Copper emissions from antifouling paint on recreational vessels

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ABSTRACT - Trace metals, especially copper, are commonly occurring contaminants in harbors and marinas. One source of copper to these environs is copper-based antifouling coatings used on vessel hulls. The objective of this study was to measure dissolved copper contributions from recreational vessel antifouling coatings for both passive leaching and hull cleaning activities. To accomplish this goal, three coating formulations including hard vinyl, modified epoxy, and a biocide-free bottom paint were applied on fiberglass panels and placed in a harbor environment. *In situ* measurements of passive leaching were made using a recirculating dome system. Monthly average flux rates of dissolved copper for the hard vinyl and modified epoxy coatings were 3.7 and 4.3 µg/cm^2/d, respectively, while the flux rate for the biocide-free coating was 0.2 µg/cm^2/d. The highest passive flux rates were measured initially after cleaning activities and rapidly decreased to a baseline rate within 3 d, regardless of copper-based coating formulation. Hull cleaning activities generated between 8.6 and 3.8 µg dissolved copper/cm^2/event for the modified epoxy and hard vinyl coatings, respectively. Aggressive cleaning using an abrasive product doubled the copper emissions from the modified epoxy coating, but produced negligible change in the hard vinyl coating. When compared on a mass basis, roughly 95% of copper is emitted during passive leaching compared to hull cleaning activities over a monthly time period for a typical 9.1 m power boat.

INTRODUCTION

Trace metals have been identified as important constituents of concern contaminating sediments in marinas and harbors. Sediment quality surveys around the United States routinely find high copper concentrations in marinas and harbors (U.S. EPA 1996a, NOAA 1994). For example, NOAA (1991) found the highest sediment concentrations in marinas and harbors, with maxima reaching over 10^4 mg copper /dry kg, compared to other areas throughout the Southern California Bight. Dissolved trace metals in the water column frequently exceed levels of concern in marinas (Hall *et al.* 1988, Zirino *et al.* 1998). Zirino *et al.* (1978) found the highest concentrations of dissolved copper in marinas of San Diego Bay, often exceeding the U.S. EPA's chronic water quality criterion of 3.0 µg/L. These elevated trace metal concentrations in marinas partly result from the physical processes of mixing and dispersion. Marina and harbor areas are inherently protected, providing calm water for navigation, but also restricting circulation. The multitude of potential contaminant inputs found in marinas and harbors exacerbates the copper contamination in these areas. Some of these marina and harbor areas might host local point sources such as municipal or industrial wastewaters. Many mari-

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na and harbor areas receive surface runoff, which will vary in water quality as a function of the development within the adjoining watershed. However, all of these marina and harbor areas receive inputs from vessel activities. There are a variety of activities associated with vessels that could contribute trace metals including antifouling paint hull coatings, sacrificial anodes, motor exhaust, and hazardous material spills.

Of all the vessel-related activities, antifouling bottom paints are among the largest source of copper and other trace metals. Modern hull coatings are impregnated with copper and sometimes co-biocides, which retard the growth of algae and other encrusting organisms. These encrusting organisms foul hulls and other underwater parts that impede progress underway, lengthening transit times, and increasing fuel consumption (WHOI 1952). Copper-impregnated coatings are designed to slowly release copper, in the dissolved and most toxic form, so as to retard growth of these organisms and maintain a smooth underwater surface.

There are more coating formulations than there are coating manufacturers. Aside from the active ingredient, which typically varies from 20 to 76% copper content, hull coatings also have a variety of formulations for the inert matrix and delivery. There are self-polishing copolymers, ablative, and epoxy-based formulations. The passive flux of copper from each of these formulations differs as a result of the matrix. For example, epoxy-based coatings use a honeycomb matrix that enables the impregnated cuprous oxide to leach through "micro-channels" in the coating. Regardless of the release process, all coating formulations require periodic (ca. monthly) underwater hull cleaning to maintain a smooth surface and improve the copper release on pleasure craft. Hence, the biocide does not prevent fouling, it merely prolongs the natural process of hard substrate recruitment and succession.

