



**Department of Pesticide Regulation  
Environmental Monitoring Branch  
1001 I Street  
Sacramento, CA 95814**

**June 2006**

**STUDY 236: Assessing Water Quality Indicators of Antifouling Paint Pollution in California Marinas**

**I. INTRODUCTION**

In California, DPR registers antifouling paint (AFP) products since they are considered pesticides. Like other pesticides, AFP products are formulated by combining pesticide active ingredients (often referred to in AFPs as “biocides”) with other compounds (e.g., solvents, adjuvants, inert ingredients) to produce useable and effective products. Copper oxide, copper hydroxide, copper thiocyanate, zinc pyrithione, and Irgarol are the biocides that are most frequently formulated into AFP products currently registered in California (DPR, 2005). A single AFP product may actually contain multiple biocides. Copper oxide, in particular, is the most popular of these biocides, appearing in more than 90 percent of California AFP products.

The leaching of copper from AFPs used on recreational boats has been determined to be the major source pathway of copper pollution in a large boat basin known as the Shelter Island Yacht Basin (SIYB) in San Diego Bay (SDRWQCB, 2005). Water column levels of copper documented at SIYB are high enough to impair beneficial uses and exceed California Toxics Rule (CTR) standards for copper (chronic value of 3.1 µg/L and acute value of 4.8 µg/L). More recently, AFPs are suspected as being significant sources of copper in two other large boat basins in Southern California: Lower Newport Bay and Marina del Rey (U.S. EPA, 2002) (LARWQCB, 2005).

Another biocide, Irgarol, is being detected with increasing frequency at ecologically sensitive levels in coastal water worldwide. In the U.S., Irgarol (as well as its major metabolite M1) has been detected in the waters of Chesapeake Bay and Florida (Hall and Gardinali, 2004). The United States Environmental Protection Agency (U.S. EPA) has concerns about the potential phytotoxic effects of Irgarol on aquatic plants and algae (U.S. EPA, 2003a). A recent National Oceanic and Atmospheric Administration (NOAA) study recently measured Irgarol levels in a number of Southern California marinas (Y. Sapozhnikova, personal communication, 2006). However, this was the only investigation of this biocide in California to date. The results of this study have yet to be published.

Zinc from the use of AFP products is another potential contaminant in marinas. There is little documentation of zinc concentrations in marinas. With the use of zinc pyrithione AFPs growing in recent years and the possibility that more zinc-based products could enter the AFP market, current zinc levels in California marinas need to be evaluated.

In the past, monitoring data of relevance to the evaluation of AFP pollution in California

have been largely generated from the San Diego Bay region (Singhasemanon, 2005). In recent years, an increase in the development of AFP-related Total Maximum Daily Loads (TMDLs) and listing of Clean Water Act section 303(d) water bodies in other coastal areas of California challenges the presumption that this issue is only limited to San Diego Bay.

For this study, the Department of Pesticide Regulation (DPR) will collect water and sediment samples from a number of California marinas and analyze them for indicators of AFP pollution. The biocides of particular interest are copper oxide, copper hydroxide, copper thiocyanate, zinc pyrithione, and Irgarol. Findings from this monitoring study will help DPR, State Water Resources Control Board (SWRCB), Regional Water Quality Control Boards (RWQCBs), and other interested agencies more fully evaluate the potential adverse effects of current AFP use on aquatic and benthic organisms. Several basin plan-designated beneficial uses (California Water Code 13050(f)) will be addressed by this study including marine habitat, estuarine habitat, warm fresh water habitat, and cold fresh water habitat. Most importantly, these findings will help DPR determine the need for mitigation and/or regulatory actions on a regional or a statewide scale.

This monitoring study focuses on marinas because they harbor densely packed and continuously emitting sources of AFPs in the form of recreational (and occasionally commercial) boats in poorly flushed areas. Thus, AFP pollution at these locations should represent some of the worst water quality conditions resulting from the use of AFPs on boats.

## **II. OBJECTIVE**

Primary objective:

- Determine the occurrences and concentrations of dissolved copper, dissolved zinc, and Irgarol in the water and sediment of selected California marinas and establish whether these levels exceed established water quality standards (i.e., CTR standards for dissolved copper and dissolved zinc), criteria (i.e., U.S. EPA's proposed updated aquatic life criteria for copper, NOAA's sediment quality criteria), guidelines, and other ecologically relevant values (e.g., LC<sub>50</sub>, EC<sub>50</sub>).

