Estuaries Vol. 27, No. 3, p. 437–447 June 2004

Spatial and Temporal Variations in Copper Speciation in San Diego Bay

A. C. Blake[1,*], D. B. Chadwick[1], A. Zirino[2], and I. Rivera-Duarte[1]

[1] *Space and Naval Warfare Systems Center, Marine Environmental Quality Branch, Code 2362, 53475 Strothe Road, San Diego, California 92152*
[2] *Scripps Institution of Oceanography, Mail Code 0202, La Jolla, California 92093*

ABSTRACT: Copper in estuaries has been an issue of concern for its toxicity to marine organisms. The ability to understand the processes that control copper speciation is a key factor towards achieving an improved assessment of the ecological risk it poses in the marine environment. Field measurements were made in August 2000, January 2001, May 2001, and September 2001 to provide a comprehensive view of circulation and water quality both spatially and temporally for the entire San Diego Bay. Rapid, underway, analysis of copper provided a unique, high-resolution view of total and labile copper species. The data show that total copper concentrations in San Diego Bay have been close to or above water quality criteria, increasing gradually from the lowest values in the mouth region (8 nM) to the innermost region (approximately 55 nM) with elevated concentrations existing in the Shelter Island and Commercial Basins. This work indicates that free copper activity lies between 10^{-11} and 10^{-13}, and declines from the entrance to the head of San Diego Bay, even though the total copper concentration increases, a likely result of complexation with organic and particulate matter. Free copper measurements also show a seasonal dependence with the highest concentrations occurring 2 wk after a winter rain event in January 2001, reaching close to or above toxic levels in some locations.

Introduction

Copper is one of the most ubiquitous contaminants found in many industrial and nonpoint source effluents that enter the marine environment. Sources of copper include leaching from antifouling hull coatings on ships, discharges from industrial facilities, ships, and small craft, stormwater and nonpoint source runoff, and resuspension of previously contaminated sediments disrupted during dredging operations and ship movements.

Copper in seawater exists as a number of chemical species, including the free hydrated ion ($Cu(II)_{aq}$), dissolved organic and inorganic complexes, colloidal complexes, and particulate copper (Santschi et al. 1997). All of the species exchange copper with one another at various rates via $Cu(II)_{aq}$; those that exchange most rapidly are in steady-state equilibrium with one another. While water quality criteria for copper are typically based on the total or dissolved concentration, a large body of scientific data indicates that it is the free or aqueous cupric ion, $Cu(II)_{aq}$, that relates best to copper toxicity in marine organisms (i.e., Sunda and Guillard 1976; Buffle 1988; Buffle et al. 1990; Campbell 1995; Eriksen et al. 2001). This is because copper is strongly complexed by organic chelators (or ligands) in seawater, which lowers its biological availability and consequently its toxicity (Sunda and Guillard 1976; Anderson and Morel 1978; Seligman and Zirino 1998). Free copper in estuaries has been reported in the ranges of 0.16–3.16 pM (12.8–11.5 pCu) in the Scheldt estuary (Van den Berg et al. 1987), 0.16–6.31 pM (12.8–11.2 pCu) in the Severn estuary (Apte et al. 1990), and 0.32–10.00 pM (12.5–11 pCu) in Chesapeake Bay (Donat 1995). Previous field studies in San Diego Bay have shown that the concentration of $Cu(II)_{aq}$ ranges from 0.5–19.9 pM (12.3–10.4 pCu; Zirino et al. 1998a), which is $<0.01\%$ of the total copper measured.

To study the fate and ecological effects of copper loading in estuarine environments, a whole-basin project was launched in San Diego Bay in 1999. The objective of the project was to study the relationship between copper species and ecological risk in order to evaluate the relationship between various copper species in an estuarine system, determine the mass balance of copper in the system, and relate the observed speciation to a range of biological and ecological indicators of bay health. This paper represents one part of this study, focusing on the spatial and temporal distribution of copper species in San Diego Bay.

Study Location

San Diego Bay is a semi-enclosed, crescent-shaped embayment bordering the city of San Diego on the southernmost coast of California (Fig.

---

[*] Corresponding author; tele: 619/553-5753; fax: 619/553-3097; e-mail: amy.blake@navy.mil

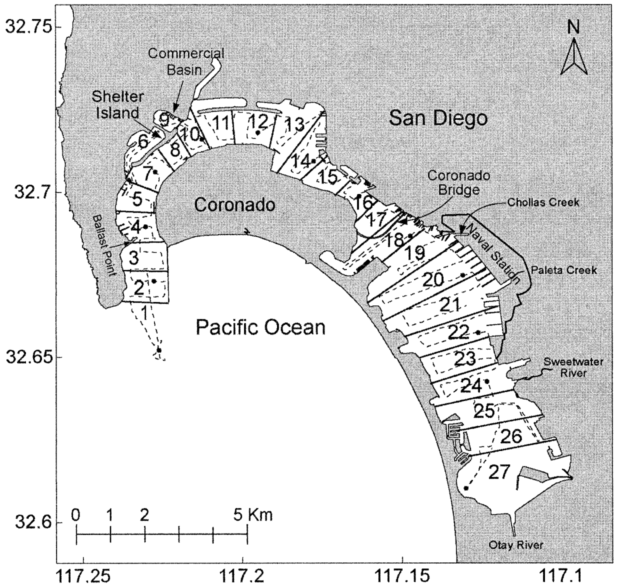

Fig. 1. Sampling transect in relation to the 1-dimensional model grid for San Diego Bay. The Bay was broken up into 27 box segments for data averaging.

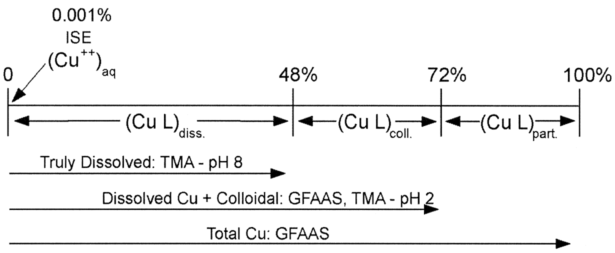

Fig. 2. A schematic diagram showing the relative distribution of copper species in San Diego Bay for the August 2000 survey.

1). The region south of the Coronado Bridge is commonly referred to as south bay or back bay, and the region north of the bridge to the bay's connection to the Pacific Ocean is considered north bay. Several creeks feed fresh water and particulate material into San Diego Bay, including the Sweetwater River, Otay River, Paleta Creek, and Chollas Creek. Freshwater inflow occurs infrequently during the winter and is insignificant during the majority of the year (Largier et al. 1997).

