Department of Pesticide Regulation

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M E M O R A N D U M

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VIA: Charles M. Andrews
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FROM: David Duncan *Original Signed By*
Environmental Program Manager II
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DATE: January 30, 2014

SUBJECT: DETERMINATION OF MAXIMUM ALLOWABLE LEACH RATE AND MITIGATION RECOMMENDATIONS FOR COPPER ANTIFOULING PAINTS PER AB 425

The Department of Pesticide Regulation (DPR) placed copper-based antifouling paint (AFP) products into reevaluation in June 2010 to address elevated copper concentrations in salt water marinas that are primarily a result of extensive use of copper AFPs on recreational boat hulls.

To date, affected pesticide registrants have complied with the reevaluation data requirements, including disclosure of product copper leach rate, paint types, and potential mitigation strategies that have been valuable to the Environmental Monitoring Branch (EMB) as our staff evaluate mitigation approaches to address the issue. The registrants also funded a passive leaching and hull cleaning study (Earley *et al.*, 2013) to provide DPR with data on copper loading and the water quality impacts of in-water hull cleaning. Reevaluation continues as DPR works toward implementing solutions that will reduce copper concentrations in California marinas.

In October 2013, the Governor signed Assembly Bill (AB) 425 (Atkins) into law. AB 425 states, "No later than February 1, 2014, the Department of Pesticide Regulation shall determine a leach rate for copper-based antifouling paint used on recreational vessels and make recommendations for appropriate mitigation measures that may be implemented to address the protection of aquatic environments from the effects of exposure to that paint if it is registered as a pesticide."

The purpose of this memorandum is to present: 1) DPR's modeling approach and rationale for decision making; 2) DPR's recommendations for mitigation; and 3) the selected maximum allowable leach rate.

Modeling Approach and Rationale for Decision Making

EMB utilized the Marine Antifoulant Model to Predict Environmental Concentrations (MAM-PEC) as a reliable modeling tool to simulate the fate of copper in typical California marinas. Scientists and regulators worldwide (including the U.S. Environmental Protection Agency and the European Union) commonly utilize MAM-PEC to predict environmental concentrations of AFP biocides in a variety of marine environments. In our case, we used MAM-PEC in a manner that ultimately generated a maximum allowable copper leach rate for boats painted with copper AFPs.

DPR selected the California Toxics Rule (CTR) chronic criterion of 3.1 µg/l or parts per billion (ppb) dissolved copper as the statewide target for the reduction of copper loading from AFPs in California marinas. The CTR acute and chronic criteria are currently being enforced by the State Water Resources Control Board and the nine Regional Water Quality Control Boards (collectively referred to as the Water Boards).

With the CTR reduction target in mind, EMB relied on data for 20 California salt water marinas to accurately construct marina scenarios that reflected various levels of copper loading (for detailed modeling analysis see Appendix 1). Five scenarios were subsequently established to define distinct risk management levels. The lowest marina scenario (i.e., #1) represents marinas with 733 boats, which is the median size among the 20 sampled marinas. Scenario 2 represents marinas with 1,270 boats (75th percentile in size); scenario 3 represents marinas with 1,833 boats (90th percentile in size); scenario 4 represents marinas with 2,263 boats (95th percentile in size). Scenario 5 represents marinas with 4,754 boats (largest in size among the sampled marinas), which is comparable to Marina del Rey in Los Angeles County.

As an initial step in determining the maximum allowable leach rate for the five scenarios, EMB modeled the leach rates produced under the condition that the average predicted concentration of dissolved copper within a marina is below the CTR of 3.1 µg/l. This modeling procedure produced the maximum allowable leach rates for each of the five scenarios that range from 1.12 to 24.60 $\mu g/cm^2/day$ (Appendix 1, Table 6, "LR_0" column).

Since in-water hull cleaning commonly occurs in California marina waters, we must adjust these leach rates appropriately to account for the impacts of this activity on passive leaching. Note that cleaning produces particulate copper as well as dissolved copper; however, for the purpose of our analysis, we focused only on dissolved copper.

Although Earley *et al.* (2013) showed that the in-water hull cleaning event itself represents only about 1–3% of dissolved copper loading to the 3-year life span of the AFP, their data also showed that the refreshment of the painted hull surface ultimately causes a spike in passive leaching that gradually declines to the baseline or steady state leach rate within about four weeks.

Therefore, as a direct result of this activity, the regular refreshment of the painted hull can contribute to 59% (average for epoxy and ablative AFPs) of the dissolved copper loading over the 3-year life span of the paint if a relatively abrasive 3M™ pad is used for scrubbing. Note that the use of this material is not considered to be a best management practice (BMP) and therefore we consider this to be a worst case cleaning scenario. For the purpose of determining a maximum allowable leach rate, EMB conservatively assumed that this non-BMP practice is used by all in-water hull cleaners on all boats in every marina. Adjustments for non-BMP in-water hull cleaning lower the initial leach rates to a range of 0.46 to 10.09 $\mu g/cm^2/day$ (Appendix 1, Table 6, "LR_2" column).

EMB compiled a list of leach rates for 169 copper AFP products that were actively registered as of December 2013, using data submitted by registrants. Leach rates ranged from 1.0 to 29.6 $\mu g/cm^2/day$ with a mean of 11.1 $\mu g/cm^2/day$. With this list, EMB determined that for scenarios 1, 2, 3, 4 and 5, the percentage of currently registered copper AFP products that exceed each scenario's associated leach rate were 50, 85, 91, 97 and 100, respectively. Note that the calculated maximum allowable leach rates could change if other actions that impact copper leaching from boat hulls are taken.

Recommendations for Mitigation

EMB assumes that the AB 425 requirement for the "determination of a leach rate" means a maximum allowable leach rate that will serve as a limit for California registered copper AFP products. As noted above, this would mean some percentage of currently registered products would be required to reformulate. EMB has determined that reformulation to AFP products to reduce copper leach rates will dramatically decrease copper loading in marinas. This impact will be pronounced in any of the five scenarios we have defined. However, if product reformulation is to play a key part in the mitigation of copper in marinas, other critical activities need to also be implemented to ensure the overall success of this endeavor. Appendix 2 contains a list of mitigation recommendations from EMB and includes the identification of the parties likely to be involved and a short rationale for the recommendation. Besides reformulation of copper AFP products, these recommendations also include:

- Require in-water hull cleaners to implement BMPs for in-water hull cleaning.
- Reduce in-water hull cleaning frequency to no more than once per month.
- Include painted-hull maintenance information as part of product labels.
- Develop for distribution hull maintenance brochures to be provided to boaters via boatyards at the time of painting.
- Increase boater awareness and acceptance of copper AFP alternatives.
- Foster new incentive programs and continue support for existing programs to convert copper-painted boat hulls to those painted with alternatives.

