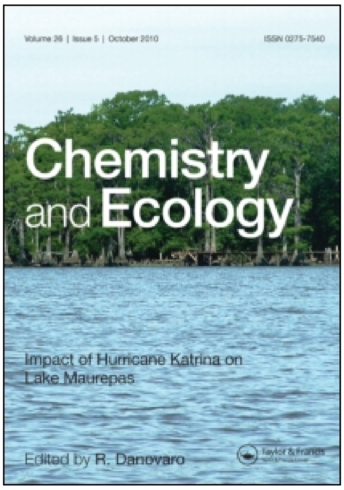

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Spatial distribution of copper in relation to recreational boating in a California shallow-water basin

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Spatial distribution of copper in relation to recreational boating in a California shallow-water basin

Carlos Neira[a]*, Francisco Delgadillo-Hinojosa[b], Alberto Zirino[c,d], Guillermo Mendoza[a], Lisa A. Levin[a], Magali Porrachia[d] and Dimitri D. Deheyn[d]

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The overall effect of the number of boats on the copper (Cu) levels in the water column and sediment, along with their spatial variability within Shelter Island Yacht Basin (SIYB), San Diego Bay, California was examined. We identified a horizontal gradient of increasing dissolved Cu and Cu in sediment from outside to the head of SIYB which was coincident with the increasing number of boats. Spatial models of Cu distribution in water and sediment indicated the presence of 'hotspots' of Cu concentration. From outside to the head of SIYB, dissolved Cu ranged from 1.3 $\mu g\,L^{-1}$ to 14.6 $\mu g\,L^{-1}$ in surface water, and 2.0 $\mu g\,L^{-1}$ to 10.2 $\mu g\,L^{-1}$ in bottom water. Cu in sediment exceeded the Effect Range Low of 34 $mg\,kg^{-1}$ (i.e. where adverse effects to fauna may occur), with a peak concentration of 442 $mg\,kg^{-1}$ at the head of the basin. Free Cu^{++} in surface water was several orders of magnitude higher than in sediment porewater. High-resolution data of Cu species together with probability maps presented in this paper will allow managers to easily visualise and localise areas of impaired quality and to prioritise which areas should be targeted to improve Cu-related conditions.

Keywords: copper hotspots; recreational boats; water column; sediments; copper complexation capacity; Shelter Island Yacht Basin; San Diego Bay

1. Introduction

In the marine environment, Cu is normally found at trace levels and in many physicochemical forms or chemical species. Trace Cu is essential for proper function of many life processes, but can be toxic at high levels [1]. Due to its use as a biocide in antifouling paints, leached Cu can be found at levels that approach or exceed state and federal water quality criteria. This is especially likely in semi-enclosed environments with a high density of boats. Copper-based antifouling paints are applied to boats to prevent the growth of fouling organisms by leaching Cu slowly into the water surrounding the hull [2]. There is increasing concern regarding the ecological risk that Cu pollution poses in small marinas because Cu is toxic not only to the targeted fouling organisms but also to other animals in the environment. Overall loading and spatial distribution of the different

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chemical species of Cu must be understood because studies indicate that Cu toxicity to aquatic biota is primarily related to Cu^{++} rather than to the total dissolved Cu concentration [1].

San Diego Bay has long been recognised to have some of the highest Cu levels reported in natural waters [3–4,41]. This embayment berths more than 17,000 recreational vessels, of which about 2,300 ($\sim$13.5%) are moored permanently in Shelter Island Yacht Basin. A total Cu load of 2,163 $\mathrm{kg\,y^{-1}}$ has been estimated to enter the water column of Shelter Island Yacht Basin [3,5], about 92% of which has been attributed to passive leaching of Cu from antifouling paints. The remaining 8% enters the water column via underwater hull cleaning (5%), urban runoff (1%), background sources of dissolved Cu found in ambient water (1%), and direct atmospheric deposition ($<$1%) [3,5]. Recently, Leon and Warnken [6] showed that vessel activity (e.g. hull cleaning, painting) and associated Cu load in Australian coastal waters increase during vacation periods. This boat activity occurs in San Diego Bay as well, where boat maintenance and traffic peak in Spring and Summer (B. Rocco, Aquarius Yacht Services, pers. comm.).

In this study we tested the hypothesis that the presence of 'hotspots' of Cu concentration is linked to boat distribution (number of boats and distance from the boats) and to basin environmental characteristics. Our objectives were to: (i) measure the actual Cu levels in sediments (solid phase) over a range of exposures to boat hulls, distance from the mouth and degree of flushing; (ii) measure dissolved Cu and free Cu^{++} in three vertical water zones (surface, bottom and porewater); (iii) identify trends and 'hotspots' in Cu concentrations along the basin associated with distance from boat docks and boat density; (iv) generate spatial probability models of Cu distribution in surface and bottom water, sediment, and porewater in Shelter Island Yacht Basin; (v) determine the percentage of particulate Cu in the total Cu pool in the water column; and (vi) assess the Cu complexation capacity (a measure of the self-detoxification capacity of the system) in selected regions of the basin. Detailed knowledge of the actual concentrations of total dissolved Cu and Cu^{++} in surface and porewater, solid-phase Cu in sediments, and the Cu complexation capacity of the water body will contribute to a better assessment of biological effects. It will also serve as a baseline for further studies examining any future recovery trajectory of one of the most Cu contaminated areas in the United States.

2. Materials and methods

2.1. *Study site*

Shelter Island Yacht Basin is a semi-enclosed basin approximately 3.2 km long constructed by the Army Corps of Engineers in the late 1930s and early 1940s. It is located in the north end of San Diego Bay (32°43'N; 117°13'W), with its opening facing the main (and only) entrance channel of San Diego Bay (Figure 1). The mean width of the basin is 475 m with a mouth width of 200 m, a greatest width of 750 m in the centre, and an average seawater volume estimated at $5.9 \times 10^6\ \mathrm{m^3}$ [7]. The mean depth at mean lower low water (MLLW) is about 5 m, with depths ranging from 3 m (near Kellogg Beach) to 7 m (at the entrance). Shelter Island Yacht Basin is heavily used for boat berthing as well as boat repair and repainting. It has the largest number of boats of any basin in San Diego Bay [8].