Secondary objectives:

- Quantify copper and zinc in the water and sediment of water areas that are adjacent to each marina to determine if concentrations in marinas are significantly higher than local reference concentrations.
- Determine whether AFP analyte concentrations differ between salt water, brackish water, and fresh water marinas.
- Estimate bioavailability and toxicity of copper using U.S. EPA's Biotic Ligand Model (BLM).
- Measure the toxicity of marina waters using mussel embryo (*Mydulis galloprovincialis*) development, compare measured toxicity with copper concentrations and BLM-predicted toxicity, and identify the likely cause of

observed toxicity using Toxicity Identification Evaluation (TIE) procedures.

### III. PERSONNEL

The study will be conducted primarily by staff from DPR's Environmental Monitoring Branch, Surface Water Protection Program under the general direction of Marshall Lee, Senior Environmental Research Scientist (Supervisor). Key personnel are listed below:

**Project Leader:** Nan Singhasemanon, Program Specialist  
**Field Coordinator:** Nina Bacey, Associate Environmental Research Scientist  
**Senior Scientist:** Frank Spurlock, Research Scientist III  
**Laboratory Liaison:** Carissa Ganapathy, Program Specialist  
**Chemists:** Dirk Holstege, Traci Francis  
University of California Agriculture and Natural Resources  
Analytical Laboratory, Davis, CA

Ed Wirth, Yelena Sapozhnikova  
NOAA Hollings Marine Laboratory, Charleston, SC

Ken Schiff, Darrin Greenstein  
Southern California Coastal Water Research Project,  
Westminster, CA

Amrith Gunasekara  
Department of Land, Air, and Water Resources,  
University of California, Davis, CA

**Technical Advisors:** Ray Arnold, Consultant, Copper Development Association  
Inc., New York, NY

Linda Candelaria, Environmental Scientist, Santa Ana  
Regional Water Quality Control Board, Riverside, CA

Richard Looker, Engineer, TMDL Unit, San Francisco Bay  
Regional Water Quality Control Board, Oakland, CA

Kelly Moran, Consultant/Scientist, TDC Environmental,  
LLC, San Mateo, CA

Paul Salop, Marine Ecologist, Applied Marine Sciences,  
Inc., Livermore, CA

Ken Schiff, Deputy Director, Southern California Coastal  
Water Research Project, Westminster, CA

Sampling assistance will be provided by Harbor Masters and marina managers through collaboration with the California Association of Harbor Masters and Port Captains and the Marina Recreation Association.

Note that part of this study may be funded by the SWRCB and/or U.S. EPA. DPR staff are currently engaged in funding discussions with California and federal water quality agencies.

Questions concerning this monitoring study should be directed to Nan Singhasemanon, at [nsinghasemanon@cdpr.ca.gov](mailto:nsinghasemanon@cdpr.ca.gov) or (916) 324-4122.

#### **IV. STUDY PLAN**

Copper, zinc, and Irgarol are the principal AFP analytes of interest. Water and sediment samples will be taken from inside and outside of marinas areas and analyzed for these constituents as well as a number of other water quality parameters. If marina levels of AFP analytes are consistently and statistically higher than ambient levels outside of the marina (local reference), this should provide strong evidence that marinas are a significant source of AFP pollutants. Moreover, if other in-marina sources of AFP analytes can be shown to be primarily attributable to boat AFP use, then we can further deduce that boats are the most important local source of these analytes, particularly during dry periods. Irgarol will not be analyzed for in local reference samples as boat AFPs are the only expected source of this active ingredient.

Recent research on the fate of zinc pyrithione in sea water suggests that its use could result in the formation of a more stable and toxic compound: copper pyrithione (Grunnet and Dahllöf, 2005). The use of copper pyrithione may actually be more indicative of zinc pyrithione use than dissolved zinc. However, the assessment of zinc pyrithione and copper pyrithione is currently beyond the scope of this study. In the future, if DPR finds the environmental risk posed by copper pyrithione to be significant and available analytical methods to be reliable, DPR may initiate investigations of the water quality impacts of this active ingredient.

The sampling period will be confined to California's summer months (July through October) to avoid confounding hydrologic factors that would be introduced by storm events. Processes such as flushing, dilution, mixing, and sediment resuspension affect the water and sediment concentrations of AFP indicators and other analytes. Moreover, during storm periods, other non-marina inputs of AFP analytes into the marina could exceed AFP sources within the marina. Because DPR is interested in evaluating pollution from AFP use, sampling for this study has been scheduled for the warm summer months when storm runoff is minimal and the density of boats in marinas is highest.

At each marina, concentrations of AFP analytes will be measured at marina and local reference sites three times during this study. This translates to a sampling frequency of approximately once per month. Site means for the sampling period will be calculated from these three sampling rounds. These means will also be averaged to generate a

marina mean for the entire sampling period.

