Bay during a two and one-half-year period. While total copper concentrations in bay waters were rapidly elevated near hull cleaning operations, the biologically active species of copper complexed rapidly, returning actual toxic copper potential to near ambient conditions within minutes to hours after hull cleaning ceased. With the Ion Selective Electrode (ISE), a good technique was developed for tracking and modelling a copper plume formed during hull cleaning. The small changes in free copper ion activity detected by the electrode indicate that most copper released during hull cleaning operations is in the particulate form and is rapidly incorporated into bottom sediments. Estimates of toxicity from the hull cleaning plume to resident nontarget biota from site-specific bioassays were used to evaluate potential effects on the marine ecosystem. These data are consistent with other studies and show toxicity thresholds above the actual copper levels contributed to San Diego Bay by hull cleaning activities.

RECOMMENDATIONS

It is essential that the Navy employ a database to evaluate the environmental risks from potential contaminant-introducing activities such as in-water hull cleaning and the general use of antifouling paints.

Because of increasingly stringent environmental regulation and escalating concern over the status of bays and estuaries, in-water hull cleaning has recently come under the scrutiny of regulatory agencies. We recommend that local, state, and federal regulatory personnel be shown these data and encourage open discussions to revise compliance standards and regulations based on realistic environmental concentrations.

Site-specific water quality criteria for copper should be developed using recent EPA methods comparing reference water and site-specific water toxicity testing. This approach more effectively addresses the bioavailable copper on a site-specific basis and is consistent with our findings that less than the total amount of copper measured is in a form toxic to organisms.

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ACRONYMS

μg	microgram
μl	microliter
μm	micron, micrometer
AA	atomic absorption
ADCP	acoustic Doppler current profiler
AF	antifouling
APDC	ammonium pyrrolidinedithiocarbamate
ASTM	American Society for Testing and Materials
ASV	anodic stripping voltametry
cm	centimeter
CTD	conductivity, temperature, depth
Cu	copper
DIW	deionized water
EC	effect concentration
EDTA	ethylene diamine tetraacetic acid
EPA	United States Environmental Protection Agency
GFAA	graphite furnace atomic absorption
HDPE	high density polyethylene
HMDE	hanging mercury drop electrode
HNO_3	nitric acid
IC	inhibition concentration
ISE	ion selective electrode
kg	kilogram
L	liter
LC	lethal concentration
LOEC	lowest observable effect concentration
m	meter
M	moles
MΩ	megohm
MIBK	methyl isobutyl ketone
ml	milliliter
MLC	median lethal concentration
mV	millivolt

NATO	North Atlantic Treaty Organization
NAVSEA	Naval Sea Systems Command
NCCOSC	Naval Command, Control and Ocean Surveillance Center
ng	nanogram
NOAA	National Oceanic and Atmospheric Administration
NOEC	no observable effect concentration
NPDES	National Pollutant Discharge Elimination System
NRaD	NCCOSC RDT&E Division
NRCC	National Research Council of Canada
NURP	National Urban Runoff Program
OCNR	Office of the Chief of Naval Research
pCu	logarithm of the reciprocal of the copper ion concentration
PE	polyethylene
pH	logarithm of the reciprocal of the hydrogen ion concentration
ppb	parts per billion
ppm	parts per million
SDG&E	San Diego Gas and Electric Company
TLM	median tolerance limit
WRCB	State of California Water Resources Control Board

BACKGROUND

With the desired extension of U.S. Navy vessel drydocking periods to 5 to 7 years, the requirement for in-water hull cleaning of the new ablative copper antifouling coatings has increased greatly. Because of increasingly stringent environmental regulation and escalating concern over the status of bays and estuaries, in-water hull cleaning has come under scrutiny of regulatory agencies. There is increasing likelihood that use and maintenance of copper antifouling paints will be regulated by measures such as release rate restrictions, discharge limits, debris cleanup, and monitoring requirements.

It is essential that the Navy develop a base of information that can be used to evaluate the environmental risks from its copper-producing activities such as in-water hull cleaning and general use of antifouling paints. Studies performed about 15 years ago to evaluate the fate and effects of hull cleaning wastes from conventional copper-based paints provided some useful input for the database, but similar data need to be obtained for the newer ablative copper paints that are now used on most Navy vessel hulls. Past and present experience shows that ablative paints may require cleaning at some point during their operational cycle. Environmental assessment information will be needed to (1) address compliance issues with state and federal regulators on an ecological risk basis; (2) support formulation of remediation strategies if necessary; and (3) develop, improve, and optimize hull husbandry practices.

OBJECTIVES

- To define the overall environmental loading and mass balance of copper in typical Navy harbor environs and to evaluate the magnitude and fate of those materials derived from in-water hull cleaning operations.
- To examine the possible toxicity of hull cleaning by-products of copper ablative coatings and to identify the biological effects of chemical species of that material.

TECHNICAL APPROACH

Field efforts for these studies were performed in San Diego Bay, where many U.S. Navy vessels receive in-water hull cleaning. Additionally, the existing environmental database is extensive, since NRaD and other organizations have performed many water quality, biological, and ships husbandry studies in this harbor.

During the course of this investigation, six detailed measurement/sampling series were accomplished during in-water hull cleaning operations. Hull cleaning effluent plumes were monitored for several hours while copper levels were measured. These measurements assist in defining the composition, amounts, and fates of typical hull cleaning effluents. The Naval Command, Control and Ocean Surveillance Center (NCCOSC) RDT&E Division’s (NRaD’s) marine environmental survey craft, R/V *ECOS*, with equipment capable of obtaining real-time measurements of supporting oceanographic parameters, supported the San Diego Bay survey operations. Harbor-wide surveys of copper levels and related oceanographic parameters were performed during periods when hull cleanings were not taking place to characterize background levels and ambient copper distribution.

The fate and effects of three primary by-products of hull cleaning were evaluated:

- Dissolved copper—mostly released during and shortly after hull cleaning activities from brushed and fragmented paint surfaces: lower levels may be released from the same sources after cleaning and some may leach copper from debris on and in bottom sediments. Maximal effects are likely pulsed, having relatively short-term effects.

- Particulate copper—present largely as paint chips associated with bottom sediments; some fine material is suspended in the water column for varying lengths of time. Potential effects are probably long-term in nature, depending on dissolution rate of the copper and degree of uptake of particulate and dissolved copper fractions by sediment-dwelling organisms.

- Organic fouling debris—present mostly on and in sediments near hull cleaning areas (derived from fouling growth brushed from hulls). Effects are expected to be primarily short-term, being caused by autotrophic consumption of oxygen and production of dissolved nutrients during decomposition of the organic material.

In the aquatic environment, dissolved copper actually exists in many forms and compounds, referred to here as copper species. In most studies of copper toxicity, “total copper,” which includes copper of all species, is measured and is assumed to be responsible for any noted toxic effects. In reality, considerable differences exist in the biological availability and toxicity of various copper species. Thus, although total copper values may be high in an area, the amount of toxic copper present may be low, because most copper is tightly bound in complex organic compounds or is adsorbed onto particulate material.

The measurement of biologically active and ligand exchangeable copper was an important aspect of this program. These are the two groups of copper species having the greatest biological availability and mobility. Total dissolved copper concentrations were measured in water samples using standard atomic absorption techniques. Additionally, approximately 20% of all water samples was analyzed for copper speciation using electrochemical (anodic stripping voltametry) techniques. In later phases of the program, toxicity of the more commonly encountered copper species was tested for toxicity using a standard laboratory bioassay test (Microtox®). Total particulate copper (associated with filtered particles larger than 0.45 µm in size) was measured for approximately 50% of all water samples.

INTRODUCTION

TOXICITY, ENVIRONMENTAL CHEMISTRY, AND FATE

Trace element speciation in surface waters and its ecological implications was explored during a NATO conference (Leppard, 1983). The toxicity of essential and non-essential metals was also discussed. It is generally acknowledged that essential elements are less toxic than non-essential elements, with trace metals becoming toxic when the nutritional supply exceeds the optimal amount by a factor of 40 to 200 fold. However, copper is considered to be toxic at relatively low levels. Copper toxicity seems to be higher for lower organisms than for more advanced organisms. The high toxicity of copper has been tentatively correlated with the electronegativity, or other properties, of its salts or of chelates. The more electronegative metals and all the divalent transition metals are particularly active in the chemical inactivation of enzymes (Albergoni and Piccinni, 1983).

The toxicity of copper in environmental waters and sediments is directly linked to its availability, and hence its physico-chemical form. Metals may vary widely in their natural environmental forms including "...the hydrated ion; simple organic and inorganic complexes; stable organic and inorganic complexes; adsorbed on inorganic colloids; adsorbed on organic colloids; bound in various ways to large particles which include solid organics, minerals and mixtures of various kinds of these. In terms of transport, the chemical species can be: truly dissolved; insoluble but suspended; or a component of colloids having intermediate characteristics between those of dissolved substances and sedimenting particles" (Leppard and Burnison, 1983). Colloidal forms of copper complexes have particular relevance to this study. In coastal seawater, the combined forms of organic and inorganic colloidal copper complexes accounted for 56% of total copper (Batley, 1983).

In sediments, the issues of availability to organisms and physico-chemical form are complex as well. In a 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..." (Tessier and Campbell, 1987). Heavy metals in sediments may be associated with clay surfaces, clay structural matrices, humic acids, surfaces of iron and manganese hydrous oxides, detrital and freshly precipitated carbonates, nodules, detrital organic matter, and crystalline and amorphous sulfides. Where copper is present in sediments containing sulfide, it is primarily a precipitated sulfide and not bioavailable (Loring, 1981, 1982). When the molar sum of the acid volatile sulfides exceeds the molar sum of the non-iron heavy metals in sediments, the heavy metals in the sediments are not available, and hence non-toxic to aquatic species (DiToro et al., 1990).

As might be expected, the nature of copper in interstitial waters is also complex. Approximately 80% of the dissolved copper in interstitial water from anoxic sediment from Narragansett Bay was complexed with natural dissolved organic matter, or associated with colloidal organic matter (Elderfield, 1981). It was reported that insoluble sulfide was a major factor controlling copper availability resulting in low interstitial water copper concentrations, and a low flux of copper from sediment to the interstitial water (Elderfield, 1981; Elderfield *et al.*, 1981).

REGULATORY STATUS

The water quality criterion for copper in marine waters is a 1-hour average not to exceed 2.9 $\mu g\ L^{-1}$ (U.S. EPA, 1985). This criterion has been adopted by the state of California in its enclosed bays and estuaries plan as the state water quality objective for the protection of marine organisms (Water Resources Control Board [WRCB], 1991). In the state of California's ocean plan for the protection of marine organisms in open waters, a 6-month median concentration of 3 μg L^{-1} is targeted. A daily maximum concentration of 12 μg L^{-1} and an instantaneous maximum concentration of 30 μg L^{-1} are also allowed (WRCB, 1990). It should be noted that these target concentrations reflect total copper, and therefore are conservative since the active component or bioavailable copper in a natural water sample would certainly be less than total copper.

The most recent EPA view of the water quality criterion for copper in marine waters has changed, however. The 1-hour average concentration limit of 2.9 μg L^{-1} now may address that copper fraction which passes through a 0.45-micron filter operationally defined as dissolved copper (U.S. EPA, 1992). The EPA acknowledges that this fraction still contains colloidal copper complexes and its bioavailability remains to be defined. This change is, however, a significant development regarding the estimation of bioavailable copper in the aquatic environment. The EPA has further stated that a ratio of copper toxicity in ambient site water and toxicity measured in reference water (Narragansett Bay) may be used to adjust site water copper criteria (water effect ratio). This would have the effect of raising the allowable copper concentration in waters having less bioavailable copper than that in the reference water. The ratios measured in seawater have not been particularly large, however, being on the order of a factor of two (Delos, 1993, personal communication). These recent EPA recommendations have not as yet been endorsed by the WRCB.

SAN DIEGO BAY—GENERAL CHARACTERISTICS

PHYSICAL DESCRIPTION

In a recent study addressing the distribution and fate of organotins from antifouling paint sources in U.S. harbors (Grovhoug et al., 1987), San Diego Bay was described as a semi-enclosed water body extending approximately 28 kilometers in length and varying from 0.5 to 4.6 kilometers in width, with a depth of generally less than 4.5 meters. The sediment is characterized by primarily grey, brown, or black mud, silt, gravel, and sand. In many of the dredged areas, the mud layer has been removed exposing the underlying sandy strata (Kram et al., 1989). A channel 7.5 to 20 meters deep runs lengthwise through most of the bay. Currents generally flow in the direction of the channel with velocities ranging from 0.5 to 3 knots dependent on tidal fluctuations (Kram et al., 1989). The salinity is near oceanic throughout most of the bay due to minimal freshwater input. Seligman et al. (1986) have discussed the bay in terms of four regions characterized by current velocity patterns and use characteristics. The northern region has relatively high current velocities and rapid flushing rates. This region includes most of the shipping channels and dredged areas of the bay. The southern region is largely shallow having low-velocity currents and longer water residence times. Nursery grounds for fish and invertebrate species are located in this region. The naval region includes several ship berthing areas and is moderately well-flushed. Marinas and commercial boat basins compose a fourth region of the bay and are generally characterized by moderate to dense aggregations of vessels in enclosed embayments with reduced flushing characteristics (Seligman et al., 1989).

In the context of the general current velocities seen in the bay, the Submarine Support Facility should have the highest flushing rate of naval facilities located in San Diego Bay due to its location near the entrance channel. The carrier pier has a moderately high flushing rate due to its location in and parallel to the deep channel. Water circulation at the Naval Station is reduced due to its inner position relative to the long axis of the bay and the interference of piers and ships.

Based on tidal dispersion, Ridley (1959) calculated an exchange ratio of 0.06 for San Diego Bay, or a 6% reduction of a contaminant per tidal cycle assuming little mixing. Using this figure, an 80% reduction in contaminants present would be achieved in 13 tidal cycles (7.5 days). If a higher degree of mixing is assumed, the 80% flushing level might require 18 tidal cycles (9 days).

BIOTA

San Diego Bay is an important spawning area for ocean fishes, with the bay habitats providing an integral element in the interconnected food web of adjacent ocean waters. Benthic studies in the vicinity of the Naval Station reveal communities indicative of a moderately disrupted habitat, however. Frequently observed benthic organisms include the snail *Nassarius tegulus*, the burrowing shrimp *Callianassa* spp., the gobiid fish *Clevelandia ios*, and numerous polychaete worms (U.S. Army Corps of Engineers, 1975a). Fish and invertebrate species tend to be most abundant on the western side of the bay, where generally the water is shallower and there is improved water quality. Black croaker (*Cheilotrema saturnum*) and bonito (*Sarda chiliensis*) were the most numerous fish collected during a Naval Ocean Systems Center bay-wide survey (Peeling, 1974) in both the bay in general, and a sampling site near Pier 8 at the

Naval Station. Thirty-eight fish species were identified. Spiny lobsters (*Panulirus interruptus*) also move into San Diego Bay during their spawning season (March–July).

The principal vegetation in most of the bay includes several species of algae and the eel grass, *Zostera marina*. Much of the original marshland surrounding the bay has been replaced by urban development. The southern portion of the bay is relatively undisturbed by industrial activity.

COPPER CONTAMINATION

To evaluate the potential effects of copper released from hull cleaning activities, this study focused on copper values in water and bay sediments. Some historical data concerning copper values in the naval region is provided prior to initiation of hull cleaning operations in the mid-1970s. Data collected by the California Regional Water Quality Control Board in 1972 (in Peeling, 1974) indicate that sediment copper values off the end of the mole pier near Pier 8 at the Naval Station ranged from 57 to 170 mg kg^{-1}. The Army Corps of Engineers reported a sediment copper concentration of 57 mg kg^{-1} off Pier 3 at the Naval Station in 1971 (in Peeling, 1974). During 1973 and 1974, a heavy metal survey of sediments was conducted in San Diego Bay at two locations in the Naval region where hull cleaning activities would later take place (Yamamoto et al., 1975). Figure 1 shows the locations of the sampling stations in the Naval region. Copper concentrations in sediment from the Naval Station region are given in table 1.

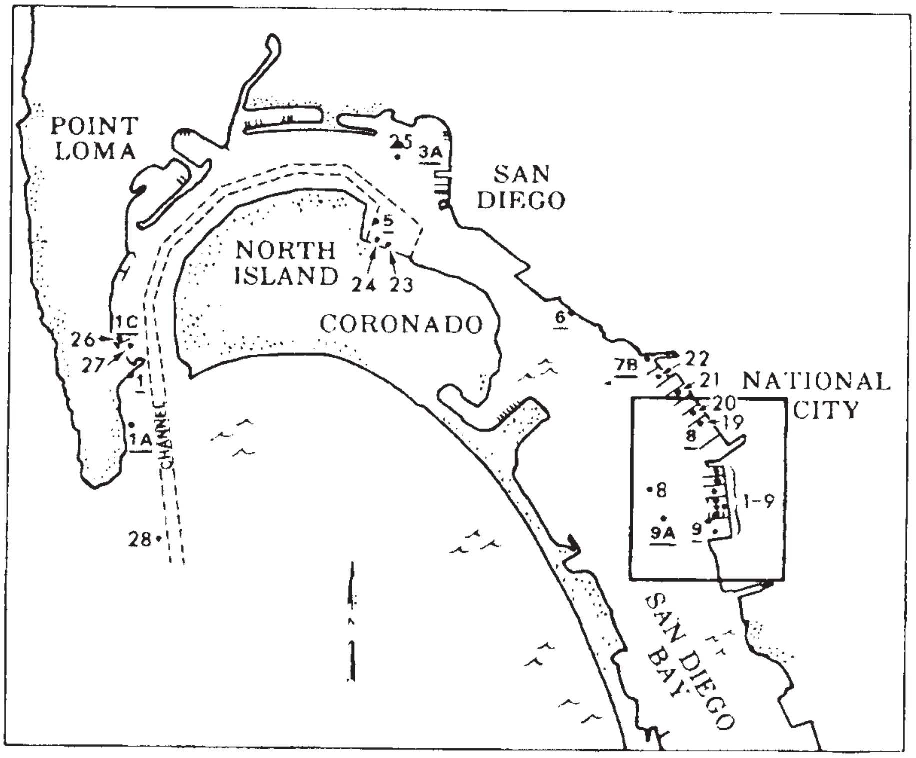


Figure 1. Naval Station sediment copper collection sites several years prior to hull cleaning operations (from Yamamoto et al., 1975).

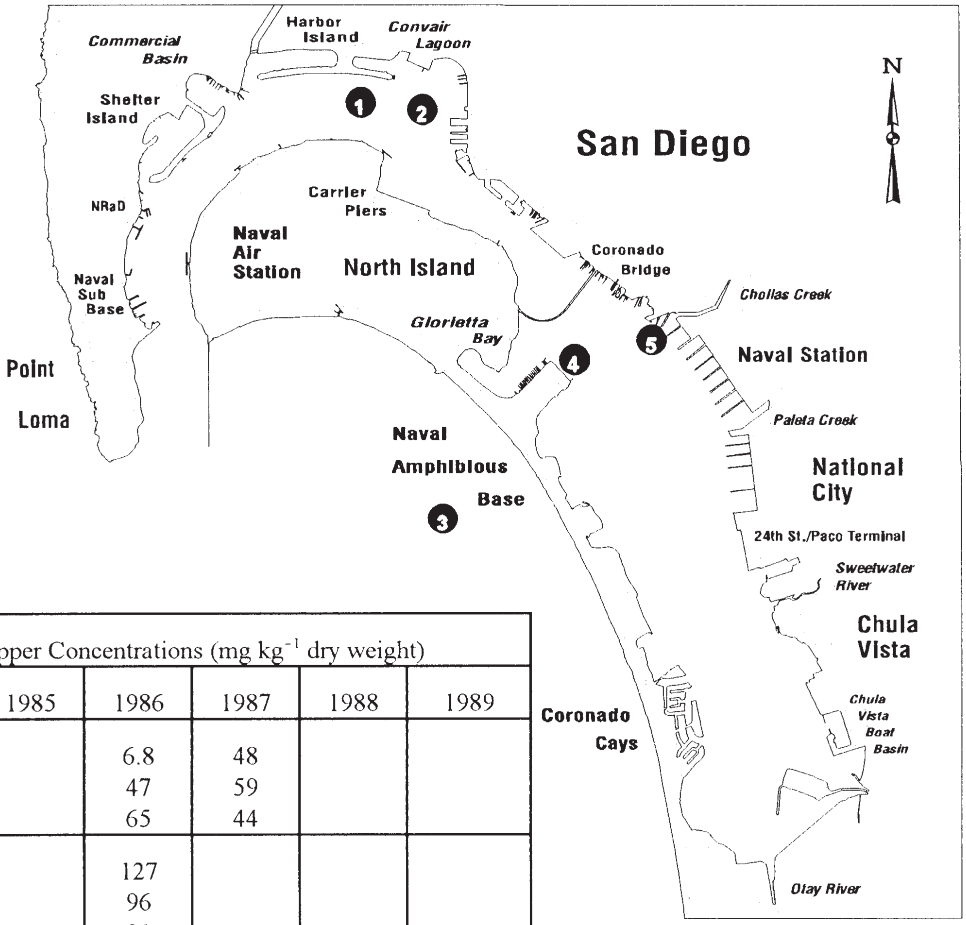
Table 1. Sediment copper concentrations in San Diego Bay prior to hull cleaning operations. Values are mg kg^{-1} dry weight (Yamamoto et al., 1975; Peeling, NOSC, unpublished data).

Inactive Fleet Sites (see figure 1)	Copper
Station 1	231
Station 2	197
Station 3	207
Station 4	264
Station 5	271
Station 6	284
Station 7	253
Active Fleet Sites (see figure 1)	
Station 19	133
Station 20	360
Station 21	301
Station 22	189
Station 23	86
Station 24	111
Station 25	82
Station 26	40
Station 27	42
Peeling, NOSC, Unpublished Data	
1C	25
1A	6.3
1	1.2
3	11
5	12
6	64
7B	20
8	270
9	39
9A	60

The highest copper concentrations in sediment were found at the Naval Station and inactive fleet areas, followed by the carrier piers and the submarine support facility. The Naval Station sediments averaged 246 ± 83 mg kg^{-1}, while the carrier and submarine facilities collectively averaged 72 ± 3 mg kg^{-1} copper. Water concentrations ranged from 3 to 15 µg L^{-1} at the inactive fleet site, and from 3 to 16 µg L^{-1} at the active fleet site (Yamamoto, et al., 1975). During later studies, sediment copper concentrations averaged 415 mg kg^{-1}, while average water copper concentrations in San Diego Bay were reported to be about 3 µg L^{-1} (Salazar et al., 1980; Zirino et al., 1978; Kenis et al., 1978). This latter value is similar to the lower copper concentrations measured in surface waters from the naval region over a 1-year period which ranged from 2.2 to 23 µg L^{-1} (Krett, 1980). These earlier studies cited serve as a historical reference point for later comparisons of copper concentrations in water and sediment samples collected during hull cleaning operations at the Naval Station.

Additional data for sediment copper measurements made in the 1980s are summarized in Woodward–Clyde (1991) from data cited in NOAA (1991). Sediment copper data from the Naval Station ranged from 92 to 241 mg kg^{-1} (dry weight) during 1984 to 1986 (figure 2).

The copper values measured in sediment at the Naval Station (Site 5) are very similar to the mean sediment copper value of 246 mg kg^{-1} for Naval Station sediments from the data of Yamamoto et al. (1975) indicating little change in sediment copper concentration during an interval of a decade. More recent and abundant data (San Diego Bay Integrated Risk Assessment, K. Richter unpublished data, 1993, figure 3) indicate that sediment copper values may have increased at Naval Station Piers 3–4, 11–12, and 13 to levels ranging from approximately 360 to 480 mg kg^{-1} dry weight (figure 3). Sampling took place on 1–2 July 1993. Hull cleaning operations took place during May 1991 and February 1993 (Pier 12), and August 1991, June 1992, and February 1993 (Pier 13). Probable causes for the observed increases are varied, however. Storm runoff from the Naval Base and the proximity of Pier 13 to the PACO Ore terminal, where copper ore was spilled into San Diego Bay for a number of years, complicate isolation of copper inputs for these areas. The high copper value measured at station B-1 between Piers 3 and 4 was not likely to be due to hull cleaning activity because of the distance from Piers 12 and 13 and direction of the prevailing circulatory current pattern. Since this station is located close to the Naval Station at the head of Piers 3 and 4, it is quite possible that storm runoff has contributed significantly to copper input at this area. Gadbois (1992) reported copper in storm runoff ranging from 0.32 to 1.9 mg L^{-1} in samples collected from areas 10 and 14 located near the head of Pier 4. The variable copper concentrations measured in storm runoff complicate predictions of input. Unfortunately, no “end of pipe” flow volumes are available for the Pier 3–4 area precluding any estimate of input. Considering the time span over studies done in 1971 to the present, it is quite likely that urban development in San Diego has contributed significantly to the input of copper to the Naval Station and the bay in general.