- Consider site-specific objectives (SSOs) for copper for certain marinas or harbors.

In Appendix 1, EMB further quantitatively explored the impacts that the implementation of many of these recommendations could have on bringing California salt water marinas to compliance with the CTR chronic criterion. Two of these quantitative evaluations that relate to in-water hull cleaning are summarized below.

Earley *et al.* (2013) tested an in-water hull cleaning BMP that employed soft pile carpet as the scrubbing material. This BMP came directly out of the California Professional Divers Association's (CPDA's) hull cleaning BMP certification manual (CPDA, 2008). The BMP material was tested against a more abrasive non-BMP 3M™ pad. Data showed that the BMP cleaning only contributed to 43% (average for epoxy and ablative AFPs) of the copper loading over the 3-year lifespan of the paint compared to 59% from the non-BMP cleaning.

EMB staff also observed that by limiting the frequency of cleaning to monthly during the entire year, up to five less passive leaching spikes are eliminated over the 3-year lifespan of the paint. The cleaning schedule used by Earley *et al.* (2013) was once every three weeks in the summer (June, July, August) and once every four weeks the rest of the year. Loading comparisons showed that a monthly frequency of cleaning lowers copper loading from 43% to 29% over the 3-year lifespan of the paint. Implementation of an even lower frequency of cleaning (e.g., every five weeks, bimonthly) could further reduce copper loading; however, reduction in frequency should be carefully weighted with the benefits of cleaning.

Implementation of these two proposed actions to decrease the magnitude of passive leaching of copper allows DPR to work with a higher range of leach rates that provides greater flexibility in maintaining sufficient product efficacy in reformulated products. Efficacy is critical for the effective control of native fouling species as well as non-native aquatic invasive species. If monthly, soft-pile carpet BMP becomes the accepted industry norm for a cleaning regime, this will allow DPR to work with scenarios with maximum allowable leach rates that range from 0.79 to 17.47 $\mu g/cm^2/day$ (Appendix 1, Table 6, "LR_3" column).

<u>Selected Maximum Allowable Copper Leach Rate</u>

Based on our modeling analysis, DPR recommends the establishment of the maximum allowable copper leach rate for AFP products at 9.5 $\mu g/cm^2/day$ under the condition that in-water hull cleaners follow CPDA's BMP method with soft-pile carpet and that cleaning cannot be performed more frequently than once per month.

For copper AFP products that do not require in-water cleaning, DPR recommends the establishment of the maximum allowable copper leach rate at 13.4 $\mu g/cm^2/day$ under the condition that in-water hull cleaning of any type is prohibited. Registrants will need to prove this

specific product claim to DPR via studies that are conducted in appropriate California marine settings.

In order to reinforce product-specific requirements for in-water hull maintenance for both categories of AFPs to boat owners, brochures or other forms of outreach materials need to also be provided to them. The most logical strategy for product-specific outreach is probably to have boatyards provide brochures to boat owners at the time of painting. More general outreach is important as well in the overall mitigation effort. Other points of distribution (e.g., marinas, AFP retailers, and boating events) will need to be explored.

Setting a maximum allowable leach rate at 9.5 $\mu g/cm^2$/day should result in about 58% of the currently registered copper AFP products or approximately 100 products having to be reformulated. The highest leaching product currently available has the leach rate of 29.6 $\mu g/cm^2$/day. This is equivalent to a maximum of 68% reduction in leaching rate.

The selection of these two leach rates is protective of marinas in scenario 2 where EMB expects waters in marinas that contain as many as 1,270 boats to be in complete compliance with the chronic CTR criterion of 3.1 ppb. Nearly all California salt water marinas are addressed in scenario 2. EMB expects to also observe a significant reduction in dissolved copper concentrations in the larger marinas of scenarios 3, 4, and 5. Although dissolved copper concentrations in these marinas may still at times exceed the CTR criterion, the eventual reduction in copper loading will increase protection of aquatic organisms in all of California's marinas.

EMB expects to see increased adoption of non-copper alternatives (i.e., coatings or technologies) in the future considering the amount of research, development, testing, and demonstration of alternatives that has taken place in recent years. Using our model, we estimated that a 12% adoption rate of non-copper alternatives will bring the marinas belonging in scenario 3 (those with 1,833 boats or less) into compliance with the CTR criterion. A larger adoption rate will bring even larger marinas into compliance. EMB will continue to work with stakeholders groups to facilitate greater adoption of AFP alternatives, including biocide-free products that are a growing presence in the marketplace.

Interested parties may also pursue development of SSOs for consideration by the Water Boards. Before undertaking this effort, parties should discuss the various approaches available to them with a representative of the Water Boards. The Water Effects Ratio approach already exists as option. The Biotic Ligand Model (BLM), which represents a reliable and economical way to calculate site-specific standards in fresh water, is being evaluated by U.S. EPA for use in the salt water environment. Note that in a letter from its Executive Director to the San Diego Port Tenants Association dated September 13, 2013, the State Water Resources Control Board (State Water Board) stated its support of the U.S. EPA in pursuing and making it a priority to complete

development of salt water copper criteria using the BLM. In that letter, the State Water Board also stated that if a BLM for salt water copper criteria was completed, then it would provide another tool that could be used by the Water Boards in developing SSOs for copper.

It is important to stress that reformulation alone based on the selection of any of the five scenarios we developed represents a significant reduction of copper loading to all salt water marinas in California. Reductions should also benefit brackish and fresh water marinas that harbor boats with copper AFPs. The full water quality impact of the this mitigation effort may not be realized for many years due to the timeframes involved with reformulation, relabeling, registration approval, and market distribution. Moreover, the rate at which boatyards can convert boat hulls (i.e., strip existing AFP and apply a new one) is limited. Therefore, the eventual transition to reformulated AFP products will also be dependent on this factor. We would, however, expect to see more immediate improvements in water quality from changes to in-water hull cleaning practices.

As a part of the copper AFP reevaluation, DPR will begin immediate discussions with copper AFP registrants and U.S. EPA regarding reformulation, data requirements (e.g., efficacy), label restrictions and outreach for boaters, boatyards, and marinas. DPR will additionally engage with the Water Boards, registrants and key stakeholder groups to further refine and implement the overall mitigation effort.

We request your approval of this determination. If you or your staff have any questions or require additional information, please contact Nan Singhasemanon, of my staff, at 916-324-4122 or <nsinghasemanon@cdpr.ca.gov>.