Dissolved copper concentrations at any given time are heavily influenced by the level of suspended solids in solution. Copper that becomes bound to solids will not be measurable as a dissolved analyte, but will instead be accounted for in the total copper measurement. To improve the understanding and interpretation of dissolved copper results, concentrations of total copper and total suspended solids (TSS) will be assessed along with dissolved copper.

To provide input into U.S. EPA's copper BLM, a number of water quality parameters and constituents will have to be measured for each water sample taken. These include: alkalinity, calcium, salinity (as chloride), dissolved organic carbon, magnesium, pH (*in situ*), potassium, sodium, sulfate, and temperature (*in situ*). This model determines the bioavailability of copper and predicts its toxicity to aquatic organisms. It is based on the concept that toxicity is determined by the amount of copper that binds onto a biotic ligand site (target organism's biochemical receptor site). The amount of copper that is available to bind to these sites is dependent on the amount of dissolved copper and the presence of various complexing substances in the water. The fresh water BLM has proven to be so reliable that U.S. EPA has adopted it to establish future copper water quality criteria for the protection of aquatic organisms in fresh water (U.S. EPA, 2003b).

The BLM is currently being evaluated for salt and brackish water applications (Arnold et al., 2005). Thus far, the model appears to require identical input parameters that are needed for the fresh water application. Based on the overall acceptance of the model's scientific basis for fresh water, it will likely be adopted by U.S. EPA for use on estuarine and marine waters in the near future. Thus, we will measure for the current fresh water BLM input parameters. BLM-predicted toxicity results (i.e., LC<sub>50</sub>, EC<sub>50</sub>) will have dissolved copper concentrations associated with them since all metal samples will be taken concurrently with BLM-associated samples.

Although we anticipate that the BLM will eventually provide an estimate of toxicity for a large number of our study samples, a subset of salt and brackish marina water samples will still be assessed for actual toxicity using U.S. EPA's method for short-term chronic toxicity test on mussel (*Mytilus galloprovincialis*) embryo development. Since this test is fairly sensitive to copper levels, the results will help establish whether elevated levels of dissolved copper correspond to sample toxicity. The determination of actual toxicity will also help DPR evaluate the usability of the current version of the salt water BLM by comparing actual to estimated toxicity.

TIEs will be employed to better link chemistry results with biological effects. TIE procedures will be performed on a subset of toxic samples to confirm the cause of the observed toxicity. TIE treatments are designed to selectively remove or neutralize classes of compounds and their associated toxicity to identify the most likely cause of the toxicity. Toxicity/TIE samples will have dissolved copper and predicted toxicity results associated with them since metals and BLM-associated toxicity samples will be taken concurrently with the toxicity/TIEs samples.

## **Study Design Considerations:**

For the selected study design to satisfy the objectives of this study, DPR staff made certain assumptions and accepted certain limitations:

### *Assumptions*

- AFP-painted boats represent notable sources of copper, zinc, Irgarol, and other AFP pollutants to marina waters and sediments.
- The pathways that introduce AFP pollutants to marina waters and sediments are passive leaching and underwater hull-cleaning of AFP-painted boats.
- Non-AFP, in-marina inputs of copper (e.g., wood preservative use on marina structures) are small compared to AFP input. (DPR staff will gather information from each marina that may support or challenge this assumption.)
- AFP-painted boats in the marina represent the most significant source of Irgarol detected in the marina.

### *Limitations*

- It will be difficult to attribute in-marina concentrations of zinc mainly to AFP sources since there are several marine applications of zinc in marina areas. A combination of zinc sources: AFP products, sacrificial anodes, galvanized surfaces, other in-marina sources, and local reference likely contributes to the concentrations observed in marinas. Moreover, the use of zinc pyrithione is not as significant as the use of copper oxide in AFP products. Although it is informative to compare in-marina zinc concentrations with established water quality standards and criteria, linkages of in-marina water and sediment concentrations of zinc to AFP use will be limited by these factors.
- Dissolved copper and zinc concentrations at any given site may vary over time due to a number of factors including tidal influence, site-specific hydrology, and changes in total suspended solid levels. The design of this study attempts to address these limitations; however, these factors will still have some effects on study results.

## **Site Selection Criteria:**

DPR staff evaluated hundreds of California marinas using information produced by the Marina Mapping Sub-Workgroup of the Non-Point Source Interagency Coordinating Committee's Marina and Recreational Boating Workgroup. The pool of candidate marinas were then reduced from the large initial list with the use of maps and application of the following considerations (in descending order of importance):

- 1) Marina contains a relatively high number of slips for its water body type.
- 2) Marina is located in an area that receives poor flushing (the likelihood of finding elevated levels of marina-borne pollutants over an extended period is high.)
- 3) Marinas are distributed somewhat evenly across various regions of the state.