Sediment Copper Concentrations (mg kg^{-1} dry weight)						
	1984	1985	1986	1987	1988	1989
Site 1			6.8 47 65	48 59 44		
Site 2			127 96 91			
Site 3	7.3 7.7 8	6.9 7.9 11.2				
Site 4						14 13 28
Site 5	228 92 236	200 241 147	134 202 143			

Figure 2. Copper concentrations in San Diego Bay sediments, 1984 – 1989 (NOAA, 1991).

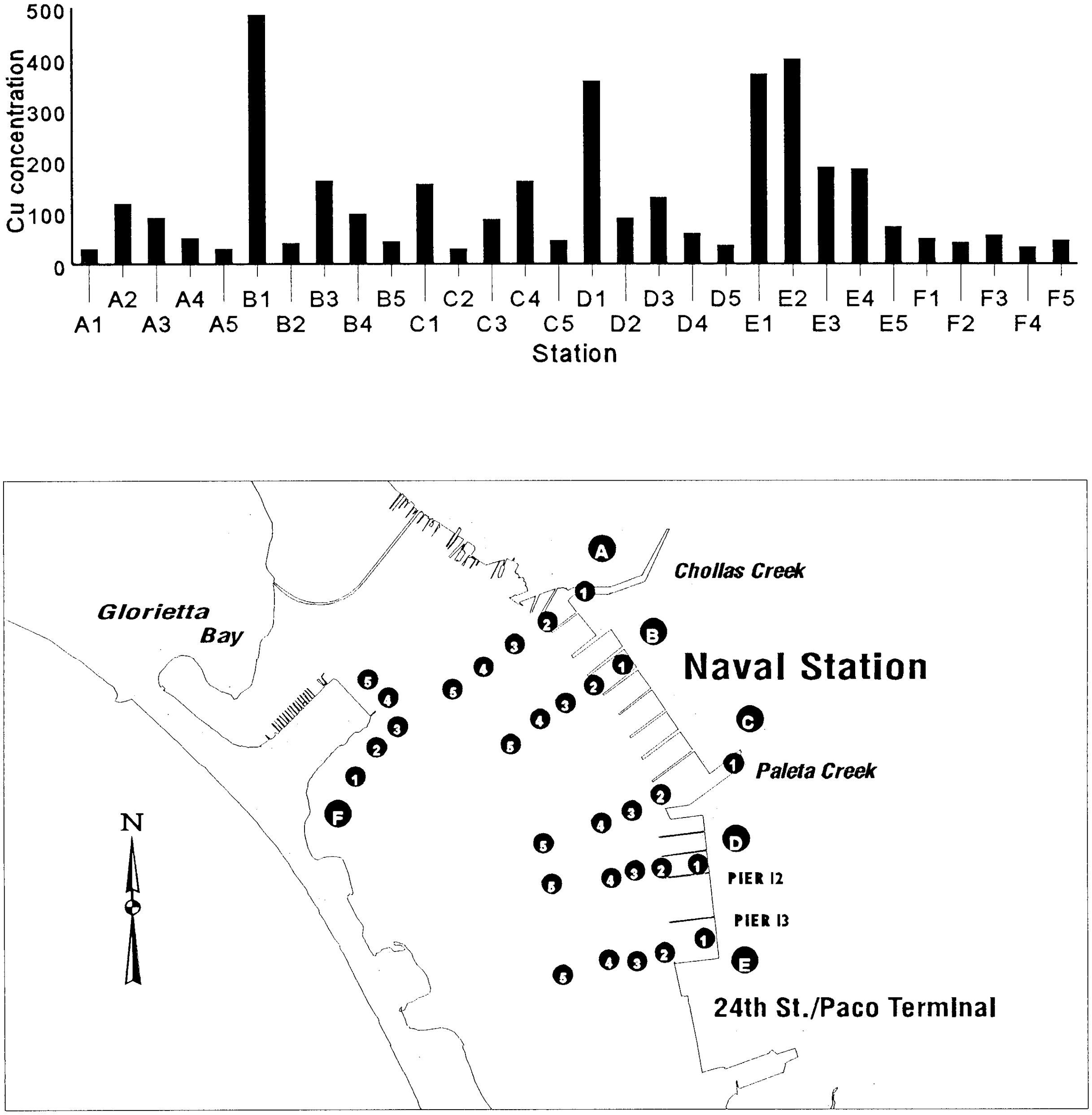


Figure 3. Sediment copper concentrations in San Diego Bay at Integrated Risk Assessment stations, July 1993 (Richter, unpublished data). Copper concentrations in mg kg^{-1} dry weight.

BIOLOGICAL EFFECTS

OVERVIEW OF COPPER TOXICITY

A general summary of copper toxicity to marine organisms is provided in table 2. These data are provided to give an indication of the copper levels found toxic to various species under various testing conditions.

Table 2. Copper concentrations reported toxic and/or inhibitory to marine organisms.

Organism	Effect	Concentrations (ppm, mg L^{-1})	Reference
Algae			
Mixed diatoms	Toxic	0.050	Zeituon et al., 1969
Dinoflagellates	2-day LC_{50}	0.020	Saifullah, 1978
Mixed phytoplankton	Inhibition of growth	0.100	Thomas et al., 1977
Exuviaella sp.	Inhibition of growth	0.025	Mandelli, 1969
Gymnodinium breve	Toxic	0.030	Marvin et al., 1961
Laminaria hyperborea	Inhibition of growth (28-day exposure)	0.050	Hopkins and Kain, 1971
Invertebrates			
Colonial hydroid, *Campanularia flexuosa*	11-day growth rate inhibition	0.010–0.013	Stebbing, 1976
Colonial hydroid, *Campanularia flexuosa*	Enzyme inhibition	0.0014	Moore and Stebbing, 1976
Colonial hydroid, *Eirene viridula*	14- to 21-day growth rate inhibition	0.030–0.060	Karbe, 1972
Ctenophore, *Mnemiopsis mccrodyl*	24-hr LC_{50}	0.017-0.029	Reeve et al., 1976
Pleurobrachia pileus	24-hr LC_{50}	0.033	Reeve et al., 1976
Polychaetes	Lethal	0.120-0.250	McLusky and Phillips, 1975
	Abnormal larvae	0.010	Reish, 1964
Nereis vireus	4-day LC_{100}	0.500	Raymont and Shields, 1963
Nereis vireus	2-day LC_{100}	1.5	Raymont and Shields, 1963
Cirriformia spirabracha	26-day LC_{50}	0.040	U.S. EPA, 1980
Phyllodoce maculata	9-day LC_{50}	0.080	McLusky and Phillips, 1975
Neanthes arenaceodentata	28-day LC_{50}	0.044	Pesch and Morgan, 1978
Neanthes arenaceodentata	28-day LC_{50}	0.100	Pesch and Morgan, 1978
Larval annelids, mixed species	24-hr LC_{50}	0.089	Reeve et al., 1976

Organism	Effect	Concentrations (ppm, mg L^{-1})	Reference
Echinoderms			
Sea urchin, *Arbacia punctatum*	58% decrease in sperm motility	0.300	Young and Nelson, 1974
Paracentrotus lividus	Retardation of pluteal larval growth 4-day test	0.010-0.020	Bougis, 1965
Crustaceans			
Acartia clausi	2.5-hr LC_{50}	5.0	Corner and Sparrow, 1956
Acartia clausi	2-day LC_{50}	0.034-0.082	Moraitou and Apostolopoulou, 1978
Acartia tonsa	6-day LC_{50}	0.009-0.073	Sosnowski et al., 1979
Acartia tonsa	24-hr LC_{50}	0.104-0.311	Reeve et al., 1976
Euchaeta marina	24-hr LC_{50}	0.188	Reeve et al., 1976
Metridia pacifica	24-hr LC_{50}	0.176	Reeve et al., 1976
Phialidaum sp.	24-hr LC_{50}	0.036	Reeve et al., 1976
Undinula vulgaris	24-hr LC_{50}	0.192	Reeve et al., 1976
Copepod nauplii, mixed species	24-hr LC_{50}	0.090	Reeve et al., 1976
Labidocera scotti	24-hr LC_{50}	0.132	Reeve et al., 1976
Barnacle larvae	2-hr LC_{50}	200	Corner and Sparrow, 1956
Barnacle larvae	Inhibition of attachment	0.024	U.S. Naval Institute, 1952
Carcinus maenas	12-day lethal	1-2	Raymont and Shields, 1963
Cancer magister zoea	96-hr LC_{50}	0.049	Bretler et al., 1984
Cancer maenas	48-hr LC_{50}	100	Portmann, 1968
Crangon crangon	48-hr LC_{50}	30	Portmann, 1968
Leander squilla	Toxic	0.500	Raymont and Shields, 1963
Pandalus montagui	48-hr LC_{50}	0.200	Portmann, 1968
Lobster, *Homarus americanus*	13-day LC_{50}	0.056	McLeese, 1974
Molluscs			
Acmaea scabra	3-day LC_{50}	0.100	Marks, 1938
Cardium edule	48-hr LC_{50}	1.0	Portmann, 1968
Busycon canaliculatum	77-day LC_{50}	0.470	Betzer and Yevich, 1975
Nassarius obsoletus	Decrease in O_2 consumption, 3 days	0.100	MacInnes and Thurberg, 1973
Crassostrea gigas	96-hr TLM	1.9	Fujiya, 1960
Crassostrea gigas embryos	48-hr EC_{50}	0.0053	Bretler et al., 1984
Crassostrea virginica	48-hr LC_{50}	0.103	Bretler et al., 1984
Crassostrea virginica larvae	12-day LC_{50}	0.046	Calabrese et al., 1977
Oyster larvae	Lethal	3.0	Reish, 1964
Oyster larvae	48-hr LC_{50}	0.103	Calabrese et al., 1973
Oyster larvae	Inhibition and Tolerance Level	0.8-2.5	Reish, 1964

Organism	Effect	Concentrations (ppm, mg L^{-1})	Reference
Oyster larvae	48-hr MLC	0.001-0.003	Connor, 1972
Oyster larvae	96-hr TLM	0.01	Mandelli and McIlhenny, 1971
Mya arenaria	Toxic	0.02	Pringle et al., 1968
Mya arenaria	7-day LC_{50}	0.035	Eisler, 1977
Mytilus edulis	96-hr LC_{50}	0.28	Abel, 1976
Mytilus edulis	17-day LC_{100}	200	Marks, 1938
Mytilus edulis embryos	48-hr EC_{50}	0.0058	Bretler et al., 1984
Mytilus edulis	7-day LC_{50}	200	Scott and Major, 1972
Mytilus edulis embryos	Mean Acute Value	0.0058	U.S. EPA, 1985
Mercenaria mercenaria	10-day LC_{50}	0.016	Calabrese et al., 1977
Mercenaria mercenaria	77-day LC_{50}	0.025	Shuster and Pringle, 1968
Bay scallop, *Argopecten irradians*	42-day EC_{50} (growth)	0.0058	U.S. EPA, 1980
Argopecten irradians	119-day LC_{100}	0.005	U.S. EPA, 1980
Black abalone, *Haliotis cracherodii*	Histopathological gill abnormalities, 4-day treatment	> 0.032	Martin et al., 1977
Red abalone, *Haliotis rufescens*	Histopathological gill abnormalities, 4-day treatment	> 0.032	Martin et al., 1977
Fish			
Fundulus heteroclitus	50% inhibition of hatching	0.250	Gardner and LaRoche, 1973
Fundulus heteroclitus	96-hr LC_{50}	3.2	Jackim et al., 1970
Fundulus heteroclitus	Histopathological lesions, 21-day test	<0.500	Gardner and LaRoche, 1973
Fundulus heteroclitus	Enzyme inhibition, 4-day exposure	0.600	Jackim, 1973
Menidia menidia	Histopathological lesions, 4-day test	<0.500	Gardner and LaRoche, 1973
Clupea harengus pallasi, embryo	Incipient LC_{50}, 6-day exposure	0.033	Rice and Harrison, 1977
Clupea harengus pallasi, larva	Incipient LC_{50}, 2 day exposure	0.900	Rice and Harrison, 1977
Brevoortia tyrannus	14-day LC_{50}	0.610	Engel et al., 1976
Leiostomus xanthurus	14-day LC_{50}	0.160	Engel et al., 1976
Micropagen undulatus	14-day LC_{50}	0.210	Engel et al., 1976
Lagodon rhomboides	14-day LC_{50}	0.150	Engel et al., 1976
Pleuronectes platessa	4-day LC_{50}	0.750	Saward et al., 1975
Pseudopleuronectes americanus	Histopathological lesions, 14-day exposure	0.180	Baker, 1969
Atlantic salmon, adults in fresh water	Lethal	48	Sprague, 1964
Juvenile Coho salmon	96-hr LC_{50}	0.06-0.074	Lorz and McPherson, 1977

Organism	Effect	Concentrations (ppm, mg L^{-1})	Reference
Oncorhynchus tschawytscha	Acute toxicity	0.04	Hazel and Meith, 1970
Atherinops affinis, fertilization, embryo	EC_{50}	0.024-0.190	Anderson et al., 1991
Atherinops affinis, development	NOEC	0.032-0.123	Anderson et al., 1991
Atherinops affinis, larval survival	LC_{50}	0.212-0.288	Anderson et al., 1991
Atherinops affinis, larval survival	NOEC	0.090-0.160	Anderson et al., 1991

HISTORICAL SAN DIEGO BAY DATA

Several studies have contributed data on copper toxicity to indigenous species in San Diego Bay. Krett (1980) reported that soluble copper water concentrations measured by anodic stripping voltametry (ASV) at the Naval Station and Shelter Island yacht basin averaged 4.0 μg L^{-1} compared to a site near the open bay side of Shelter Island that averaged less than 1 μg L^{-1}. Although the copper concentrations were significantly higher at the Naval Station and Shelter Island sites, phytoplankton productivity and biomass were not reduced in those regions relative to the open bay Shelter Island pier site. Diversity indices revealed no significant differences among sites; however, phytoplankton genera reported to be sensitive to copper were absent from the Shelter Island inlet and Naval Station sites. Subsequent laboratory bioassay testing indicated that the phytoplankton genera from the Shelter Island inlet site were more copper tolerant. Six genera were present at ambient copper concentrations decreasing to four genera when the copper concentration was increased to 40 μg L^{-1} by addition of copper sulfate. The pier phytoplankton genera decreased from 12 genera at ambient copper levels to four genera when the copper concentration was increased to 40 μg L^{-1}. Productivity and biomass also decreased drastically at 5 μg L^{-1} copper. Field and laboratory evidence therefore indicated that the phytoplankton species exposed to higher ambient copper concentrations were generally more tolerant to copper exposure (Krett, 1980).

Johnston (1990) reported dissolved (ASV) copper concentrations of 2.6 μg L^{-1} at the Naval Ocean Systems Center pier and 8.9 and 11 μg L^{-1} within the Shelter Island yacht basin. The mean number of fouling species per area was higher where lower concentrations of copper and organotin compounds were measured in water samples.

Salazar and Salazar (1985) reported that sediment collected from the commercial basin area of San Diego Bay and used in bioassay tests to determine its toxicity was acceptable for ocean disposal under existing guidelines administered by EPA and the Army Corps of Engineers. The species tested were a copepod (*A. tonsa*), a mysid (*A. sculpta*), and a bottom fish (*C. stigmaeus*). Copper was measured at 210 mg kg^{-1} (ppm wet wt.) in the sediment tested. In a bioaccumulation test, copper was significantly accumulated in clam (*M. nasuta*) and polychaete worm (*N. arenaceodentata*) tissues over control concentrations. The clams tested accumulated 3.3 mg kg^{-1} copper, while the polychaete worms accumulated 16 mg kg^{-1} copper. The significant accumulation noted indicates that copper was bioavailable to the test species in sediment from this area of the bay. Percent clay was 14.3 percent in this area, which is similar to that measured in sediments from the Naval sites sampled in this study (8.4 to 13.2% clay). (See table 5 in the "Monitoring Data" section of this report.)

Copper is present in very high concentrations at a site approximately 300 yards south of the Naval Station's southern boundary (Pier 13). Copper ore was stockpiled and loaded onto ships at the National City Marine Terminal from 1979 to 1985. Sediment copper concentrations as high as 58,269 mg kg^{-1} dry weight were measured near the wharf (Woodward–Clyde Consultants, 1991). The Woodward–Clyde report extensively defines the spatial distribution of copper in the sediment and discusses physical-chemical factors that would act to bind copper in the sediments and therefore render it less bioavailable to organisms. The report further indicates that the crystalline sulfides in the copper-ore bind the copper into a highly insoluble nontoxic form. Bioassay tests with nine different bioassay test organisms and 14 biotic response characteristics were used to evaluate the toxicity of sediments from areas of high and low sediment copper concentration. Tests were conducted with flatfish, shrimp, sea urchin eggs and embryos, clams, worms, two different amphipods, fish larvae, and oyster larvae. Eight of the nine species tested exhibited no toxicity under standard test conditions. One of the amphipod species not found in San Diego Bay exhibited a toxic response independent of the copper concentration in the sediment tested. Other studies of numbers and types of species present in the sediments showed that differences and similarities between numbers, types, and diversity of species in the area were not related to sediment copper concentrations. The report concluded that the 1000 mg Cu kg^{-1} remediation objective defined by the Water Quality Control Board, San Diego Region, for the copper containing sediments in this area was highly protective of aquatic life (Woodward–Clyde Consultants, 1991).

CHLOROPHYLL BIOASSAY

This section of the study provides environmental toxicity data for copper on the potential effects of an effluent collected during the underwater hull cleaning of USS TUSCALOOSA (LST 1187) coated with International Paint Company formulation BRA-540 paint, and USS RANGER (CV 61) coated with International Paint Company formulation BRA-540/542 paint. The Qwik-Lite chlorophyll assay was used to produce the results discussed in this report.

The Qwik-Lite chlorophyll assay uses microalgae as test organisms in a static non-renewal exposure system. The premise of this assay is that a toxic response of microalgae to chemical exposure can be a change in growth rate or biomass. This change can be quantified indirectly by measuring chlorophyll fluorometrically. This bioassay was conducted in accordance with the American Society for Testing and Materials (ASTM) Standard Guide for Conducting Static 96-hr Toxicity Test with Microalgae (E1218) (ASTM, 1992). Relative fluorescence (expressed as a percent of control) and an inhibition concentration ($IC50_{72}$) were used as endpoints. The $IC50_{72}$ is defined as a statistical or graphically estimated concentration that is likely to cause a 50% inhibition of one or more biological processes in 72 hours.

MATERIAL AND METHODS

The test medium was seawater effluent discharged from a hull cleaning device as it was being used in the hull cleaning process. The effluent was filtered through 0.45-micron filters prior to bioassay testing. The samples were collected in an acid-washed 5-gallon Nalgene® carboy by a method that directed a small portion of the discharge effluent of the scamping device through a 3/4-inch hose over a distance of approximately 25 feet. Thus, the toxicity potential was a conservative estimate based on samples collected in the centroid of the effluent discharge of a hull cleaning machine prior to dispersion due to currents.

The instrumentation used for measuring *in-vivo* chlorophyll via relative fluorescence from algal cells was a Turner Model 112 Fluorometer equipped with a 110-853 (Blue T-5) lamp, a photomultiplier type R-136 (red sensitive), sliding window orifices 1X, 3X, 10X, and 30X, a 5–60 filter for excitation, and a 2–64 filter for emission to detect fluorescence at > 640 nm. The optimum sensitivity for chlorophyll α measurements is obtained at an excitation wavelength of 430 nm and emission wavelength of 663 nm. The instrument was blanked between readings with filtered (0.22 μm) seawater, and samples were read on a static digital readout. Borosilicate glass vials and 125-ml flasks were used as test containers. Prior to testing, all borosilicate containers were soaked in RBS®, 10% nitric acid and finally triple-rinsed with deionized water. All vials and flasks were seawater-aged prior to use.

Isochrysis sp. was obtained from the North East Pacific Culture collection at the University of British Columbia, Canada. Monocultures were maintained in Enriched Seawater Medium in accordance with appendix A2 of ASTM Standard E1218 in 2-liter borosilicate erlenmeyer flasks under a light regime of 12:12 hours (light:dark) at approximately 100 foot-candles delivered from cool white fluorescent bulbs. Ambient temperature was 22 to 25° centigrade.

The same amount of algal inoculate was exposed to different concentrations of the initial effluent for a period of 72 hours. Three replications at six different concentrations were tested. Tested effluent copper concentrations in the first assay were 6.25% (14 ppb), 12.5% (28 ppb), 50.0% (110 ppb), 75.0% (165 ppb), and 100% (220 ppb) of effluent as the test article. The control groups were exposed to 0% of effluent. The test was repeated for the second assay using the following effluent copper concentrations: 6.25% (15 ppb), 12.5% (30 ppb), 25.0% (60 ppb), 50.0% (120 ppb), 75.0% (180 ppb), and 100% (240 ppb) effluent. Copper concentrations were determined by GFAA following the bioassay procedure.

At the beginning of each bioassay, the same amount of algal stock culture (≈150 μl) was introduced into three 125-ml erlenmeyer flasks containing 25 ml of dilution water for the controls and each of six different concentrations of the effluent mixture as treatments. The dilution water was San Diego Bay water collected off of NCCOSC RDT&E's (NRaD's) Pier 136. The water had been filtered and enriched with the same media as the stock cultures, except for micronutrients (trace metals). The control group received no effluent. The effluent mixture did not exhibit background fluorescence or color when tested as a reagent control.

The filtered effluent was clear and exhibited no phase separation. There was approximately 7.5 mm of headspace in each flask. All flasks were read immediately after introduction of the algae into the flasks (t=1) and at 24-hour intervals thereafter for a period of 72 hours. Nominal concentrations were analyzed for inorganic copper after the bioassay was completed. Fifty ml of each effluent concentration and test control water (0% effluent) were collected in acid-washed nalgene bottles and stabilized with 0.2% Ultrex nitric acid. Samples were then analyzed by graphite furnace atomic absorption (GFAA) utilizing a direct seawater vaporization methodology. Results were adjusted to coincide with known dilution factors.

The following deviations from prescribed procedures occurred during this investigation:

> *Assay was completed after 72 hours vice 96 hours*. Previous assays indicated that significant differences in exposure groups can be determined within the 72-hr period. Also, growth of the inoculate in control groups normally exceeds the range of the fluorometer after 72 hours.

Samples were not filtered immediately after collection. Initial sampling procedures failed to account for continued leaching of particulates that apparently occurred in the unfiltered water contained in carboys. This leaching resulted in increased concentrations of copper. Comparison of values from the 18- and 6-hr filtered samples and on-site filtered samples collected from the plume in the same location indicated that copper had approximately doubled in the filtered fraction during the 18- and 6-hr storage periods. Some alteration of dissolved and complexed copper species may have occurred from that characteristic of the initial sample.

The dilution of the 25% effluent concentration in the first bioassay was incorrect. Results of the 25% effluent exposure group were eliminated due to human error in making the dilution.

There was no attempt to fully characterize the effluent. A complete analysis or a full characterization of the effluent of all chemical components was not performed, thus other factors may have been present that could interact with available copper and/or contribute to the toxic loading.

The Enriched Seawater Media micronutrient (trace metal and ethylene diamine tetraacetic acid [EDTA]) solution was not added to the dilution water. This was done to avoid chelating the metal(s) in the environmental sample and possibly affecting their bioavailability.