2.2. *Sampling design*

In Spring 2006, a preliminary sampling model was designed which consisted of a spatial grid with 32 stations distributed at roughly equal distances from each other ($\sim$165 m). The grid was then projected on an orthophoto of Shelter Island Yacht Basin using ArcGIS (ESRI, 2006). The design

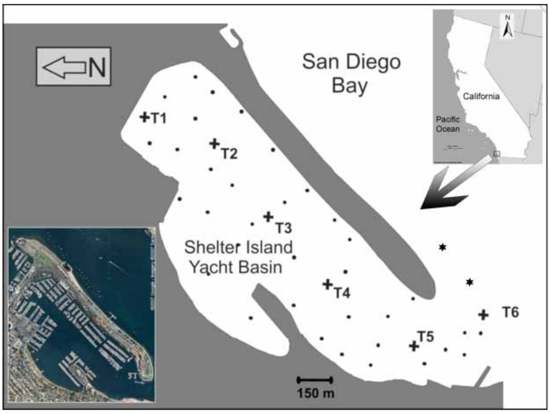

Figure 1. Sampling stations at Shelter Island Yacht Basin (SIYB), San Diego Bay, California. 'Reference' stations outside Shelter Island Yacht Basin are indicated by ⋆.

ensured that the whole basin was equally sampled and represented, including both open areas and areas with moored boats. One location outside the basin in San Diego Bay served as a reference site. Stations were sampled during ebb tide as close as possible to the original grid locations using a global positioning system (GPS). Because of pier locations and boat transit constraints, some stations had to be shifted from the original theoretical sampling grid, resulting in the actual sampling grid (Figure 1).

Based on the 2006 Cu sediment distribution results, we conducted a second sampling in Spring 2007, at a total of 27 sites, focused on areas of high (9 stations), medium (8 stations) and low Cu concentration (8 stations). This time we selected two reference sites located outside of the basin. To examine whether or not increased seasonal boat activity was reflected in differences in dissolved Cu, Cu^{++}, and/or in a shift in the percent contribution of particulate Cu to the total Cu pool, we collected samples of surface, bottom, and porewater at six sites along a transect from outside to the head of the basin in March and August 2008 (Figure 1). Additional samples of surface and bottom water were collected to determine the Cu complexation capacity.

2.3. *Sample collection and processing*

Samples of surface sediment (0–5 cm) were collected at each station by SCUBA divers using plastic tube cores (8.1 cm internal diameter, 51.5 cm^2). Once back onboard, the overlying water was gently removed and sediment redox potential was immediately measured in the top 1 cm using a portable Eh-meter (Mettler Toledo). In addition, a small syringe core (1.13 $cm^2 \times 1$ cm depth) was taken from the sample for sediment chlorophyll *a* and phaeopigments (an estimate of the amount of organic matter that is derived from primary production) in pre-weighed 15 mL polypropylene tubes and stored at −20°C until analysis. Finally, the top 5 cm fraction of sediment was transferred into an acid-cleaned Nalgene® jar and transported on ice to the laboratory for further analysis.

Surface and bottom water samples were collected at each site with acid-washed 250 mL Nalgene® bottles at a depth of 50 cm below the surface and at about 30 cm above the bottom. For the determination of dissolved Cu in the laboratory, 200 mL of seawater was filtered through a pre-weighed polycarbonate membrane (0.45 μm, 47 mm) using an acid-cleaned Nalgene® analytical filter unit. All filtered water samples were then acidified to pH <2 with Optima grade HNO_3 (Fisher) and stored until analysis. Filters containing suspended particulate matter were stored in pre-cleaned Petri dishes and kept frozen inside Ziploc® bags.

For determination of suspended particulate matter, the pre-weighed polycarbonate filter membranes (details above) were air dried to constant weight under laminar flow conditions in a class 100 ultra clean room and reweighed.

Sediment porewater was extracted by centrifuging ~30 cc of homogenised sediment at 4,000 rpm for 10 min. The supernatant was filtered through a 13 mm, 0.45 µm PTFE filter. The filtered porewater (~5 mL) was acidified to pH <2 with Optima grade HNO_3 and stored until analysis of dissolved Cu.

The total organic matter content of sediment samples was determined from mass loss after 30 g portions of dried (60°C), homogenised, sediment were combusted at 500°C for 4 h [9].

For grain size analysis, approximately 100 g of sediment were mixed with 25 ml of 30% hydrogen peroxide to remove the organic matter. The slurry was allowed to stand for 3–4 days until no trace of organic matter was left. After adding distilled water, the mixture was sieved wet through a 63 µm mesh sieve. Both fractions of the sample (>63 and <63 µm) were dried at 60°C and weighed to determine percent sand and silt-clay, respectively.

Sediment chlorophyll a (chl a) and phaeopigments were determined spectrophotometrically (Thermo Spectronics, Genesis 20) from freeze-dried sediment [10] after extraction with 90% acetone [11]. The sum of chl a and phaeopigments is referred as chloroplastic pigment equivalent [12].

3. Cu analysis

3.1. *Cu in sediments (solid phase)*

Approximately 300 mg of dried, homogenised sediment was weighed into precleaned, acid-washed Teflon beakers and digested with concentrated trace-grade HNO_3, $HClO_4$ and HF. The strength of acid treatment used may have dissolved constitutive metal from the mineral matrix, which could overestimate Cu bioavailability. The acidified samples were heated at 250°C and maintained with constant reflux for 12 h. After cooling, the digest solutions were transferred to polypropylene tubes, and 8 ml of MilliQ water was added. Cu concentrations were measured in triplicate by atomic absorption spectrometry (Varian model SpectrAA 220 fast sequential). Blanks and certified reference material (CRM) MESS-3 (National Research Council, Canada) were used for quality control. One CRM measurement was performed for every batch of 6 samples and all samples were randomly analysed. Results indicated good agreement between analytical and certified values (Table 1).

3.2. *Dissolved Cu (surface and bottom water, and sediment porewater)*

The filtered and acidified samples of pore, bottom, and surface water were preconcentrated under class-100 clean laboratory conditions using a modified Chelex-100 ion-exchange technique [13,14] as described by [15]. In order to analyse the Cu content of porewater, samples (~5 mL) were diluted in 50 mL of MilliQ water. Prior to pre-concentration, the pH of seawater

Table 1. Analysis of certified standards for seawater (CASS-4) and sediment (MESS-3). The 95% confidence interval is given in parentheses.