When about 40 candidate marinas were left after this initial reduction, DPR staff used aerial photos and more detailed maps to evaluate further evaluate individual marina layouts and relevant anthropogenic, geologic, and hydrologic features. A list of 24 potential study marinas was generated and is shown below in Table 1. With the approval of this protocol, DPR staff will make site visits to these candidate marinas to talk to individual marina managers and gauge their collaborative interests. Moreover, staff will discuss logistical and site-specific concerns with them. Additional selection criteria may be used to further reduce the number of marinas. These criteria include:

- 1) The marina owner/operator is cooperative.
- 2) The marina has a boat on-site that can be used for sampling.
- 3) The marina contains slip areas that are sufficiently isolated from adjacent or surrounding sources (e.g., boatyards, industrial discharges, mining discharges).
- 4) Historical and current activities (e.g., dredging, construction) in the marina area will not significantly interfere with the interpretation of results.

**Table 1: List of Potential Study Marinas\***

<b>FRESHWATER</b>	<b>BODY OF WATER</b>	<b>COUNTY</b>	<b>CITY</b>	<b>TOTAL SLIPS</b>
1) Folsom Lake Marina	Folsom Lake	El Dorado	Folsom	675
2) Tahoe Keys Marina	Lake Tahoe	El Dorado	Lake Tahoe	250
3) Sacramento City Marina	Sacramento River	Sacramento	Sacramento	547
4) Village West Marina	Sacramento-San Joaquin	San Joaquin	Stockton	700
<b>BRACKISH WATER</b>				
1) Antioch Marina	San Joaquin River	Contra Costa	Antioch	310
2) Benicia Marina	Carquinez Strait	Solano	Benicia	320
3) Vallejo Municipal Marina	Mare Island Strait	Solano	Vallejo	800
4) Pittsburg Marina	Sacramento-San Joaquin	Contra Costa	Pittsburg	486
<b>SALTWATER</b>				
1) Clipper Yacht Harbor	Richardson Bay	Marin	Sausalito	735
2) San Francisco Marina	San Francisco Bay	San Francisco	San Francisco	700
3) South Beach Harbor	San Francisco Bay West	San Francisco	San Francisco	700
4) City of Berkeley Marina	San Francisco Bay East	Alameda	Berkeley	1,052
5) Marina Bay Yacht Harbor	San Francisco Bay East	Contra Costa	Richmond	850
6) Loch Lomond Marina	San Francisco Bay North	Marin	San Rafael	517
7) San Leandro Marina	San Francisco Bay East	Alameda	San Leandro	455
8) Ballena Isle Marina	San Francisco Bay East	Alameda	Alameda	504
9) Coyote Point Marina	San Francisco Bay West	San Mateo	San Mateo	565
10) Santa Cruz Harbor	Santa Cruz Harbor	Santa Cruz	Santa Cruz	1,000

11) Monterey Harbor	Monterey Bay	Monterey	Monterey	413
12) Santa Barbara Harbor	Santa Barbara Channel	Santa Barbara	Santa Barbara	1,133
13) Marina del Rey Basins D, E, F	Marina del Rey Harbor	Los Angeles	Marina del Rey	~ 3,000
14) Marina del Rey Basins A, B, C, G, H	Marina del Rey Harbor	Los Angeles	Marina del Rey	~5,000
15) Alamitos Bay Marina	Alamitos Bay	Los Angeles	Long Beach	1,191
16) Downtown Shoreline Marina	L. A. - Long Beach H.	Los Angeles	Long Beach	1,800

\* Source: Marina and Recreational Boating Workgroup – Mapping Sub-Workgroup

Since copper levels in marinas have been documented to some extent in San Diego Bay, Mission Bay, Oceanside Harbor, and Dana Point Harbor, these regions will be excluded from the geographic scope of this study (Singhasemanon, 2005) (Schiff, 2006).

Moreover, the Santa Ana Regional Water Quality Control Board will be initiating a monitoring study of metals in Newport Bay area marinas in the summer of 2006 (L. Candelaria, personal communication, 2006). Therefore, our study will not include sites in the Newport Bay region.