APPROVED: *Original Approved By* DATE: 01/30/14
Brain R. Leahy, Director

Attachments

cc: Victoria Whitney, SWRCB, Deputy Director (w/Attachments)
Chris Reardon, DPR, Chief Deputy Director (w/Attachments)
Nan Singhasemanon, DPR, Sr. Environmental Scientist (w/Attachments)

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Appendix 1

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Modeling to determine the maximum allowable leach rate for copper-based antifouling products in California marinas

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Abstract

DPR is required by law to determine a copper leach rate for antifouling paint pesticides for the protection of aquatic environments. Five scenarios representing various levels of copper loading were defined. For each scenario, a leach rate was calculated by the MAM-PEC model that limits dissolved copper concentrations in the marina to below the California saltwater chronic water quality standard of 3.1µg/L. Copper leach rates were calculated for 5 different marina scenarios based on hull cleaning techniques and frequency of cleaning events. The maximum allowable leach rate ranged from 0.46 to 24.6 µg/cm^2/day depending on the scenario, cleaning frequency, and cleaning methods. About 5–100% of current registered products have leach rates that are higher than the derived leach rates. Leach rates calculated for the BMP and non-BMP decreased from those determined for no cleaning. When the cleaning frequency was decreased to monthly, leach rates were increased by 25% for BMP scenarios and 9% for the non-BMP scenarios. Converting to non-copper alternatives can also reduce copper loading and consequently affect the selection of maximum allowable leach rates. This analysis will serve as a basis for decision making on scenario selection and final leach rate determination.

Introduction

Copper has been found in California marinas at concentrations exceeding water quality criteria (Singhasemanon *et al*., 2009). Copper-based antifouling paint (AFP) pesticides are commonly applied on the underwater portion of a vessel as a biocide to protect boats from fouling. These copper AFPs have been identified as the primary source of copper pollution in marinas, particularly in salt and brackish water marinas along the California coast. In 2010, the Department of Pesticide Regulation (DPR) initiated the re-evaluation of 212 copper-based AFP products. In October 2013, assembly bill AB 425 was passed. This bill requires DPR to determine a leach rate for copper AFPs used on recreational vessels and to make recommendations for appropriate mitigation measures that may be implemented to protect aquatic environments from the effects of exposure to these paints. The objective of this analysis is to determine the maximum allowable leach rates for AFPs that would limit copper concentrations to the levels that are within compliance of current California Toxics Rule (CTR) water quality standards.

Materials and Methods

The MAM-PEC model

The Marine Antifoulant Model to Predict Environmental Concentrations (MAM-PEC) is a hydrodynamic model designed to predict dissolved and total concentrations of antifouling compounds within marine environments. The model takes into account emission factors (e.g., leaching rates, shipping intensities, residence times, vessel hull underwater surface areas), compound-related properties and processes (e.g., K_d, K_{ow}, K_{oc}, volatilization, speciation, hydrolysis, photolysis, bacterial degradation), and properties and processes related to the specific environment (e.g., currents, tides, salinity, DOC, suspended matter load) (van Hattum *et al*., 2002).

MAM-PEC was developed in the Netherlands in 1999 and has been widely used worldwide including the European countries, New Zealand, and the United States. Recently, the model was used by U.S. EPA in their reregistration for copper products. The MAM-PEC was selected for this study due to its wide-acceptance, adaptability, and its capability of providing predicted environmental concentrations (PECs) for generic marine environments including marinas.

The MAM-PEC model is normally used to predict copper concentrations (PEC) in a marina based on input parameters including the leach rate for a copper AFP. For this study, however, DPR used the saltwater copper CTR criterion (3.1 µg/L) as target output to back-calculate the leach rate needed to achieve the desired dissolved copper concentration in a marina. The reverse approach included the following steps: (1) run the model with an initial estimate of the leach rate value; (2) compare the model generated average PEC value for DCu to the target concentration value of 3.1 µg/L; (3) adjust the leach rate according to the difference between the average PEC and the target value and re-run the model; and (4) repeat step 1 to 3 until the PEC for DCu equals the target value.

Definition of marina scenarios

MAM-PEC can simulate various marine environments including marinas, harbors and shipping lanes. In addition to the EU standard scenarios, the model also allows users to define their customized environments. In California, monitoring studies have shown that high copper concentrations were found mainly in salt and brackish water marinas (Singhasemanon *et al.*, 2009). Therefore, this study defines the copper AFP use scenarios for California marinas and uses the option of user-defined marina in the MAM-PEC environmental setting.

To define the marina scenarios, a dataset containing physical dimension and environmental chemistry information from 20 California marinas was used (sample dataset). International Paint, Inc. developed this dataset and included it in their mitigation proposal to DPR (International Paint, 2010). It contains measurements for 15 variables including total number of vessels, marina length, width, surface area, outlet width, fraction of total vessels in the marina painted with copper, tidal period, mean tidal range, water depth, median total suspended solids (TSS), median DOC, background DCu concentration, pH, salinity, and temperature (Appendix I). The physical dimension such as marina length, width, and outlet width data were obtained from Google Maps satellite imaging. Water depth was determined by taking the depth from the website of the

marina or data from local National Oceanic and Atmospheric Administration (NOAA) stations, Singhasemanon *et al*., (2009) or San Diego Regional Water Board (2005). The physicochemical data such as TSS, pH, and temperature were taken from the nearest NOAA stations. The full list of data is attached in Appendix I.

Five California marina scenarios were defined reflecting various levels of copper loading with scenario 1 having a lower level of copper loading and scenario 5 having a higher level of copper loading (Table 1 and 2). The five scenarios were differentiated by assigning different values to the nine key parameters that reflect the total number of vessels, physical dimension and physicochemical properties of marinas (Table 1 and 2). The percentile values for each of the 9 parameters from the sampled dataset were used. For example, for the total number of vessels, 50th, 75th, 90th, 95th percentile and the maximum values were used for scenario 1, 2, 3, 4, and 5, respectively (Table 1). However, while some variables are positively correlated with the PEC of DCu some others are negatively correlated. Therefore, for the variables that are positively correlated with the PEC (e.g., number of vessels, background concentration of DCu) values at 50th, 75th, 90th, 95th percentile and the maximum values were used for scenario 1, 2, 3, 4, and 5, respectively. For variables that are negatively correlated with PEC (e.g., TSS, tidal range, water depth, outlet width), values at 50th, 25th, 10th, 5^{th}percentile and the minimum values were used instead. This approach ensures that the copper loading levels incrementally increase from scenario 1 to 5.