Mean relative fluorescence, standard deviation, and coefficient of variation were calculated for each control and effluent concentration replicate. Relative fluorescence calculated as a percentage of control values was plotted versus exposure time. The $IC50_{72}$ was then estimated by plotting percent reduction of chlorophyll fluorescence versus concentration of the effluent, fitting a sigmoidal dose-response curve to the data, and then determining the concentration corresponding to the 50% reduction level. No Observable Effect Concentration (NOEC) and Lowest Observable Effect Concentration (LOEC) values could not be estimated because significant differences were found between the control groups and all exposure groups concentrations making it difficult to identify a NOEC.

RESULTS AND DISCUSSION

USS TUSCALOOSA Hull Cleaning Plume Assay: Based on published literature the IC_{50} for algae has been estimated to be approximately 50 ppb (Cu). Results are displayed in figure 4. Response across concentrations was measured. Algal growth rate decreased as effluent concentration increased and growth was arrested at 75% (165 ppb (Cu)) effluent exposure. The observed IC_{50} value was approximately 42 ppb (Cu).

USS RANGER Hull Cleaning Plume Assay: Results are displayed in figure 5. Response across concentrations was measured, and algal growth decreased as effluent concentration increased, and growth was again arrested at 75% (180 ppb (Cu)) effluent exposure. The observed IC_{50} value was approximately 45 ppb (Cu).

Both bioassays demonstrated a concentration-response where relative fluorescence decreased with increased effluent exposure. This is a direct measure of chlorophyll α presence in each sample, which is an indication of algal growth (or number of viable algal cells present in the sample) relative to effluent exposure. IC_{50} values for both assays ranged between 42 to 45 ppb.

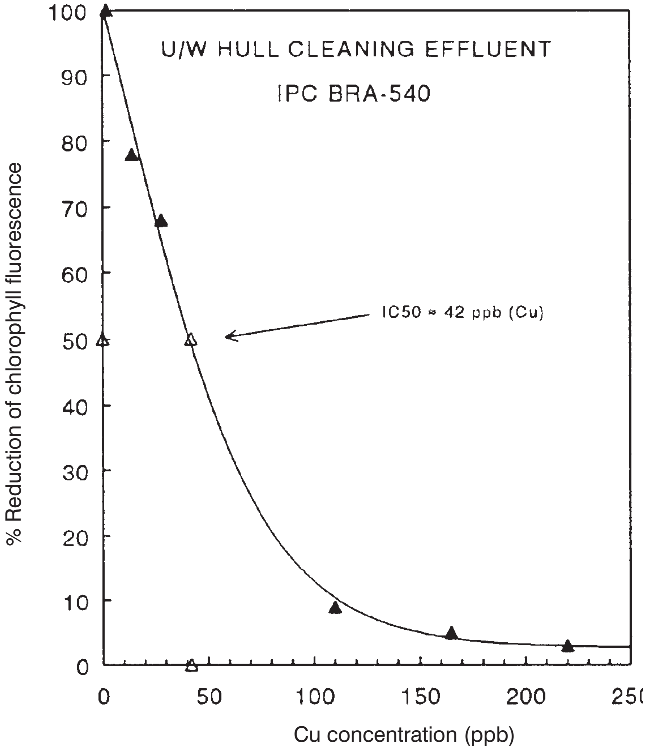


Figure 4. Hull cleaning plume IC_{50} graph, USS TUSCALOOSA, March 1993.

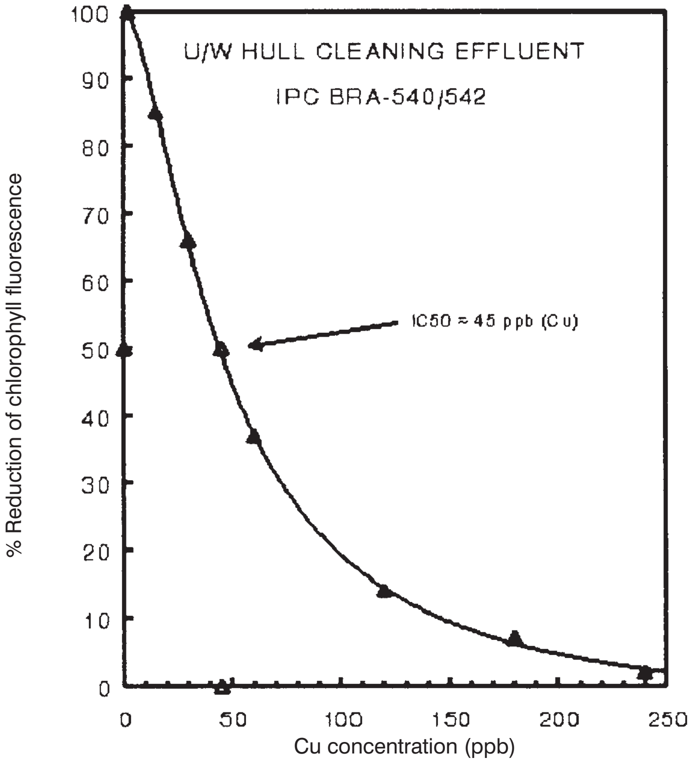


Figure 5. Hull cleaning plume IC_{50} graph, USS RANGER, July 1993.

The results of this test should be viewed as one test of effluent copper toxicity. Additional testing is necessary to confirm the results, and, if possible, should include more complete chemical analysis of the effluent. Also, special caution should be taken to ensure that samples are processed upon collection as quickly as possible. The available information on the effluent mixture demonstrates toxicity to this species of microalgae similar to literature values in a controlled laboratory setting. The steep response curve indicates a rapid toxic response to the effluent.

Since holding the unfiltered effluent water sample greatly increased the 0.45-μm filtered water copper concentration, the importance of determination of copper toxicity based on available copper is emphasized. The recent EPA approach involving bioassay testing of ambient and reference waters to develop a water-effect ratio would likely raise the site-specific copper water quality criteria in an area such as San Diego Bay where dissolved organic matter is more likely to interact with free copper ion than in water from a cleaner reference site.

MICROTOX®

The Microtox® bacterial bioassay was used to measure the toxicity of water samples collected from the hull cleaning plumes of three ships. Samples were collected during the cleaning operations within the brushing plume area. Microtox® bioassays were performed on filtered and/or on unfiltered samples. Additionally, a reference water sample was collected approximately midway between the Naval Station and the Amphibious Base in the center of the bay (SDCH4). Toxicity values are expressed as the percent of the original seawater sample that yielded either a 20% or 50% (EC_{20} or EC_{50}) reduction in light output after 5- and 15-minute exposures using the Microtox® system. Light-emitting bacteria were employed as the test source. An EC_{50} of 100% means the seawater sample was tested with no dilution. An EC_{20} of 25% refers to a 1:3 dilution of the sample with reference seawater. Typically, an EC_{50} is used to express toxicity. This is the concentration that produces a 50% reduction in light output relative to a seawater control sample (reference sample) after 5 or 15 minutes. Data from these tests are summarized in table 3.

When Microtox® tests reveal no measurable toxicity relative to controls using an undiluted test sample, an EC_{20} may be obtainable. For example, a filtered water sample from the cleaning plume of USS RANGER did not exhibit a 5-minute EC_{50} using an undiluted sample (100%), while a 5-minute EC_{20} was recorded with a 58% sample (see table 3). The lower percent effect level (EC_{20}) provided a measurable toxic effect.

Plume samples from USS FORT FISHER and the filtered samples from USS TUSCALOOSA exhibited no measurable toxicity with undiluted samples. The unfiltered sample from USS TUSCALOOSA exhibited EC_{20} values of 93 and 48% at 5 and 15 minutes, respectively, demonstrating slight toxicity. USS RANGER plume samples exhibited the greatest toxic responses measured among cleaning samples collected. The unfiltered sample was the most toxic tested exhibiting 5- and 15-minute EC_{50} values of 73 and 43%, respectively. The undiluted filtered sample exhibited no measurable toxicity after 5 minutes, while after 15 minutes, an EC_{50} of 95% was recorded. EC_{20} values of 58 and 56% were measured at 5 and 15 minutes, respectively.

The Microtox® testing was performed to assist in evaluation of the potential plume toxicity. However, due to the nonspecific nature of the test, no clear assessment of copper toxicity is possible from the Microtox data alone. The results indicate that the plume samples were generally not acutely toxic.

Table 3. Results of Microtox tests of cleaning plume effluent.

	Filtered Water				Unfiltered Water			
	EC_{20}		EC_{50}		EC_{20}		EC_{50}	
	5 min	15 min	5 min	15 min	5 min	15 min	5 min	15 min
USS RANGER	58% SD=9 n=3	56% SD=5 n=3	***	95% SD=3 n=3			73% SD=6 n=3	43% SD=2 n=3
USS TUSCALOOSA	***	***	***	***	93% SD=6 n=3	48% SD=3 n=3	***	***
SDCH4	***	***	***	***				
USS FORT FISHER					***	***	***	***

*** insufficient toxic response to calculate EC_{50} or EC_{20}

MONITORING DATA

BAY-WIDE SURVEYS

Bay-wide water and sediment samples were collected to compare copper concentrations in samples collected during hull cleaning activity to those in open bay areas. Samples were collected onboard the R/V *ECOS* by a flow-through (5 liters per minute) pumping system composed of Teflon® tubing and an all-plastic centrifugal pump head. Samples collected from the hull cleaning plume were collected by a submerged rubber hose connected to an impellerless deck pump onboard an 18-foot skiff. The following procedures discuss sample preparation and analysis for bay-wide survey samples as well as for hull cleaning samples. Sample stations are shown in figure 6. Sample collection dates and codes per ship cleaned are listed in table 4.

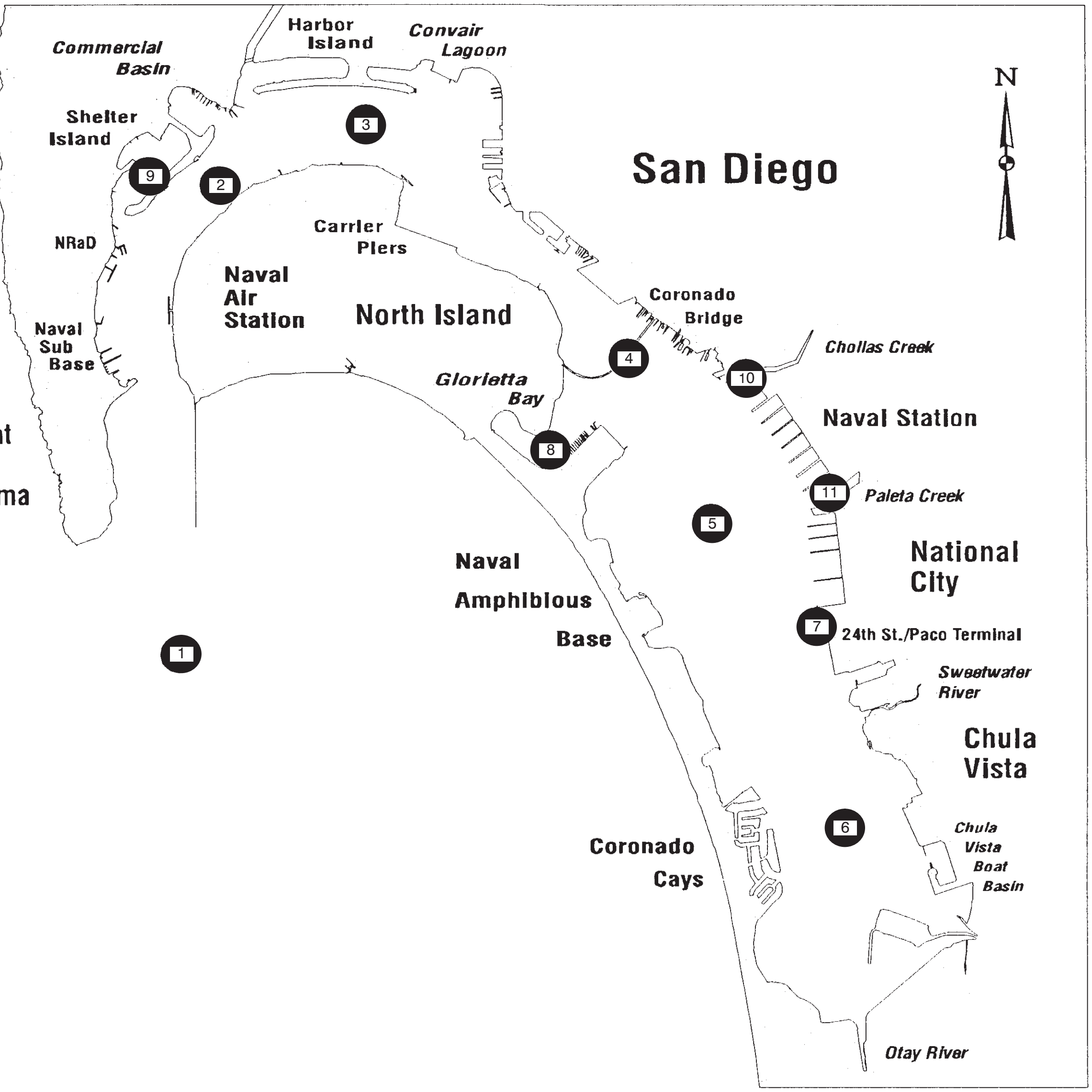


Figure 6. Bay-wide sample station locations in San Diego Bay.

Table 4. In-water hull cleaning surveys.

Vessel	Paint Type	Date	Survey Code
USS DURHAM (LKA 114)	ABC-3	15–16 May 91	SDC1
USS ENGLAND (CG 22)	BRA-540	8–9 August 91	SDC2
USS MARVIN SHIELDS (FF 1066)	ABC-3/BRA-540	22 June 92	SDC3
USS FORT FISHER (LSD 40)	F-121	23 February 93	SDC4
USS TUSCALOOSA (LST 1187)	BRA-540	26 February 93	SDC5
USS RANGER (CV 61)	BRA-540	22 March 93	SDC6

WATER SAMPLES

Seawater samples were collected in 125-ml precleaned (I-Chem) Nalgene® HDPE bottles and were filtered using 115-ml capacity Nalgene analytical filter units, with 0.45-µm cellulose nitrate filters. Filters were retained for analysis from surveys 1 and 2 for particulate [Cu], which was added to the dissolved fraction [Cu] for total [Cu]. For surveys 3 through 6, nonfiltered seawater was retained for total [Cu], and particulate [Cu] was determined indirectly by subtracting the dissolved fraction [Cu]. All water samples were acidified to an approximate pH of 1.6 (0.2% v/v Ultrex HNO_3) and stored frozen. The term “dissolved” is used in this report to refer to the sample passing the 0.45-µm filter unit. It is so used to facilitate comparison with literature data and is not meant to imply that this fraction is actually that containing only dissolved copper. The discussion of ion-specific electrode measurements that follows in this document addresses dissolved copper in detail.

Water samples were analyzed using a Perkin-Elmer® Zeeman 5100™ Graphite Furnace Atomic Absorption Spectrometer. L’vov platforms were used in pyro-coated tubes. Survey 1 and 2 water and survey 2 dome leachate samples were analyzed by direct injection using $Pd(NO_3)_2$ and $Mg(NO_3)_2$ as matrix modifiers. Concentrations were determined from a 6-point calibration curve (0, 5, 10, 20, 50, 100 µg L^{-1}). Standards were created instrumentally from 20 and 100 µg L^{-1} stock solutions made serially from a 1000 µg ml^{-1} reference standard solution. Recovery percentages and recalibrations (based on 20 µg L^{-1} standard) typically were performed after every 10 samples.

Prior to analysis, surveys 3 through 6 water and dome samples were extracted using the APDC-MIBK (ammonium pyrrolidinedithiocarbamate; methyl isobutyl ketone) method, for the purpose of matrix cleanup, and, in the case of the SDC3 dome leachate samples, for dilution-extraction. A 10-ml volume of APDC solution (generally 1% w/w) was made daily from crystalline APDC in 18-MΩ double-deionized water (DIW) (any reference to DIW in this section refers to this water), and cleaned 3 to 4 times with 1-ml aliquots of MIBK prior to use. The APDC solution was used at 0.125-mg APDC per ml sample extracted (i.e., 25 µl of 1% APDC per ml sample). Survey samples were extracted at the proportion of 2 ml sample: 2 ml MIBK, as were dome leachate samples from SDC4-6. SDC3 dome leachate sample: MIBK ratios varied depending on the expected concentration, from 1:3 to 0.2:4. Survey 3 water and dome leachate sample concentrations were determined using method of addition calibration. Additions of 5, 12.5, and 25 µg L^{-1} were made to the first of each group of survey samples to develop the calibration curve for that group. Dome samples were processed in three groups and concentrations added to the first sample in each group varied depending on the expected concentration range. Surveys 4 through 6 water and dome sample concentrations were determined from a 6-point calibration curve generated using extracted standards made from MIBK-cleaned seawater (0, 5, 10, 20, 50, and 100 μg L^{-1}). Samples out of range of the calibration curve were diluted instrumentally with MIBK.

Nonfiltered plume samples were diluted 0.1 ml:5 ml DIW (pre-acidified DIW, 0.2% HNO_3), and concentrations were determined from a 4-point calibration curve generated from filtered, pre-acidified seawater standards (0, 1000, 2000, and 3000 μg L^{-1}) that were then diluted in the same manner as the samples. Extraction was not necessary because of the large dilution factor.

FILTERS

Filters were removed from the filter units with Teflon forceps and stored frozen in 50-mm disposable petri dishes. Because the filters themselves contained some copper, 12 filters from the only lot used for surveys 1 and 2 were digested and analyzed to determine this background [Cu]. All filters were digested with 10-ml Ultrex HNO_3 in lined digestion vessels (CEM®). Digestates were diluted 1:9 with DIW. Concentrations were determined from a 6-point calibration curve generated from standards (0, 5, 10, 20, 50, and 100 μg L^{-1}) made instrumentally from 20 and 100 μg L^{-1} stock solutions (in 10% HNO_3 v/v in DIW), which were made serially from a 1000 μg ml^{-1} reference standard solution.

SEDIMENTS

Sediments were stored frozen in precleaned (I-Chem®) Nalgene® HDPE bottles or PE zipper closure bags. After thawing, samples were homogenized before and between sub-sampling. Three aliquots of each sample were dried at 250°C, ground with a Diamonite mortar and pestle, and placed in X-ray cells with mylar window film. Samples were analyzed using a Spectrace 9000™ portable X-Ray Fluorescence Spectrometer for 200 seconds on the ^{109}Cd source. The National Research Council of Canada (NRCC) standard reference material PACS-1 was analyzed routinely for comparative purposes.

Sediment samples were collected with either a Van Veen stainless steel sampler from the R/V *ECOS*, or by a cylindrical corer fitted with a plastic inner cylinder. Samples were placed in zip-lock plastic bags and stored frozen until grain size analysis was performed. Samples were passed through a series of standard screens, and subsequently hydrometer (ASTM No. 152H) readings were taken to define the percentage sand, silt, and clay fractions (Black, 1965).

WATER COLUMN MEASUREMENTS

Water column samples were collected concurrently with hull cleaning operations in order to compare background levels of copper throughout the bay with those measured in the vicinity of hull cleaning operations. The bay-wide water column copper data are summarized in figures 7 through 12. Copper measured in the bay-wide samples is referred to as “dissolved” copper again simply to indicate that this fraction passed a 0.45-μm filter and to facilitate comparisons with literature values. Measurements of dissolved copper are discussed in the “Ion Selective Electrode” section of this document.

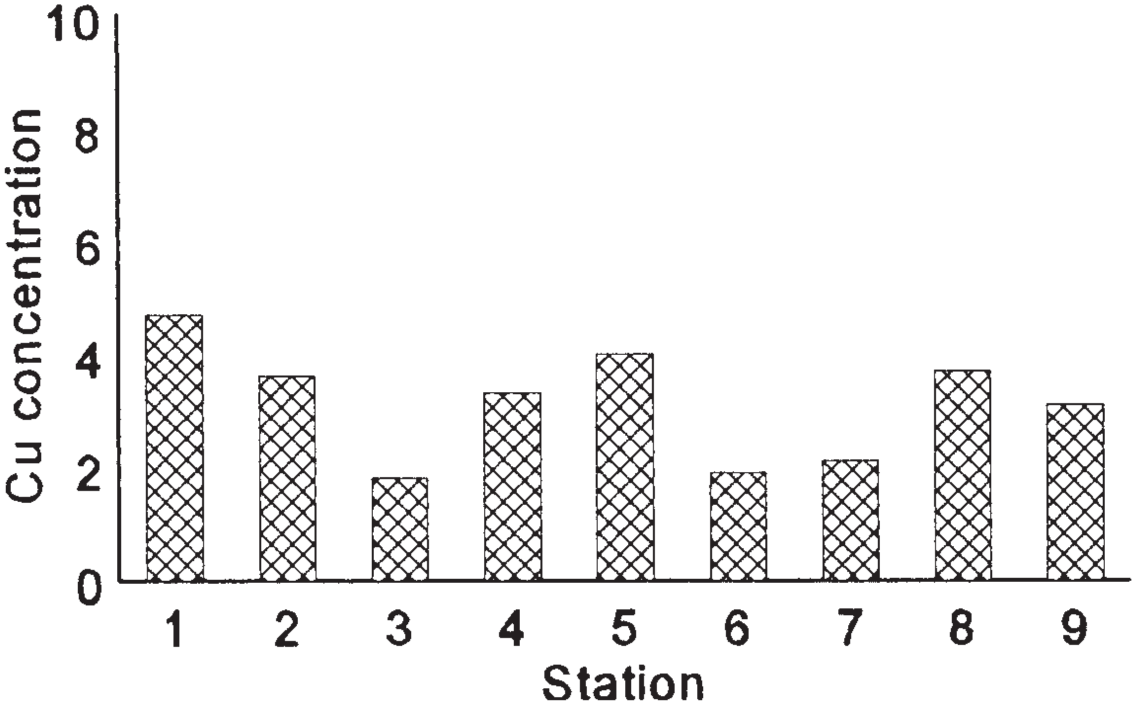


Figure 7. Mean bay-wide surface water dissolved copper concentrations in μg L^{-1}, May 1991.

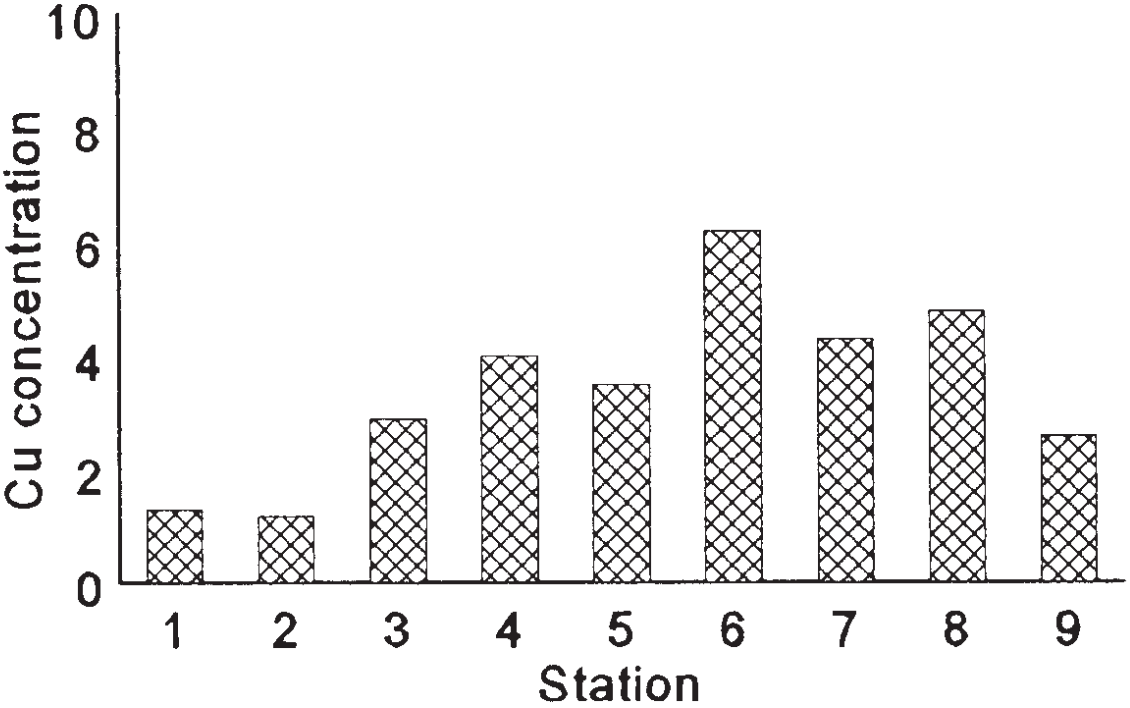


Figure 8. Mean bay-wide midwater dissolved copper concentrations in μg L^{-1}, May 1991.