AFPs are not applied to boats in fresh water areas because hull fouling is not a major operational concern and because these boats may spend a significant amount of time out of the water when they are not being used. AFP use for boats maintained in brackish water areas tend to be somewhat higher than freshwater areas since these boat do occasionally have to deal with salt water fouling. However, the highest level of fouling by far occurs on boats that regularly operate in salt water regions. In general, these boats also spend more time in the water and therefore experience higher fouling. As such, AFPs are widely employed for boats moored in salt water areas.

Since the highest amount of AFP use occurs in salt water areas, there is an emphasis on salt water marinas in this study. The proposed distribution of marina types is 16 salt water marinas, four brackish water marinas, and four fresh water marinas. This distribution may change once sampling logistics and other factors are considered. If necessary, sites may have to be substituted.

Local reference sites will also be determined for each marina to help support the hypothesis that concentrations of AFP pollutants are significantly higher in the marina than in surrounding areas. Each marina operator, manager, dock master, or harbor master (these individuals will be collectively referred to as marina managers) will be consulted to ascertain viable locations near each marina area in which analyzable local reference samples can be collected. Local reference sites will be identified and selected using the following criteria (in descending order of importance):

- 1) The site should be located outside the influence of marina activities and potential sources of AFPs, but adjacent to the marina area and within the same body of water.
- 2) The site should be sufficiently isolated from potentially confounding inputs (e.g., boatyards, industrial discharges, and various historical contamination).
- 3) Historical and current activities (e.g., dredging, construction) in the immediate area will not significantly interfere with the interpretation of results.



- 4) The site contains underlying sediment that can be collected and analyzed.
- 5) There is suitable and safe access to the site.

The exact location of local reference sites will have to be determined on the first day of sampling at each marina when site-specific conditions can be considered. Once local reference sites have been determined in the first sampling round, they will be revisited in the second and third round.

### **Sampling Vessels:**

Every marina has a unique facility administrator in the marina manager. These individuals almost always operate or have staff that operates at least one vessel on site. They are very knowledgeable of each marina's layout, history, hydrology, and site-specific features. During the site selection process, DPR staff established verbal agreements with each marina manager to verify that a boat and an operator will be available during the study period.

As the initial sampling period approaches, DPR will establish a sampling schedule that will be used to coordinate marina visits with each marina manager and his or her staff. DPR's sampling crew, who are based out of Sacramento, California, will bring all necessary supplies and sampling equipment with them to each sampling site.