Since there are numerous variations in copper content and matrix formulations, paint manufacturers have developed a standard method for estimating biocide release rates (ASTM 2000, Kiil *et al*. 2001). Copper release rates are measured from coated rotating cylinders exposed to artificial standard seawater under controlled temperature and pH conditions. After an initially high flux and when the release rate has stabilized, the copper release rate is calculated by sampling the seawater in which the drum is immersed. Other investigators have reported that the ASTM methods generate flux rates that are higher than *in situ* measurements under static conditions, and under environmental exposure (Schatzberg 1996, Thomas *et al.* 1999)

The goal of this study was to assess the contributions of dissolved copper to receiving waters *via* antifouling coatings from recreational vessels. The objective was to measure these contributions *in-situ* to estimate flux rates under environmentally relevant conditions. The primary question addressed by this study is a comparison of dissolved copper flux rates for both passive leaching and hull cleaning activities. Three subquestions were also addressed in this study relevant to dissolved copper release rates from antifouling coatings. The first subquestion focused on quantifying the change in dissolved copper flux during passive leaching between cleaning events as biofilms, algae, and other encrusting organisms begin to grow on coated surfaces. The second subquestion focused on quantifying the effect of best management practices (BMPs) on hull cleaning activities. This is important since BMPs are a potentially important mechanism for controlling antifouling coating discharges. The third subquestion focused on evaluating the effect of different coating formulations. Differences among coating formulations may produce differential flux rates for copper during both passive leaching and underwater hull cleaning activities.

METHODS

Three design factors were investigated including: coating formulation, cleaning method, and time since underwater cleaning (Table 1). Three basic types of bottom coatings available to boat owners, each varying in its biocide content and mode of action, were also evaluated: hard vinyl, modified epoxy, and biocide-free coatings. The copper flux of each coating type was measured during passive leaching, and again during underwater hull cleaning activities.

The flux of copper was quantified using two different methods of underwater hull cleaning. The first method was a hand method by a professional underwater hull cleaning company using BMPs. The BMP paradigm mandates using the softest cleaning materials possible in order to minimize copper contributions and maximize the lifetime of hull coatings. The second method was a non-BMP hand cleaning method using a more abrasive cleaning material than was necessary to remove fouling.

Table 1. Number of treatments for each of three factors evaluated during the antifouling coating project. All treatments had three replicates.

Treatment Factor	No. of Treatments	Passive Leaching	Underwater Hull Cleaning	Notes
Coating Types	3	Yes	Yes	Modified Epoxy, Hard Vinyl, Biocide-free
Cleaning Types	2	No	Yes	BMP (nonabrasive) vs nonBMP (abrasive) on all three coatings
Time Since Cleaning	7	Yes	No	Day 1, 3, 5, 7, 14, 21, 28 on all three coatings

Time since cleaning was evaluated by measuring the flux of copper during passive leaching at periodic intervals following a cleaning event. Since most recreational vessels are cleaned on monthly schedules (sometimes slightly less during winter or slightly more during summer) by professional services, intervals of 1, 3, 5, 7, 14, and 28 d were selected.

Hull Surfaces and Coatings

Fiberglass panels from a local boat manufacturer were used to simulate a recreational boat hull. These 40.6 cm wide x 40.6 cm high x 0.48 cm thick panels were prepared for antifouling coating application by removing wax, lightly sanding the gel-coat, and applying two coats of non-sanding primer. Two coats of paint were then applied onto the panels with a roller. After drying, panels were hung from the side of a boat dock in ambient seawater 40 cm below the surface in a randomly assigned order. Similar to any recreational vessel, a professional boat hull cleaning service provided monthly maintenance beginning 60 d after submersion prior to the initiation of the sampling phase. Biocide-free coated panels were cleaned every two weeks as a result of rapid fouling.