Certified standard	Certified value	Measured value	% Recovery	Detection limit	N
For seawater: CASS-4	0.59 (±0.06) $\mu g\, l^{-1}$	0.54 (±0.02) $\mu g\, l^{-1}$	90.7 (±3.9)%	0.05 $\mu g\, l^{-1}$	6
For sediment: MESS-3	33.90 (±1.60) $mg\, kg^{-1}$	31.88 (±1.17) $mg\, kg^{-1}$	94.0 (±3.4)%	0.03 ($mg\, kg^{-1}$)	6

(~150 mL) or diluted porewater was adjusted to 6 ± 0.5 with a Suprapur NH_4OH solution. Cu was measured on a single sample for each station using a Varian 880Z graphite furnace atomic absorption spectrometer (GFAAS) equipped with Zeeman background correction. Cu determination was made using the method of standard addition to correct for sample matrix interference. Accuracy and precision were assessed by analysis of coastal seawater certified standards (CASS-4) (National Research Council, Canada) (Table 1).

3.3. *Particulate Cu*

Polycarbonate filter membranes with suspended particulate matter collected in Spring 2006, and March and August 2008 were transferred into acid-cleaned polypropylene vials, and digested in two steps: first with 1 mL concentrated HNO_3 (Optima) in a microwave unit (Milestone ETHOS EZ system) at 100°C (350 W) for 1 h 40 min, followed by a 12 h digestion with a mixture HNO_3/HCl after addition of 1 mL trace metal-grade concentrated HCl (J.T. Baker). Because this acid treatment ensured a complete extraction of leachable and particle bound Cu (i.e. bioavailable [16] but not necessarily the constitutive fraction from the mineral matrix), we refer to this fraction as bioavailable particulate Cu. In order to estimate the percent contribution of bioavailable particulate Cu to the Cu pool in the water column, we are reporting bioavailable particulate Cu in $\mu g\,L^{-1}$. To get a final solution containing ~5% of acid, a 350 µl aliquot of the original solution was transferred into a sterile disposable polystyrene tube and ~4.7 mL of MilliQ water were added. Samples were analysed in triplicate by inductively-coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 3000DV). An internal control (1 ppm multi-element solution) was run every 20 samples to ensure the stability of the instrument throughout the process. Internal blanks were processed exactly as regular samples but containing only HNO_3/HCl.

3.4. *Free copper (Cu^{++})*

The Orion 94-29 Cu-Ion Selective Electrode (ISE) was used to determine the concentration of Cu^{++} in unfiltered seawater samples collected from the surface, bottom and porewater. The ISE electrode measures Cu^{++} in seawater in terms of pCu, where $pCu = -\log_{10}(Cu^{++})$ when calibrated with ethylenediamine Cu buffers at three different pH values prepared in 0.45 µm filtered seawater [17–19]. The electrode is precise at ± 0.06 pCu units, and covers a range of pCu between 9.4 to 13 (or more) since the response of the electrode to these buffers is linear [17]. The cell used for measurements and procedure were described by [20].

3.5. *Cu complexing capacity*

In August 2008, we conducted Cu titrations on unfiltered seawater collected at two depths (surface and bottom water). We collected 1 L of surface and bottom water with a special Niskin bottle at six selected sites along a N-SW transect from outside to the head of Shelter Island Yacht Basin (Figure 1). In the laboratory, about 15 mL were pipetted into a series of thirteen 60 mL pre-weighed FEP bottles in accordance with the procedure described by [20].

4. Data analysis

To examine the relationship between Cu concentrations and boat proximity, we measured the distance from each station to the nearest cluster of boats using ArcGIS 9.2 (ESRI, 2006) on a georeferenced map overlain on a 2004 orthophoto of San Diego Bay. The number of boats moored within the basin was estimated by counting them on a digital orthophoto (Google Earth, 2008). The number of boats estimated by this method is rather accurate and valid for all periods considered in this study since the percent occupancy in Shelter Island Yacht Basin is over 95% and, according the literature, the number of boats estimated agreed with early studies (e.g. [3,57]).

Spearman rank correlation analysis was performed to test for possible relationships among the investigated variables [21]. Analysis of variance (ANOVA) with a-posteriori Tukey's HSD tests was used to test for significant differences of Cu concentrations in zones (a) corresponding to sediment Cu levels, and (b) number of boats and sediment Cu. Data were tested for normality, and when necessary, square root transformed. The non-parametric Wilcoxon test was used when transformed data failed to fulfill parametric assumptions. The JMP v6.0 (SAS Inc.) statistical package was used. Differences between surface and bottom water dissolved Cu were tested using a paired t-test. Regression analysis was applied to relate sediment Cu and distance to the nearest boats. Given the fact that only one basin was studied, we acknowledge that all of our within-basin samples, grouped into zones are effectively pseudoreplicates (*sensu* Hulbert 1984 [58]). This limits the inferences that can be made to Shelter Island Yacht Basin. We found no significant time effect in copper concentrations among the zones that were defined during the first sampling period. This provided us with more confidence in combining the data sets to perform traditional statistical tests, but does not remove the constraints imposed by the lack of true replication in the experimental design.

To create Cu probability maps, Cu concentrations were interpolated on a regular grid by ordinary point kriging. Ordinary point kriging uses a weighted average of the neighboring points to estimate the value of an unobserved value [22]. In order to visually identify the spatial distribution of Cu, probability data were produced using kriging calculations performed in Matlab 2008 [23] and then mapped using ArcGIS (ESRI, 2006). These probability maps represent one tool by which agencies and decision makers can easily identify areas with high concentrations of Cu.

5. Results

5.1. *Basin sediment properties*

In Spring 2006 the mud content, total organic matter and chl a increased progressively from outside the Shelter Island Yacht Basin mouth to the head of the basin, while the sediment redox potential became progressively lower (Figure 2). There were positive correlations between total organic matter and content of fine particles (<63 mm) ($p < 0.001$), and pigments (chl a, phaeopigments and chloroplastic pigment equivalent, $p < 0.001$) (Table 2A). Sediment redox potential was inversely correlated with total organic matter ($p < 0.05$) and pigments ($p < 0.01$). Similar trends and relationships were observed in Spring 2007 (Table 2B).