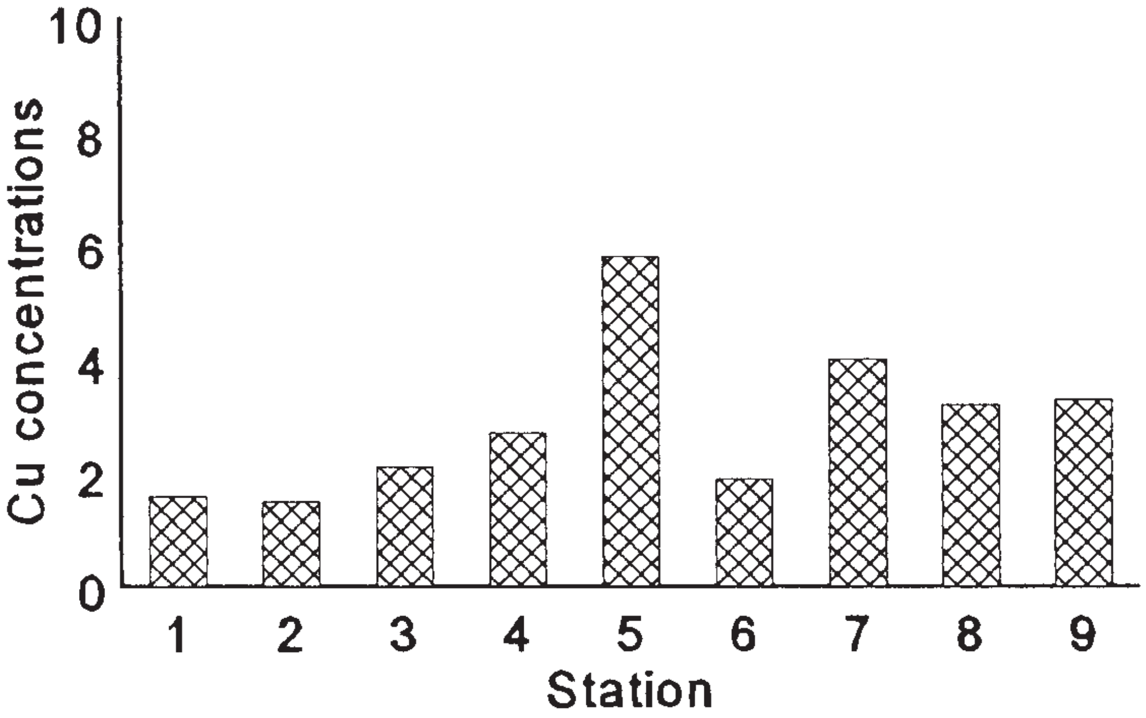


Figure 9. Mean bay-wide deep water dissolved copper concentrations in μg L^{-1}, May 1991.

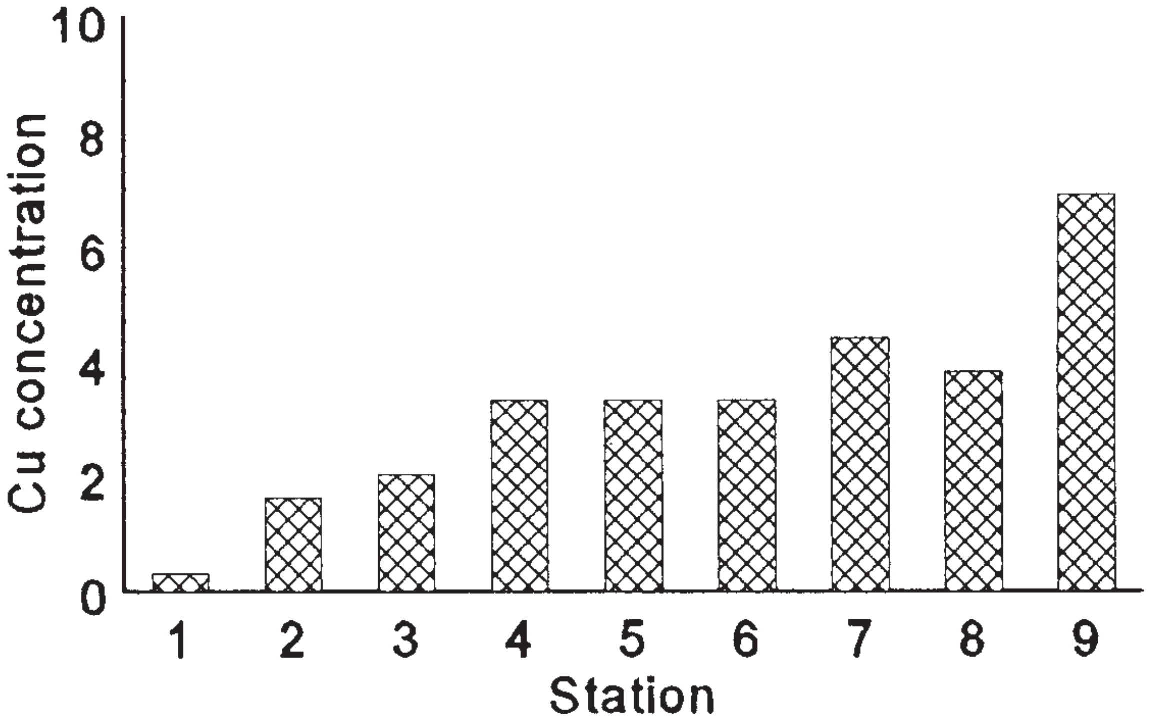


Figure 10. Mean bay-wide surface water dissolved copper concentrations in μg L^{-1}, June 1992.

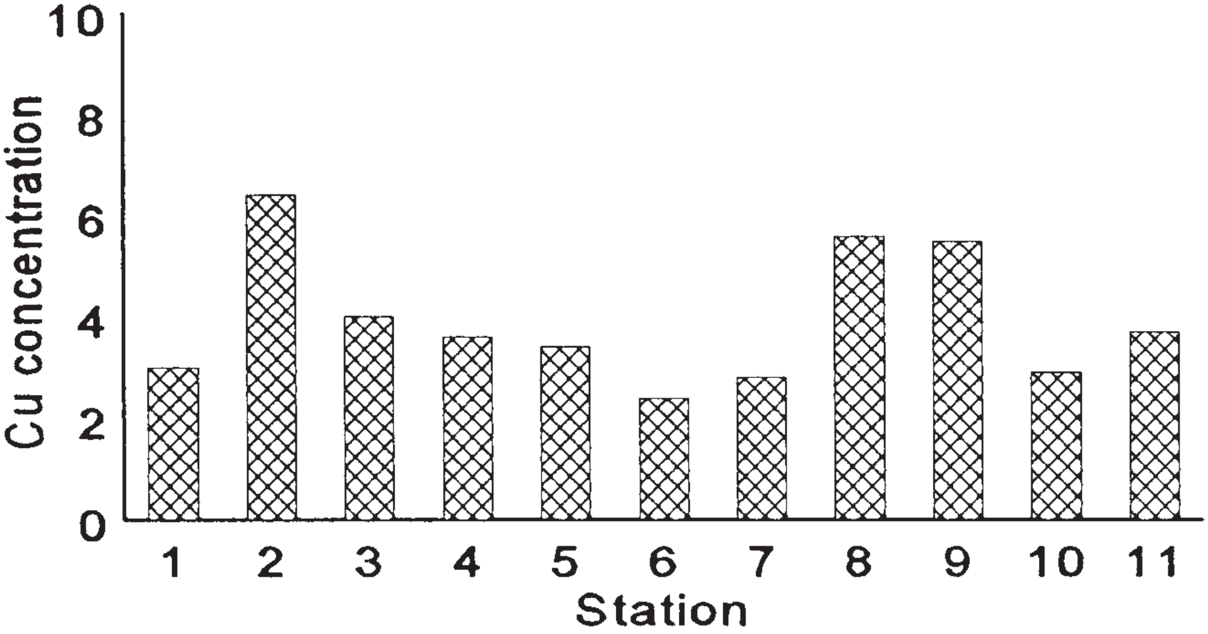


Figure 11. Mean bay-wide surface water dissolved copper concentrations in μg L^{-1}, February 1993.

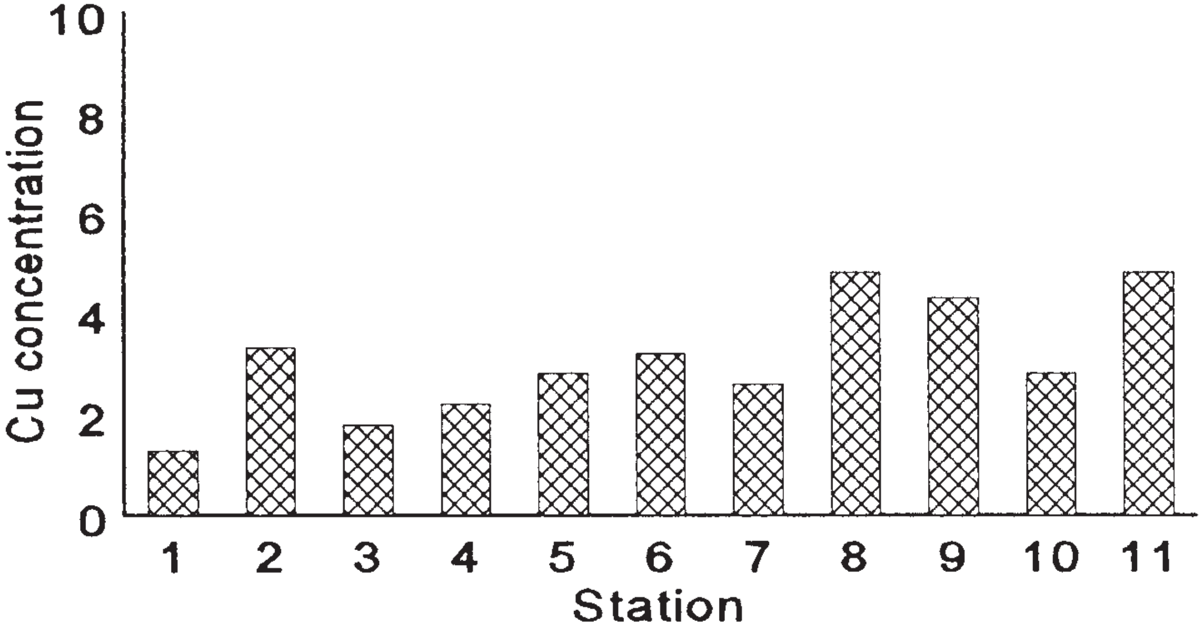


Figure 12. Mean bay-wide deep water dissolved copper concentrations in μg L^{-1}, February 1993.

Of the 58 measurements (sum of measurement intervals over all stations reported in figures 7 through 12) made throughout the bay during the three hull cleaning operations, 24 were at or below 2.9 µg L^{-1}, which is the EPA 1-hour average water quality criterion for copper. The Shelter Island (Station 9) and Glorietta Bay (Station 8) yacht harbor stations exhibited intermediate to high copper values relative to other stations. The highest concentrations recorded in these areas were 6.9 and 5.6 µg L^{-1}, respectively. These values are similar to the mean dissolved copper concentration reported by Krett (1980), but not as high as the 8.9 to 11 µg L^{-1} dissolved copper levels reported in Johnston (1990). Both the Krett and Johnston studies measured "dissolved" copper by ASV in water samples from Shelter Island. Labile copper values measured at pH 2.2 by ASV, and copper extracted on Chelex 100-AA and measured by atomic absorption compared very well (Zirino et al., 1978), suggesting that labile copper concentrations measured by ASV at pH 2 may also be similar to copper concentrations measured by atomic absorption after separation using a 0.45-µm filter. It appears that "dissolved" copper concentrations may not have changed a great deal in the bay over a period of 10 years.

Background water column copper levels in the main channel adjacent to the Naval Station (Station 5) ranged from 2.8 to 5.8 µg L^{-1} with an overall average value of 3.8 µg L^{-1}. The majority of the main channel samples exceeded the EPA water quality criterion of 2.9 µg L^{-1}. As mentioned above, approximately 50% of the samples analyzed during the bay-wide study exceeded this criterion indicating that copper concentrations are elevated throughout the bay. If compared to earlier studies, it appears that this elevation may have been so for a decade or possibly longer. The constant input by leaching of copper from the antifouling paints of pleasure, commercial, and military vessels is a likely primary source of copper in the bay. This input will be discussed further in this document under the topic of "Loading Factors."

SEDIMENT MEASUREMENTS

Copper concentrations in bay-wide sediment samples collected during hull cleaning operations are summarized in figures 13 through 15. Concentrations were quite variable exhibiting no particular patterns. The sediment copper concentrations measured at the main channel station off the Naval Station (Station 5) ranged from 132 to 268 mg kg^{-1} and were similar to those reported by Yamamoto et al. (1975) and NOAA (1991) from sediment samples collected yet closer to the Naval Station in the early 1970s and 80s. Copper in sediment collected from Station 8 (table 1) in the early 1970s was much lower (28 mg kg^{-1}) than that reported in the present study at the main channel off the Naval Station (Station 5) and approximate to the location of Station 8. Sediment copper concentrations at the Shelter Island yacht harbor and PACO Ore terminal were relatively high, ranging from 133 to 212 and 140 to 647 mg kg^{-1}, respectively.

SEDIMENT GRAIN SIZE ANALYSIS

Sediment grain size analysis was performed to identify sample composition and permit comparison to literature values. A sediment grain size analysis summary is presented in table 5. Sediments at the main channel station near the Naval Station were relatively high in percentage clay indicating a high capacity for binding copper.

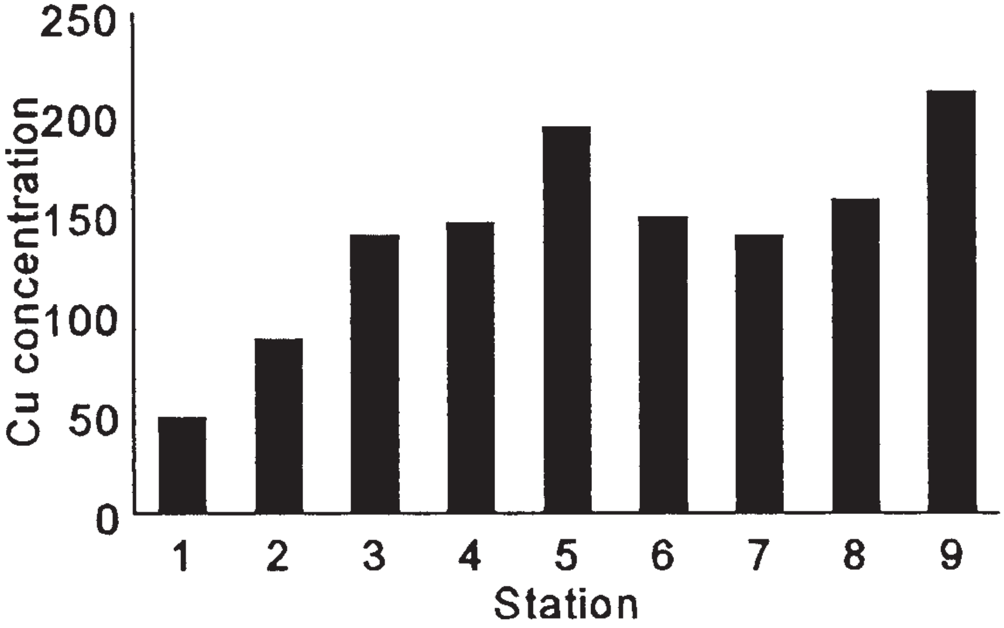


Figure 13. Mean bay-wide sediment copper concentrations in mg kg^{-1} dry weight, May 1991.

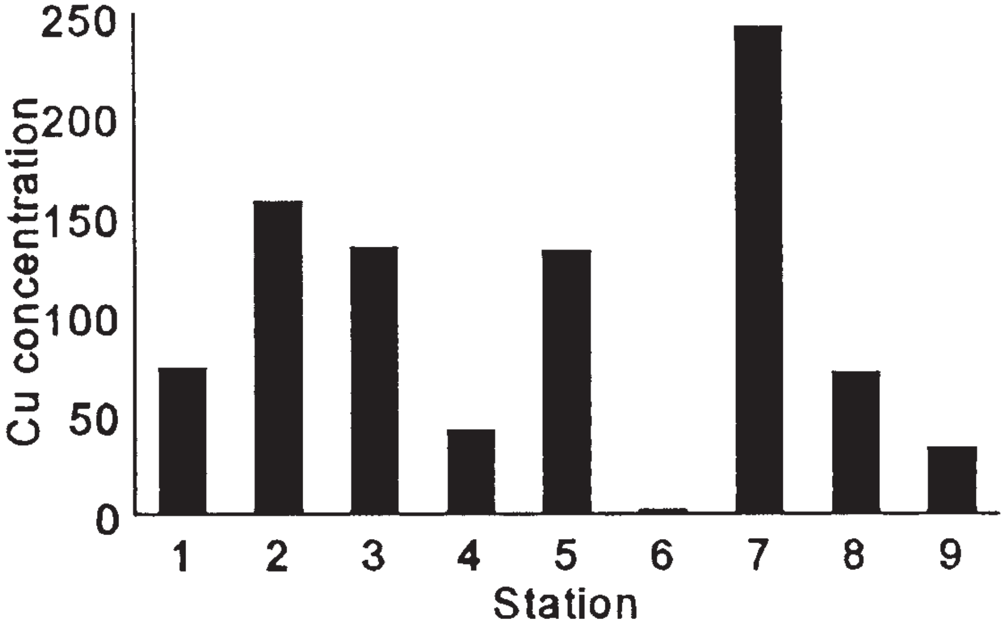


Figure 14. Mean bay-wide sediment copper concentrations in mg kg^{-1} dry weight, August 1991.

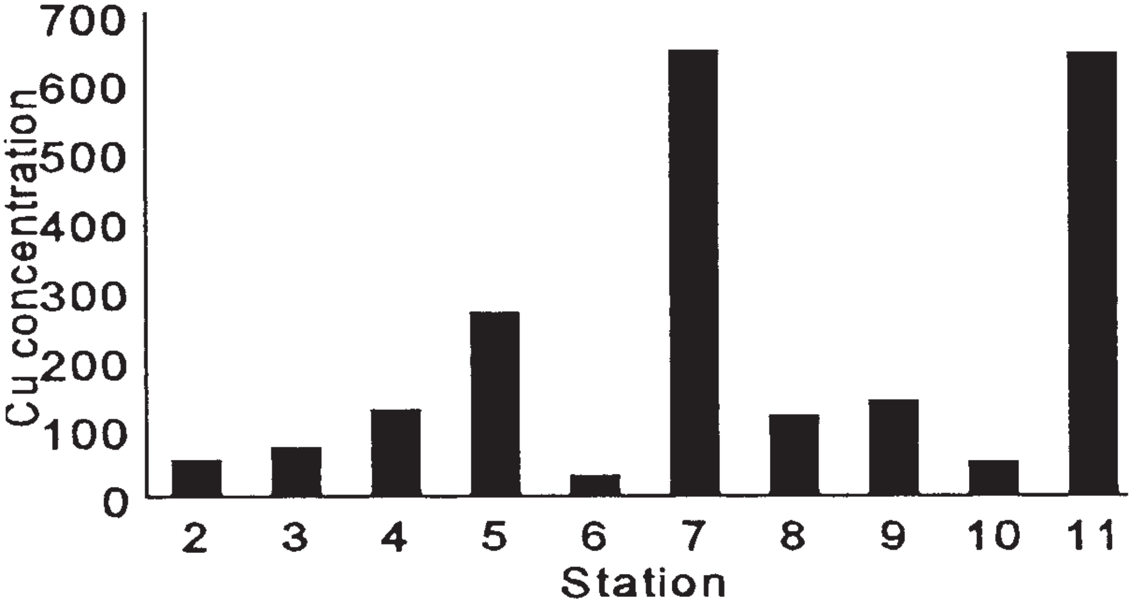


Figure 15. Mean bay-wide sediment copper concentrations in mg kg^{-1} dry weight, February 1993.

Table 5. Sediment grain size analysis summary. Data as percent of sample.

	Coarse Sand	Sand					Silt						Clay	
Sample Number	>2 mm	1.00–2.00	0.500–1.00	0.250–0.250	0.125–0.250	0.063–0.125	0.046–0.063	0.026–0.046	0.015–0.026	0.009–0.015	0.005–0.009	0.003–0.005	0.001–0.003	<0.001
Bay Entrance Channel														
01–S1	1.3	0.3	0.6	2.4	71.9	19.9	0.3	0	0	0	2.5	0	0	0.2
01–S2	0.9	0.3	0.4	5.8	76	17.3	0.5	<1						
01–S3	0.7	0.3	0.4	1.6	73.4	21.7	0.8	<1						
Shelter Island Bay Channel														
02–S1	0.3	0.4	1.6	5.1	55.7	17.1	2.5	1.0	2.9	0.7	0.3	2.5	0.7	7.1
02–S2	0.1	0.1	0.2	2.6	53.8	23.1	2.6	1.7	1.8	2.9	2.1	1.1	1.1	4.6
02–S3	0.8	0.4	0.8	3.6	48.2	24.4	2.9	1.4	1.0	1.8	2.4	1.4	1.5	7.0
Harbor Island Bay Channel														
03–S1	1.6	1.8	4.1	15.3	32.1	21.7	3.3	5.1	3.6	1.8	1.8	1.1	1.8	10.5
03–S2	1.6	1.7	3.0	9.8	30.7	23.6	4.4	3.7	3.7	3.4	2.2	1.8	1.5	8.9
03–S3	1.8	1.8	5.1	19	33.9	16.4	3.0	1.8	1.6	2.8	1.0	2.1	1.0	7.2
Coronado Bay Bridge														
04–S1	0.3	0.7	1.5	9.2	33.8	21.4	4.4	6.6	2.6	3.1	3.5	2.6	2.2	14.9
04–S2	*	*	sand	fraction	lost	*	4.0	1.1	3.5	3.1	3.6	3.5	4.1	14.3
04–S3	0.3	0.8	1.8	10.3	45.3	15.2	2.9	1.1	2.1	3.6	1.0	1.5	1.1	10.3

Table 5. Sediment grain size analysis summary. Data as percent of sample (continued).