Two commercially available antifouling coatings and a biocide-free coating were tested in the study. The antifouling coatings had cuprous oxide (Cu_2O) as the primary biocide within an insoluble matrix of modified epoxy or hard vinyl enhanced with Teflon™. The matrix for the biocide-free coating was a two-part epoxy with Teflon™. A standard application technique was applied to all panels regardless of coating types to ensure biocide release rates would not vary as a result of coating thickness or other application variables.

Sampling for Passive Leaching of Coated Surfaces

Passive leaching was measured using a closed, recirculating system (520 mL min^{-1}) developed by the U.S. Navy (Seligman *et al.* 2001, Valkirs *et al.* 2003). Each system consisted of a 30.5 cm diameter polycarbonate dome with a double-edge gasket connected to Teflon™ hoses and a peristaltic pump. For each coating type, a randomly selected panel was placed in a pre-cleaned 59 L plastic tub filled with ambient seawater. Each panel was gently placed into the tub and the dome system was positioned over the top. After purging all air from the system, the dome was pressed onto the sunny side of the panel and was hydrostatically attached using negative pressure by removing a small volume of water from the system. Water samples were then drawn from the system every 15 min for 1 hr. A pressure gauge monitored the system for leakage and allowed dome volume calculations. Filtered samples were collected from each composite using a 50 mL syringe fitted with a 25 mm diameter filter cassette using 0.45 μm pore size Metricel™ filters. Samples were preserved with nitric acid to pH < 2.

Sampling for Cleaning Activities

Panel cleaning activities were sampled using precleaned 59 L plastic tubs filled with ambient seawater, which prevented advective losses of copper due to currents and harbor mixing. Three panels were selected randomly from each coating type and gently placed in individual tubs. At time zero, a sample was collected from each tub as a blank. Immediately following, each panel was cleaned using either a BMP or non-BMP method, then removed at the end of 5 min. Particles were allowed to settle for 1 hr and a second water sample was collected from the tub. The BMPs vary among underwater hull-cleaning services. The BMP procedure selected for this study by a professional service agency used a low abrasive shag carpet and minimal applied pressure. The non-BMP procedure selected for this study used a non-professional with a nylon 3M™ scouring pad and greater applied pressure. Filtered samples were collected from each composite using a 50 mL syringe fitted with a 25 mm diameter filter cassette using 0.45 µm pore size Metricel™ filters. Samples were acidified with nitric acid to pH < 2.

A validation experiment was conducted using actual vessels and a BottomLiner™ boat bag to evaluate any bias between the smaller panel system and a vessel hull. The boat bag is a rectangular plastic liner with a partially filled volume of 8,400L that is submerged into the marina slip. The boat bag is closed on three sides to allow a boat to enter, then the fourth side is closed to isolate the hull from the ambient environment. A total of 12 L of water were collected at multiple locations and depths throughout the bag with time zero as a blank sample. The vessel then was cleaned using a professional cleaning service using identical BMPs to those used in the panel experiments. Particles were allowed to settle for 1 hr and a second 12 L composite water sample was collected. Filtered samples were collected from each composite using a 50 mL syringe fitted with a 25 mm diameter filter cassette using 0.45 µm pore size Metricel™ filters. Samples were acidified with nitric acid to pH < 2.

Analytical Chemistry

Filtered and acidified seawater samples were extracted using an iron-palladium precipitation technique following Bloom and Crecilius (1983). This extraction method removes matrix-related interferences to quantify copper at low levels (0.1 µg/L) in seawater. The extract was reconstituted in deionized water and analyzed using inductive coupled plasma mass spectrometry (ICP-MS) using EPA Method 1640 (U.S. EPA 1996b). Quality assurance measurements indicated that all laboratory blanks were below method detection limits and duplicate samples were within a 10% reproducible difference.

Data Analysis

Three types of data analysis were conducted for this study. The first analysis calculated dissolved copper flux rates for passive leaching from each coating type. The second analysis calculated dissolved copper flux rates for each hull cleaning method from each coating type. The third analysis compared the relative copper input of passive leaching to hull cleaning by estimating dissolved copper mass emissions for a typical vessel using the rates calculated in this study.