5.2. *Distribution of dissolved copper in surface, bottom and porewater*

In spring 2006, dissolved copper concentrations in surface water ranged from 1.3 μg L^{-1} (outside the mouth) to 14.6 μg L^{-1} at the innermost part of Shelter Island Yacht Basin, with a mean value (±1 SE) of 9.1 ± 0.5 μg L^{-1}. Dissolved Cu in bottom water ranged from 2.0 μg L^{-1} (near mouth) to 10.2 μg L^{-1} (northwest side of the basin head), with an average of 4.3 ± 0.4 μg L^{-1} (Figure 3). The situation in Spring 2007 was similar, and dissolved Cu in surface water averaged 8.0 ± 0.4 μg L^{-1}. We identified a horizontal gradient of increasing dissolved Cu from outside to the head of the basin (Figure 3). This gradient was larger in surface water than in near-bottom water, and it is coincident with the number of boats progressively increasing toward the head of the

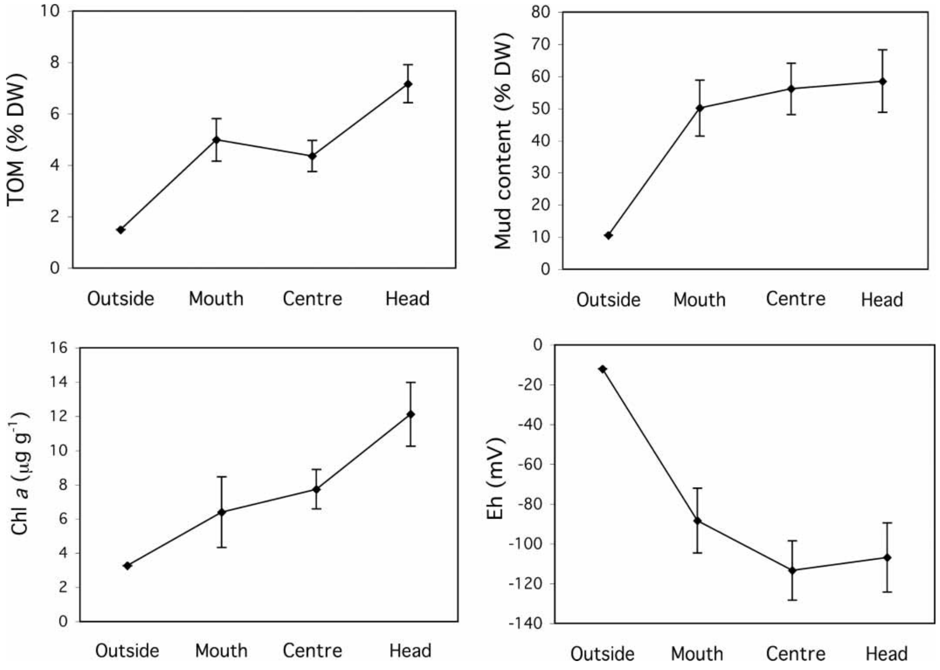

Figure 2. Sediment properties at different sectors along Shelter Island Yacht Basin (Spring 2006). Each point indicates the mean (±1 SE) for Mouth (10 stations), Centre (11 stations), and Head (10 stations). Grouped stations are indicated by vertical lines in Figures 3 and 4. A single station outside served as the 'reference'. TOM, total organic matter; Chl *a*, chlorophyll *a*; Eh, redox potential.

basin. We note that despite the shallowness of the basin (∼5 m), a clear depth-related difference in concentrations occurred; surface dissolved Cu was significantly higher than in bottom water (paired *t*-test, $t_{31} = 8.59$; $p < 0.0001$) across the entire basin (Figure 3).

In Spring 2006, dissolved Cu concentrations in sediment porewater did not exhibit large variation among stations, ranging from 5.2–12.8 μg L^{-1} (8.1 μg L^{-1} on average). Similar concentrations were found in 2007, ranging from 4.0 to 12. 7 (7.3 μg L^{-1} on average). Consistently, the highest concentrations of dissolved Cu in porewater were recorded at the head of the basin (in 2006 ranging from 7.0–12.8 μg L^{-1}, and in 2007 from 5.7–12.7 μg L^{-1}).

5.3. *Cu in sediments*

Cu concentrations in sediments ranged from 15.4 mg kg^{-1} outside of the basin to 442.3 mg kg^{-1} at the head of the basin and were consistent in time (Spring 2006 and 2007) (Figure 4). Cu concentrations inside the entire basin exceeded the Effects Range Low of 34 mg kg^{-1}, i.e. where adverse effects to fauna may occur [24], and six sites exceeded the Effects Range Medium of 270 mg kg^{-1}, i.e. where concentrations are frequently toxic [24]. Sediment Cu was significantly correlated with sediment-related environmental variables such as OM, grain size, chl *a* and chloroplastic pigment equivalent (Table 2A, B). Sediment Cu was significantly higher with increasing number of moored boats (Anova $F_{3,25} = 8.2$; $p = 0.0007$, Spring 2007; $F_{3,31} = 2.9$, $p = 0.048$, Spring 2006) (Figure 5A). There was a consistent exponential decrease of Cu in sediment with increasing distance to boats (i.e. the distance from each site to the nearest boat dock) (Spring 2007: $y = 215.47e^{-0.093x}$, $r^2 = 0.61$, $P < 0.001$; Spring 2006: $y = 139.45e^{-0.0072x}$, $r^2 = 0.48$, $p = 0.0003$) (Figure 5B).

Table 2. Spearman's rank correlation coefficients between studied variables in Shelter Island Yacht Basin. OM = organic matter; Chl *a* = chlorophyll *a*; Phaeo = phaeopigments; CPE = chloroplastic pigment equivalent; Eh = redox potential; DCu = dissolved copper.

(A) Surface-area exploratory sampling (Spring 2006).

Variable	OM	Mud	Sand	Chl *a*	Phaeo	CPE	Eh	DCu surface	DCu porewater	Cu sediment	DCu bottom	No. of boats	Distance to boat
OM	–												
Mud	0.841***	–											
Sand	−0.841***	−1.000***	–										
Chl *a*	0.556***	0.464**	−0.464**	–									
Phaeo	0.736***	0.558***	−0.558***	0.913***	–								
CPE	0.710***	0.568***	−0.568***	0.952***	0.986***	–							
Eh	−0.541*	−0.351*	0.351*	−0.613**	−0.551**	−0.513**	–						
DCu surface	0.066	0.087	−0.087	0.492**	0.300	0.359*	−0.266	–					
DCu porewater	0.269	0.323	−0.323	0.377*	0.321	0.367*	0.019	0.203	–				
Cu sediment	0.470**	0.394*	−0.395**	0.588***	0.574***	0.593***	0.075	0.372*	0.230	–			
DCu bottom	−0.025	−0.128	0.128	0.168	0.136	0.116	0.254	0.217	0.072	0.230	–		
No. of boats	0.149	0.153	−0.153	0.574***	0.386*	0.455**	−0.228	0.904***	0.341	0.400*	0.284	–	
Distance to boat	0.042	0.157	−0.157	−0.382	−0.296	−0.309	−0.044	−0.410	−0.040	−0.540	−0.470	−0.449*	–

(B) Focused sampling (Spring 2007) based on the distribution of Cu concentration in sediment as determined during the exploratory sampling.