Historical data have shown that total copper concentrations in San Diego Bay increase gradually from the lowest concentrations at the mouth to the innermost region (Zirino et al. 1978; Flegal and Sañudo-Wilhelmy 1993; Esser and Volpe 2002). Particularly in the south bay region, dissolved copper concentrations are close to or above water quality criteria of 49 nM for chronic exposure (U.S. Environmental Protection Agency [EPA] 1995). The primary source of dissolved copper to the Bay is from copper-based antifouling paints used on ship and pleasure boat hulls (Valkirs et al. 1994; Johnson et al. 1998). Studies have shown that passive leaching and release during in-water hull cleaning account for 67% of the total loading to the bay (Valkirs et al. 2003; Chadwick et al. 2004). Several hot spots with concentrations consistently exceeding the criteria also exist: the Shelter Island Basin (Phillips 1988; Stevens 1988; Van der Weele 1996) and Commercial Basin (Katz 1998). Both are semi-enclosed basins where a large number of pleasure craft are located. A survey of boat owners and maintenance companies with boats moored in San Diego Bay revealed that over 90% of the vessels used conventional leaching paints that had copper as the primary biocide (Nichols 1988). Hull cleanings also add an additional source of copper into the water.

Methods

Data was collected using the Marine Environmental Survey Capability (MESC) system to characterize spatial and temporal conditions in San Diego Bay. The MESC system is a real-time data acquisition and processing system designed and built by the Navy to provide integrated, rapid, continuous measurement and synoptic mapping of oceanographic and environmental parameters in coastal and estuarine environments (Chadwick and Salazar 1991; Katz and Chadwick 1993). The MESC system measures physical, chemical, and biological characteristics from a moving vessel using state-of-the-art sensors, computer systems, and navigation equipment. This approach allows for direct, in situ measurements at a frequency commensurate with scales of natural and anthropogenic variability. To assess bay conditions and contaminant distributions, surveys were conducted in August 2000, January 2001, May 2001, and September 2001. Data were collected along a transect outlining 27 contiguous box-like segments following the axis of the Bay (Fig. 1). Real-time data were typically collected while moving at speeds up to 6 kts, which at a 4-Hz sampling rate, enabled along-track spatial resolution of data to less than 1 m.

The MESC real-time system employs both a towed sensor package and a seawater flow-through system that provides a continuous stream of seawater to a suite of onboard sensors. Sensors in the towed package consisted of a Seabird conductivity, temperature, and depth profiler (CTD), outfitted with a pH probe and dissolved oxygen sensor, a SeaTech light transmissometer, and a Chelsea Instruments UV Aquatracka ultraviolet fluorometer for hydrocarbon detection. Onboard sensors included two fluorometers (Turner Instruments) in-

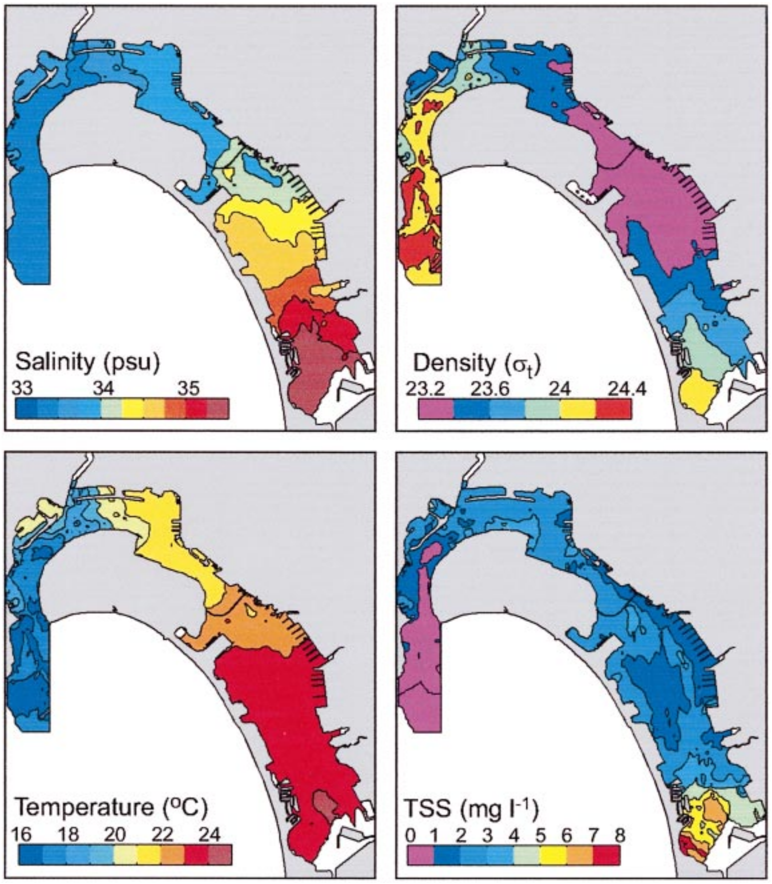

Fig. 3. Contour plots of salinity, temperature, density, and total suspended sediments (TSS) for the August 2000 survey. These distributions are typical of steady-state summer conditions in the San Diego Bay.

dependently set up to measure hydrocarbon and chlorophyll fluorescence, an automated trace metal analyzer (TMA), and an RD Instruments Workhorse acoustic doppler current profiler.

In addition to the real-time measurements, the MESC flow-though system was used to collect integrated seawater samples in a 16-l carboy, pumped from approximately 2 m below the surface during the transect through each box. Discrete samples were used to calibrate the real-time sensors and to provide additional analyses. Subsamples were analyzed for total and dissolved Cu concentrations and total suspended sediments (TSS). TSS was measured by filtering water samples from each box and drying to determine the total weight of dry sediments.