Dissolved copper emissions and flux rates were determined for each coating type. Determination of passive leaching flux rates for each dome sampling event was estimated by first plotting each of the sample copper mass emissions, calculated as the product of the sample concentration and known volume of the dome sampling system, versus time over the course of the 1 hr sampling event. Flux rates, given as µg/cm^2/d, were derived from the slope of the line based on linear regression of these samples (Zar 1984). Since these individual flux rates can vary by time since cleaning, an average flux rate for each coating type was calculated by integrating the area under the curve of the one-month passive leaching experiments. Since replicate curves were derived for each coating type, a t-test of slopes was used to test for significant differences in passive leaching copper fluxes among coating types.

Hull cleaning flux rates, either in tubs or boat bags, were calculated using 1 hr samples corrected for time zero blank samples and any passive leaching that may have occurred during this time period. The resultant concentrations were converted to dissolved copper mass using the known surface area of the fiberglass panel or vessel hull, and the known volume of the tub or boat bag. The comparison among coating types and hull cleaning methods was accomplished using a non-parametric two-factor analysis of variance (ANOVA) (Zar 1984).

In an effort to compare the relative contributions of copper during passive leaching and hull cleaning, copper mass emissions were estimated for a typical 9.1 m by 2.7 m powerboat. Surface area was estimated using the coating manufacturer's formula (Length * Beam * 0.85). Since hull cleaning occurs on a monthly basis, dissolved copper emissions were calculated over a 28-d period.

RESULTS

Passive Leaching

The enclosed system was able to measure *in situ* passive dissolved copper leach rates from fiberglass panels (Figure 1). Dissolved copper mass within the recirculating dome system for hard vinyl coatings originated near 10 µg at time zero, then increased more than one order of magnitude to 130 µg after1 hr. Sequential samples collected over this time period increased in a linear fashion. We used this rela-

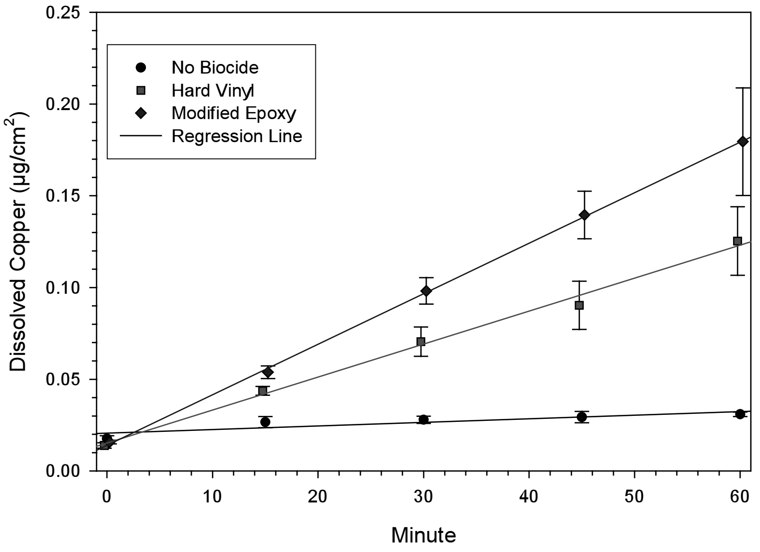

Figure 1. Passive leach rate curve for dissolved copper from a hard vinyl, modified epoxy, and biocide free antifouling paint. All data were collected 14 days after underwater cleaning.

tionship to fit curves that approximated passive leaching rates. The passive leaching rates for modified epoxy resulted in a curve that was very similar to that of hard vinyl coatings. In contrast, the biocide-free coatings had a flat curve, demonstrating minimal leaching.

Passive leaching rates varied between copper-based and biocide-free antifouling coatings (Table 2). As expected, biocide-free coatings had passive leaching rates that were near zero. In contrast, mean passive leaching rates for copper-based antifouling coatings varied from 3.7 to 4.3 µg/cm^2/d. Although these copper-based passive leach rates varied by 15%, they were not significantly different.