Variable	OM	Mud	Sand	Chl *a*	Phaeo	CPE	Eh	DCu surface	DCu porewater	Cu sediment	Cu^{++} Surf.W	Cu^{++} poreW	No. of boats	Distance to boat
OM	–													
Mud	0.615***	–												
Sand	−0.6145***	−0.999***	–											
Chl *a*	0.708***	0.453*	−0.453*	–										
Phaeo	0.847***	0.586**	−0.586**	0.921***	–									
CPE	0.831***	0.567**	−0.568**	0.941***	0.996***	–								
Eh	−0.573**	−0.305	0.303	−0.720***	−0.646***	−0.667***	–							
DCu surface	0.262	0.688***	−0.692***	0.009	0.115	0.086	0.031	–						
DCu porewater	−0.165	−0.233	0.208	−0.196	−0.158	−0.148	0.175	−0.085	–					
Cu sediment	0.858***	0.623***	−0.625***	0.668***	0.790***	0.778***	−0.640***	0.318	−0.098	–				
Cu^{++} surface	0.259	0.484*	−0.497**	0.237	0.288	0.268	−0.189	0.595**	0.195	0.274	–			
Cu^{++} porewater	−0.541**	−0.255	0.252	−0.327	−0.382	−0.381	0.610***	−0.326	0.050	−0.559**	−0.348	–		
No. of boats	0.409*	0.241	−0.247	0.256	0.382	0.366	−0.181	0.427*	0.189	0.635***	0.209	−0.442*	–	
Distance to boat	−0.270	−0.443	0.448*	−0.107	−0.239	−0.213	−0.053	−0.371	−0.117	−0.437*	−0.324	0.181	−0.708***	–

Note: Significance: *0.01 $\leq p < 0.05$; **0.001 $\leq p < 0.01$; *** $p < 0.001$.

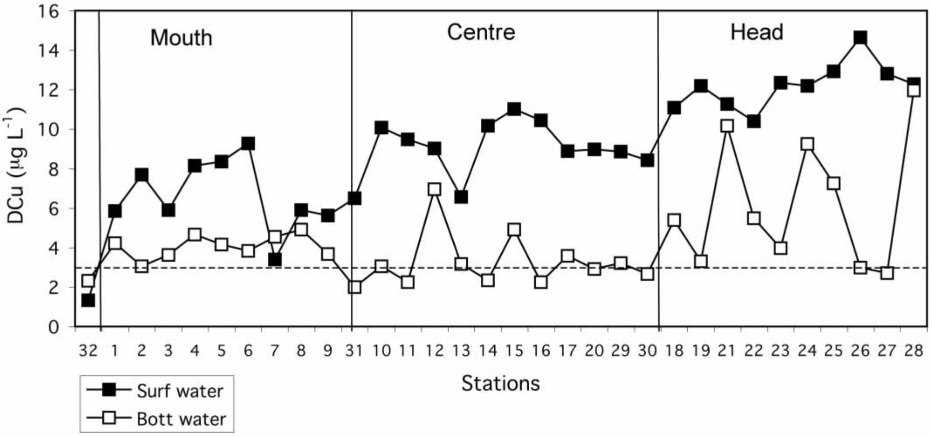

Figure 3. Dissolved Cu concentrations ($\mu g\,L^{-1}$) in surface and bottom water of Shelter Island Yacht Basin (Spring 2006). Horizontal dash line indicates value of US EPA water quality criteria of $3.1\,\mu g\,L^{-1}$ (49 nM).

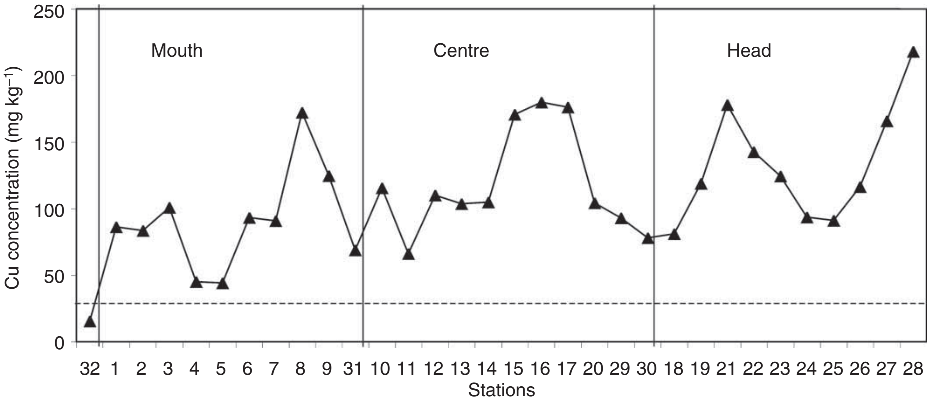

Figure 4. Horizontal distribution of Cu in sediment from outside to the head of the basin. Horizontal dash line indicates the threshold for Effects Range Low (ERL) of $34\,mg\,kg^{-1}$; i.e. range where adverse effects to fauna may occur [24].

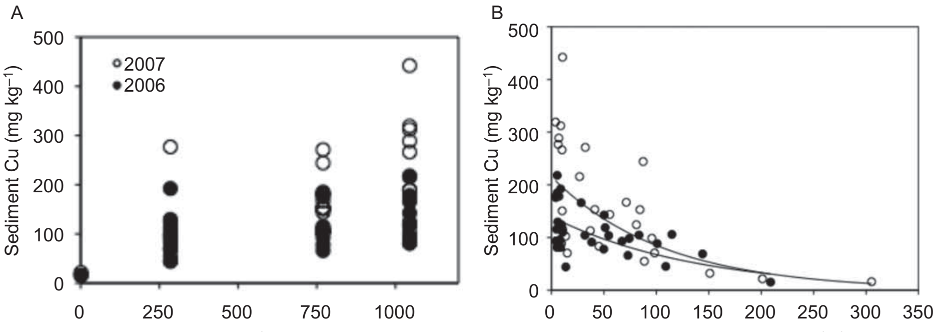

Figure 5. Relationships between sediment Cu concentration and (A) number of boats (Spring 2007: Anova $F_{3,25} = 8.2$, $p = 0.0007$; spring 2006: Anova $F_{3,31} = 2.9$. $p = 0.048$), and (B) distance from each station to the nearest boat dock (2007: $y = 215.47e^{-0.093x}$, $r^2 = 0.61$; $p = 0.0019$; 2006: $y = 139.45e^{-0.0072x}$, $r^2 = 0.48$, $p = 0.0003$).