	Coarse Sand	Sand					Silt						Clay	
Sample Number	>2 mm	1.00–2.00	0.500–1.00	0.250–0.250	0.125–0.250	0.063–0.125	0.046–0.063	0.026–0.046	0.015–0.026	0.009–0.015	0.005–0.009	0.003–0.005	0.001–0.003	<0.001
Naval Station Bay Channel														
05–S1	0.3	0.3	0.3	4.8	29.2	11.4	3.6	6.0	8.3	5.5	5.0	2.8	5.0	17.9
05–S2	0.4	0.0	0.4	3.3	18.4	13.1	2.0	11.6	9.1	7.6	5.1	5.0	5.0	25.3
05–S3	0.3	0.1	0.3	1.3	12.1	15.0	5.1	9.8	10.3	8.3	7.7	3.1	4.7	21.6
South Basin														
06–S1	5.9	1.0	2.0	13.4	26.5	12.8	3.6	0.8	3.6	3.2	3.9	3.6	4.0	18.6
06–S2	2.1	0.8	0.9	9.2	30.9	13.5	4.2	0.9	3.3	4.2	4.2	3.4	4.2	21.4
06–S3	2.4	1.0	2.7	10.0	27.5	16.5	4.8	4.1	3.2	3.3	3.3	1.6	3.6	16.7
Paco Ore Terminal														
07–S1	0.5	0.1	0.3	2.5	23.6	20.6	3.6	2.5	5.3	4.4	5.7	4.99	4.5	20.3
07–S2	0.6	0.2	0.8	4.2	25.1	16.3	4.1	6.3	4.5	5.4	4.5	3.6	4.9	17.6
07–S3	0.1	0.1	0.2	1.3	13.6	16.5	5.7	7.1	7.0	5.2	5.7	4.2	5.2	25.0
Glorietta Bay Entrance														
08–S1	0.1	0.1	0.1	0.9	20.2	46.5	7.2	1.5	3.6	3.2	3.6	2.2	2.5	9.7
08–S2	0.1	0.1	0.1	0.7	12.1	40.0	8.2	5.1	7.3	5.1	4.3	1.7	4.7	14.5
08–S3	0.1	0.1	0.1	1.1	14.8	47.5	7.0	0.8	4.6	5.1	3.0	2.0	1.5	13.6
Shelter Island Yacht Harbor														
09–S1	0.1	0.1	0.1	1.3	13.3	15.9	5.7	6.9	11.8	8.7	6.0	4.4	3.9	20.0
09–S2	0.1	0.1	0.1	1.0	12.7	17.9	6.5	9.0	10.4	8.5	5.0	3.1	4.5	16.7
09–S3	0.0	0.05	0.05	1.2	26.8	22.8	4.8	6.0	6.8	5.6	2.4	2.4	2.4	12.4
USS DURHAM (LKA 114)														
S4		0.2	0.2	1.7	13.3	9.4	2.1	12.1	12.6	8.5	5.7	4.8	5.2	21.1
S5	5.8	7.2	6.7	9.9	28.7	5.9	2.4	2.0	6.0	4.8	4.8	3.2	4.4	12.4

LOADING FACTORS

BRUSHING ACTIVITY AND PLUME CONCENTRATIONS

The discrete sample data collected during hull cleanings are summarized in figures 16 through 25. Only filtered (“dissolved”) sample copper concentrations are presented since this fraction most closely approximates the copper available to organisms. It is not intended, however, to imply that all copper in the filtered samples is available. (See Ion Selective Electrode discussion, p. 44 and tables 7a and 7b.) Reference to the EPA marine water quality criteria for copper of 2.9 µg L^{-1} is made to characterize the existing and post cleaning copper levels relative to the current regulatory standard.

USS DURHAM (LKA 114)

Surface water dissolved copper concentrations decreased rapidly with distance from the ship’s hull during cleaning operations (figure 16). Before cleaning and after cleaning surface water copper concentrations were essentially the same. All surface water copper concentrations measured were greater than the EPA water quality criteria of 2.9 µg L^{-1}, including those measured in surface water before cleaning operations commenced. Samples collected at midwater depth remained essentially the same before and after cleaning operations, ranging from 2.5 to 8.7 µg L^{-1} (figure 17). Comparatively, samples collected before cleaning were similar to those collected after cleaning 1/2 to 2 hours later. Samples collected along the middle transect (where most of the measurements were made) exhibited a decrease in copper concentration from 19.1 to 5.3 µg L^{-1} at 18 and 96 m from the ship’s hull, respectively. Four of 27 samples collected before, during, and after hull cleaning at midwater depth were at or below the copper water criteria of 2.9 µg L^{-1}.

If the copper concentrations during hull cleaning and distance from the hull are regressed, the mean water copper concentration prior to cleaning (4.3 µg L^{-1}) is met at 101 m from the hull. Data from the middle transect at midwater depth were used since these measurements gave the best correlation with copper concentration and distance. The area of hull cleaning influence may be estimated to be a cylinder with a radius of 101 m and a depth of 9 m. The area is calculated to be 288,280 m^3, or approximately 0.001% of the bay volume (taken to be 2.5 x 10^8 m^3).

USS ENGLAND (CG 22)

During the hull cleaning of USS ENGLAND, surface water dissolved copper concentrations ranged from levels approximating before and after hull cleaning concentrations to levels nearly twice initial concentrations (figures 18 and 19). All surface water copper concentrations were above 2.9 µg L^{-1}. Midwater copper concentrations measured during hull cleaning were not generally highly elevated above pre-cleaning values. At 42 m from the hull, along the middle transect, a sample collected during cleaning was nearly three times the pre-cleaning level. At 10 m from the hull, a post-cleaning sample was approximately twice the pre-cleaning concentration. The sample collected during cleaning at 10 m was, however, less than the concentration measured prior to cleaning. Clearly the fixed-point sampling performed gives only an approximate characterization of the water column copper concentration. Many more discrete samples would be necessary to clearly define the entire area where elevated copper concentrations occurred. All samples measured were above 2.9 µg L^{-1} copper.

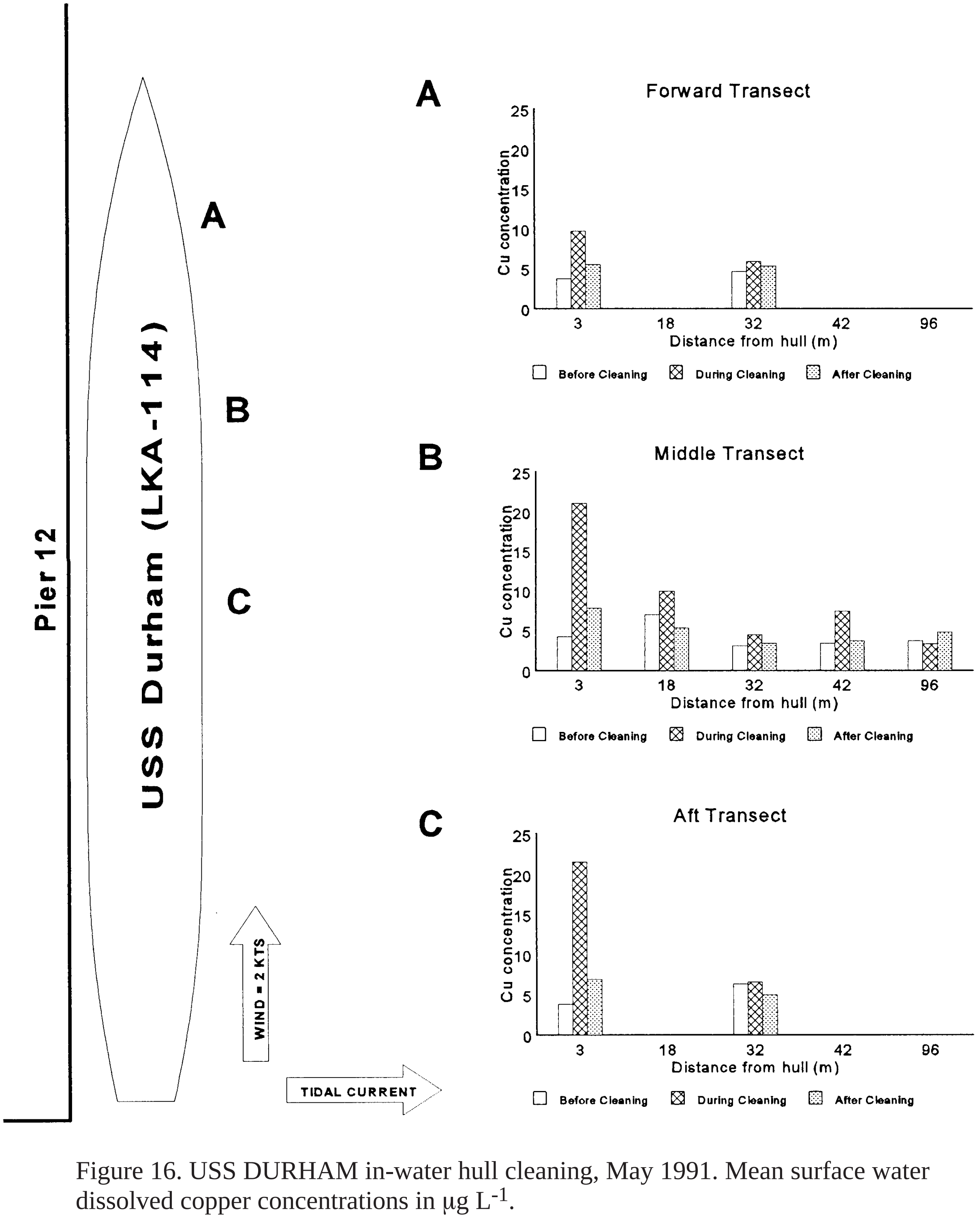


Figure 16. USS DURHAM in-water hull cleaning, May 1991. Mean surface water dissolved copper concentrations in µg L^{-1}.

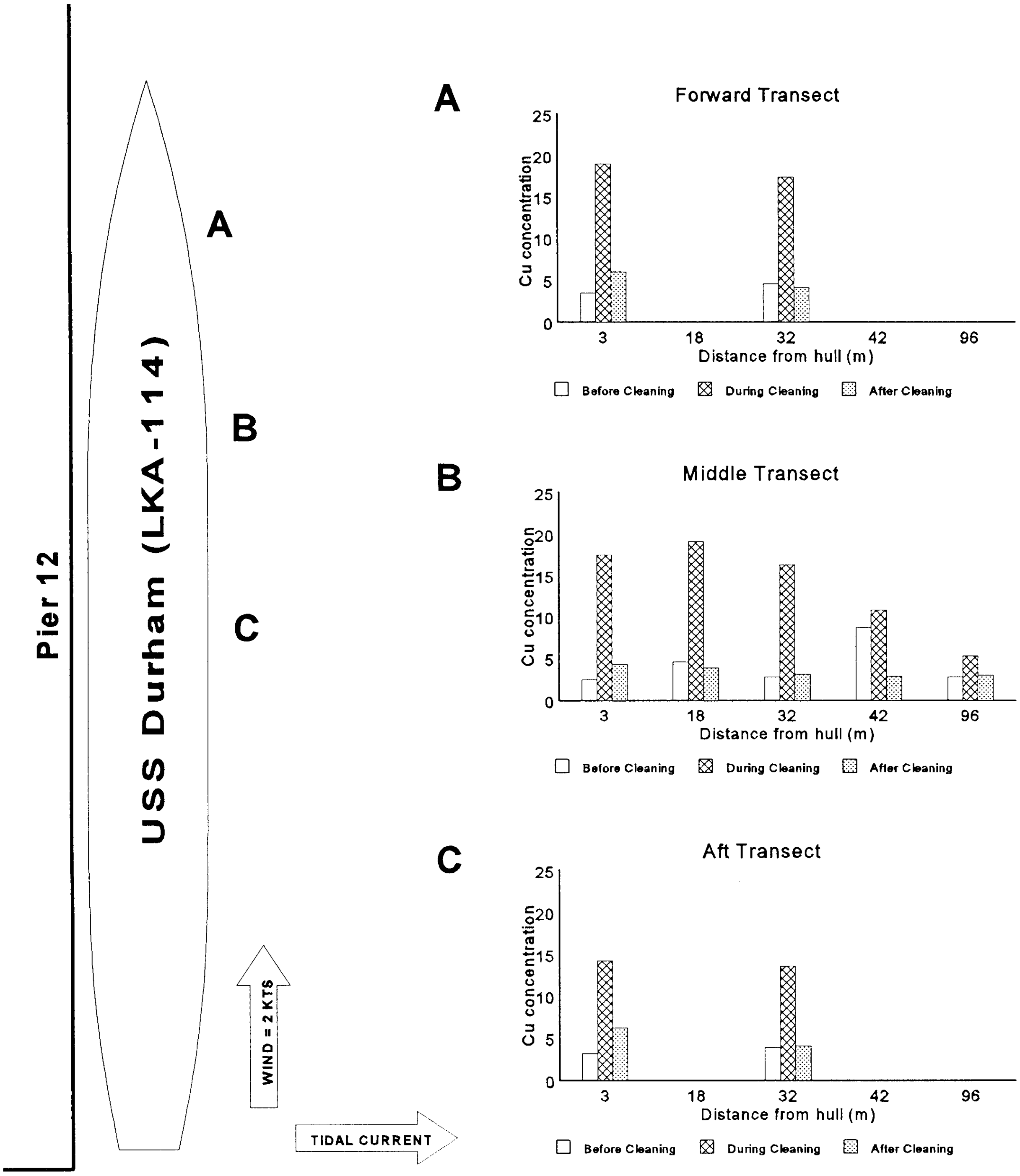


Figure 17. USS DURHAM in-water hull cleaning, May 1991. Mean midwater dissolved copper concentrations in µg L^{-1}.

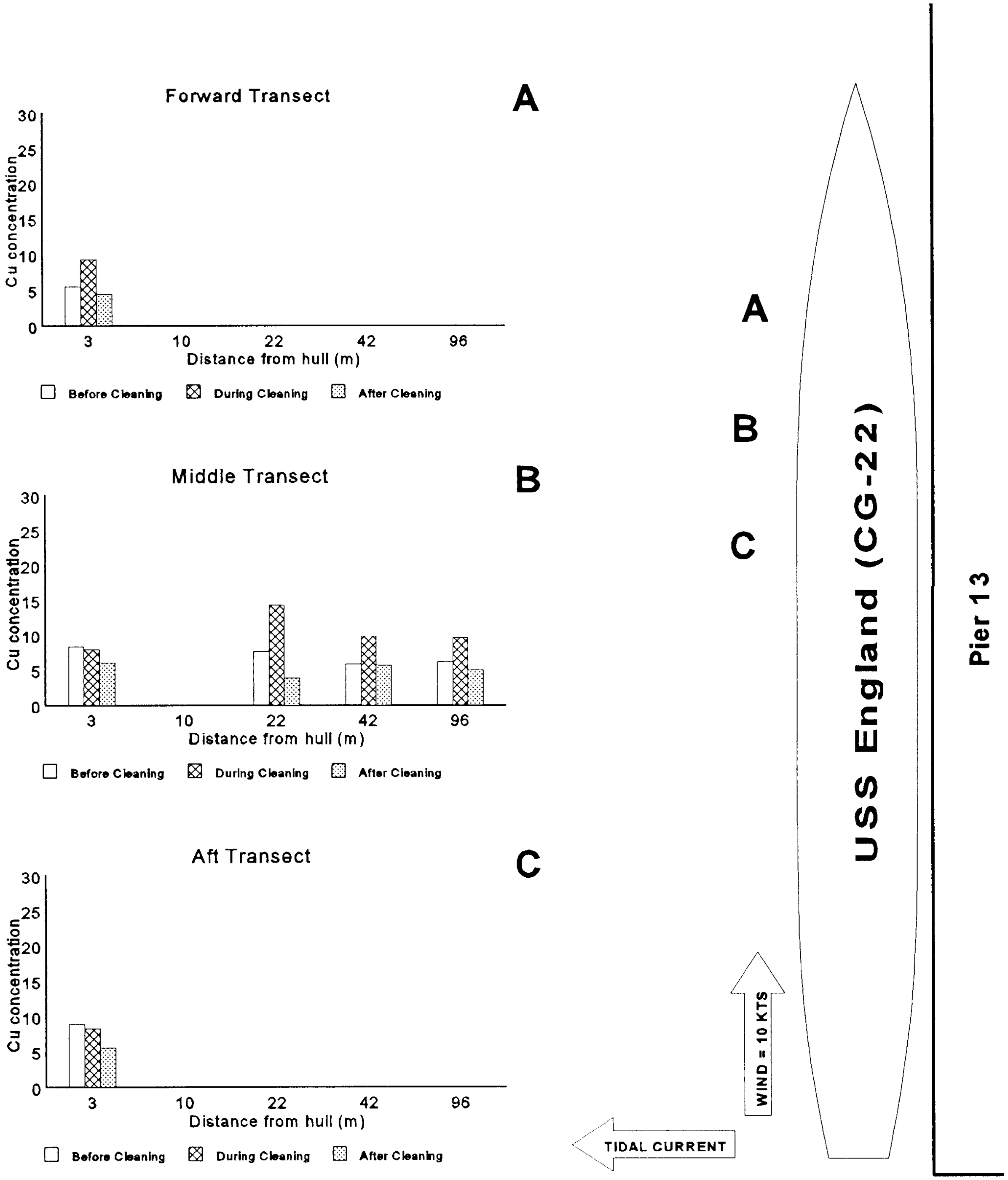


Figure 18. USS ENGLAND in-water hull cleaning, August 1991. Mean surface water dissolved copper concentrations in µg L^{-1}.

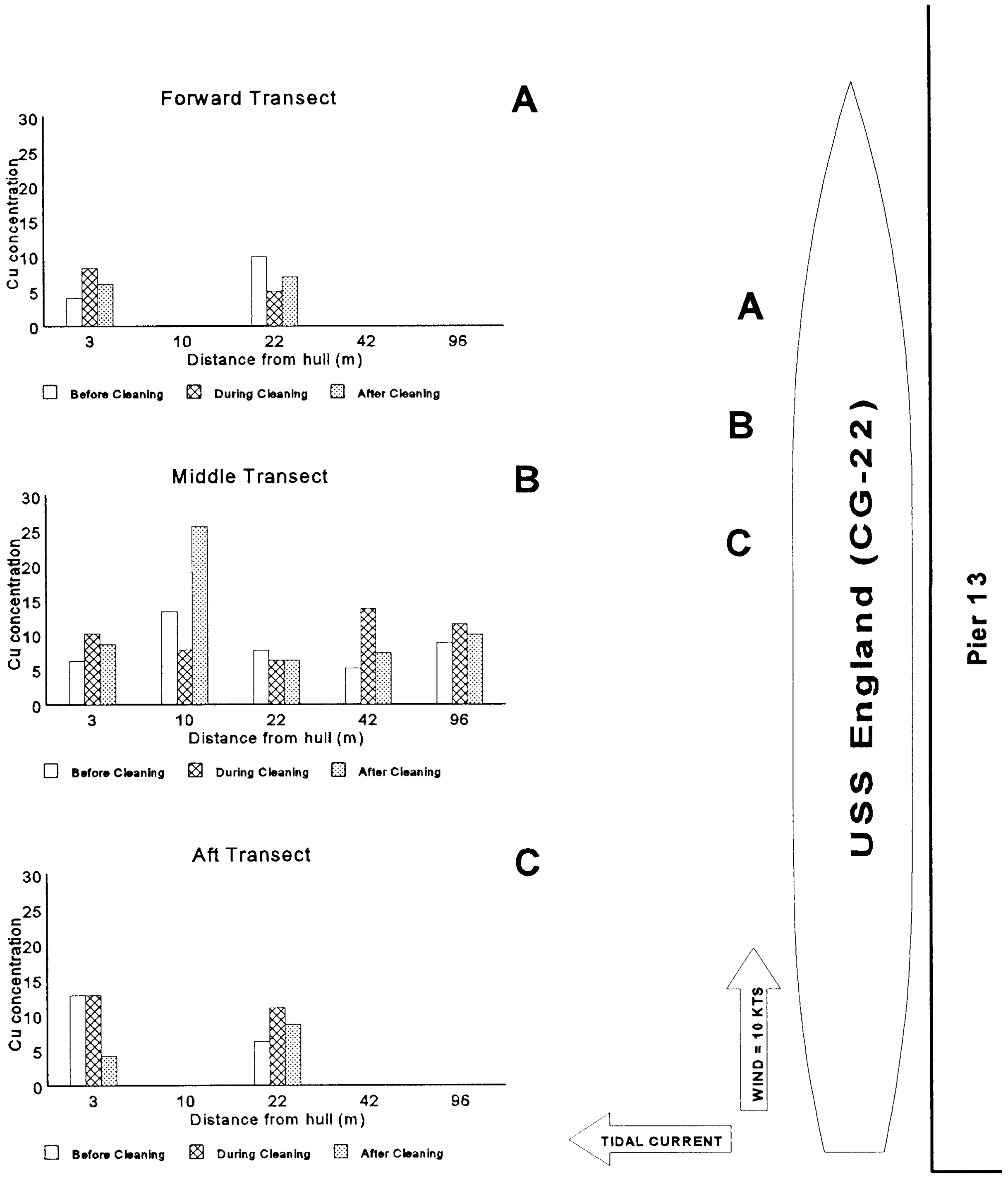


Figure 19. USS ENGLAND in-water hull cleaning, August 1991. Mean midwater dissolved copper concentrations in μg L^{-1}.

USS MARVIN SHIELDS (FF 1066)

Less copper data are available for USS MARVIN SHIELDS hull cleaning operation. This paint-test vessel was painted primarily with equal distributions of ABC-3 and BRA-540 (figure 20). Samples collected during hull cleaning were generally slightly higher in copper concentration than those collected prior to cleaning. At 2 m from the hull, approximately twice as much copper was measured during cleaning than prior to cleaning. Dissolved copper concentrations in all samples, including pre-cleaning samples, were above 2.9 μg L^{-1}.

USS FORT FISHER (LSD 40)

Copper data are available only during USS FORT FISHER hull cleaning operation (figure 21). Dissolved copper concentrations measured ranged from 4.1-5.1 μg L^{-1}. These levels are similar to pre-cleaning levels measured during other hull cleanings, suggesting that little dissolved copper was released during USS FORT FISHER hull cleaning. This pattern was expected, as USS FORT FISHER was coated with Formula 121 antifouling paint 6 years previously.

Sediment samples collected prior to cleaning and after hull cleaning operations did not show any indication of increased copper in sediments as a result of cleaning operations (figure 22). The notably higher sediment copper value measured at point E (1037 mg kg^{-1}) suggests that paint particles may have been abundant in this sample.

USS TUSCALOOSA (LST 1187)

Copper data collected during the hull cleaning of USS TUSCALOOSA ranged from 1.2 to 8.4 μg L^{-1} (figure 23). Less copper was measured during this hull cleaning operation than during others. It is possible that the paint coating on this vessel was nearly exhausted and well beyond its operational life. Five of eight samples measured had less than 2.9 μg L^{-1} dissolved copper.

Of five prior and after cleaning sediment sample comparisons, only one location (A) indicated a clear difference in sediment copper values after cleaning operations (figure 24). The other locations had similar copper concentrations before and after cleaning operations. The sediment copper concentrations measured at the site of USS TUSCALOOSA and USS FORT FISHER hull cleanings were higher than those measured during the bay-wide surveys off the Naval Station (Station 5), but similar to values measured in this same area several months later (figure 3; Richter unpublished data). The sediment copper data collected in the Naval area at Piers 12 and 13 are higher than those measured in these areas in the mid-1970s (Yamamoto et al., 1975) and may indicate a long-term increase due to ship presence and cleaning activity or proximity to the PACO Ore Terminal.

USS RANGER (CV 61)

Dissolved copper concentrations measured in hull cleaning samples collected near USS RANGER were also similar to previously measured ambient values ranging from 2.4 to 5.6 μg L^{-1} (figure 25). Seven of nine samples collected were less than 2.9 μg L^{-1} copper.