## **V. SAMPLING METHOD**

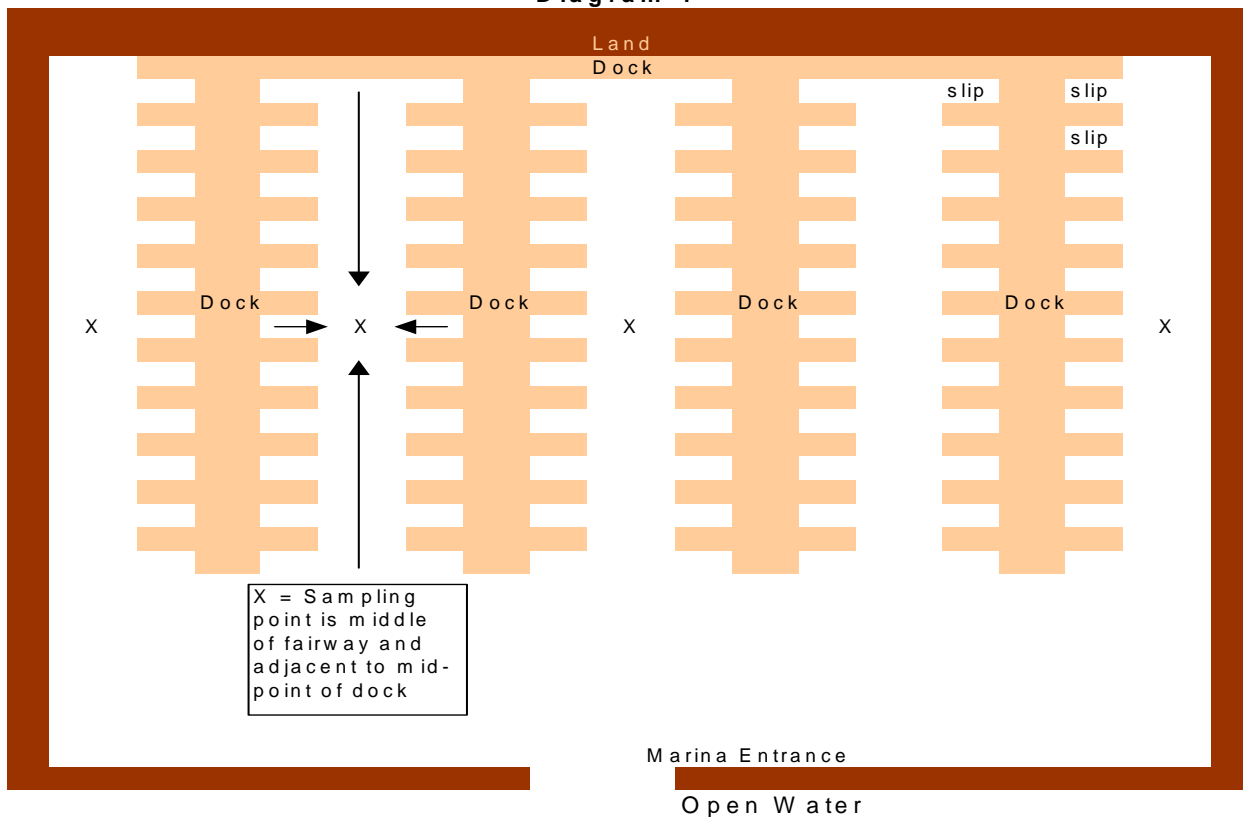
### **Sampling Method and Frequency:**

#### *Marina Sites – Copper, Zinc, TSS, and BLM-Associated Parameters*

A table showing sampling locations, frequencies, and analytes is attached in [Appendix 1](#). Water and sediment samples will be taken by boat from four points within each marina for dissolved copper, dissolved zinc, total copper, TSS, and BLM-associated parameters. Water samples will be collected once a month at each site over a three-month period for a total of three rounds. Sediment samples will only be collected in the third sampling round. Water samples will be collected prior to sediment samples at each sampling point; this will minimize contamination of the water samples.

Past copper monitoring suggests that copper levels in both water and sediment tend to be highest near the area of moored vessels and lower toward the entrance of the marina (SDRWQCB, 2005) (Pap, 2004). Marina sampling sites will therefore be located near moored vessels to focus on areas with potentially high AFP analyte concentrations. To maintain site-to-site consistency, DPR staff will chose sampling sites that are located near the center of the fairway (common term for the channels between the docks) and adjacent to the midway point of the dock/pier structure (see Diagram 1, below).

Diagram 1



Although each marina will have a unique layout of docks and slips, DPR staff will identify each marina's candidate fairways. Fairways that are adjacent to docks with less than 50% of their slips filled will not be considered viable for the initial sampling round (and therefore excluded from subsequent rounds). If there are more than four viable fairways, the fairways that will contain the final sampling sites will be randomly chosen.

To accurately revisit sampling sites during subsequent rounds, each sampling location will be initially identified using a global positioning system (GPS) unit to mark the exact latitudinal and longitudinal coordinates. If a site becomes inaccessible during subsequent rounds, attempts will be made to collect samples within three days of the visit.

#### *Marina Sites – Irgarol*

Both water and sediment samples will be taken for Irgarol from a subset of marinas. Two water samples will be taken from 12 marinas in the first sampling round and the third sampling round. Holding times constraints and shipping schedules will dictate which marinas the Irgarol samples will come from. Once these marinas are determined, these two sites will be randomly selected from the four sampling sites associated with copper, zinc, TSS, and BLM-associated parameters. There will be a maximum of 48 water samples taken for Irgarol. There will be no Irgarol samples taken during the second sampling round.

One sediment sample will also be taken from each of the same 12 marinas during the

third sampling round for a total of 12 Irgarol sediment samples. The sediment sampling sites will be randomly chosen from one of the two Irgarol water sampling sites.

#### *Marina Sites – Toxicity and TIEs*

Water samples will be taken for toxicity from a subset of marinas. Four samples will be taken from 12 marinas in the second sampling round (same 12 marinas as for the Irgarol samples). Toxicity samples will be taken from the four sampling sites associated with copper, zinc, TSS, and BLM-associated parameters. There will be a maximum of 48 toxicity samples taken for toxicity. There will be no toxicity samples taken during the first or third sampling round.

A maximum of four TIE samples will be chosen from toxicity samples that exhibit greater than 50% toxicity. The toxicity testing laboratory will determine which toxicity samples are the best candidates for the TIEs. If possible, the four TIE samples will come from four different marinas.

There will be no sediment samples taken for toxicity or TIE analysis.

#### *Local Reference Sites - Copper, Zinc, TSS, and BLM-Associated Parameters*

Water and sediment samples will be taken by boat from four points outside of each marina area. Water samples will be collected once a month at each site over a three-month period for a total of three sampling rounds. Sediment samples will only be collected in the third sampling round. In this round, water samples will be collected prior to sediment samples at each sampling point; this will minimize contamination of the water samples.