5.4. *Bioavailable particulate Cu*

In Spring 2006, concentrations of bioavailable particulate Cu fluctuated from 0.48–3.52 $\mu g\,L^{-1}$ in surface water; whereas in bottom water they varied from 0.46–10.05 $\mu g\,L^{-1}$. The contribution of bioavailable particulate Cu to the total Cu pool in surface water averaged 13.5% inside the basin; whereas in bottom water bioavailable particulate Cu contributed 27% on average. Outside the basin the contribution of bioavailable particulate Cu in surface waters was greater (56%) than dissolved Cu, possibly due to resuspension of sediment. In bottom waters, the bioavailable particulate Cu contribution increased toward the centre of the basin to about 32% of total Cu.

We found a clear difference between March 2008 and August 2008 in the relative importance of bioavailable particulate Cu relative to dissolved Cu, and between surface and bottom water (Table 3). In March 2008, more than 90% of Cu in the surface water was in dissolved form. A similar situation was observed for bottom water, except at station T6 (outside the basin) where bioavailable particulate Cu contributed 32% of the 'total' Cu. In contrast, in August 2008, bioavailable particulate Cu increased both in surface (16.2%) and bottom water (42.2%) relative to dissolved Cu (Table 3), probably reflecting Spring–Summer peak boat cleaning activities.

5.5. *Free copper (Cu^{++})*

Measurements of pCu in porewater revealed that concentrations varied between 14.6–11.7; whereas in surface water pCu values ranged between 11.3–10.9. Decreasing pCu values represent increasing concentrations of Cu^{++}. Thus, Cu^{++} concentrations were several orders of magnitude higher in surface water than in sediment pore water, suggesting that the main source of Cu is boat hulls at the water surface. As the total dissolved Cu increases in surface waters, a linear increase in Cu^{++}occurs ($r^2 = 0.64$, $p < 0.0001$) (Figure 6). In contrast, a weak, but significant inverse relationship was observed between dissolved Cu and Cu^{++} in pore water ($r^2 = 0.20$, $p = 0.020$ (Figure 6).

Measurements of pCu carried out in March and August 2008 confirmed the differences in free Cu^{++} concentrations in three vertical horizons. Free Cu^{++} decreased from surface to bottom water to interstitial pore water (Table 3). In addition, concentration of free Cu^{++} was greater (i.e. lower pCu) in August relative to March (Table 3). These data were consistent with the enhanced contribution of bioavailable particulate Cu in August relative to March, and in bottom waters relative to surface waters.

5.6. *Cu complexation capacity*

The copper-ion selective electrode titrations conducted on water samples collected from six sites along the transect in Shelter Island Yacht Basin yielded typical titration curves, having a steeper slope with increasing Cu concentration. In August 2008, there was a gradual of declining Cu complexation capacity in surface waters, from the head (T1: 529 nM) to outside Shelter Island Yacht Basin (T6: 330 nM) (Table 3). In contrast, in bottom water the Cu complexation capacity was in general more uniform with no distinct gradient, ranging from 484 to 510 nM. In March 2008 the general pattern of Cu complexation capacity was similar to August 2008 but with a more abrupt reduction from the head (T1) to the centre (T4) in surface water. Cu complexation capacity in bottom averaged 405 nM (Table 3).

5.7. *Spatial distribution of Cu*

Based on our results of Cu concentration in the water column and sediments, we generated probability maps of the spatial distribution of dissolved Cu in surface water (Figure 7A), dissolved

Table 3. Contribution (%) of dissolved Cu (DCu) and bioavailable particulate Cu (CuPB) to total Cu pool in surface and bottom water; free copper concentration (Cu^{++}) in surface, bottom, and porewater; Cu complexation capacity (CuCC) in surface and bottom water. Top panel represents Winter (March 2008); bottom panel represents Summer (August 2008). pM = picomolar; nM = nanomolar.

March 2008

Transect station	%Dcu Surface water	%CuPB Surface water	%Dcu Bottom water	%CuPB Bottom water	Cu^{++} (pM) Surface water	Cu^{++} (pM) Bottom water	Cu^{++} (pM) Pore water	CuCC (nM) Surface water	CuCC (nM) Bottom water
T1	92.3	7.7	89.1	10.9	5.92	1.42	0.72	589	370
T2	100.2	0.0	100.0	0.0	2.94	1.83	1.00	485	410
T3	99.0	1.0	100.0	0.0	6.34	2.43	1.03	381	450
T4	93.0	7.0	91.3	8.7	3.78	2.17	1.20	343	484
T5	>99.9	<0.01	100.0	0.0	5.40	1.87	0.45	338	338
T6	>99.9	<0.01	68.2	31.8	3.84	1.51	0.26	306	381

August 2008

Transect station	%CuPB Surface water	%Dcu Surface water	%CuPB Bottom water	%DCu Bottom water	Cu^{++} (pM) Surface water	Cu^{++} (pM) Bottom water	Cu^{++} (pM) Pore water	CuCC (nM) Surface water	CuCC (nM) Bottom water
T1	16.5	83.5	63.2	36.8	13.4	8.6	4.1	530	491
T2	11.6	88.4	38.7	61.3	11.9	10.2	5.4	521	506
T3	13.3	86.7	50.5	49.5	11.1	8.9	4.0	497	502
T4	15.2	84.8	36.2	63.8	12.2	9.2	4.3	468	484
T5	25.5	74.8	31.4	68.6	9.7	9.9	3.9	411	489
T6	15.5	84.5	33.1	66.9	9.1	9.2	4.3	330	510

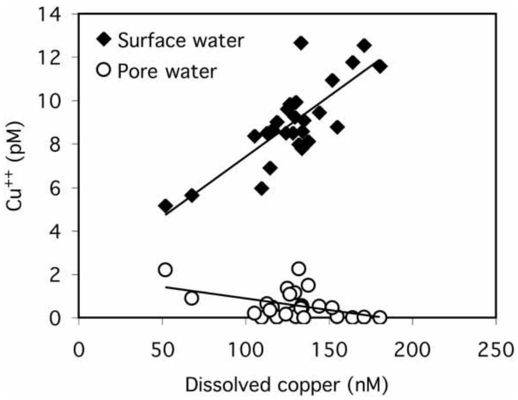

Figure 6. Relationship between free aqueous copper (Cu^{++}) and dissolved copper concentrations in surface water ($y = 0.0559x + 1.82$; $r^2 = 0.64$; $p < 0.0001$) and pore water ($y = -0.0108 + 1.98$; $r^2 = 0.20$; $p = 0.020$). (Sampled Spring 2007).