There is one complication with the above approach. Some variables are strongly correlated with each other but have the opposite impact on DCu PECs. For example, the total number of vessels is strongly correlated with surface area of marinas (product of marina width and length) (Fig 1). While the number of vessels is positively correlated with DCu PECs, marina width is negatively correlated with DCu PECs. In this case, percentile values for the number of vessels and marina width were used directly as model input. Then, the surface area and marina length were calculated based on the number of vessels using equations (1) and (2). Equation 1 is the regression equation from Figure 1. For marina width, the maximum value, and the values at 95th, 90th, 75th and 50th percentiles were used for scenario 1, 2, 3, 4, and 5, respectively. The values for the total number of vessels and the physical dimensions of marinas are shown in Table 1. The values for the physicochemical properties for each of the scenarios are shown in Table 2.

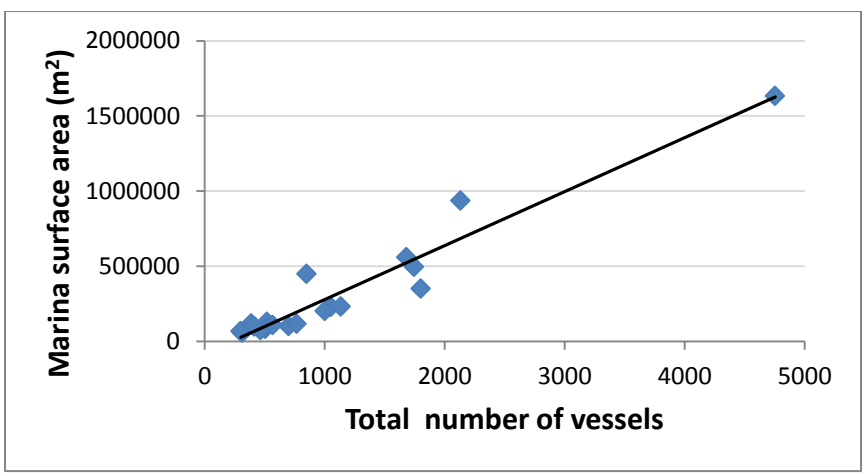

Fig 1: Regression between total number of vessels and marina surface area; $P < 0.0001$, $R^2 = 0.93$

$$Marina\ Surface\ Area \quad 359 \quad Total\ Vessels - 80073 \qquad \text{Equation (1)}$$

$$Marina\ Length \quad Surface\ Area \quad Marina\ Width \qquad \text{Equation (2)}$$

The rest of the variables were not listed on tables 1 and 2 because they do not vary significantly among the 20 marinas or the variables are not critical for producing the DCu PEC. These variables are tidal period, copper application rate, pH, DOC, and salinity. The mean values of these variables were used as model input and were identically set for all the 5 scenarios.

Table 1: Physical dimensions and number of vessels defined in the five scenarios

Marina Scenarios	Copper loading	Number of vessels		Outlet width X3 (m)		Marina width Y1 (m)		Surface Area (m^2)	Marina length X2 (m)
		Value	Percentile	Value	Percentile	Value	Percentile		
1	Low	733	50%	95	50%	1,600	100%	182,895	114
2		1270	75%	63	25%	1,594	95%	375,857	236
3		1833	90%	49	10%	1,543	90%	578,046	375
4		2263	95%	43	5%	751	75%	732,344	975
5	high	4754	100%	40	0%	473	50%	1,626,613	3443

Table 2: Physiochemical properties for marinas in the five scenarios

Marina Scenarios	Copper loading	Tidal range (m)		Water depth (m)		TSS (mg/L)		Background concentration of DCu (µg/L)	
		Value	Percentile	Value	Percentile	Value	Percentile	Value	Percentile
1	Low	1.24	50%	3.66	50%	18.20	50%	0.70	50%
2		1.16	25%	2.44	25%	17.10	25%	1.23	75%
3		1.11	10%	2.12	10%	14.52	10%	1.61	90%
4		1.08	5%	2.03	5%	13.66	5%	1.70	95%
5	high	1.08	0%	2.03	0%	13.00	0%	1.70	100%

<u>Estimation of underwater area of vessels</u>

The underwater area of vessels is a very important parameter in MAM-PEC because copper emission is calculated based on the underwater area and leach rate. The study used the following equation to estimate underwater area of vessels:

$$UnderWaterArea \quad length \quad beam \quad 0.85 \qquad \text{Equation (3)}$$

This equation is widely used by paint manufactures to provide an estimate of underwater areas of vessels for paint application (Schiff et al., 2004). Vessel length was estimated based on a dataset from a boat survey. The survey was conducted by researchers from San Francisco State on vessel sizes and types in California's marinas during 2007-2009 (Godard and Browning, 2011). Table 3 shows their survey results on vessel lengths. The percentages of vessels in each length category are similar for the survey conducted in 2007-2008 and 2009. The percentage numbers from 2009

survey were used to derive number of vessels of certain length category for each scenario (Table 4).

To estimate vessel beam size, a set of survey data obtained from the Shelter Island Yacht Basin (SIYB) was used. The data contain beam width and vessel length for marinas in the SIYB (2012 Shelter Island Yacht Basin TMDL monitoring and progress report, March, 2013; Appendix Table B-3). Using this dataset, the following relationship between beam width and length were derived:

- Vessel length < 16 ft: Beam width = 5
- Vessel length > 16 ft: Beam width $-21.1 + 9.2 \ln$ length) Equation (4)

The regression in Equation (4) was significant with P-value < 0.0001 and R^2 value of 0.70. This equation is similar to the California Department of Boating and Waterways guidelines (2005), where beam width is estimated as:

Beam width = -14 + 8 * Ln (Length) for power boats and
Beam width = -10.5 + 6.5 * Ln (Length) for sail boats

Using the above method, vessel underwater areas were estimated for each vessel length categories as shown in Table 5.

Table 3: Vessel length in California's marinas*

Length of vessel	Count 07-08	Percent 07-08 (%)	Count 09	Percent 2009 (%)
< 16 ft	228	8.7	283	9.4
16-19 ft	450	17.1	595	19.8
20-25 ft	846	32.2	919	30.6
26-39 ft	792	30.1	870	29.0
40-65 ft	295	11.2	315	10.5
> 65 ft	17	0.6	18	0.6
Total	2628	100.0	3000	100.0

* Source: Godard and Browning, 2011

Table 4: Number of vessels within each length category for the 5 scenarios

Length of vessel	Percent from survey (%)	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
8- 16 ft	9.4	69	120	173	213	448
16-19 ft	19.8	145	252	364	449	943
19-25 ft	30.6	225	389	562	693	1456
25-39 ft	29.0	213	368	532	656	1379
39-65 ft	10.5	77	133	192	238	499
65-160 ft	0.6	4	8	11	14	29
total	100.0	733	1270	1833	2263	4754

Table 5: Estimated beam width and underwater areas for each vessel length category

Length of vessel (ft)	Average length (ft)	Estimated beam (ft)	Underwater area (ft^2)	Underwater area (m^2)
8- 16	12	5.0	51.0	4.7
16-19	17.5	5.2	77.8	7.2
19-25	22.5	7.5	144.3	13.4
25-39	32.5	10.9	301.9	28.0
39-65	52.5	15.3	684.5	63.6
65-160	115	22.6	2204.6	204.8

During the model runs, all vessels were assumed to be berthed in the marina rather than moving in or out of the marina. This is because the amount of time a vessel is moving in a marina is minor compared to it being berthed according to the survey by Godard and Browning (2011).