The passive leaching rates were highest immediately following cleaning events, then declined rapidly until asymptotically reaching a baseline rate (Figure 2). Mean passive leach rates for modified epoxy and hard vinyl coatings 1 d following cleaning activities were 18 and 15 µg/cm^2/d, respectively. This is the interval when panels were free of fouling by biofilms, algae, or other organisms. These rates decreased three-fold within 3 d following cleaning activities, dropping to between 4 and 5 µg/cm^2/d. Passive leach rates decreased slowly following day three, dropping to only 3 µg/cm^2/d after 28 d following cleaning activities. Biocide-free coatings exhibited minimal variability in copper concentration over time, remaining uniformly low to non-detectable.

Hull Cleaning

Contributions of dissolved copper during normal cleaning activities varied among all three coating types (Table 2). Modified epoxy-coated surfaces showed the greatest fluxes, averaging 8.6 µg/cm^2/event. Hard vinyl-coated surfaces produced dissolved copper fluxes that averaged roughly half of the modified epoxy fluxes. Dissolved copper fluxes of biocide-free coatings were essentially zero.

The effect of BMPs can alter the flux of dissolved copper, depending upon the type of coating being cleaned (Table 2). The lack of BMPs during cleaning events doubled the flux of dissolved copper from surfaces painted with modified epoxy antifouling coatings. The flux of dissolved copper did not change with or without the use of BMPs for either the hard vinyl or biocide-free coated surfaces. The mean flux of dissolved copper from hard vinyl coated surfaces remained near 4 µg/cm^2/cleaning. The flux of dissolved copper from the surfaces coated with the biocidefree formulation remained essentially zero.

Estimates of Combined Mass Emissions

Passive leaching contributed more dissolved copper than hull cleaning activities for a typical recreational vessel on a monthly basis (Table 3). A 9.1 m powerboat that is cleaned every four weeks using BMPs was estimated to contribute between 22 to 26 g/mo of dissolved copper. Between 4 and 7% of these emissions arise from hull cleaning activities, depending upon the type of coating. The remaining 93 to 96% of the copper emissions arose from passive leaching. The relative difference in loadings between passive leaching and hull cleaning activities is a function of frequency. On a daily basis, the flux of dissolved copper was slightly higher for cleaning activities than passive leaching (Table 2). However, most vessels are cleaned once per month, whereas passive leaching is a continuous process.

DISCUSSION

Flux rates of dissolved copper varied in our study as a function of biocide content within the coating, hardness of the coating matrix, development

Table 2. Mean flux rates (95% confidence intervals) of dissolved copper for three types of commercially available antifouling coatings for passive leaching, hull cleaning using best management practices (BMPs), and hull cleaning without BMPs.

	Mean Dissolved Copper Flux		
	Modified Epoxy	Hard Vinyl	Biocide Free
Passive Leaching (µg/cm^2/day)	4.32 (0.44)	3.71 (0.86)	0.24 (0.08)
Hull Cleaning (µg/cm^2/event)			
BMP	8.57 (0.70)	3.84 (1.55)	0.03 (0.02)
No BMP	17.45 (1.65)	4.18 (0.35)	0.05 (0.03)