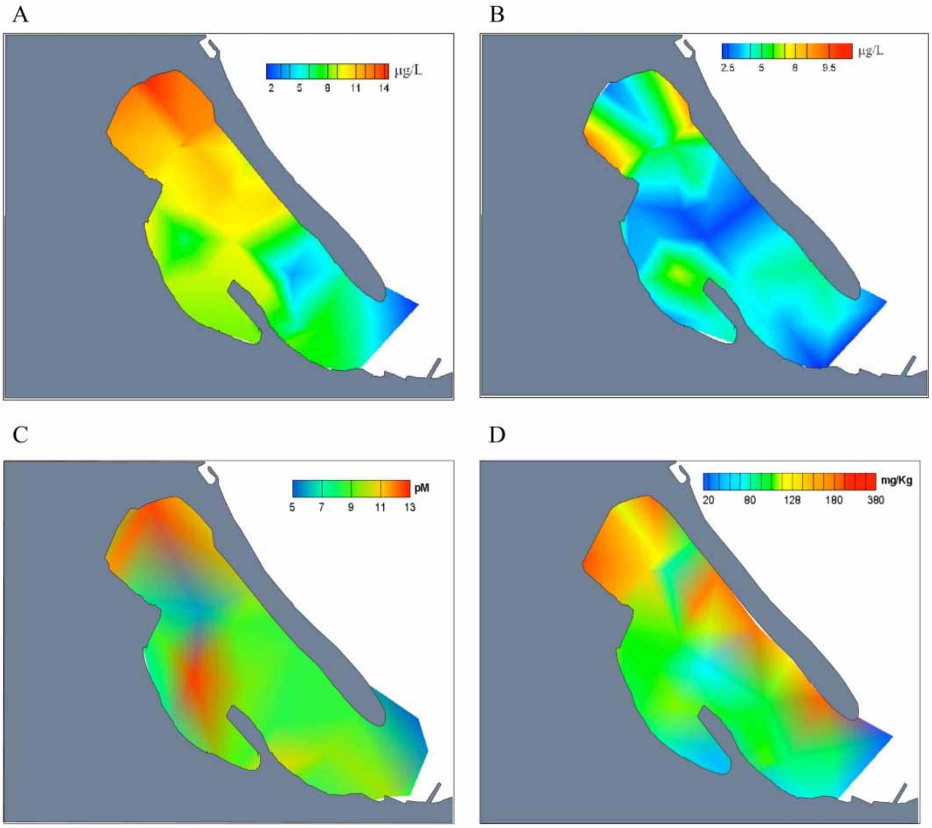

Figure 7. Probability maps of spatial distribution of Cu concentration. (A) Dissolved Cu surface water, (B) dissolved Cu bottom water, (C) free Cu^{++} in surface water, (D) sediment copper. Note the different scales and units.

Cu in bottom water (Figure 7B), and Cu^{++} in surface water (Figure 7C), and Cu in sediment (solid phase) (Figure 7D). These probability maps show ‘hotspots’ of high Cu concentrations that correspond to locations with boats. They reveal the horizontal gradient in dissolved Cu and Cu^{++} in surface water resulting from boat leaching and Cu accumulated in sediments.

6. Discussion

6.1. *Horizontal and vertical gradients of dissolved Cu*

This study provides strong evidence that dissolved Cu concentrations in water of Shelter Island Yacht Basin are associated with the presence of boats within the basin. The higher dissolved Cu in near-surface water and the positive correlation between dissolved Cu and the number of boats (Spearman $r = 0.90$; $p < 0.001$), indicates that the source of Cu is at the surface. On average, the levels of dissolved Cu in surface water exceeded by a factor of 3 (up to a factor of ∼5) the threshold of water quality of $3.1\,\mu g\,L^{-1}$ established by [25,26]. Early studies carried out in San Diego Bay show that dissolved Cu has been consistently higher over many years in Shelter Island Yacht Basin than the US EPA threshold [25]. For example, in the 1980s, values of $4.0\,\mu g\,L^{-1}$ dissolved Cu were recorded by [27], whereas [7] reported concentrations ranging from 8.9 to $11\,\mu g\,L^{-1}$. In the period of 1991 to 1993, mean concentrations of $6.9\,\mu g\,L^{-1}$ were reported by [28]. More recently, average concentrations as high as of $12\,\mu g\,L^{-1}$ [29] of dissolved Cu were documented for Shelter Island Yacht Basin.

The increasing differences between surface water and bottom water dissolved Cu concentrations (ΔCu), from outside to the head of the basin can be explained by poor tidal flushing and vertical water mixing towards the inner basin relative to the mouth, where dissolved Cu levels are lower and tend to be more similar. The lower concentration of dissolved Cu in bottom waters can be attributed to a net transport of Cu from the surface to the bottom sediments via complexation and adsorption to suspended particulate matter including clays and organic particles [30–32]. Suspended particulate matter is an important element in the process of trapping and transfer of trace elements towards the sediments because it contains organic matter with strong adsorption capacities [32]. The longer residence time of finer particles in the water column toward the head of the basin relative to mouth area offers more time for Cu removal through adsorption and binding. This is supported by the higher change in dissolved Cu toward the head of the basin.

The relatively uniform distribution of dissolved Cu in the interstitial water suggests that the interstitial system is spatially and temporally stable and that most of this dissolved Cu is complexed. Reducing sediment conditions in Shelter Island Yacht Basin, as indicated by low Eh values (< -100 mV) usually associated with sulfide, can also limit Cu availability and hence reduce dissolved Cu concentration in the interstitial water [33].