ION SELECTIVE ELECTRODE/VOLTAMMETRIC SPECIATION

“Dissolved“ copper can exist in estuarine or ocean water in many forms: as the free ion or as a labile or inert complex. The complex itself may be either organic or inorganic, or possibly,

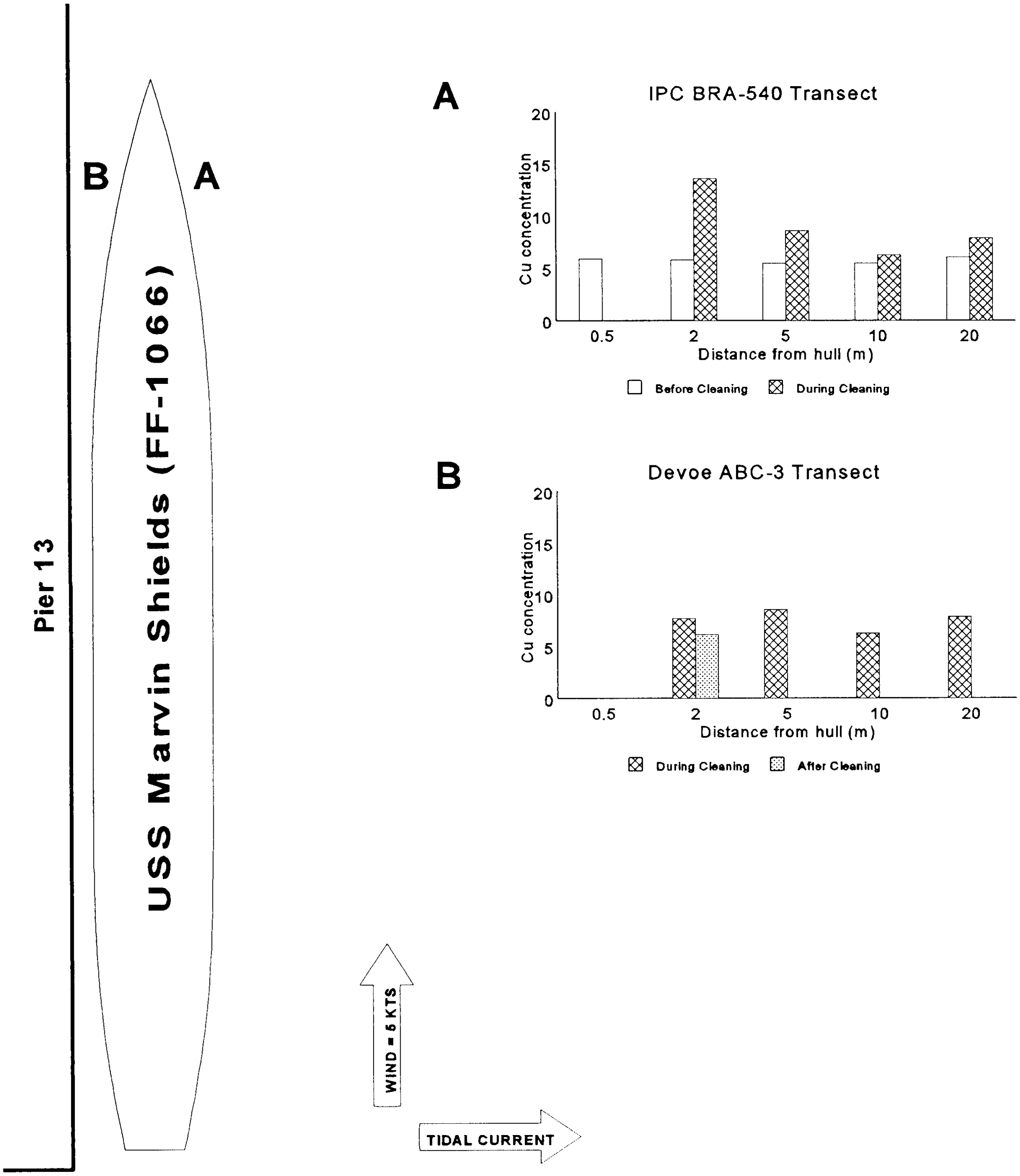


Figure 20. USS MARVIN SHIELDS in-water hull cleaning, June 1992. Mean midwater dissolved copper concentrations in μg L^{-1}.

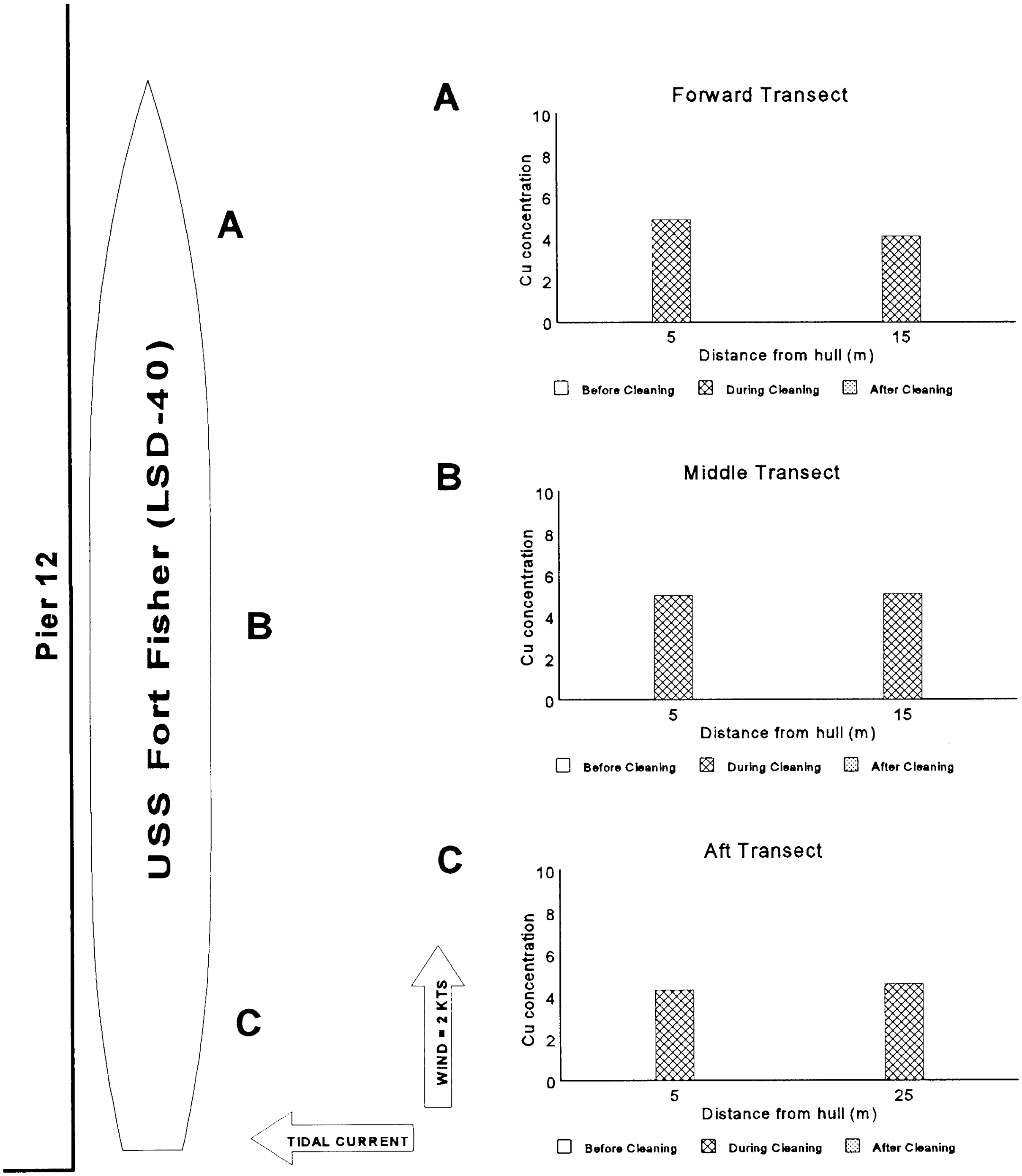


Figure 21. USS FORT FISHER in-water hull cleaning, February 1993. Mean midwater dissolved copper concentrations in $\mu g\ L^{-1}$.

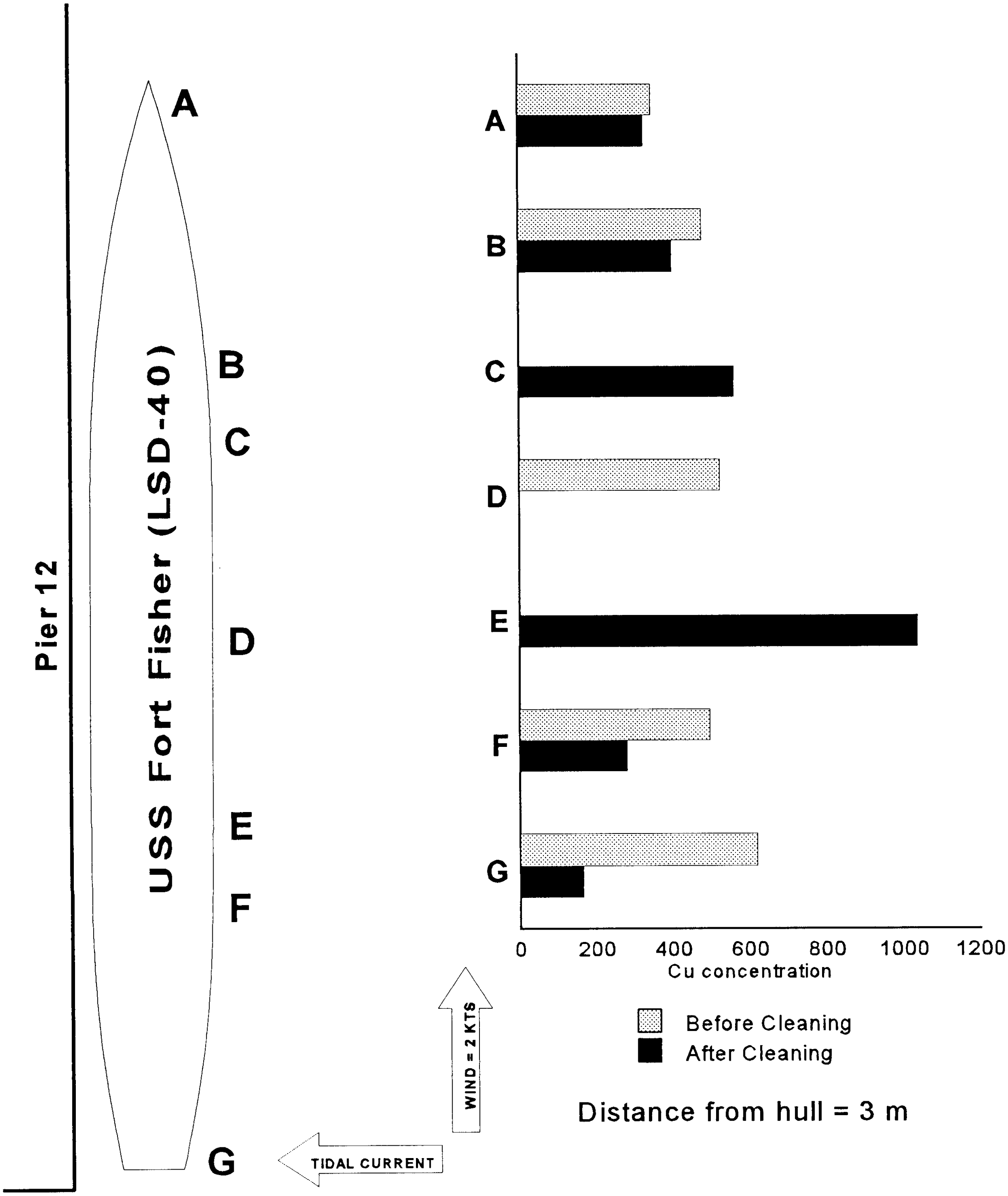


Figure 22. USS FORT FISHER in-water hull cleaning, August 1991. Mean sediment copper concentrations in mg kg^{-1} dry weight.

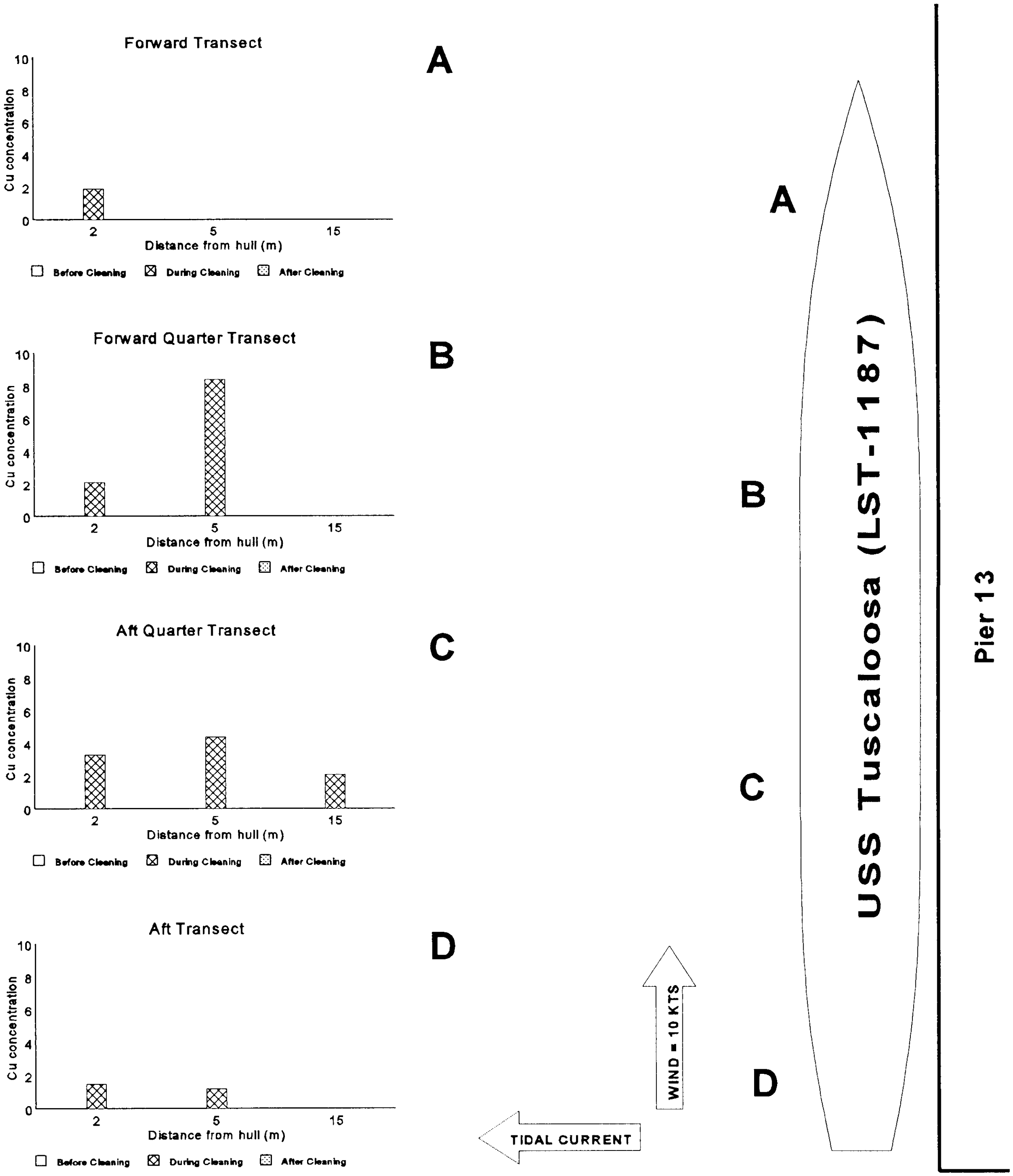


Figure 23. USS TUSCALOOSA in-water hull cleaning, February 1993. Mean midwater dissolved copper concentrations in µg L^{-1}.

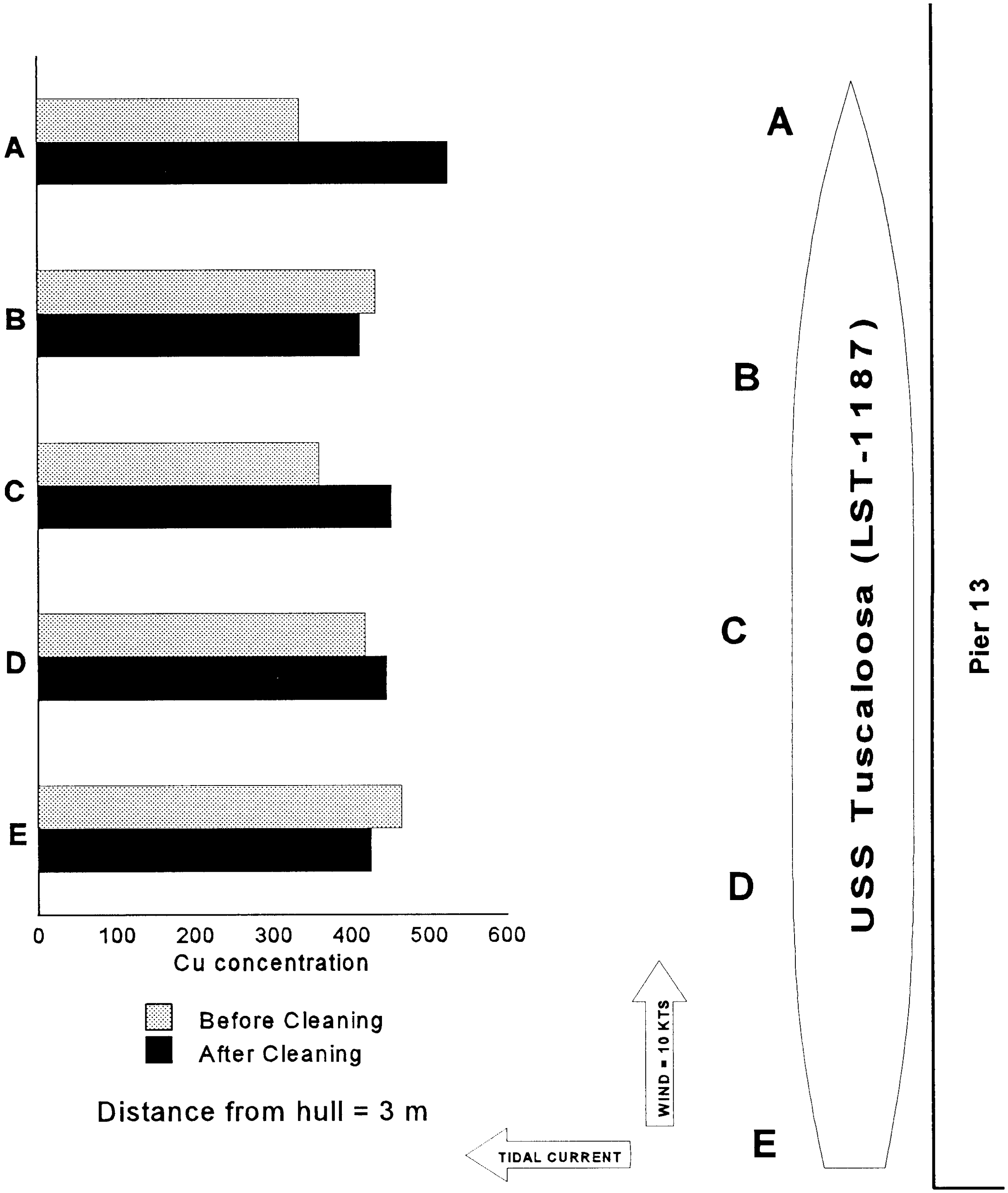


Figure 24. USS TUSCALOOSA in-water hull cleaning, August 1991. Mean sediment copper concentrations in mg kg^{-1} dry weight.

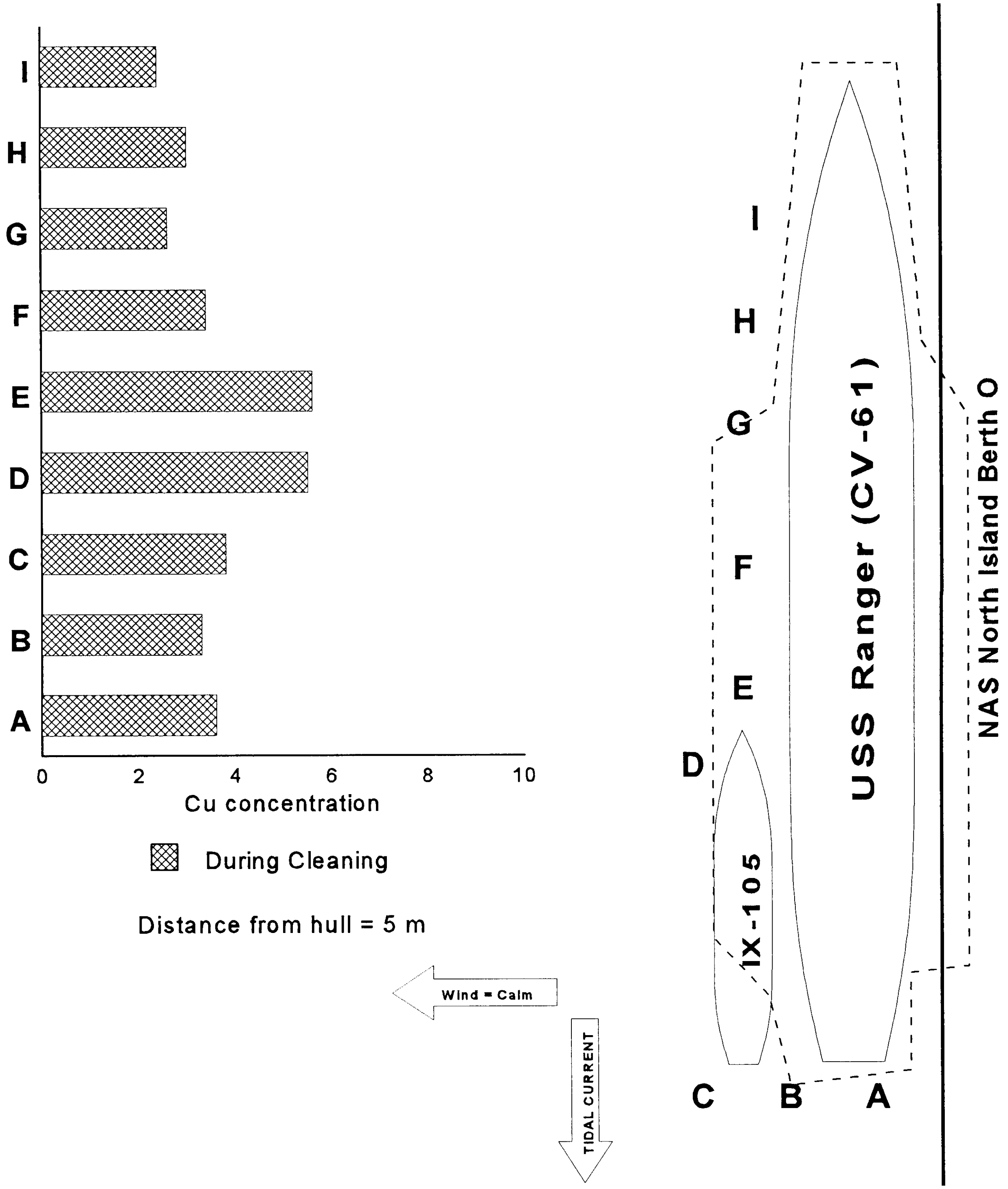


Figure 25. USS RANGER in-water hull cleaning, July 1993. Mean surface water dissolved copper concentrations in μg L^{-1}.

both. The inert forms are most likely colloidal (Mackey and Zirino, 1994). The toxicity of the different fractions may vary; indeed, the work of Sunda and Guillard (1976) and Anderson and

Morel (1978) have shown that it is the concentration of free ion (and not the total concentration of Cu) that correlates best with plankton toxicity.

To assess the environmental impact of hull cleaning operations, we have applied some newly developed speciation tests to samples collected during the hull cleaning procedure. Similarly, we have used the Orion® Cu ion selective electrode (ISE) to detect the release of Cu^{++} during hull cleaning and to determine the base or ground level of free Cu^{++} at various locations in San Diego Bay.

The relationship between the millivolt output of the Orion® Cu^{++} ISE and free Cu^{++} was established by calibrating the electrode with Cu^{++} activity buffers prepared according to Belli and Zirino (1993). These workers also showed that the electrode was able to provide accurate measurements of the free Cu^{++} activity or concentration in seawater media and demonstrated that the problem known as the "chloride interference problem" was likely due to the incorrect usage of the electrode by previous workers.

We have also measured hull cleaning and ambient waters in San Diego Bay for certain copper fractions according to a speciation scheme published by Scarano et al., (1990). This voltammetric method detects the "labile" fraction of Cu present at pH 8, the "ligand exchangeable" fraction, which includes the labile fraction and that portion of the "bound" fraction that would exchange with ethylenediamine (En-exchangeable, Scarano et al., 1992), and the "inert" fraction, e.g., that portion of the sample that can only be detected by lowering the pH to 2.

It should be noted that the speciation scheme above separates the fractions by increasing the "strength" of the chemical treatment, and if a sample is composed entirely of labile Cu, then all three voltammetric fractions would have identical concentrations. On the other hand, the potentiometric measurements do indeed measure the free Cu^{++} ion. Even the most labile complexes, such as $CuCl_2$, are not detected by the ISE. Thus, Cu^{++} activity values detected by potentiometry are much smaller than any of the fractions measurable by voltammetry.

Inorganic models may be constructed that describe the speciation of seawater in terms of its inorganic components (Zirino and Yamamoto, 1972). All of these models essentially predict that the concentration of the free Cu^{++} ion is approximately 1% of the total copper concentration. Therefore, for a seawater concentration of 5×10^{-8} M (3.2 μg L^{-1}), the activity of the free ion should be approximately 5×10^{-10} (0.032 μg L^{-1}), or pCu = 9.3.