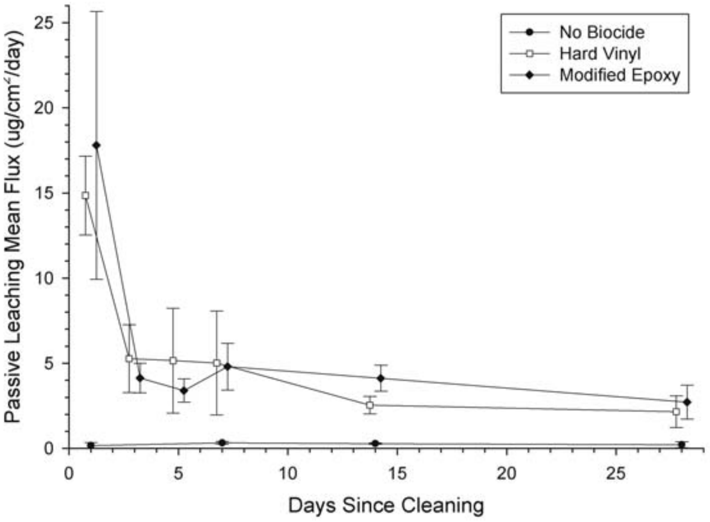

Figure 2. Mean (+ std dev) changes in passive leaching of dissolved copper from three types of hull coatings (hard vinyl, modified epoxy, biocide free) over 28 days following a cleaning event.

of biofilms and other fouling organisms, amongst others. Release rates were highest for the modified epoxy coating in this study. This paint had a greater copper content (57.7%) than the hard vinyl (37.25%) or biocide-free (0%) coating based on the ingredients listed on the product container. Our study used three types of coatings, but there are many available on the commercial and industrial markets including ablative and self-polishing copolymer coatings. Passive *in-situ* leach rates of dissolved copper from ablative paints used by the U.S. Navy were measured to average 3.9 µg/cm^2/d (Zirino and Seligman 2002). Valkirs *et al.* (2003) measured passive leach rates that ranged from 8-22 µg/cm^2/d after two months at steady-state conditions from ablative in service and copolymer self-polishing test coatings used on military vessels. In the United Kingdom, Thomas *et al*. (1999) found ablative leach rates that ranged from 18.6-21.6 µg/cm^2/d in 17-d experiments. Although ablative coatings appear to have a slightly higher flux rate, the use of these coatings has diminished in recent years in civilian pleasure craft. Interestingly, the reduction in ablative coatings stems not from concerns about water quality, but rather from concerns about air quality. It appears that these coatings have a large volatile component that makes it difficult for most boatyards, at least in southern California, to comply with clean air standards (Leigh Johnson *personal communication*).

The hardness of the coating matrix appeared to alter the flux rates of dissolved copper, particularly during cleaning events. In the present study, both the modified epoxy and hard vinyl coatings were classified by the manufacturer as hard, insoluble types that release biocide through contact leaching. However, water discoloration by coating particles was observed during cleaning operations on panels with modified epoxy, but not with the hard vinyl matrix. Moreover, the concentration of dissolved copper was higher following cleaning activities in the softer modified epoxy coating, which was only exacerbated when more abrasive cleaning techniques were applied. In contrast, the most abrasive cleaning technique did not alter dissolved copper flux rates for the hard vinyl coating.

Biofouling quickly reduced and, ultimately, equalized the passive leaching rates of both copper-containing coatings examined in this study. Biofilms have been shown to alter release rates (WHOI 1952, Mihm and Loeb 1988, Valkirs *et al.* 2003). Cleaning events allowed the passive leach rates of the paints

Table 3. Estimated mean dissolved copper mass emissions (grams per month) for three coating types (hard vinyl, modified epoxy, and biocide free) for a 9.1 m powerboat.

	Flux (g/mo)		
	Modified Epoxy	Hard Vinyl	Biocide Free
Passive Leaching	24.9	21.4	1.4
(Min - Max)	23.3 - 27.8	15.7 - 24.5	0.9 - 1.8
Underwater Hull Cleaning with BMPs	1.8	0.8	<0.01
(Min - Max)	1.7 - 2.0	0.5 - 1.2	0.00 - 0.01
Total Emissions	26.7	22.2	1.4
(Min - Max)	20.5 - 33.6	15.0 - 31.5	0.9 - 1.8

to temporarily function above 10 μg/cm^2/d, a leach rate known to retard biofouling (WHOI 1952, Caprari *et al.* 1986). However, as the biofilm layer increases it may sequester leached metals. As evidence of this, biofilms have been reported to contain high (1.3-3.5 μg/mg dry wt) copper concentrations (French *et al.* 1984).