COPPER MEASUREMENTS

A unique, high-resolution measure of near-total and labile Cu species was obtained by using two TMAs, one at pH 2 and the other at pH 8. Data from the pH 8 instrument was only collected during August 2000, after which the TMA was dedicated to underway measurements of Zn. The TMA enables near real-time (1 sample per 5 min), unattended measurement of trace metals in the field with a significant cost savings over traditional graphite furnace atomic adsorption spectroscopy (GFAAS) and inductively coupled plasma mass spectroscopy methods. Using the TMA for in situ surveys also minimizes errors associated with sample collection and storage (Tercier and Buffle 1993). The TMA measured dissolved metals using an automated Au-film (pH 2) or Hg-film (pH 8) and a potentiometric stripping analysis technique (Wang et al. 1995). The pH 2 technique provides results comparable to traditional methods for truly dissolved and colloidal copper species combined; the pH 8 analysis provides results comparable to the truly dissolved species, which includes Cu complexed with strong chelating ligands such as ethylenediamine (Zirino et al. 1998a; Fig. 2). For measurements made at pH 2, approximately 3 ml of unfiltered water from the flow-through system were brought into an analysis cell where hydrochloric acid was added (to pH 2) to aid in sepa-

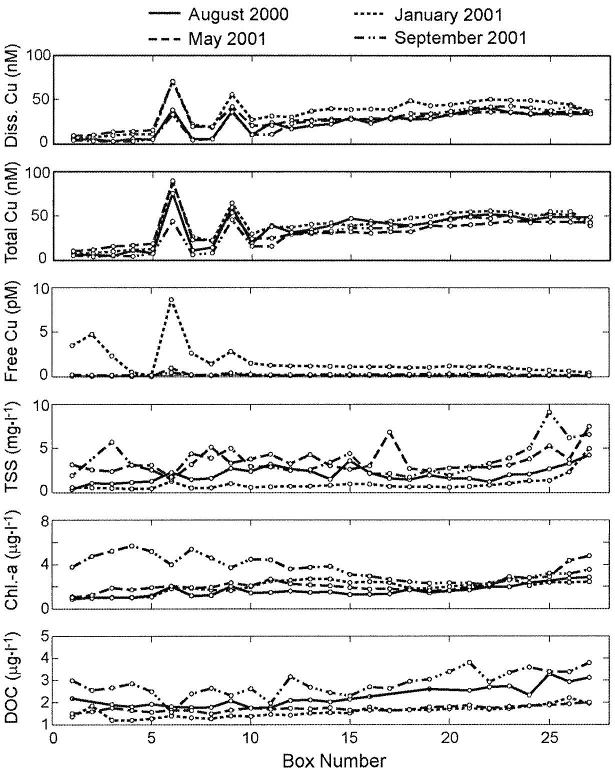

Fig. 4. Box-averaged concentrations of dissolved copper, total copper, free copper, TSS, chl *a,* and DOC show trends along the axis of the Bay for the four surveys. Boxes 6 and 9 represent the Shelter Island and Commercial Basins, respectively.

rating the metal ions from the organic complexing matrix and transferring to the Au-film. Dissolved and colloidal copper were plated onto the Au-film using a potential of −0.4 V for 60 s, then stripped off at a constant 2-μA current. Serial additions of a copper standard were made with each run to quantify the amount of metal present in the seawater sample. The nominal sampling interval for the analysis was 7 min. For the pH 8 analysis, approximately 3 ml of unfiltered water from the MESC's flow-through system was brought into an analysis cell where sodium citrate and mercuric chloride were added to aid in the transfer of metal ions to the Hg-film, but no adjustment was made to the pH of the solution (ambient pH approximately 8). Dissolved copper was plated onto the Hg-film using a potential of −1.1 V for 120 s, then stripped off at a constant 2-μA current. Ethylenediamine was added to the cell just before stripping to promote the oxidation of copper (Scarano et al. 1990). Serial additions of a Cu standard were made with each run to quantify the amount of metal present in the seawater sample. The nominal sampling interval for the analysis was 9 min. The method detection limit for the TMA is 11 nM.

The concentration of Cu(II)$_{aq}$ was measured using a jalpaite copper ion selective electrode (Cu-ISE), which permits the precise measurements of pCu in seawater (Belli and Zirino 1993; DeMarco et al. 1997; Zirino et al. 1998b). The Orion electrode measures hydrated divalent copper ions (Cu(II)$_{aq}$) in terms of pCu, where pCu = $-\log_{10}(\text{Cu[II]}_{aq})$, when calibrated with glycine and ethylenediamine copper buffers (Belli and Zirino 1993; DeMarco et al. 1997). The precision of the Cu-ISE is ±0.06 pCu units (Zirino et al. 1998b), and the electrode is effective at total copper concentrations <3 nM (Zirino et al. 2002). Cu(II)$_{aq}$ concentrations were measured using the onboard flow-through water system. In this mode, the continuous flow of water past the sensor permits accurate measurement without rotating the electrode. The Orion Cu-ISE has been shown to leach copper when used in seawater; however, this is not a problem in flowing systems (Zirino et al. 2002).

Discrete samples were collected through an acid-cleaned tow system on the bow of the boat for the measurement of filtered ($\leq$0.45 μm) and unfiltered total copper concentrations. Samples were collected using trace metal clean techniques in 1-l acid-cleaned, low-density polyethylene bottles, using acid-cleaned Teflon and Masterflex tubing and a peristaltic pump. Filtered samples were collected simultaneously through in-line, acid-cleaned Calix all-polypropylene 0.45 μm pore-size cartridge filters. The copper in the samples was pre-concentrated by liquid-liquid extraction with ammonium 1-pyrrolidinedithiocarbamate (APDC) and diethylammonium diethyldithiocarbamate (DDDC; Bruland et al. 1985) and was measured by GFAAS using stabilized temperature platforms and the method of standard additions. The efficiency of the extraction was 102 ± 8.6% (average ± standard deviation, n = 4) for the standard reference material NIST-SRM 1643d (trace elements in water), and 98% ± 8.8% (n = 18) for certified reference materials CASS3 and CASS4. The variation of replicate analysis was $\leq$12%, and the method limit of detection was 0.06 ± 0.03 nM (n = 8).

Results

AUGUST 2000

Salinity and temperature values increase towards the back of the bay, ranging from 33.5 psu and 16.3°C, respectively, at the mouth to 36.0 psu and 25.1°C, respectively, in the back bay. TSS values were generally low throughout the bay (<4 mg l^{-1}) with a sharp increase in the back bay reaching concentrations of 8.5 mg l^{-1}. A plume characterized by higher TSS concentrations and often a distinct thermal signal, has been observed to persist in the southernmost region of the Bay. Figure 3 shows salinity, temperature, density, and TSS for the survey, which are typical of steady-state summer conditions in the bay. Chl *a* concentrations were lowest at the mouth of the Bay and increased progressively to the southernmost sampling site. Chlorophyll values ranged 0.76–3.43 $\mu g\ l^{-1}$, with the highest measured values occurring in the south Bay and the Shelter Island Basin (Fig. 4).