Effects of underwater hull cleaning

Studies have shown that underwater hull cleaning increases copper release from AFPs both during and after cleaning (Schiff *et al.*, 2004; Earley *et al*., 2013); therefore, the allowable leach rate is adjusted to account for additional copper loading over no cleaning. Since the MAM-PEC model has no input parameter for hull cleaning, an adjustment factor was calculated for loading from the BMP and non-BMP cleaning and applied to the leach rates calculated from the model.

The adjustment factors were derived from the copper leaching measurement by Earley *et al.*, (2013). Earley *et al.* (2013) measured the life cycle of copper leach rate including before, during and after hull cleaning events using the U.S Navy's Dome measurement method. The study showed that for a 3-year life cycle, copper loading from hull cleaning using the BMP was 41.2 and 44.6% higher for epoxy and ablative AFPs, respectively, over loading from no cleaning; and loading using the non-BMP was 56.2 and 62.3% higher for epoxy and ablative AFPs, respectively, than loading from no cleaning. The adjustment factors were calculated as follows:

$$(100 - ((41.2 + 44.6)/2))/100 = 0.57 \text{ for BMP}$$
$$(100 - ((56.2 + 62.3)/2))/100 = 0.41 \text{ for non-BMP}$$

These factors were then applied to adjust the no-cleaning leach rates calculated from the MAM-PEC model. For example, if the leach rate from modeling was 10 $\mu g/cm^2/day$, the final values of 5.7 and 4.1 $\mu g/cm^2/day$ would be produced to account for the effects of hull cleaning using BMP and non-BMP methods, respectively.

In addition, adjustment factors were calculated for a reduced cleaning frequency with BMP and non-BMP methods. The cleaning schedule used by Earley *et al.* (2013) was once every three weeks in the summer (June, July, August) and once every four weeks in September through May, which is consistent with the current regime. In this analysis, a cleaning schedule with a lower frequency (monthly) was used. Using the leach rate data in Earley *et al.* (2013), we calculated the loading from hull cleaning. For a 3-year-lifecycle, an average of 29 and 55.2% of the dissolved copper were from monthly hull cleaning via BMP and non-BMP method, respectively. Consequently, the adjustment factors of 0.71 and 0.448 were used to account for the effects of monthly cleaning.

Results and Discussion

Table 6 shows the leach rates from the modeling (LR_0) and the adjusted leach rate to account for the effects of underwater hull cleaning using BMP (LR_1, LR_3) and non-BMP (LR_2, LR_4) methods. The rates from modeling with no cleaning ranged from 1.12 µg/cm^2/day for scenario 5 to 24.6 µg/cm^2/day for scenario 1. The adjusted leach rates for BMP cleaning ranged from 0.64 µg/cm^2/day for scenario 5 to 14.02 µg/cm^2/day for scenario 1. The adjusted leach rates for non-BMP cleaning ranged from 0.46 µg/cm^2/day for scenario 5 to 10.09 µg/cm^2/day for scenario 1. With less frequent cleaning (monthly), the adjusted leach rates for BMP (LR_3) and non-BMP (LR_4) ranged from 0.79 to 17.47 and 0.50 to 11.02 µg/cm^2/day, respectively. Note that when the cleaning frequency was decreased to monthly, leach rates were increased by 25% for BMP scenarios and 9% for the non-BMP scenarios.

Table 6: Leach rates from modeling (LR_0) adjusted leach rates accounting for cleaning effects (LR_1: current cleaning schedule using BMP method; LR_2: current cleaning schedule using non-BMP method; LR_3: monthly cleaning using BMP method; LR_4: monthly cleaning using non-BMP method)

Scenario	LR_0 (µg/cm^2/day)	LR_1 (µg/cm^2/day)	LR_2 (µg/cm^2/day)	LR_3 (µg/cm^2/day)	LR_4 (µg/cm^2/day)
1	24.60	14.02	10.09	17.47	11.02
2	13.35	7.61	5.47	9.48	5.98
3	8.60	4.90	3.53	6.11	3.85
4	2.90	1.65	1.19	2.06	1.30
5	1.12	0.64	0.46	0.79	0.50

In addition to BMP and less frequent cleaning, conversion to non-copper alternatives can also reduce DCu loading in marinas. This reduction can be modeled by MAM-PEC by adjusting the input parameter of application factor. The current analysis assumes that all the vessels in the marina were coated with copper (application factor = 100%). The application factor can be lowered if vessels convert to non-copper products. A 10% conversion would result in about 10% reduction in PEC of DCu since the emission component of the MAM-PEC is linear.

This suggests that conversion to non-copper alternatives can provide additional levels of mitigation and it affects the final selection of maximum allowable leach rates. For example, if the maximum allowable leach rate was set to 9.48 µg/cm2/day (LR_3 for scenario 2), marinas represented in scenario 2 would meet the target CTR of 3.1 µg/L with monthly cleaning using BMP. Marinas with higher copper exposure levels, such as those in scenario 3, may not meet the target CTR. However, if 12% of vessels in scenario 3 marinas convert to non-copper alternatives, they will be able to meet the target CTR.

A dataset containing copper leach rates calculated by the International Organization for Standardization (ISO) method for 169 AFP products was obtained from registrants as a requirement of DPR's copper AFP reevaluation (Appendix II). ISO method is known to over-predict the actual leach rates (i.e., quantified by the Dome method). Therefore, we applied a commonly-used adjustment factor of 2.9 that has been established by Finnie (2006).

The adjusted leach rates (similar to the Dome method leach rates) for current AFPs ranged from 1.0 to 29.6 µg/cm^2/day, with a median rate of 10.1 µg/cm^2/day (Fig. 2, Appendix II). Table 7 shows the percentage of these AFP products that have the adjusted ISO leach rates above LR_0,

LR_1, LR_2, LR_3, and LR_4. For scenario 1, about 5, 23, 50, 17, and 41% of products exceeded LR_0, LR_1, LR_2, LR_3, and LR_4, respectively. For the most conservative case (scenario 5), 97-100% of these products exceeded LR_0, LR_1, LR_2, LR_3, and LR_4. The products with leach rates higher than the allowable leach rates would be targeted for reformulation if reformulation is used as a mitigation approach. These percentage numbers will change if the leach rate information for existing AFP products changes.