THE RELATIONSHIP BETWEEN Cu^{++} AND TOXICITY

As was stated above, the argument for Cu^{++} ion activity being a more reliable measure of toxicity than the total copper ion concentration goes back to the work Sunda and Guillard (*op. cit.*). They showed that cultures of the estuarine diatom *Thalassiosira pseudonana* (clone 3H) and of the estuarine green alga *Nannochloris atomus* in highly chelated media showed growth rate inhibition at calculated Cu^{++} activities above 3×10^{-11} (1.9 ng L^{-1}). Growth rate inhibition was not related to the total Cu concentration that ranged from 10^{-3} M to 10^{-6} M (63.5 mg L^{-1} to 63.5 μg L^{-1}). Cu^{++} ion activity was calculated because it could not be measured directly at that time. Two years later, Anderson and Morel (op. cit.) repeated Sunda and Guillard's experiment using cultures of the marine dinoflagellate *Gonyaulax tamarensis*. They also found that a Cu^{++} activity level of 4×10^{-11} (2.5 ng L^{-1}) also inhibited motility. They pointed out that for some marine environments, this value was relatively close to the value that could be calculated assuming only inorganic complexation.

MEASUREMENTS IN SAN DIEGO BAY

USS DURHAM (LKA 114)

Cu^{++} activity measurements were made in the field during the last five hull cleaning operations. Initial measurements were made during the hull cleaning operations of USS DURHAM. Figure 26 shows the raw millivolt response of the Cu^{++} ISE during the hull cleaning event of May 16, 1991. For this operation, the sensor was actually placed on the R/V *ECOS*, 9 m from the side of USS DURHAM. Seawater near USS DURHAM was collected by holding the open end of a 50-m Teflon® hose near the hull and aspirating the sample through the hose to the electrodes on the *ECOS*. The effect of brushing on the ambient water is clearly evident in the figure, producing a peak from about 10:30 to 15:00. The peak in potential (mV) values also coincides with a peak in the plot of the discrete samples collected at the same time and analyzed by ASV (table 6). However, pCu values could not be assigned at this time because seawater-copper buffers had not yet been developed.

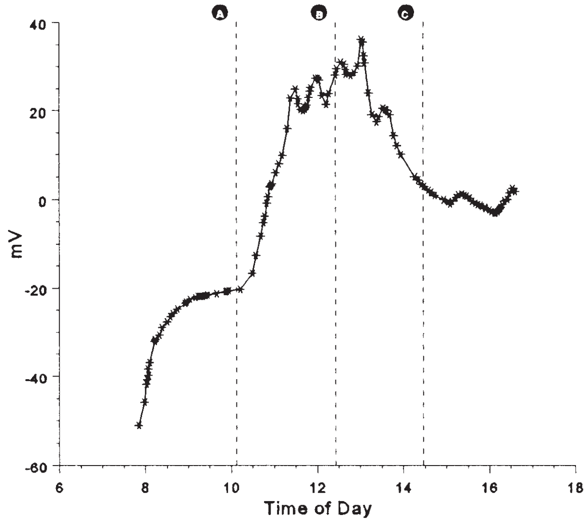


Figure 26. Ion Selective Electrode response profile, USS DURHAM in-water hull cleaning, 16 May 1991. (A) Initial hull cleaning pass; (B) slack low tide; (C) hull cleaning operations end.

Nevertheless, assuming an ideal electrode response of 29.6 mV decade^{-1}, we see that during the hull cleaning operation, Cu^{++} values rose by about two orders of magnitude. The high values did not persist, however, and dissipated after the hull cleaning ceased (table 6).

That the electrode response reflected the dissolution of hull cleaning residue is confirmed by table 6, which shows the results of the ASV analysis of the discrete samples collected at various distances from the hull. It is clearly evident that the ambient water has been significantly (though temporarily) impacted. The “labile” content of the water next to the ship is seen to increase by two orders of magnitude, in agreement with the ISE results.

Table 6. Results of samples collected before, during, and after hull cleaning operation, 16 May 1991. All copper concentrations in parts per billion (ppb).

Sample	Labile	En-exchangable	Acid-exchangable	AA (F)	Comments
3 METERS FROM SHIP HULL					
CSU-67	217	227		30.1	Approx. 30 min after hull clean. ops. began
CSU-85	12.4	26.2	151.2	12.1	Approx. 45 min after scrubber pass
CSU-103	3.5	6.3	10.1	4.6	Approx. 40 min after hull clean. ops. ended
CSU-121	6.0	10.3	28.9	11.1	Approx. 2 hrs after hull clean. ops. ended
21 METERS FROM SHIP HULL					
FSU-11	4.9	8.9	49.2	2.9	Pre hull cleaning (5/15/91)
FSU-73	16.3	16.3	12.2	6.7	Approx. 30 min after scrubber pass
FSU-127	4.6	10.9	12.7	3.6	Approx. 2 hrs after hull clean. ops. ended
45 METERS FROM SHIP HULL					
HSU-33	1.8	4.7	9.1		Pre hull cleaning (5/15/91)
HSU-55	2.4	3.6	11.8	3.8	Pre hull cleaning (5/16/93)
HSU-95	9.4	15.6	67.3	10.8	Approx. 45 min after scrubber pass
HSU-131		5.7	9.0	4.2	Approx. 2 hrs after hull clean. ops. ended

Discrete samples were also collected during the week of the USS DURHAM hull cleaning operation and were measured for the various fractions: labile, ethylenediamine exchangeable, and acid exchangeable. Some were associated with the hull cleaning operations while others were taken around San Diego Bay in a bay-wide survey. The first are presented in table 7a, while the results of the bay-wide survey are presented in table 7b. With the exception of a few discrepancies, a clear pattern emerges from all the samples:

labile < ion exchangeable < acid-exchangeable

We notice that data from the bay-wide survey indicate that the acid-exchangeable fraction is approximately twice the labile fraction with the En-exchangeable fraction being somewhere in between. This pattern appears to be typical of Cu in San Diego Bay waters and is supported by additional data obtained by Venderweel (in preparation). However, near ship operations, the acid exchangeable value is often five times higher than the En-exchangeable fraction. We suggest that this result is due to the presence of particulate copper, presumably from paint particles.

Since the paint is largely of copper oxide, the oxide particles would be dissolved quickly by the acid and not by the ethylenediamine. In general, analysis of the same samples by atomic absorption (AA) did not produce the very high values, but gave concentrations similar to the En-exchangeable fraction. Because the AA determination of the samples occurred after filtration through a 0.45-μm filter, this also suggests the presence of particulates.

Table 7a. Samples collected near and around pier area, USS DURHAM, 17 May 1991. All copper concentrations in parts per billion (ppb).

Sample	Labile	En-exchangable	Acid-exchangable	Location
ZMU-1	6.1	8.2	14.8	Outside of pier
ZMU-5	9.6	16.0	20.9	Outside of pier
ZMU-11	4.5	5.9	8.2	End of pier
ZMU-14	13.0	17.6	21.5	Inside pier area
ZMU-20	12.2	15.0	20.5	Inside pier area

Table 7b. Results of bay-wide survey, 21 May 1991. All copper concentrations in parts per billion (ppb).

Sample	Labile	En-exchangable	Acid-exchangable	AA (F)	Location
CSD1SU-29	5.3	8.8	10.3	4.7	Bay-mouth
CSD2SU-32	1.6	2.0	4.5	3.6	Center of channel btw Shelter Is. and NAS
CSD3SU-35	2.1	3.6	N/A	1.8	Center of channel, south of Harbor Is.
CSD4SU-38	2.3	3.1	5.0	3.3	Center of channel, under Coronado Bridge
CSD5SU-41	3.9	4.8	6.3	4.0	Off of San Diego Naval Station
CSD6SU-44	3.7	3.9	2.1	1.9	South San Diego Bay
CSD7SU-47	1.7	2.4	2.0	2.1	Overload Facility
CSD8SU-50	4.7	6.2	9.7	3.7	Glorietta Bay
CSD9SU-53	1.6	2.9	3.1	3.1	Shelter Island

USS MARVIN SHIELDS (FF 1066)

Participation in the USS MARVIN SHIELDS hull cleaning survey was limited to making Cu ISE measurements before, during, and after the hull cleaning operation (June 22, 1992). Once again, the R/V *ECOS* was stationed about 25 m off MARVIN SHIELD’s beam, and the Cu ISE was aboard the *ECOS*. Using a 25-m Tygon hose, water was sampled at 2, 5, 10, and 20 m from the hull and pumped to the *ECOS* where it was measured for copper activity. This time, the electrode was calibrated for activity by using a single ethylenediamine buffer and varying the pH. The electrode potential became more positive after the hull cleaning event.

Also measurements closest to the ship were more positive, indicating more available copper. Unlike for USS DURHAM, only a 15-mV increase was registered, indicating a six-fold increase in free Cu ion next to the hull during the event. pCu values (the negative logarithm of the free Cu^{++} activity) were in the range of approximately 12 with high Cu^{++} of 11.8 (equal to 1.6×10^{-12} M, or 0.1 ng L^{-1}) to a low of 12.7 (equal to 2.0×10^{-13} M, or 0.013 ng L^{-1}). The potential of the electrode returned to background value after about 30 minutes. No samples were analyzed by voltammetry.

USS FORT FISHER (LSD 40)

For the USS FORT FISHER hull cleaning event, the electrode was mounted on a CTD (conductivity, temperature, depth) probe (IDRONAUT 301™ – Milan, Italy) with direct readout to a portable computer via a cable. The Cu-electrode-equipped CTD, which also measures pH and dissolved oxygen, was hand-lowered in the water from a small boat situated in the hull cleaning regions. Profiles were taken throughout the hull cleaning operations at various distances from the hull.

Calibrations of the electrode were effected using the Belli and Zirino (1993) buffers. The IDRONAUT 301™ possesses a reference electrode of unusual stability for a field device. This makes it possible to compare Cu ISE readings over long periods of time. We carried out calibrations of the electrode in the laboratory and in the field over a 6-month period and found that the Cu ISE electrode potential readings in freshly made buffers varied only by a few millivolts. There is also very little drift with the pH electrode associated with the CTD. Thus, a secondary measure of the stability of the reference is whether the pH electrode on the CTD returns the pH value of the fresh ethylenediamine and glycine buffers (8.22). Electrode potentials were related to Cu^{++} ion activity using the formula:

$$\text{pCu} = (-65\text{ mV} - (-\text{ potential reading}))/(29.6\text{ mV}) + 13.33$$

Three approximately equidistant stations were located along the starboard side of USS FORT FISHER and were sampled approximately three times during the hull cleaning. Profiles were made from surface to near bottom. In summary, all profiles for all variables indicated a well-mixed water column. Cu ISE values varied from about –13 mV (pCu = 11.6) nearest the ship, at the onset of the hull cleaning, to approximately –50 mV (pCu = 12.8) during a lull in the operation. Similar changes and ranges were noted during the USS MARVIN SHIELDS operation.

USS TUSCALOOSA (LST 1187)

The procedure used for sampling during the USS TUSCALOOSA survey was very similar to that used for USS FORT FISHER. Four stations were set up approximately 10 m from the starboard hull and sampled throughout the hull cleaning procedure. Measurements were made by lowering the CTD to near bottom at several distances (2, 5, and 15 m) from the hull.

For all stations at all depths, the electrode potentials varied between –30 mV and –33 mV, giving a pCu of approximately 12.1. No copper was detected by ISE from this hull cleaning operation. All stations around USS TUSCALOOSA were well-mixed. No samples were collected for analysis by voltammetry.

USS RANGER (CV 61)

The final hull cleaning survey was of USS RANGER. As in the last two surveys, stations were set up along the port side, under the flight deck and sampled periodically during the hull cleaning operation. Sampling was effected at each station by manually lowering the CTD from a small boat.

All stations showed a nearly isopycnal water column and Cu ISE potentials varied from –11 mV to –14 mV, giving a pCu value of approximately 11.6. A sample of the “red water” discharged by the hull cleaning “brush” was trapped and measured directly with the electrode on the CTD. The potential immediately moved toward the positive and in a few minutes, the potential rose to +85 mV (pCu = 8). No samples were collected for analysis by voltammetry.

RESULTS AND DISCUSSION

The results of our work with the Cu ISE indicate that the free Cu^{++} level in San Diego Bay is approximately 10^{-12} M (0.06 ng L^{-1}; pCu = 12) and that the *in situ* hull cleaning procedure may temporarily raise the pCu to about 11, but that the impacted waters quickly return to the ambient level in a matter of hours or less. This strongly suggests that the hull cleaning debris is largely particulate and that its contact with the ambient waters is brief before settling to the bottom. In the cases of USS TUSCALOOSA and USS RANGER, no impact from hull cleaning could be noted at all, even a few meters from the hull.

A pCu value of near 12 is at least one order of magnitude below the toxicity value for microalgae established by Sunda and Guillard (1976) as well as Anderson and Morel (1978). Thus, by this criterion, the temporary changes in pCu due to hull cleaning cannot be construed to be a danger to microalgae. In fact, a pCu of 12 lies in the optimum region established by Sunda and Guillard (1976), for the growth of *Thalassiosira pseudonana*. Higher values of Cu^{++} are toxic, and lower values lead to a nutrient deficiency.

Interesting is the relatively large fraction of labile Cu present in the bay as determined by stripping voltammetry. This fraction is present at pCu from 7 to 8. At this point, it is important to define labile in terms of the over-voltage applied to the electrode. For this work, we applied a reducing potential of –1.0 V to the hanging mercury drop electrode (HMDE). This constitutes an over-voltage of approximately 500 mV over the reduction of copper in organic free seawater. Scarano et al. (1992) showed that for Tyrrhenian Sea samples, this over-voltage did not produce significantly higher currents than an applied potential of 500 mV, e.g., there were no additional voltammetrically labile compounds to be reduced in addition to those already reduced at 500 mV. In San Diego Bay, the labile fraction turned out to be anywhere from 50 to 70% of the ethylenediamine exchangeable fraction. This is exactly the same fraction observed for the Tyrrhenian Sea samples.

Thus, the labile fraction in San Diego Bay represents easily reduced copper compounds; compounds as easily reduced as $CuCl_2$. This poses two questions: (1) Is the labile fraction as toxic as Cu^{++}? and (2) What is its composition? What raises the pCu to 12 and is labile to voltammetry? (In San Diego Bay, inorganic complexation, as predicted by speciation models, can only take the pCu to about 10).

The answer to the first question appears to be “no.” The labile fraction is not toxic to microalgae. From the criteria developed by Sunda and Guillard (1976) and Anderson and Morel

(1978) for cultures, the values found in San Diego Bay would completely inhibit growth, and thus, there would be no microalgae in the bay! Thus, either the labile fraction is not toxic or the existing microflora is very resistant. Indeed, Krett (1980) showed that copper tolerant species of microalgae existed in the bay. Nevertheless, Krett did note toxicity at about 2×10^{-7} M (12.7 μg L^{-1} = ppb) ionic copper for plankton samples from the Shelter Island inlet, a relatively polluted area. In any case, it does not appear that the labile fraction is toxic to microalgae in the bay.

Even a tentative answer to the second question, "What is the physico-chemical nature of the labile fraction?" is more difficult and awaits further speciation work.

Detection of Cu^{+}

It should be pointed out that our entire discussion has been in terms of the cupric (Cu^{++}) ion, the stable form in oxygenated seawater, while copper in antifouling paints is in the cuprous or +1 state. Nevertheless, our results are still valid because (1) we expect the cuprous form to oxidize spontaneously in the water; (2) ASV does not distinguish between the two valence states; and (3) our laboratory tests showed that the Cu ISE also responds well to additions of cuprous ion.

RELEASE RATES/SHIP LOADING FLUX

The *in situ* copper release rates measured with a closed recirculating polycarbonate plastic dome system (Lieberman et al., 1985) attached to the ship's hull by divers are presented in table 8. Water is circulated through the closed system under a slight negative vacuum during the period of 1 hour while samples are withdrawn for copper analysis. The copper concentration increases with time in a linear fashion as more and more copper is leached into the closed system. The release rate is then calculated as a linear function with time.

The copper leach rates summarized in table 8 are low and less than the required leach rate (10 $\mu g/cm^2/day$) to prevent fouling of hulls (Preiser et al., 1977). The physical appearance of the hulls tested supported this assumption as they were heavily fouled. Divers communicated that paint appeared to be missing in some hull areas. The age of the paint tested was likely responsible for the low leach rates measured.

SEDIMENT DEPOSITION/BENTHIC FLUX CHAMBER

As has been stated previously, the availability of copper is an essential aspect of its potential toxicity both in water and in sediments. In water samples copper partitioning and availability have been investigated by separation techniques and chemical measurements. The availability of copper in sediments is controlled by unique factors as well. It is generally known that if interstitial water concentrations are higher than water concentrations above the sediments (water column concentrations) then a pollutant contained in the sediment is available via a positive flux. Hence, in addition to the issue of increased copper in the water column from hull cleaning operations, that of increasing sediment copper concentrations and possible availability to sediment dwelling organisms is also of concern.

Table 8. *In situ* antifouling paint copper release rate measurements.

USS RANGER (CV 61)

	Before Brushing		After Brushing	
Paint Type	μg Cu cm^2 day^{-1}	Loading g day^{-1}	μg Cu cm^2 day^{-1}	Loading g day^{-1}
BRA-540	1.2	158	3.8	500
			5.7	748

USS FORT FISHER (LSD 40)

Paint Type			μg Cu cm^2 day^{-1}	Loading g day^{-1}
F-121	Samples		4.0	188
	Not Taken Due to		3.5	166
	Dome Failure		9.6	454

USS TUSCALOOSA (LST 1187)

Paint Type	μg Cu cm^2 day^{-1}	Loading g day^{-1}	μg Cu cm^2 day^{-1}	Loading g day^{-1}
BRA-540	3.1	100	3.0	96
	2.6	84	2.9	94

USS MARVIN SHIELDS (FF 1066)

Paint Type	μg Cu cm^2 day^{-1}	Loading g day^{-1}	μg Cu cm^2 day^{-1}	Loading g day^{-1}
BRA-540	5.9	52	5.5	48
	5.7	50	2.8	25
APC-3	1.1	10		
	1.2	11	3.2	28

USS ENGLAND (CG 22)

Paint Type	μg Cu cm^2 day^{-1}	Loading g day^{-1}	μg Cu cm^2 day^{-1}	Loading g day^{-1}
BRA-540	3.6	112	5.0	155
	4.6	143	5.5	171
	4.7	146	5.4	168
	6.0	186	4.8	149

Since evaluating the availability of a pollutant in a sediment sample introduces problems associated with disturbance of its physical-chemical structure and hence potentially artifactual results, the Navy has developed a novel *in situ* sampling device that measures the positive or negative flux of a contaminant from a sediment (Chadwick and Stanley, 1993; Chadwick et al., 1993). This is accomplished by isolating a volume of water above the sediment, drawing off samples from this volume over time, and analyzing these samples for increases or decreases in contaminant concentration. An increasing contaminant concentration indicates that the contaminant is effusing from the sediment, while a decreasing concentration indicates that the contaminant is partitioning to the sediment. The chamber, sensors, sampling devices, control systems, power supply, and deployment/retrieval equipment are all mounted on a tripod frame that can be placed *in situ* and left to sample a site for as long as 7 days.

Sediment copper flux data collected in San Diego Bay at the Shelter Island yacht basin in 1993, at the Naval Station in 1993, and at the NRaD pier in 1990 are presented in figures 27 through 30. Although the dates and exact areas of investigation are not synoptic with the naval hull cleaning sites, the data serve to indicate that no positive flux of copper was calculated from these areas. The Shelter Island sediment site is relatively high in percent clay and would be expected to bind copper. The naval site near Paleta Creek is close to the sites where ship hulls were cleaned. Sediments collected at the hull cleaning sites also had relatively high percentage clay content (table 5). The copper deposited in the underlying sediments after hull cleanings would not likely become available given the occurrence of natural binding processes judging from the *in situ* copper flux data collected.

ADDITIONAL NONNAVAL SITES

Municipal Yacht Harbors/Commercial Shipping

Among several principle sources of copper input to San Diego Bay, that from municipal yacht harbors and commercial shipping must be considered significant. The presence of several thousand pleasure craft (currently 7600 as of April 1993, San Diego Harbor Police census) in various yacht basins throughout the bay, and routine commercial shipping activity leads to a constant input of copper into the surrounding waters as a result of leaching release from copper containing antifouling paints. The application of copper from antifouling paint to pleasure craft was estimated, together with that of commercial vessels and military vessels, to total 50 metric tons per year (Young et al., 1979) in San Diego Bay. A total of 84,000 liters of copper containing antifouling paint was estimated to be applied to pleasure craft, commercial, and military vessels on a yearly basis. The contribution by pleasure craft is calculated to be approximately 10,000 liters per year. Since this information was collected in 1973, we have used recent yacht census data (April, 1993) to recalculate the copper applied to pleasure, commercial, and military vessels on a yearly basis. The total amount of copper applied using an updated pleasure craft census is calculated to be 56 metric tons per year. The number of pleasure craft has increased from 3600 in 1973 to 7600 presently. The estimated yearly application of copper-based antifouling paint to pleasure craft has increased to approximately 22,000 liters. We have assumed that commercial and military inputs have remained similar, and that the copper content of antifouling paints has also remained similar to those used in 1973.

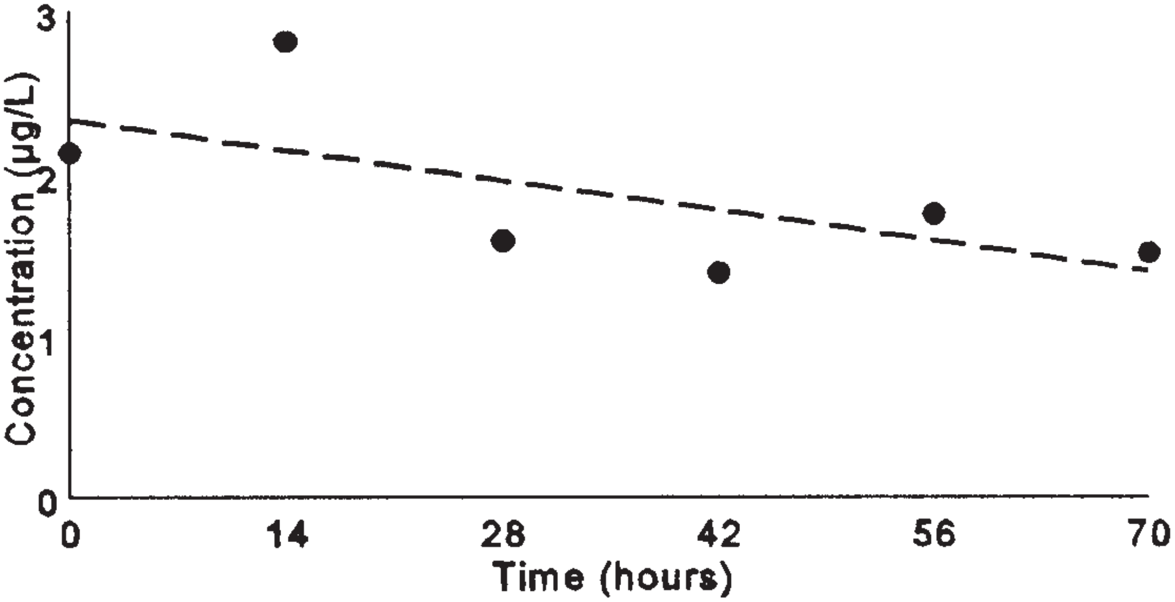


Figure 27. Sediment copper flux, Shelter Island, 19 June 1993. Copper concentrations in µg L^{-1}. Flux rate: –81 µg m^{-2} day^{-1} ($r^2 = 0.42$).