TMA measurements at both pH 2 and pH 8 show an increase in copper concentration towards the south Bay region. The TMA operating at pH 2 showed concentrations ranging from below the detection limit (<5 nM) to 60 nM (Fig. 5) with maximum concentrations in the main channel just outside of Naval Station San Diego (Box 20–21). The TMA operating at pH 8 showed concentrations ranging from <5 to 45 nM with high concentrations recorded with both the pH 8 and pH 2 meters occurring in the Shelter Island Basin. Free copper concentrations were generally constant throughout the main channel of the Bay (0.12 pM or 12.9 pCu), with increased values (0.50 pM or 12.3 pCu) in localized regions of high vessel surface area to water volume ratio, including the Shelter Island and Commercial Basins (Fig. 6). Total copper concentrations measured using GFAAS show increasing values from the mouth (6 nM) to the south bay (approximately 52 nM) with large peaks in the Shelter Island and Commercial Basins (Fig. 4).

JANUARY 2001

This survey took place after the onset of the winter rainy season, and illustrates the changes that take place during this time of year. Salinity decreased towards the back of the Bay, ranging from 33.5 psu at the mouth to 32.0 psu in the south Bay. Temperature values were relatively constant throughout the Bay (13.0–14.4°C), with the exception of a distinct thermal plume in the south Bay that reached 17.0°C. TSS values throughout the bay were relatively uniform but very low, ranging from 0.3 to approximately 2 $mg\ l^{-1}$. Increased TSS values in the vicinity of the thermal plume were observed, reaching 10.9 $mg\ l^{-1}$. Box-averaged data for salinity, temperature, and density are shown in Fig. 7.

Measurements from the trace metal analyzer at pH 2 show a general increase in copper concentration towards the mid bay region (Box 20–21). In the main body of the bay, concentrations ranged from below the detection limit to 32 nM (Fig. 5) with maximum concentrations in the main channel just outside of Naval Station San Diego. Hot spots were detected in the Shelter Island and Commercial Basins with concentrations reaching 94 nM. Free copper concentrations ranged from 0.32 to 1.26 pM (12.5–11.9 pCu) throughout the main channel of the bay, with the exception of a sharp decrease in values near Ballast Point (Box 4; Fig. 6). A marked increase in concentration is seen in regions of high vessel surface area to water volume ratio, including the Shelter Island and Commercial Basins. Total copper concentrations measured using GFAAS show increasing values from the mouth (7.8 nM) to the mid bay (55 nM; Box 22) and then decrease slightly towards the back Bay to 39 nM. Large peaks occur in the Shelter Island (87 nM) and Commercial Basins (63 nM; Fig. 4).

MAY 2001

Salinity increased towards the back of the Bay, ranging from 33.5 psu at the mouth to 34.4 psu in the south Bay, with a strong longitudinal gradient in the south Bay (Boxes 24–27; Fig. 7). Temperature values increase from 13.0°C at the mouth, warming to 23.7°C in the south bay. A thermal plume is evident, as well as high TSS values within the plume reaching 30.4 $mg\ l^{-1}$ (Fig. 4). TSS values through the rest of the Bay range from 1.5–7.5 $mg\ l^{-1}$ and chlorophyll values increased from 1.0 $\mu g\ l^{-1}$ at the mouth to 4.8 $\mu g\ l^{-1}$ in the south Bay.

Measurements from the trace metal analyzer at pH 2 (Fig. 5) show an increase in copper concentration from the mouth (below detection limit) with a maximum of 47 nM in the mid bay region (Boxes 20–21). Hotspots are located in the Shelter Island and Commercial Basins with concentrations reaching 72 nM. Free copper concentrations were generally uniform throughout the main channel of the bay (~0.10 pM or ~13 pCu), with the exception of a sharp decrease to 0.012 pM (13.9 pCu) near Ballast Point (Box 4; Fig. 6). An increase in free copper concentrations is seen in the Shelter Island (5.01 pM or 11.3 pCu) and Commercial Basins (1.0 pM or 12 pCu). Total copper concentrations measured using GFAAS show values increasing from the mouth (~11 nM) and leveling off at 44 nM in the south Bay from Boxes 23–27. Large peaks occur in the Shelter Island (90 nM) and Commercial Basins (54 nM; Fig. 4).

SEPTEMBER 2001

Salinity increased towards the back of the Bay, ranging from 33.4 psu at the mouth to 35.8 psu in the south Bay (Fig. 7). Temperature values increase from 15.0°C at the mouth to 25.4°C in the south Bay. A thermal plume is evident. TSS values ranged from 0.0 to 4.0 $mg\ l^{-1}$ throughout most of the Bay with values reaching 18.8 $mg\ l^{-1}$ within the plume (Fig. 4). Chlorophyll values ranged from 1.5 to 4.0 $\mu g\ l^{-1}$ throughout most of the Bay with an increase at the mouth on the eastern side of the