Table 7: Percent of current AFP products with adjusted leach rates exceeding LR_0, LR_1, LR_2, LR_3 and LR_4

Scenario	Percent of products exceeding LR_0 (%)	Percent of products exceeding LR_1 (%)	Percent of products exceeding LR_2 (%)	Percent of products exceeding LR_3 (%)	Percent of products exceeding LR_4 (%)
1	5	23	50	17	41
2	23	72	85	58	83
3	67	88	91	83	91
4	93	93	97	93	97
5	97	100	100	100	100

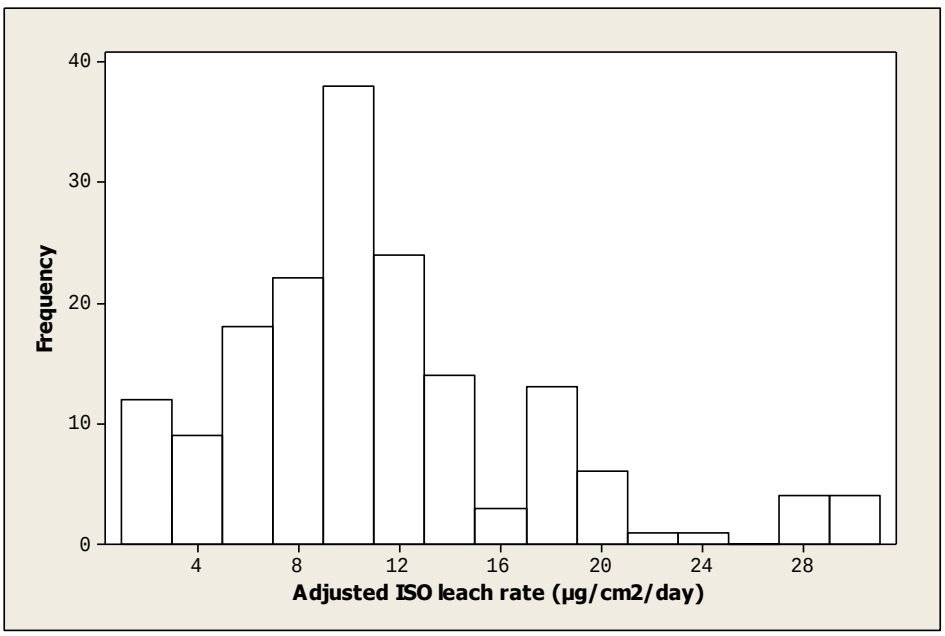

Fig 2. Histogram of adjusted product leach rate

Uncertainties

The uncertainties of the modeling are mainly from two groups of input variables that the modeling results are heavily dependent on: the physical dimensions of the modeled marina and the copper emission inputs. The important parameters related to physical dimensions include marina width (Y1), length (X2) and outlet width (X3). Marina width and length affect water volume, dilution, exchange and therefore PECs of copper. Outlet width affects tidal exchange rates and therefore the PECs of copper within the marina. MAM-PEC assumes a rectangular/square shape of marina (Fig 3), while in reality, not all marinas are of this shape.

This inconsistency introduces uncertainties to the modeling results. However, there is little we can do to reduce this source of uncertainty due to two reasons: (1) this analysis was not based on any particular marina but a generic case, and (2) in reality, marinas in California vary greatly in shape and there is no particular shape design that can be considered as highly "representative."

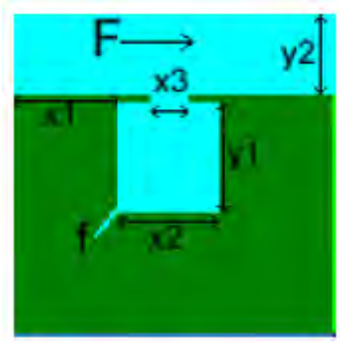

Fig 3: Conceptual model of a marina in MAM-PEC (van Hattum *et al*., 2002)

In addition to physical dimension inputs, there are uncertainties associated with copper emission inputs including vessel size distribution, number of vessels moving, number of vessels at berth, application factor (percentage of vessels applied with copper paint) and the underwater surface area of vessels. Information regarding vessel sizes in California marinas was based on recent surveys (2009) conducted on California marinas. Thus, the size distribution is likely representative for marinas within the State. However, considering that vessel size distributions do change over time, our analysis will have to be adjusted accordingly if major shifts in vessel size distribution do occur. We also formed the assumption that all vessels are at berth based on this survey's results, which shows that the time a vessel spent moving is minor compared to the time it spent at berth.

The largest uncertainties are perhaps associated with the estimate of underwater surface areas of vessels. Equation (3) provides a rule-of-thumb estimate. Methods for more accurate estimations are currently not available. Underwater surface area is one of the most important input variables for MAM-PEC. Doubling the values of underwater area would almost double the PECs of dissolved copper. Therefore, a good method for estimating vessel underwater surface area would greatly reduce model uncertainties. Studies are needed to obtain better estimations on the antifouled underwater areas for vessels in California marinas.

Conclusions

Five scenarios representing various levels of copper loading were defined with scenario 1 having a lower level of copper loading and scenario 5 having the maximum level of copper loading. The leach rates ranged from 1.12 to 24.60 $\mu g/cm^2/day$ without considering the effects of underwater hull cleaning (no cleaning). Factors of 0.57 and 0.41 were applied to adjust the leach rate to account for cleaning with BMP and non-BMP methods, respectively. The adjusted leach rates ranged from 0.64 for scenario 5 with the non-BMP to 14.02 $\mu g/cm^2/day$ for scenario 1 with BMP. The impact of limiting underwater hull cleaning to monthly can result in increasing the adjusted leach rates by 25% for BMP scenarios and 9% for the non-BMP scenarios. A transition from using copper antifouling paint products to non-copper alternatives can further reduce DCu concentrations and consequently affects the selection of maximum allowable leach rates. A comparison of all these maximum allowable leach rate thresholds to the leach rates of currently-

registered AFPs shows that 4.7–100% of these products would need to be reformulated depending on the scenario. The findings from this analysis serve as a basis for decision making on the scenario selection and the final leach rate determination.