The determination of viable local reference sites will have to be done on a site specific basis using the criteria listed under the Site Selection Criteria section.

#### *Local Reference Sites - Irgarol, Toxicity, and TIEs*

There will be no samples taken at local reference sites for Irgarol, toxicity, and TIE analysis.

#### **Sample Collection:**

*Water Samples* - Water samples will be taken from approximately 1 meter below the surface. Schiff et al. (2006) found a depth-related gradient for copper in marinas with the highest concentrations near the surface. Furthermore, to avoid AFP contamination from the sampling vessel itself, samples will be taken approximately 2 meters from the side of the boat.

The water sampling apparatus will consist of plastic tubing attached to a plastic pole. On one end, a peristaltic pump will draw water directly into the sample container. For metals, U.S. EPA certified, pre-cleaned 250 ml polyethylene plastic bottles will be used. For Irgarol, U.S. EPA-certified, pre-cleaned 1-L amber glass bottles will be used. For

TSS and BLM-associated parameters 250 ml polyethylene bottles will be used. For toxicity samples, 1-L polyethylene containers will be used.

Samples to be analyzed for dissolved copper, dissolved zinc, magnesium, calcium, sodium, and potassium, and dissolved organic carbon will be filtered (in-line 0.45µm filter) and acidified with Optima®, ultra-pure nitric acid to a pH level of < 2.0.

Samples to be analyzed for sulfate, chloride, and alkalinity will be filtered/non-acidified.

Samples to be analyzed for total copper will be unfiltered/acidified.

Samples to be analyzed for TSS, Irgarol, and toxicity/TIE will be unfiltered/non-acidified.

For salt water and brackish water sites, samples will be collected during slack tide or as close to it as possible in order to minimize the possible effect of tidal flows on sample integrity.

*Sediment Samples* - Sediment will be collected using a Van Veen® grab sampler. The jaws and doors will be coated with Teflon® to achieve metal inertness. Each grab must satisfy the following criteria in order to be an acceptable sample:

- Complete closure of the Van Veen sampler
- No evidence of sediment washout through the doors
- Minimum disturbance of the sediment surface

The overlying water in the sampler must first be drained by slightly opening the sampler. Care will be taken to minimize disturbance of the fine-grained top layer of sediment during this process. The top 2 cm of sediment will then be collected with a clean Teflon® coated scoop and placed into a 4 oz., U.S. EPA-certified, pre-cleaned polyethylene container. This will be repeated until sufficient sediment has been collected to fill the sample container.

#### **Field Quality Assurance/Quality Control (QA/QC):**

Field blanks and rinse blanks will be taken to assess potential contamination of water samples in the field. Field blanks will be done by filling sample containers with de-ionized water at the site of collection. Rinse blanks will be done by running de-ionized water through the identical sample collection apparatus that is used to collect environmental samples. Rinse blanks will be taken after the sampling apparatus has been cleaned between each site. At least 5% of the study samples will be field QC samples.

#### **Sample Handling and Custody:**

Since low concentrations (low parts per billion) of metals in the water samples are expected in this study, sample collection and handling will follow U.S. EPA Method 1669 -Sampling of Ambient Water for Trace Metals at U.S. EPA Water Quality Criteria Levels (U.S. EPA, 1996a).

After samples are taken, they will be transported in coolers with wet ice. Prior to analysis, samples will be kept refrigerated at 4°C until extraction or chemical analysis. Irgarol and toxicity samples will have to be shipped to their respective analytical laboratories due to short holding times requirements. These samples will be carefully packed and shipped via the United Parcel Service (UPS) in coolers with wet or blue ice to their destinations. Some toxicity samples DPR chain-of-custody forms will be completed and will accompany each sample.

## **VI. CHEMICAL ANALYSIS AND QUALITY CONTROL**

### **Chemical Analysis:**

#### *Water Samples – Copper, Zinc, TSS, and BLM-Associated Parameters*

The University of California, Davis, Agriculture and Natural Resources (ANR) Analytical Laboratory will analyze these samples for dissolved copper, total copper, dissolved zinc, TSS, magnesium, calcium, sodium, potassium, salinity (as chloride), sulfate, and alkalinity. Note that magnesium, calcium, sodium, potassium, chloride, sulfate, and alkalinity are also measured as dissolved concentrations. However, since total concentrations of copper and zinc (sediment) are also analyzed for in this study, it is important to distinguish the difference for these two metals.