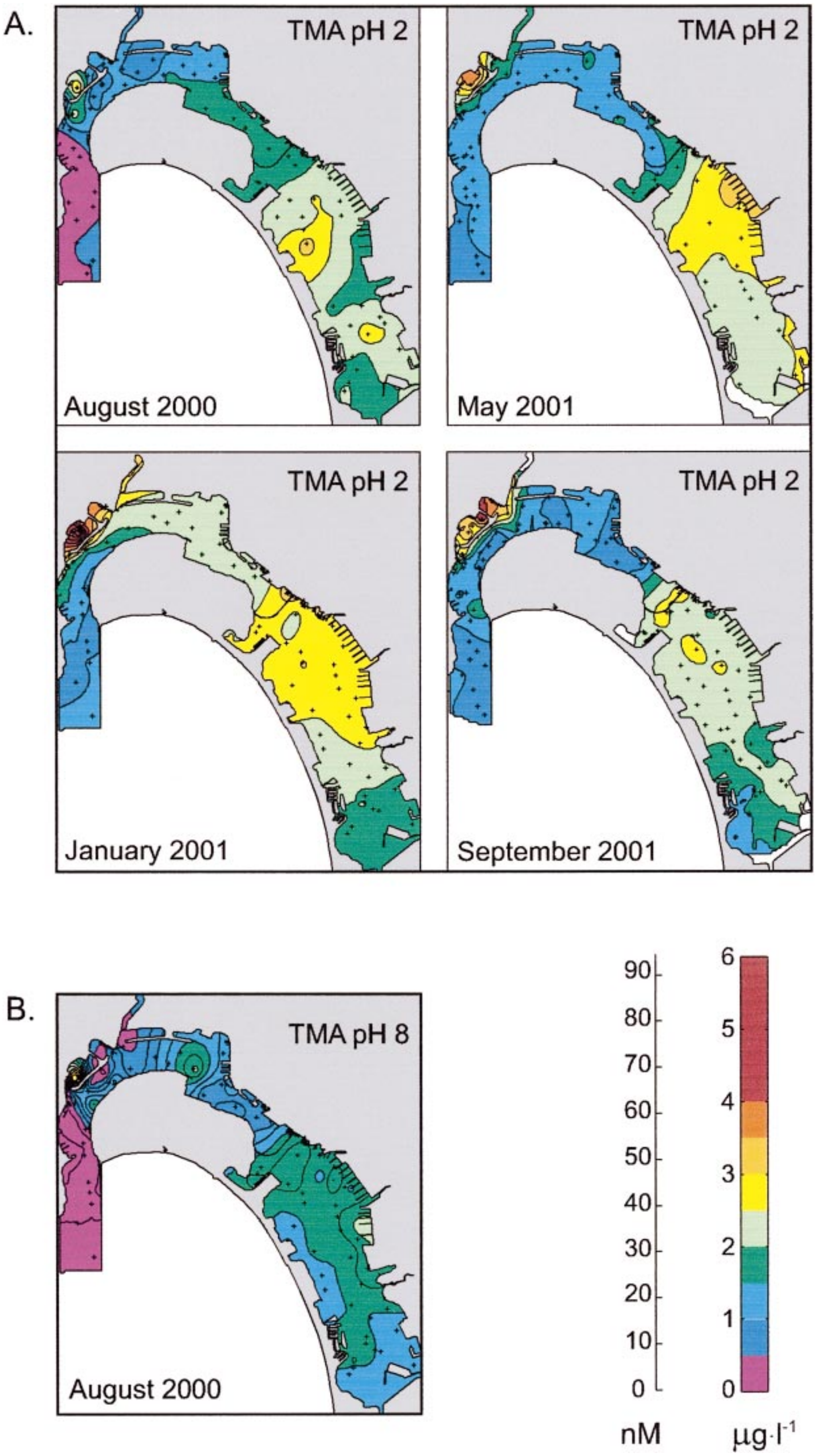

Fig. 5. Copper measurements from the pH 2 trace metal analyzer for all four surveys, which have been calibrated against discrete copper concentrations from the graphite furnace atomic adsorption spectroscopy, and copper measurements from the pH 8 trace metal analyzer during the August 2000 survey. Plus signs (+) represent sample locations.

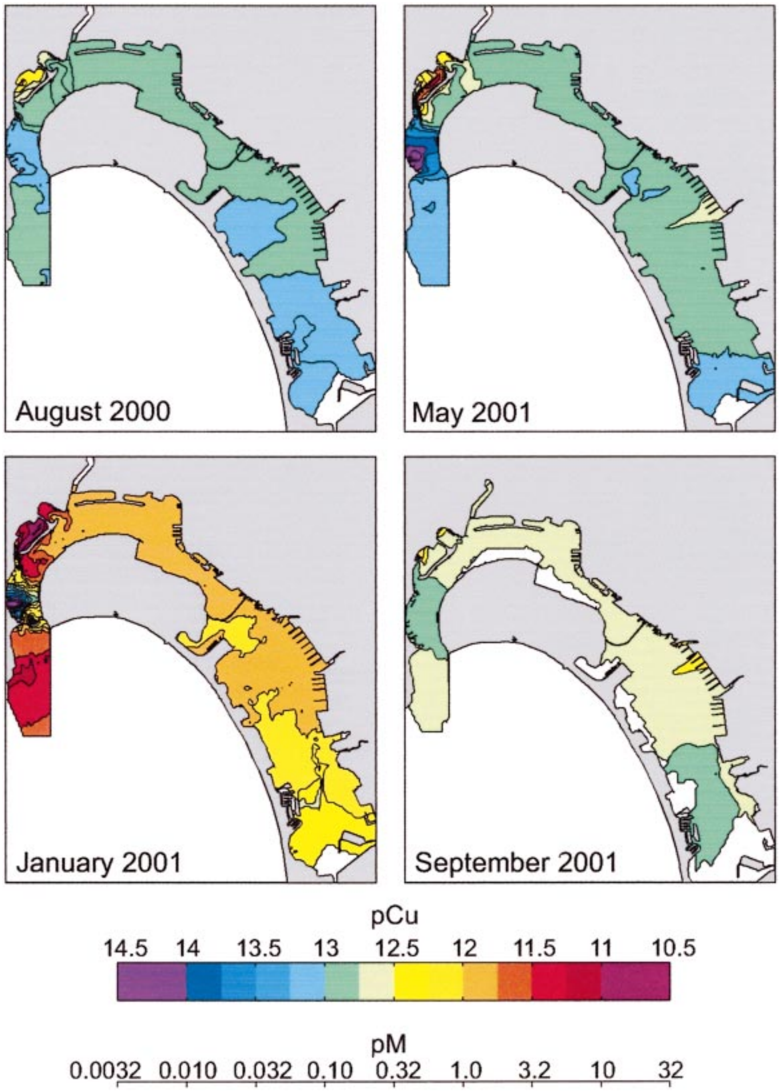

Fig. 6. Free copper activity measured with the Orion jalpaite-based ion selective electrode.

channel (~6 $\mu g\ l^{-1}$) as a result of a red tide occurring during the survey.

Measurements from the trace metal analyzer at pH 2 (Fig. 5) show an increase in copper concentration from the mouth (~4 nM) with a maximum in the mid-Bay region (31 nM; Box 20–21). Hotspots were located in the Shelter Island (63 nM) and Commercial Basins (82 nM). Free copper concentrations in the main channel of the Bay were generally uniform with a mid bay maximum (0.50 pM or 12.3 pCu; Fig. 6). A sharp increase in values is seen in the Shelter Island (2 pM or 11.7 pCu) and Commercial Basins (1 pM or 12.0 pCu). As seen in previous surveys, a decrease in free copper concentrations near Ballast Point is evident. Total copper concentrations measured using GFAAS show increasing values from the mouth (4.7 nM) to the south Bay (55 nM). Peaks occur in the Shelter Island (44 nM) and Commercial Basins (46 nM; Fig. 4).