6.2. *Spatial distribution of Cu in sediments related to boats and distance*

Cu concentration in the sediments of Shelter Island Yacht Basin increased with the number of boats moored above (Figure 5A). An inverse relationship occurred between the Cu content in sediment and the distance to the source, i.e. the closer the boats were to the sampling site the higher the Cu concentration in sediments (Figure 5B). According to a model proposed for San Diego Bay [34,30], Cu reaches the water in dissolved form before being transformed into the particulate form that ultimately sinks into the seabed sediment. Fine-grained suspended particles (including organic-mineral aggregates) act as scavengers for Cu (and heavy metals in general), and hence Cu transfer to the sediment. A removal rate of Cu from the water to the sediment ranging from 6–9% d^{-1} (a 48% of the input) has been estimated for San Diego Bay by [30]. Our results are consistent with Chadwick et al.'s model [30]. As a consequence, bottom sediments at the head of the basin are more enriched in Cu than those at the mouth of Shelter Island Yacht Basin.

The contribution of bioavailable particulate Cu was greater in August 2008 (Table 3), when there is increased boat activity (traffic) and maintenance (cleaning and painting), than in March 2008. Because underwater hull cleaning is site-specific, concentrations of particulate Cu can be elevated surrounding the area, but the released Cu is quickly incorporated into the sediment [5,28,35]. Although sediment acts primarily as a sink for Cu, sediment may also act as a source of Cu for the water column. This occurs by resuspension (highly probable in such shallow marinas), by bioturbation caused by epifauna and infauna, by efflux and diagenetic remobilisation from the sediment back into the dissolved phase [16,37], as well as by desorption from resuspended sediment particles [1,37].

6.3. *Cu^{++} and Cu complexation capacity*

6.3.1. *Cu^{++}*

The Orion 94-29 ion selective electrode has been shown to respond effectively to Cu^{++}, and its validity for pCu and Cu complexation capacity determinations has been well established [17,19,38]. In addition, it has been demonstrated that the equivalence point determined with the Cu-ion selective electrode coincided with the results obtained using US EPA-approved bioassays methods [39].

Cu toxicity to aquatic biota is related primarily to the dissolved cupric ion, which typically constitutes <0.01% of the total Cu in natural seawater [40]. Evidence indicates that over 99.9% of the dissolved Cu in coastal marine environments is complexed by organic material [1]. Nevertheless, despite its low concentration (5 orders of magnitude lower than total Cu), the free $Cu^{++}$is a better predictor of potential Cu toxicity than total dissolved Cu [39]. This is because pCu is a better measure of the availability of Cu^{++} than any other Cu species in the water [41].

In the present study, pCu values measured in surface water of Shelter Island Yacht Basin in 2007 (Spring) and 2008 (March and August) varied from 10.9 to 11.9 consistent with those previously reported for San Diego Bay and coastal areas [28,39,41,42]. pCu values of 11 or lower can become toxic to phytoplankton [43,44], copepods [45] and mussel larvae [39]. The levels of pCu in open coast surface waters of the central northeast Pacific (33 °N; 139 °W) have been reported to be ~14 pCu units [46]. In contrast, levels of free Cu^{++} near the coast and in embayments are usually two to three orders of magnitude higher. There are three main causes for higher Cu^{++} in the water in August 2008, assuming an equal number of boats: (i) enhanced boat maintenance activities; (ii) boats leach faster and dissolved Cu increases at higher temperature; and (iii) Cu complexes dissociate more when water is warmer, i.e. binding capacity may be weaker.

6.3.2. *Cu complexation capacity*

Metal titrations provide valuable information about the total metal buffering capacity within the range of Cu additions used in our procedure but do not allow us to determine the exact value of the stability constants of the different type of ligands present in the water sample [20], hence only ‘ligand concentrations’ can be discussed. The consistent decline in Cu complexation capacity in surface water from the head to outside the basin suggests that at the head of Shelter Island Yacht Basin a local source of ligands occurs, probably produced by phytoplankton. Accordingly, increasing pigment content in sediment towards the head of the basin suggests major phytoplankton production in this area that ultimately sinks to the sediment.

6.3.3. *Shelter Island Yacht Basin: a self detoxifying system?*

Total dissolved Cu concentrations in coastal waters typically range from 2 to 150 nM (0.1–9.5 $\mu g\,L^{-1}$; [47]. If Cu were complexed solely by inorganic ligands, the pCu would be in the range of 9 to 10 (free Cu^{++} concentration of 0.1–2.0 nM); this would be toxic for a variety of microalgae, bacteria and some higher organisms [43,45,48]. However, complexation by organic ligands lowers the Cu^{++} concentrations to pM levels (i.e. from <0.1 pM to 0.1 nM) [47]. Small increases in the concentrations of dissolved Cu can result in increased concentration of free Cu^{++}, as ligands become saturated [41]. In the present study, we observed the same positive relation in surface water (Figure 6). This means, that despite the continued release of dissolved Cu (and Cu^{++}) at the head region of Shelter Island Yacht Basin, Cu appears to be rapidly complexed, possibly through the *in situ* production of Cu-binding ligands. The decline of Cu complexation capacity in surface water toward the mouth of the basin, and the relatively high and uniform Cu complexation capacity distribution in bottom water, might be modulated by ligands released from the sediment, to overlying water [49] via diagenetic remobilisation and desorption [37]. The nearly three orders of magnitude lower Cu^{++} concentrations found in porewater as compared with surface water (Figure 6) suggests that in porewater a complex mixture of ligands may occur, lowering Cu^{++} below toxic levels.

6.3.4. *Ecological implications*

The high Cu concentration in water and sediments but limited free Cu^{++} raises questions about the impact of Cu on marine life in Shelter Island Yacht Basin. A central problem is knowing the uptake and potential effects of Cu on benthic animals once Cu enters the food web. Species living in soft-bottom communities have direct contact with sediment particles and interstitial water and are therefore particularly vulnerable to Cu exposure. Potential negative ecological effects of Cu on benthic fauna include lowered diversity [50], impaired reaction to predation [51], reduced colonisation and burrowing [52,55], reduced feeding rate or survivorship [53], impaired habitat selection, fertilisation, embryonic development and chemosensation [51,54], and inhibition of larval settlement [56]. However, low free Cu^{++} suggests that sediments may be relatively non-toxic to infaunal invertebrates. High-resolution sampling that matches the space and time scale of the Cu data presented here would provide a test of this idea and generate data needed to link the environmental concentrations to community and ecosystem-level consequences. The spatial and temporal dynamics of Cu reported here are likely to reflect conditions in many urban marinas.

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