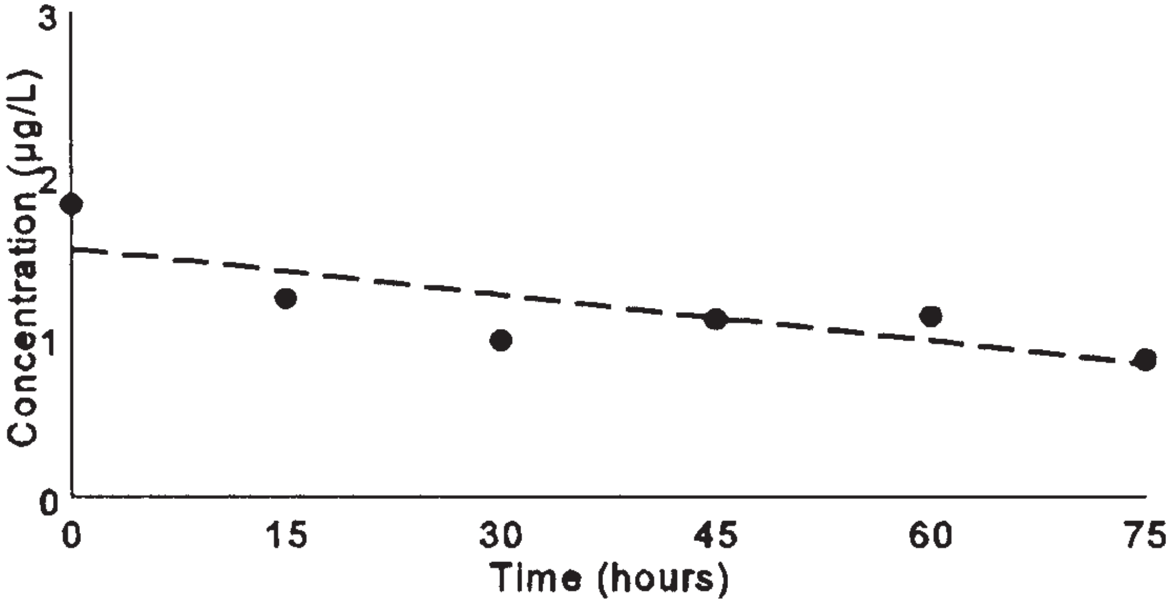


Figure 28. Sediment copper flux, Shelter Island, 25 June 1993. Copper concentrations in µg L^{-1}. Flux rate: –58 µg m^{-2} day^{-1} ($r^2 = 0.64$).

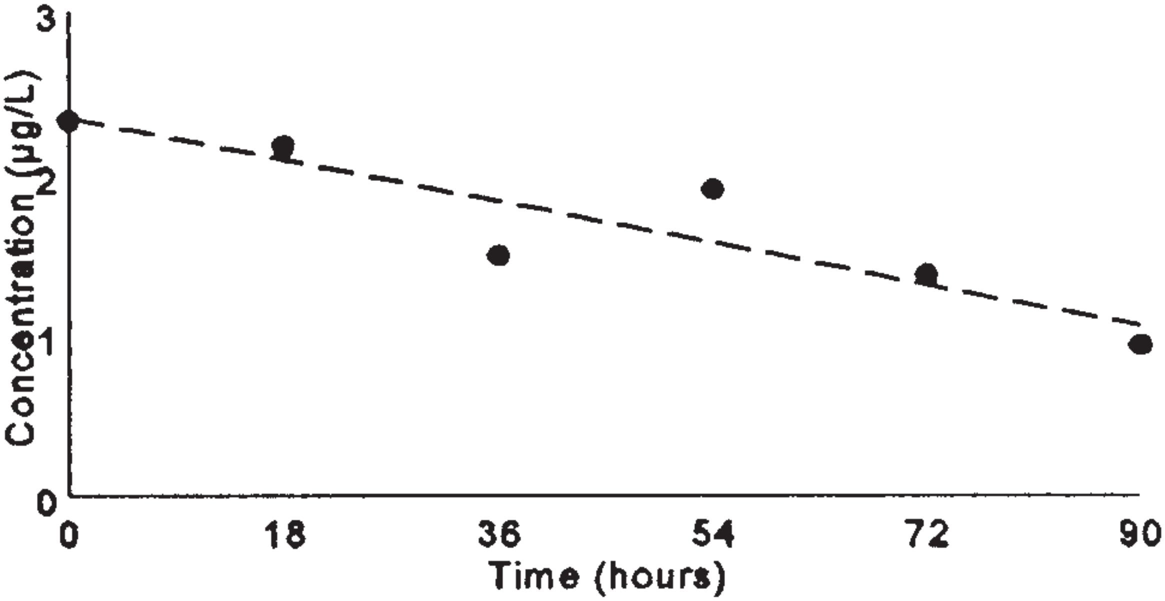


Figure 29. Sediment copper flux, Naval Station, 22 March 1993. Copper concentrations in µg L^{-1}. Flux rate: –87 µg m^{-2} day^{-1} ($r^2 = 0.82$).

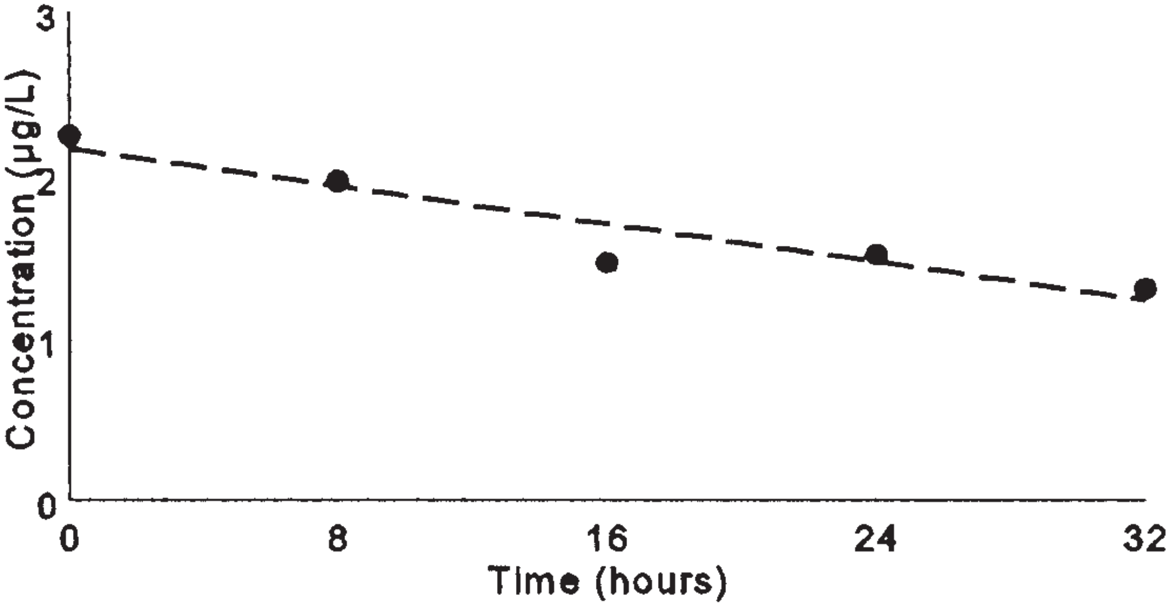


Figure 30. Sediment copper flux, NRaD Pier, 1990. Copper concentrations in µg L^{-1}. Flux rate: –158 µg m^{-2} day^{-1} ($r^2 = 0.89$).

With the input of copper to the bay from antifouling paints applied to pleasure, commercial, and military vessels, it is not surprising that several sites have been reported to have total copper concentrations in excess of the 2.9 $\mu g\ L^{-1}$ Federal water quality criteria level. Elevated copper concentrations have been reported in the yacht harbor regions and Naval Station (Zirino et al., 1978; Krett, 1980; Johnston, 1990). The dissolved copper concentrations measured in this study during hull cleaning activity (figures 16 through 25) were generally 10 $\mu g\ L^{-1}$ or less and compared with dissolved copper concentrations previously measured in the yacht harbor and Naval Station areas. The large contingent of pleasure craft in addition to commercial and military vessel presence can be expected to release copper into the bay on a continuing basis. A review of our bay wide survey data indicates that copper values will likely continue to persist throughout the bay at a concentration of 5 $\mu g\ L^{-1}$ or less (figures 7 through 12).

PACO Ore Terminal

The PACO ore terminal represents a unique historical copper input to the bay since the form of copper deposited in the surrounding sediments was a ore concentrate (cupric ferrous sulfide) from ship loading activity over-spill (Woodward–Clyde, 1991). The Regional Water Quality Control Board issued a Cleanup and Abatement Order (N. 85-91) to PACO Terminals, Inc., calling for the abatement of all copper discharge from the site and cleanup of copper-containing sediments in the site vicinity (Woodward–Clyde, 1991). Sediment copper concentrations as high as 58,269 mg kg^{-1} dry weight were measured near the pier area, thus causing concern (Woodward-Clyde, 1991). The San Diego Port Authority has taken responsibility for the cleanup process and has agreed to clean the contaminated sediment area to a 1000 mg kg^{-1} (ppm) isopleth (San Diego Port Authority, 1993, personal communication).

In the summary document cited above (Woodward–Clyde, 1991), the toxicity and bioavailability of copper from this site was evaluated. The findings of this report indicated that the copper present in the ore deposited in the surrounding sediment of the PACO ore terminal was not bioavailable and not toxic to marine species tested (including Pacific oyster embryos). Eight of nine species tested exhibited no toxicity response to sediments under standardized laboratory test conditions. The only toxic response was exhibited by the amphipod *Rhepoxynius abronius*. This response was independent of the sediment copper concentration. Natural populations of the mussel *Mytilus edulis* grow near the terminal in an area where some of the highest sediment copper concentrations were measured, suggesting that the sediment copper is not available/toxic to the mussels attached to structures in the water column. Additionally, mussels planted in the vicinity of the terminal as part of the California Mussel Watch Program, and collected from piers near the terminal, did not contain tissue copper concentrations significantly different from those in mussels collected from other areas in San Diego Bay (Woodward–Clyde, 1991).

The Woodward–Clyde study (1991) concluded that the 1000 mg kg^{-1} copper remediation objective for the sediments in the vicinity of the PACO ore terminal loading facility is highly protective of aquatic life and the designated beneficial uses of the bay. A yet higher sediment copper concentration could be accepted as well and still be protective to marine species and other resources. The principle reason for a lack of harmful effects from the elevated sediment copper concentration was concluded to be the unavailability and nontoxicity of the cupric iron sulfide in the copper ore. This form of copper is highly insoluble in anoxic sediments typified by those beneath the thin oxidized sediment layer at the surface. Additionally, there are several precipitation, complexation, and sorption reactions that convert copper into nontoxic forms in both anoxic and oxic waters limiting its availability to marine species. Some data are available for water column copper concentrations in this area (WESTEC, 1986). Samples measured 1 and 2 m above the sediment surface at high and low tides in an area where the sediment copper concentrations were high (19,800 mg kg^{-1} dry weight) ranged from 3 to 31 μg L^{-1} as total particulate copper (WESTEC, 1986). "Soluble" (that fraction passing a 0.45-μm filter) copper ranged from < 2-8 μg L^{-1}. The filtered water sample values are similar to those measured in our bay-wide surveys which ranged from 2.1 to 4.8 μg L^{-1} (figures 7 through 12).

SDG&E South Bay Power Station

In addition to input from antifouling paints, copper enters San Diego Bay waters via effluent water from the San Diego Gas and Electric (SDG&E) Company South Bay power plant. The effluent water must be monitored for heavy metals, including copper, at least semi-annually. Waste-stream effluent water containing copper from boiler cleanings (removal of deposits from the inside of the tubes) or boiler fireside washes (removal of deposits from the outside of the tubes) represents a worst-case example of effluent. Although treated prior to discharge, this effluent may still contain μg L^{-1} copper concentrations. Effluent metal cleaning water would be expected to have higher copper levels than effluent water generated during normal operations. Total copper from waste-stream metal washing effluent water measured on a semiannual basis during 1991–92 ranged from 0.03 to 0.31 lb day^{-1} (SDG&E, personal communication). No copper was detected during one sampling interval (EPA 220.1 atomic absorption direct aspiration measurement). The mean value of copper discharged during five monitoring intervals was 0.16 lb day^{-1}. The NPDES permit allows a 6 month median discharge level of 25 lb day^{-1}. These discharge concentrations are clearly within allowed limits and compare well with the majority of calculated copper loadings from hull cleaning activity (table 8).

Municipal/Naval Station Storm Water Runoff

Although it is a relatively infrequent event, storm runoff water may deposit a great deal of copper into the bay during rainy periods. Data from the EPA National Urban Runoff Program (NURP) summarized in Pitt and Field (1990) indicate that the median total copper concentration in storm-water drainage from large U.S. cities was 35 μg L^{-1}. The concentration of copper in apparently soluble forms exceeded 10 μg L^{-1} in some samples. During a storm, a great deal of copper would wash directly into San Diego Bay from the urban area via storm drains. An estimate by the U.S. Army Corps of Engineers (1975b) indicated that the runoff from city streets in the San Francisco Bay region could introduce 80 pounds of copper an hour to estuarine waters. It would not seem an unreasonable assumption that storm runoff from the city of San Diego would introduce a similar quantity of copper during storm periods.

Recent data from the Naval Station San Diego (Gadbois, 1992) indicate that storm runoff from the Naval Station contributes effluent containing a relatively high copper concentration to the adjacent bay area via storm drains. The runoff effluent is high in contaminants because there is no centralized conveyance for mixing prior to release into the bay. Gadbois (1992) reported that 70 to 80% of precipitation in the Naval Station area can be expected to enter the bay as runoff due to the high degree of paved surface and low surface permeability. If the copper runoff data reported in Gadbois (1992) are compared with data reported in the EPA nationwide urban runoff program, it is clear that a relatively high level of copper is discharged into the bay immediately surrounding the Naval Station during storm activity.

The mean copper concentration in storm runoff reported in the NURP study (U.S. EPA, 1983) ranged from 25 μg L^{-1} in a 52% industrial area to 36 μg L^{-1} in a 100% industrial area.

The copper concentrations measured in storm runoff from 14 separate sites in the Naval Base reported in Gadbois (1992) ranged from 120 to 18300 μg L^{-1} and averaged 190 μg L^{-1}. The majority of measurements reported by Gadbois (1992) were above the state water copper concentration objective of 2.9 μg L^{-1} by nearly two orders of magnitude. Action is being taken by state regulatory agencies to minimize pollutants in storm runoff. It is likely that some reduction of copper input to the surrounding bay area will occur from implementation of best management practices to minimize inputs. Some degree of copper input will, however, most likely continue from storm runoff. If best management practices decrease input by an order of magnitude, then the storm runoff input of copper would be similar to the highest copper concentrations measured in the plume samples collected 3 meters from a ship hull. If the copper concentration in storm water runoff from the Naval Station were decreased by two orders of magnitude, the input would be similar to copper concentrations measured farther from ship hulls during cleaning operations, as well as similar to concentrations measured in the bay-wide monitoring surveys.

DISCUSSION

Our bay-wide water column copper measurements and hull cleaning surveys have demonstrated that copper concentrations may exceed water quality criteria throughout the bay. Copper input due to hull cleaning operations was determined to be a short-term spatial and temporal input. In the open bay main channel off the Naval Station, water samples averaged 3.8 $\mu g\ L^{-1}$. Collectively, the average dissolved copper concentration in water samples collected from all ships studied before all hull cleanings was 5.8 $\mu g\ L^{-1}$, and 6.0 $\mu g\ L^{-1}$ after hull cleanings at Piers 12 and 13 within the Naval Station. While hull cleaning operations resulted in locally elevated water column copper concentrations in some instances, clearly, during a period of several hours, overall average concentrations returned to ambient levels.

The widespread presence of copper in the bay is not surprising when the historical presence of pleasure, commercial, and military vessels is considered. The persistent input of copper from antifouling paints (56 metric tons of copper applied yearly) may be considered a historical and continuing source of copper on a bay-wide scale. Although it is difficult to calculate the actual input from leaching processes due to a great deal of uncertainty regarding vessel size, usage, and paint type, a great deal of copper enters the bay from antifouling paints on a daily basis. Additionally, the input of copper from urban storm-water runoff, existing areas of polluted sediment, and power plant operations further contributes to the copper level of bay waters. With the exception of the input from the PACO Ore Terminal area that will undergo remedial action, the other sources of input are expected to continue on a similar scale. We do not, therefore, predict that copper levels in the bay are likely to decrease, and those recently measured may be considered characteristic of present as well as future levels.

To put the input of copper from Naval hull cleaning operations into San Diego Bay in perspective, we have composed a graphical summary of yearly inputs from several principal sources (figure 31). Clearly, pleasure craft and the naval fleet are the major sources of copper from antifouling paints to the surrounding bay waters. The inputs from a power plant and commercial shipping are quite small. The Naval hull cleanings (29 events in 1993) accounted for a comparatively small input to bay waters.

Several assumptions were made to develop these estimates. A common leach rate of 10 $\mu g/cm^2$/day was assumed for all small craft, naval vessels, and commercial vessels based on an estimate of the required amount of copper leachate necessary to control fouling (Preiser et al., 1977). Since paints may vary in their copper content and leach rate, a single estimate was used for all vessel sources. Wetted hull areas were estimated from data reported in Grovhoug et al., (1989) for pleasure and commercial vessels. An average wetted hull area of 35,000 sq. ft. was assumed for naval vessels since this would average both very large and smaller vessels. We assumed that of the 51 naval vessels currently homeported in San Diego, 40 might be in port. The area of cleaning influence described by a cylinder with a radius of 101 m and depth of 9 m multiplied by the average copper concentration from the mid-depth and mid-hull transect of the USS DURHAM cleaning was used to estimate hull cleaning input. These particular copper values were used because they have the best and most complete regression data available. Data reported for NPDES discharges from the SDG&E South Bay power plant were used to estimate the yearly power plant input. We did not estimate urban copper runoff since such an estimate is difficult due to rainfall variability in San Diego. The urban runoff input would, of course, lessen the percentages of the other input sources.

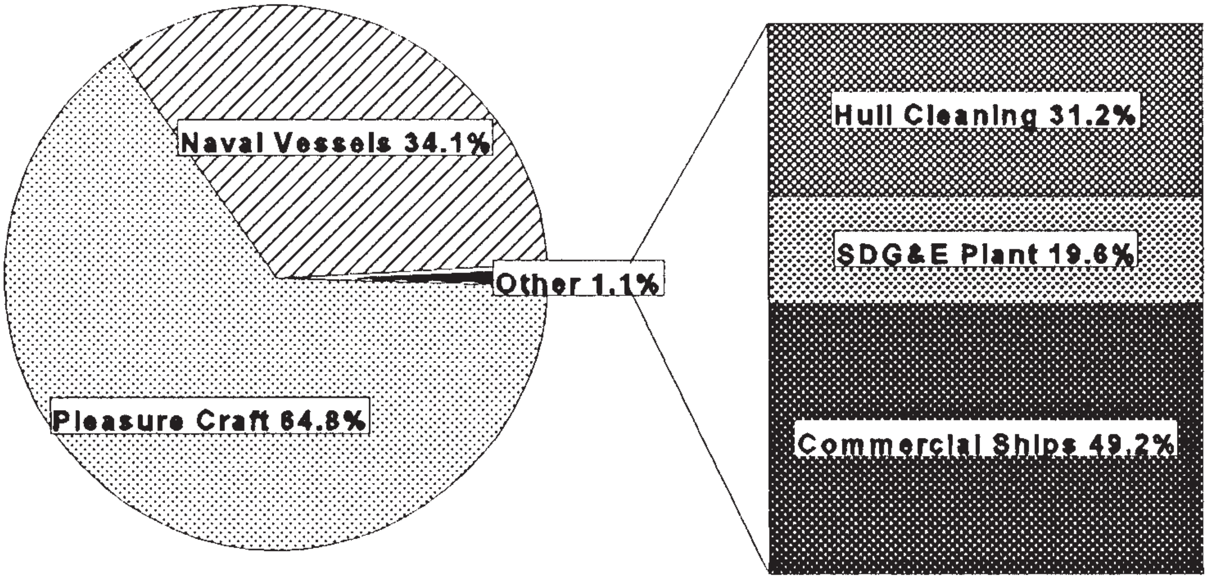


Figure 31. Relative estimated copper loading from antifouling paint and other sources into San Diego Bay per year.

With regard to current water column copper concentrations, the degree of toxicity is of fundamental importance since concentrations are frequently above the water quality criteria. The ion-selective electrode data reported in this study strongly suggest that activity of Cu^{++} (that which may be considered most available and toxic to organisms) is an extremely small fraction (concentrations as low as 0.06 ng L^{-1}) of the total copper measured. The dissolved copper fraction was elevated during cleaning activity, but quickly returned to ambient levels in a matter of a few hours. The hull cleaning debris was largely particulate copper as evidenced by comparison of total and particulate copper concentrations. Particulate copper was frequently 50 to 80% of the total copper measured and is not considered available to water column organisms. The algal test IC_{50} estimates of 42 to 45 µg L^{-1} copper from the hull cleaning effluent collected in this study emphasize the likely non-availability of copper released from cleaning operations to resident algal species, which have been shown to be resistant to copper at the Naval site as well (Krett, 1980). If copper in the hull cleaning effluent was more available (i.e., present to a greater degree in the dissolved phase than ISE measurements have shown), then the algal IC_{50} concentrations should have been much lower than those calculated in this study. The algal IC_{50} values determined in this study are in agreement with literature values cited in table 2 that summarizes the widely varying toxicity of copper to marine species.

If the estimates of dissolved copper in our study are accurate, and the labile fraction measured by ASV is not toxic, then the site specific water quality criterion for the surrounding waters of the Naval Station would be expected to be well above the general value of 2.9 µg L^{-1}. This assumption should be tested using the EPA toxicity testing protocols discussed in the regulatory status section of this report. If our assumptions are accurate, a positive water effect ratio could be determined via toxicity testing using reference and site-specific waters. If this ratio were simply a factor of two, then the resultant site-specific water quality criteria would be $2.9 \times 2 = 5.8$ µg L^{-1} copper (fraction passing a 0.45-µm filter). Such a concentration is essentially the average copper water concentration measured at the hull cleaning sites before and after hull cleaning operations.

The particulate copper released by the hull cleaning operations settles to the bottom in the vicinity of the parent ships. Our benthic flux data measured at the Paleta Creek site near Pier 8 at the Naval Station indicated that no positive copper flux was occurring. Since this area is very near and similar in sediment particle size characteristics to the sites at the Naval Station where hull cleanings occurred, we would not expect a positive flux of copper from the hull cleaning sites, given a period of equilibration where natural processes would act to bind the copper deposited in the underlying sediments. Only one sediment sample measured at the hull cleaning sites registered a total copper concentration above 1000 mg kg^{-1}, which is the clean-up limit acceptable at the PACO Ore Terminal determined by the Regional Water Quality Control Board. Therefore, the hull cleaning operations have not resulted in unacceptable deposits of copper to the underlying bay sediments.

During the hull cleaning process, biomass debris is released and settles to the sediment. Previous unpublished hull cleaning data indicated that the biomass settling to the sediment was not sufficient to cause adverse effects of burial of indigenous species. Subsequent increases in biological oxygen demand due to release of hull debris also was not a significant problem.

CONCLUSIONS

- Copper concentrations in San Diego Bay water and sediment have apparently remained similar over at least the last 10 years, including areas near the Naval Station.
- Initial and post-cleaning copper concentrations were above the EPA's 2.9-ppb water quality criteria concentration. During hull cleaning operations, initial and post-cleaning copper concentrations were well below the 42 to 45 ppb EC_{50} toxicity threshold determined for algae using the Qwik-Lite chlorophyll bioassay. The data indicate that cleaning activity did not result in copper concentrations toxic to algae. ISE measurements indicate that dissolved copper concentrations were well below values reported to be toxic.
- Sediment benthic flux measurements indicated that copper in sediment near the hull cleaning area at the Naval Station would not likely become available to the overlying water column due to a negative flux measured. It may be assumed due to the proximity and similar sediment characteristics that copper in sediments from the hull cleaning area would also bind to the sediments.
- Only a single sediment sample collected at the hull cleaning sites exceeded the copper level accepted as protective of marine species in the bay (1000 ppm). Only one before-and-after comparison of copper in sediment collected from the hull cleaning sites indicated an increase in copper from cleaning activity. Hull cleaning activities do not appear to significantly increase toxic levels of copper in bay sediments.
- Inputs of copper to San Diego Bay are varied and will likely result in continued levels of copper similar to those found during this study. The occasional cleaning of Navy ship hulls did not result in increased copper concentrations beyond a very brief period of time; nor were copper concentrations measured above levels toxic to algae. This suggests that other marine species would not be adversely affected at the copper concentrations measured.

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This field study evaluates the magnitude of environmental effects attributable to in-water hull cleaning operations in a typical Navy harbor. San Diego Bay was selected for detailed analyses of vessels coated with copper-based antifouling paint. This evaluation can be used to support discussions with environmental regulators, strengthen future compliance strategies, and provide a framework for future monitoring studies.

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