Discussion

The distribution of hydrographic parameters in San Diego Bay indicated two distinct spatial regimes. Spatial distributions of salinity and temperature indicate an outer bay area, north of the Coronado Bridge (Boxes 2–10), that is strongly influenced by neighboring coastal waters. Fall and summer conditions south of Coronado Bridge (Boxes 18–27) indicate saltier, denser waters as a result of evaporation and limited mixing of coastal water into the south bay. Between these two end points is a transitional region (Boxes 11–17) where strong

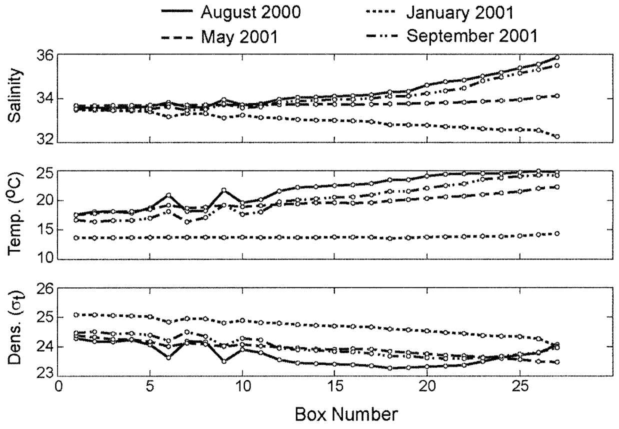

Fig. 7. Box-averaged measurements of salinity, temperature, and density show shifts in the hydrography of the system on a seasonal time scale.

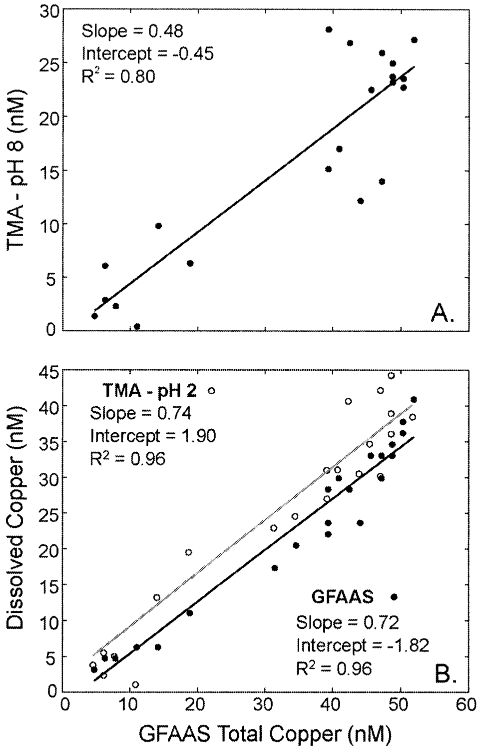

Fig. 8. Regressions of A) trace metal analyzer measurements at pH 8 and B) dissolved copper measurements from both GFAAS and trace metal analyzer (pH 2) methods to total copper. The slope of the regression shows the percent of total copper that is contributed by the copper species measured.

longitudinal gradients of salinity and temperature can be seen.

The distribution of salinity provides a tool to quantitatively assess the magnitude and extent of conservative mixing (Dyer 1997). For San Diego Bay, freshwater inflow is sporadic and steady-state conditions tend to develop in the summer and fall (August, May, and September surveys) in response to extended periods of heating and evaporation during which time hypersaline conditions persist in the back bay (Figs. 3 and 7; Largier et al. 1996, 1997). During the dry months, the salt balance is a function of the net evaporation of the system. Evaporation rates for the San Diego Bay have been estimated at 0.3–0.5 cm d^{-1} (Chadwick et al. 2004). Hypersaline basins are generally characterized by weak tidal dispersion, leading to long residence times in the basin (Largier et al. 1997). These systems are susceptible to pollution, as even small contaminant inputs during the hypersaline phase may be accumulated rather than flushed from the system. Residence times calculated for the San Diego Bay increase relatively linearly from 0 d at the mouth to 40 d at the innermost region of the bay (Chadwick et al. 2004). During the winter rainy season (January survey), freshwater input from creeks and surface water runoff is usually significant enough to reverse the salinity gradient (Fig. 7). Largier et al. (1997) terms this type of estuary, alternating between a classical estuary during wet months and a hypersaline estuary during dry months, a Mediterranean estuary. Similar systems are Elkhorn Slough, California (Smith 1973), Langebaan Lagoon, South Africa (Christie 1981), Peel-Harvey estuary, Western Australia (Hearn and Lukatelich 1990), and Tomales Bay, California (Largier et al. 1997).

Temperature measurements also show a seasonal dependence, increasing during the dry summer and fall months and decreasing in the winter with the onset of cooler air and ocean water temperatures. The salinity maximum in late summer coincides with the temperature maximum. The density structure of the outer estuary is dominated by temperature, whereas the inner estuary is dominated by salinity. During the late summer, a density minimum is seen in the mid bay, just south of the Coronado Bridge (Figs. 3 and 7).

Copper distributions in the Bay provide a means of examining the relative influence of sources, residence time, speciation, and sedimentation to the overall copper balance. The relative composition of each species to total copper for the August 2000 survey is shown in Fig. 2. A regression of raw TMA measurements at pH 8 to total copper show that the truly dissolved fraction makes up 48% of the total copper (Fig. 8). Copper concentrations from the GFAAS analysis are representative of the truly dissolved plus the colloidally-complexed fraction of copper, which constitute ~72% of the total copper. These measurements are in close agreement with discrete measurements of dissolved, colloidally-complexed copper from the TMA at pH 2, which yielded ~74% of the total copper. The remaining fraction of copper is bound by particulate matter and can be approximated as ~26% by subtracting the dissolved plus colloidally-complexed fraction (pH 2 results) from the total copper. This is consistent with the range of percent colloids in San Diego Bay as measured with an ultrafiltration system by Shafer (personal communication).

Total and dissolved copper concentrations show a strong linear relationship to one another and also show a strong correlation with residence time along the axis of the Bay ($R^2 > 0.82$; Chadwick et al. 2004). This implies that conservative mixing along the main channel of the Bay strongly influences the distributions of dissolved and total copper, regardless of the locations of the sources of these fractions. Localized areas of elevated concentration exist, predominately in small semi-enclosed basins around the Bay where strong sources are located and mixing is limited (i.e., Shelter Island and Commercial Basins). Seasonally, both total and dissolved copper concentrations change very little (Fig. 4), confirming that the sources and sinks of these copper species are not changing significantly over time. This finding reinforces results from more limited studies of San Diego Bay over the last 25 yr (Zirino et al. 1978, 1998a; Flegal and Sañudo-Wilhelmy 1993; Esser and Volpe 2002).