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Appendix I

Measured physicochemical data for 20 California marinas

Marina	Location	Total Vessels	Tidal Period (hr)	Mean Tidal Range (m)	Water Depth (m)	Surface Area (m2)	Length X2 (m)	Width Y1 (m)	Outlet Width (m)	Median TSS (mg/L)	Median DOC (mg/L)	Background DCU (µg/L)	pH	Salinity (g/kg)	Temp °C
San Francisco Marina East	San Francisco Bay	313	12.41	1.25	2.44	55696	236	236	43	21.9	0.9	0.4	7.52	38.85	16.6
San Francisco Marina West	San Francisco Bay	388	12.41	1.25	2.44	116550	185	630	130	21.9	0.9	0.4	7.52	38.85	16.6
Coyote Point Marina	San Francisco Bay West	565	12.41	1.95	3.66	105876	204	519	56	17.8	1.7	1.3	7.77	33.12	21
South Beach Harbor	San Francisco Bay West	700	12.41	1.25	9.98	100320	285	352	74	16.2	0.9	0.7	7.31	33.88	18.1
Marina Bay Yacht Harbor	San Francisco Bay East	850	12.41	1.32	7.16	446572	778	574	233	13	1.1	1.7	7.54	32.94	19.5
Ballena Isle Marina	San Francisco Bay East	504	12.41	1.48	2.74	82140	222	370	250	20.1	1.4	1.4	7.96	32.33	20.3
Berkeley Marina	San Francisco Bay East	1,052	12.41	1.32	3.66	228762	537	426	89	18.1	1	0.7	7.84	32.42	18.6
Santa Cruz Harbor	Santa Cruz Harbor	1,000	12.41	1.08	3.74	199810	130	1537	74	23.2	1	0.3	8.04	41.89	16.5
Monterey Harbor	Monterey Bay	413	12.41	1.08	3.62	98568	296	333	204	14.1	1	0.2	8	42.01	16.4
Santa Barbara Harbor	Santa Barbara Channel	1,133	12.41	1.11	6.14	230436	444	519	193	18.2	0.8	0.1	7.84	37.49	18.2

Loch Lomond Marina	San Francisco Bay North	517	12.41	1.32	2.44	128316	204	629	50	18.9	1.3	1.7	7.41	29.17	21.7
Long Beach Downtown Shoreline Marina	Long Beach	1,800	12.41	1.16	2.03	349821	827	423	100	18.5	1	0.7	7.79	49.42	21.6
Marina del Rey, Santa Monica	Santa Monica Bay	4,754	12.41	1.15	5.5	1631000	1277	1277	305	17.1	1.1	1	7.75	33.76	22.9
Fisherman's Wharf Marina	San Francisco Bay	300	12.41	1.25	2.73	65860	178	370	50	NA	NA	NA	NA	NA	15.6
San Leandro Marina	San Francisco Bay East	465	12.41	1.48	2.13	71750	287	250	65	NA	NA	NA	NA	NA	21.1
Redondo Beach Marina	Santa Monica Bay	765	12.41	1.15	5.50	115200	480	240	40	NA	NA	NA	NA	NA	17.8
San Pedro Marina	Long Beach	1,681	12.41	1.16	2.03	557500	500	1115	192	NA	NA	NA	NA	NA	19.4
Shelter Island Yacht Basin	San Diego Bay	2,132	12.41	1.23	6.00	934400	584	1600	200	NA	NA	0.5	NA	NA	22
Downtown Marina, San Diego	San Diego Bay	410	12.41	1.23	6.00	98645	545	181	74	NA	NA	NA	NA	NA	22
Harbor Island Marina	San Diego Bay	1,744	12.41	1.23	6.00	495423	311	1593	244	NA	NA	NA	NA	NA	22

Appendix II

Copper leach rates for currently registered AFP products

Product #	ISO Leach Rate	Adjusted Leach Rate
1	85.7	29.6
2	85.7	29.6
3	85.7	29.6
4	85.7	29.6
5	82.4	28.4
6	82.4	28.4
7	82.4	28.4
8	82.4	28.4
9	67.4	23.2
10	61.2	21.1
11	60.7	20.9
12	60.7	20.9
13	60.7	20.9
14	60.7	20.9
15	58.9	20.3
16	58.9	20.3
17	55.0	19.0
18	55.0	19.0
19	55.0	19.0
20	55.0	19.0
21	55.0	19.0
22	55.0	19.0
23	55.0	19.0
24	55.0	19.0
25	55.0	19.0

26	55.0	19.0
27	54.1	18.6
28	51.9	17.9
29	51.4	17.7
30	46.4	16.0
31	46.4	16.0
32	45.4	15.7
33	42.4	14.6
34	41.2	14.2
35	41.2	14.2
36	41.0	14.1
37	41.0	14.1
38	40.9	14.1
39	40.9	14.1
40	38.3	13.2
41	38.3	13.2
42	38.3	13.2
43	38.3	13.2
44	38.3	13.2
45	38.3	13.2
46	38.3	13.2
47	35.9	12.4
48	35.8	12.3
49	35.5	12.2
50	34.6	11.9
51	33.8	11.7
52	33.4	11.5
53	33.3	11.5
54	33.2	11.5
55	33.2	11.5

56	32.9	11.3
57	32.9	11.3
58	32.9	11.3
59	32.9	11.3
60	32.9	11.3
61	32.5	11.2
62	32.5	11.2
63	32.5	11.2
64	32.5	11.2
65	32.5	11.2
66	32.5	11.2
67	32.5	11.2
68	32.5	11.2
69	32.1	11.1
70	32.0	11.0
71	30.5	10.5
72	30.5	10.5
73	30.5	10.5
74	30.5	10.5
75	30.5	10.5
76	30.5	10.5
77	30.4	10.5
78	30.3	10.4
79	30.1	10.4
80	30.1	10.4
81	30.1	10.4
82	29.7	10.2
83	29.7	10.2
84	29.4	10.1
85	29.4	10.1

86	29.2	10.1
87	28.6	9.9
88	28.5	9.8
89	28.5	9.8
90	28.5	9.8
91	28.5	9.8
92	28.5	9.8
93	27.7	9.6
94	27.6	9.5
95	27.5	9.5
96	27.5	9.5
97	27.5	9.5
98	27.5	9.5
99	27.2	9.4
100	27.0	9.3
101	26.8	9.2
102	26.5	9.1
103	26.5	9.1
104	26.5	9.1
105	26.5	9.1
106	26.5	9.1
107	26.5	9.1
108	26.5	9.1
109	25.7	8.9
110	25.7	8.9
111	25.7	8.9
112	25.7	8.9
113	25.7	8.9
114	24.9	8.6
115	24.5	8.4

116	24.5	8.4
117	24.5	8.4
118	24.5	8.4
119	24.5	8.4
120	23.8	8.2
121	22.7	7.8
122	21.5	7.4
123	21.5	7.4
124	21.5	7.4
125	21.5	7.4
126	21.5	7.4
127	21.5	7.4
128	21.3	7.3
129	21.0	7.2
130	20.5	7.1
131	19.7	6.8
132	19.7	6.8
133	18.8	6.5
134	18.8	6.5
135	18.1	6.2
136	18.1	6.2
137	18.1	6.2
138	18.1	6.2
139	18.1	6.2
140	18.0	6.2
141	17.4	6.0
142	16.6	5.7
143	16.6	5.7
144	16.2	5.6
145	15.3	5.3