One potential concern about our study design was extrapolation of our results from fiberglass panels to the hulls of recreational vessels. This concern appears minimal, though, because our measurements compared favorably to measurements from recreational vessel hulls (Figure 3). Valkirs *et al.* (2003), using the *in situ* methodology used in our study, reported passive leach rates on seven different recreational vessels of varying coating formulations with different copper content, time since application, and time since cleaning. The mean passive leach rate of the recreational vessels was approximately double the fiberglass panels (8 versus 4 μg/cm^2/d), but the range of measurements for the vessels encompassed the mean of our panel system. In fact, the range of measurements for the seven different recreational vessels was within the range of measurements for the fiberglass panels (2-26 μg/cm^2/d) over the one-month test period. Likewise, the flux rates measured during hull cleaning events using fiberglass panels were comparable to results measured from recreational vessels (Figure 3). Similar to isolating fiberglass panels in a dockside tub system, we were able to measure replicate vessels by isolating them from the marina environment using a boat bag. The mean cleaning flux rate measured for the fiberglass panels and the boat bag systems were within 12% of each other. The range of hull cleaning flux rates from recreational vessels appeared much smaller than the passive leaching flux rates, perhaps because the vessels were all similar in size, coating formulation, time since application, and time since cleaning.

If managers wish to reduce dissolved copper emissions from hard vinyl or modified epoxy antifouling coatings on recreational vessels, it is most efficient to alter coating types rather than focus on hull cleaning BMPs. On a mass basis, 95% of the loading from recreational hull coatings occurs via passive leaching. Therefore, even if a BMP existed that reduced all of the dissolved copper emissions, the total cumulative reductions would amount to only 5%. Furthermore, most commercial hull cleaners attempt to clean coatings with minimal abrasiveness. These techniques not only reduce copper emissions, but also prolong the life of the coating. The use of BMPs may be more effective on softer coatings such as copper-based ablative paints. Switching to nontoxic alternatives may be the most effective mechanism to reduce overall copper emissions, but this alternative comes with a sacrifice. In this study, the nontoxic coating

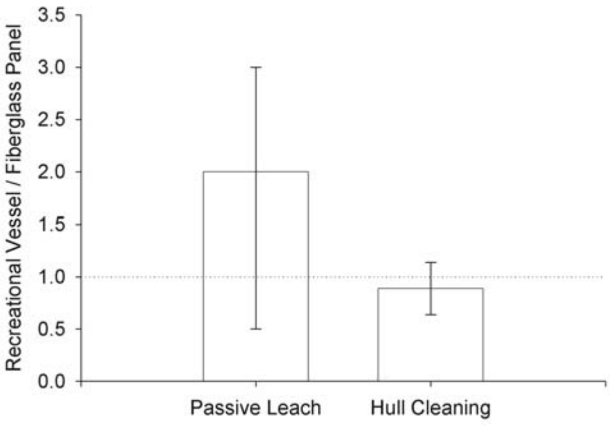

Figure 3. Ratio of mean (min, max) dissolved copper flux rates for passive leaching or hull cleaning activities from recreational vessels relative to fiberglass panels used in this experiment. Data for passive leaching from recreational vessels from Valkirs *et al* (2003).

alternative fouled much more quickly, contained more "hard" growth (i.e., barnacles), and required increased cleaning effort and time.

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ACKNOWLEDGEMENTS

The authors are deeply indebted to Dr. W.R. Crawford III, a businessman with tremendous integrity. Additional acknowledgements include F. Aquin, S. Whisnant, P. Michael, K. Kelly, P. Seligman, L. Johnson, D. Tsukada, L. Tiefenthaler, D. Ackerman, K. Ritter, and S. Bay. Laboratory analysis was conducted by CRG Marine Laboratories (Torrance, CA). Fiberglass panels were constructed by Crystaliner Corp. (Costa Mesa, CA). Boat bags were provided by Bottom Liner Corp. (Long Beach, CA). Portions of this study were funded by the San Diego Regional Water Quality Control Board and the State of California Department of Pesticide Regulation. The use of trade names does not constitute a product endorsement by funding agencies.