Free copper is generally uniform throughout the mid-Bay from Box 10–22, where concentrations begin to decrease (Fig. 6). In contrast to total and dissolved copper concentrations, a reduction in free copper from Boxes 23–27 coincides with increased DOC, chlorophyll, and TSS concentrations (Fig. 4), likely due to complexation with these binding materials. Free copper concentrations in the main channel of the Bay were on average 6 times higher during the January 2001 survey than for the other three surveys, and more than 10 times higher in the Shelter Island and Commercial Basins. This corresponds to a lack of available binding material in the Bay, as TSS (<1 mg l^{-1} throughout most of the Bay) and DOC (<2 μg l^{-1}) values were very low during this survey and the Bay water was exceedingly clear. Rivera-Duarte (personal communication) shows that toxicity to mussel larvae (*Mytilus galloprovincialis*) was reached consistently at pCu ≤ 11.0. A histogram of pCu values for all of the surveys showed that pCu < 11.0 only occurred during the January 2001 survey when the mean copper activity was ~12.0 pCu, while the mean concentration for all of the other surveys was ~13 pCu (Fig. 9).

The data presented here provide a unique, system-wide view of the seasonal and spatial variations of copper in a Mediterranean estuary. The relative uniformity of results indicates that a steady-state balance is achieved throughout most of the year for the dissolved, particulate, and colloidal fractions of copper in San Diego Bay, reflecting the continual input of copper from antifouling paint on ships, small craft, and other anthropogenic sources. While total and dissolved copper concentrations remain essentially constant over the four surveys, free copper concentrations vary as a result of changes in complexation. This shows that the concentration of dissolved copper, which is used as a measure of water quality, may remain constant from survey to survey while the amount of free copper changes based on the availability of binding materials. As a result, dissolved copper concentrations continually reach or exceed water quality thresholds; however, the Bay is shown to be below the toxic pCu limit except during winter surveys when complexation is low.

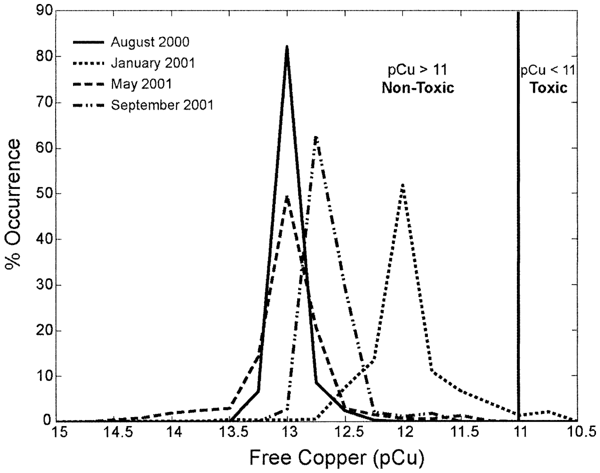

Fig. 9. Free copper concentrations for all four surveys show that values reached a toxic level (pCu < 11.0) only during the January 2001 survey. The mean concentration for the other surveys was 13 pCu, well above the level for toxicity to occur.

ACKNOWLEDGMENTS

This study was supported by the Office of Naval Research 6.2 program contract N6601-97-D-5028 and the Strategic Environmental Research and Development Program under the Project Number CP-1156. The authors acknowledge the assistance of Joel Guerrero and Lora Kear for analytical support, and Jon Groves and Brad Davidson for field support.

LITERATURE CITED

ANDERSON, D. M. AND F. M. M. MOREL. 1978. Copper sensitivity of *Gonyaulax tamarensis*. *Limnology and Oceanography* 23:282–295.

APTE, S. C., M. J. GARDNER, AND J. E. RAVENSCROFT. 1990. An investigation of copper complexation in the Severn estuary using differential pulse cathodic voltammetry. *Marine Chemistry* 29:63–75.

BELLI, S. L. AND A. ZIRINO. 1993. Behavior and calibration of the copper (II) ion-selective electrode in high chloride media and marine waters. *Analytical Chemistry* 65:2583–2589.

BRULAND, K. W., K. H. COALE, AND L. MART. 1985. Analysis of seawater for dissolved cadmium, copper and lead: An intercomparison of voltammetric and atomic absorption methods. *Marine Chemistry* 17:285–300.

BUFFLE, J. 1988. Complexation Reactions in Aquatic systems: An Analytical Approach. Ellis Horwood, Ltd., Chichester, U.K.

BUFFLE, J., R. S. ALTMAN, M. FILELLA, AND A. TESSIER. 1990. Complexation by natural heterogeneous compounds: Site occupation distribution functions, a normalized description of metal complexation. *Geochimica et Cosmochimica Acta* 54:1535–1553.

CAMPBELL, P. G. C. 1995. Interactions between trace metals and aquatic organisms: A critique of the free-ion activity model, p. 45–97. *In* A. Tessier and D. R. Turner (eds.), Metal Speciation and Bioavailability in Aquatic Systems. John Wiley and Sons, London, U.K.

CHADWICK, D. B. AND M. H. SALAZAR. 1991. Integrated measurement technologies for monitoring the marine environment, p. 343–350. *In* Proceedings of Oceans 91 Meeting, October 1–3, 1991. Oceanic Engineering Society of the Institute of Electrical and Electronics Engineers, Honolulu, Hawaii.

CHADWICK, D. B., A. ZIRINO, I. RIVERA-DUARTE, AND A. C. BLAKE. 2004. Modeling the mass balance and fate of copper in San Diego Bay. *Limnology and Oceanography* 49:355–366.

CHRISTIE, N. D. 1981. Primary production in Langebaan Lagoon, p. 101–115. *In* J. H. Day (ed.), Estuarine Ecology: With Particular Reference to South Africa. Balkema, Rotterdam, Netherlands.

DEMARCO, R., D. J. MACKEY, AND A. ZIRINO. 1997. Response of the jalpaite membrane copper(II) ion-selective electrode in marine waters. *Electroanalysis* 9:330–334.

DONAT, J. R. 1995. The speciation of dissolved copper and cadmium in the Chesapeake Bay. 209th American Chemical Society National Meeting. American Chemical Society Division of Geochemistry, Anaheim, California.

DYER, K. R. 1997. Estuaries: A Physical Introduction. John Wiley and Sons, Ltd., New York.

ERIKSEN, R. S., D. J. MACKEY, R. VAN DAM, AND B. NOWACK. 2001. Copper speciation and toxicity in Macquarie Harbor, Tasmania: An investigation using a copper ion selective electrode. *Marine Chemistry* 74:99–113.

ESSER, B. K. AND A. VOLPE. 2002. At-sea high-resolution trace element mapping: San Diego Bay and its plume in the adjacent coastal ocean. *Environmental Science and Technology* 36:2826–2832.

FLEGAL, A. R. AND S. A. SAÑUDO-WILHELMY. 1993. Comparable levels of trace metal contamination in two semi-enclosed embayments: San Diego Bay and South San Francisco Bay. *Environmental Science and Technology* 27:1934–1936.