146	15.1	5.2
147	15.0	5.2
148	15.0	5.2
149	11.9	4.1
150	11.9	4.1
151	11.8	4.1
152	11.8	4.1
153	11.4	3.9
154	11.4	3.9
155	9.5	3.3
156	9.0	3.1
157	9.0	3.1
158	8.3	2.9
159	4.7	1.6
160	4.7	1.6
161	4.7	1.6
162	4.7	1.6
163	4.7	1.6
164	4.7	1.6
165	2.9	1.0
166	2.9	1.0
167	2.9	1.0
168	2.9	1.0
169	2.9	1.0

Appendix 2

DPR Copper Antifouling Paint (AFP) Mitigation Recommendations

AB 425 requires that the Department of Pesticide Regulation (DPR), no later than February 1, 2014, determine a leach rate for copper-based antifouling paint used on recreational vessels and make recommendations for appropriate mitigation measures that may be implemented to protect aquatic environments from the effects of exposure. The following list of recommendations is being considered by DPR as part of its current reevaluation of copper AFPs and in response to AB 425 requirements.

Recommendation #1: *Copper AFP registrants reformulate existing products that have leach rates above the leaching threshold set by DPR per AB 425.*

Primary Parties Involved: DPR, U.S. EPA, and copper AFP registrants

Rationale: This mitigation action reduces passive leaching from recreational boat hulls and therefore lowers concentrations of dissolved copper in California marinas. Reformulation will eventually lead to the production and distribution of new products into the marketplace. Note that transition to new formulations may take years to ultimately complete due primarily to constraints associated with boatyard capacity to convert hulls.

Recommendation #2: *Improve the management of in-water hull cleaning practices by relying on best management practices (BMPs) or certification programs to help reduce the amount of copper leaching from boat hulls.*

Primary Parties Involved: Water Boards and in-water hull cleaners

Rationale: Using data from the Earley et al., (2013) passive leaching and in-water hull cleaning study that was conducted under DPR's reevaluation for copper AFPs, DPR calculated that in-water hull cleaning attributes 41-62% of the dissolved copper in coastal marinas depending on the paint type and whether BMPs were used or not. Therefore, management (regulatory or non-regulatory) of in-water hull cleaning could significantly help to lower dissolved copper concentrations in marinas where these activities are common. Data from this study also showed that the use of a specific California Professional Divers Association's BMP employing soft-pile carpet reduces dissolved copper loading by as much as 33% compared to typical non-BMP method. Note that some entities (e.g., Port of San Diego, individual marinas, and the Clean Marina Program) are already experimenting with various forms of restriction on in-water hull cleaning activities.

Recommendation #3: *Explore the possibility of reducing in-water hull cleaning frequency to no more than once per month.*

Primary Parties Involved: DPR, Water Boards, and in-water hull cleaners

Rationale: In some areas, an in-water hull cleaning frequency of three weeks is common in warmer months. A reduction in in-water hull cleaning frequency to once a month results in fewer cleaning events over a three-year period. Such a reduction translates to fewer passive leaching spikes associated with cleaning events. This management practice could potentially be explored in conjunction with Recommendation #2.

Recommendation #4: *As part of reformulation, copper AFP registrants should include painted-hull maintenance information as part of the revised product labels.*

Primary Parties Involved: DPR, U.S. EPA, and copper AFP registrants

Rationale: The aim of this action is to help increase boater awareness that frequent and improper underwater hull cleaning could deteriorate water quality. This manner of outreach will be most effective for boaters who buy AFPs from a retail outlet.

Recommendation #5: *Copper AFP registrants should develop a hull cleaning brochure to be distributed to boaters via boatyards.*

Primary Parties Involved: Copper AFP registrants and boatyards

Rationale: The aim of this recommendation is the same as that for recommendation #2, but it addresses cases where hull painting is done by a boatyard. Boatyard employees can provide these brochures to boat owners when hull painting is completed for their boats.

Recommendation #6: *Increase boater awareness and acceptance of copper AFP alternatives.*

Primary Parties Involved: Boater outreach groups and boating-related agencies (e.g., California Coastal Commission and Department of Parks and Recreation)

Rationale: Dozens of copper AFP alternatives have been formulated and tested for efficacy. Some alternatives, including biocide-free products, are very promising as viable options. Moreover, important product information such as cost to purchase, cost to apply, and maintenance needs and cost have been well-documented. Boaters should be provided with accurate information that could help lead them to select an alternative. Many boater programs and outreach groups exist and could play a role in this campaign.

Recommendation #7: *Foster new and support existing incentive programs to convert copper-painted boat hulls to those painted with alternatives.*

Primary Parties Involved: Dischargers and other TMDL responsible parties.

Rationale: Localized programs currently exist in San Diego Bay and Lower Newport Bay. Early roll out had limited success, but subsequent increases of incentives resulted in greater adoption. As costs associated with alternatives decrease and acceptance of alternatives increase in the future, an even higher level of conversion could be expected. Past incentive programs have been funded by U.S. EPA. The need for these programs is greatest in marinas/harbors where dissolved copper concentrations are high and where TMDLs for copper exist (e.g., Marina del Rey).

Recommendation #8: *Dischargers consider site-specific objectives for copper for marinas or harbors that have extremely high boat density and very poor flushing.*

Primary Parties Involved: Dischargers, TMDL responsible parties, and Water Boards

Rationale: Modeling by DPR suggests that some marina locations (e.g., Marina del Rey) may not achieve the current California Toxics Rule chronic water quality criterion for copper of 3.1 µg/L at all times even with the implementation of copper AFP reformulation and other mitigation approaches outlined in this document. Therefore, dischargers or TMDL responsible parties may consider pursuing site specific objectives (SSOs), which are allowed under the Water Boards' Basin Plans. Moreover, these parties could potentially rely on the Water Effects Ratio approach or on the marine Biotic Ligand Model (if and when it is accepted by U.S. EPA) as the basis for the SSOs. DPR's analysis using the draft marine Biotic Ligand Model for many California coastal marinas suggests that this approach could raise the compliance threshold to a level higher than the current 3.1 ppb criterion.

Reference:

Patrick J. Earley, Brandon L. Swope, Katherine Barbeau, Randelle Bundy, Janessa A. McDonald & Ignacio Rivera-Duarte, Biofouling (2013): Life cycle contributions of copper from vessel painting and maintenance activities, *Biofouling: The Journal of Bioadhesion and Biofilm Research*, DOI: 10.1080/08927014.2013.841891