HEARN, C. J. AND R. J. LUKATELICH. 1990. Dynamics of Peel-Harvey estuary, Southwest Australia, p. 431–450. *In* R. T. Cheng (ed.), Residual Currents and Long-term Transport. Springer-Verlag, New York.

JOHNSON, H. D., J. G. GROVHOUG, AND O. A. VALKIRS. 1998. Copper loading to U.S. Navy harbors. Technical Document #3052. Space and Naval Warfare System Center, San Diego, California.

KATZ, C. N. 1998. Seawater polynuclear aromatic hydrocarbons and copper in San Diego Bay. Technical Document #1768. Space and Naval Warfare System Center, San Diego, California.

KATZ, C. N. AND D. B. CHADWICK. 1993. Synoptic mapping and modeling of a sewage outfall plume, p. 207–215. *In* Proceedings of the Marine Technology Society 1993 Conference. Marine Technology Society, Long Beach, California.

LARGIER, J. L., C. J. HEARN, AND D. B. CHADWICK. 1996. Density structures in low inflow estuaries, p. 227–242. *In* D. G. Aubrey and C. T. Friedrichs (eds.), Buoyancy Effects on Coastal Dynamics, Volume 53. American Geophysical Union, Washington, D.C.

LARGIER, J. L., J. HOLLIBAUGH, AND S. SMITH. 1997. Seasonally hypersaline estuaries in Mediterranean-climate regions. *Estuarine, Coastal and Shelf Science* 45:789–798.

NICHOLS, J. A. 1988. Antifouling paints: Use on boats in San Diego Bay and a way to minimize adverse effects. *Environmental Management* 12:243–247.

PHILLIPS, P. T. 1988. California state mussel watch: Ten year data summary 1977–1987. Water Quality Monitoring Report No. 87-3. State Water Resources Control Board, Sacramento, California.

SANTSCHI, P. H., J. J. LENHART, AND B. D. HONEYMAN. 1997. Heterogeneous processes affecting trace metal contaminant distribution in estuaries: The role of natural organic matter. *Marine Chemistry* 58:99–125.

SCARANO, G., E. MORELLI, A. SERITTI, AND A. ZIRINO. 1990. Ethylenediamine for the measurement of copper in seawater by anodic stripping voltammetry. *Analytical Chemistry* 62:943–948.

SELIGMAN, P. F. AND A. ZIRINO (eds.). 1998. Chemistry, toxicity, and bioavailability of copper and its relationship to regulation in the marine environment. Office of Naval Research Workshop report, Technical Document 3044. Space and Naval Warfare Systems Center, San Diego, California.

SMITH, R. E. 1973. The hydrography of Elkhorn Slough; a shallow California coastal Embayment. Technical Publication 73-2. Moss Landing Marine Laboratories, Moss Landing, California.

SUNDA, W. G. AND R. L. GUILLARD. 1976. The relationship between cupric ion activity and the toxicity of copper to phytoplankton. *Journal of Marine Research* 34:511–529.

STEVENS, T. P. 1988. California state mussel watch: Marine water quality monitoring program 1986–1987. Water Quality Monitoring Report No. 88-3. California State Water Resourced Control Board, Sacramento, California.

TERCIER, M. L. AND J. BUFFLE. 1993. In situ voltammetric measurements in natural waters: Future prospects and challenges. *Electroanalysis* 5:187–200.

U.S. ENVIRONMENTAL PROTECTION AGENCY (EPA). 1995. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to west coast marine and estuarine organisms. Section 15: Purple urchin, *Stronglyocentrotus purpuratus* and sand dollar, *Dendraster excentricus* larval development test method. EPA/600/R-95/136. U.S. EPA, Washington, D.C.

VALKIRS, O. A., B. M. DAVIDSON, L. L. KEAR, R. L. FRANSHAM, A. ZIRINO, AND J. G. GROVHOUG. 1994. Environmental effects from in-water hull cleaning of ablative copper antifouling coatings. Technical Document #2662. Space and Naval Warfare System Center, San Diego, California.

VALKIRS, A. O., P. F. SELIGMAN, E. HASLBECK, AND J. S. CASO. 2003. Measurement of copper release rates from antifouling paint under laboratory and in situ conditions: Implications for loading estimation to marine water bodies. *Marine Pollution Bulletin* 46:763–779.

VAN DEN BERG, C. M. G., A. G. A. MERKS, AND E. K. DUURSMA. 1987. Organic complexation and its control of the dissolved concentrations of copper and zinc in the Scheldt estuary. *Estuarine, Coastal and Shelf Science* 24:785–797.

VAN DER WEELE, D. A. 1996. The effects of copper pollution on the bivalve, *Mytilus edulis* and the amphipod, *Grandidierella japonica* in Shelter Island yacht basin, San Diego Bay, California. M.S. Thesis, San Diego State University, San Diego, California.

WANG, J., N. S. FOSTER, S. ARMALIS, D. LARSON, A. ZIRINO, AND K. OHLSEN. 1995. Remote stripping electrode for in situ monitoring of labile copper in the marine environment. *Analytica Chimica Acta* 310:223–234.

ZIRINO, A., S. L. BELLI, AND D. A. VAN DER WEELE. 1998a. Copper concentration and Cu-II activity in San Diego Bay. *Electroanalysis* 10:423–427.

ZIRINO, A., R. DEMARCO, I. RIVERA, AND B. PEJCIC. 2002. The influence of diffusion fluxes on the detection limit of the jalpaite copper ion-selective electrode. *Electroanalysis* 14:493–498.

ZIRINO, A., S. H. LIEBERMAN, AND C. CLAVELL. 1978. Measurement of Cu and Zn in San Diego Bay by automated anodic stripping voltammetry. *Environmental Science and Technology* 12:73–79.

ZIRINO, A., D. A. VAN DER WEELE, S. L. BELLI, R. DEMARCO, AND D. J. MACKEY. 1998b. Direct measurement of $Cu(II)_{aq}$ in seawater at pH 8 with the jalpaite ion-selective electrode. *Marine Chemistry* 61:173–184.

SOURCE OF UNPUBLISHED MATERIALS

SHAFER, M. Personal Communication. 201A Water Science and Engineering Laboratory, 660 North Park Street, Madison, Wisconsin 53706

RIVERA-DUARTE, I., ROSEN, G., LAPOTA, D., CHADWICK, D. B., KEAR-PADILLA, L., AND A. ZIRINO. Personal Communication. SPAWAR Systems Center San Diego, 53475 Strothe Road, San Diego, California 92152

Received, March 21, 2003
Revised, November 14, 2003
Accepted, December 19, 2003