Assuming that method validations are successful, ANR will use:

- EPA 220.2 graphite furnace atomic absorption method (U.S. EPA, 1983) for dissolved copper and total copper
- EPA 160.2 gravimetric method for TSS
- EPA 200.7 inductively-coupled plasma method (U.S. EPA, 1994) for dissolved zinc, calcium, and magnesium
- EPA 258.1 flame atomic absorption method (U.S. EPA, 1983) for potassium
- EPA 273.1 flame atomic absorption method (U.S. EPA, 1983) for sodium
- EPA 300.0 ion chromatography conductivity method (U.S. EPA, 1993) for chloride and sulfate

DPR will analyze for dissolved organic carbon (DOC) in these samples using EPA 415.3 combustion/non-dispersive infrared method (U.S. EPA, 2005).

#### *Water Samples - Irgarol*

NOAA's Hollings Marine Laboratory (HML) in Charleston, South Carolina, will analyze these samples for Irgarol using a high performance liquid chromatography electro spray ionization tandem mass spectrometry method as published in Thomas (2002).

#### *Water Samples – Toxicity and TIEs*

SCCWRP's laboratory in Westminster, California, will test the salt and brackish water samples for sub-chronic developmental toxicity on the mussel *Mydulis galloprovincialis*

using methods in EPA/600/R-95/136 (U.S. EPA, 1995).

SCCWRP will also perform follow up TIEs on a subset of toxic samples using methods in EPA/600/R-96/054 (U.S. EPA, 1996b). The toxicity threshold that will be the trigger for TIE consideration will be 50% abnormal embryo development relative to control. SCCWRP will perform a maximum of 4 TIEs for this study.

#### *Sediment Samples – Copper and Zinc*

UCD ANR analytical laboratory will analyze these samples for total copper and total zinc using EPA 3051 flame atomic absorption method. DPR will analyze these samples for grain size and total organic carbon (TOC) using DPR method SOPMETH 004.00 (Dietrich, 2005) and SOPMETH 005.00 (Gunasekara, 2006), respectively.

#### *Sediment Samples – Irgarol*

NOAA's HML in South Carolina will analyze these samples for Irgarol. HML will use a accelerated solvent extraction liquid chromatography - tandem mass spectrometry method.

All of the parameters to be measured in this study, the methods used, and the method reporting limits are listed in Table 2 for reference.

**Table 2. Summary of Analytical Methods and Reporting Limits (BLM-associated parameters in grey)**

<b>Chemical Analytes</b>	<b>Analytical Methods</b>	<b>Reporting Limits</b>
Dissolved Copper	EPA 220.2	0.5 - 2.0 µg/L
Dissolved Zinc	EPA 200.7	1.0 – 5.0 µg/L
Irgarol (water)	<i>Thomas, 2002</i>	0.1 ng/L
Total Copper	EPA 220.2	0.5 – 2.0 µg/L
Total Suspended Solids	EPA 160.2	4 mg/L
Dissolved Organic Carbon	EPA 415.3	50 µg/L or 50 mg/L*
Chloride (Salinity)	EPA 300.0	2 mg/L
Sulfate	EPA 300.0	2 mg/L
Alkalinity	EPA 310.1	> 2 mg/L
Magnesium	EPA 200.7	2 mg/L
Calcium	EPA 200.7	2 mg/L
Sodium	EPA 273.1	2 mg/L
Potassium	EPA 258.1	1 mg/L
Total Copper (sediment)	EPA 3051/EPA 200.7	10 mg/kg (dry weight)
Total Zinc (sediment)	EPA 3051/EPA 200.7	10 mg/kg (dry weight)
Irgarol (sediment)	NOAA ASE LC/MS/MS	TBD
Total Organic Carbon (sediment)	DPR SOP METH005.00	5 mg/kg (dry weight)
Grain Size (sediment)	DPR SOP METH004.00	2 µm smallest particle size
Toxicity	EPA/600/R-95/136	N/A
Toxicant Identification Evaluation	EPA/600/R-96/054	N/A

\* Two possible reporting limits depending on the catalyst used.

In addition to the previously listed target parameters, the following *in-situ* field measurements (some of which are also required for the BLM) will be collected using a variety of water quality meters:

- Depth
- pH
- Specific conductance
- Temperature
- Turbidity

DPR staff will also record information on site-specific activities and factors (e.g., high boat traffic, nearby dredging operations, active construction activities) which may have an influence on field and laboratory data.

#### **Laboratory Quality Assurance/Quality Control:**

Laboratory QA/QC and additional information for this study are outlined in detail in the associated QAPP document titled *Monitoring for Antifouling Paint Active Ingredients in California Marinas*. The web link to this document is provided next to the link to this protocol.

### **VII. DATA ANALYSIS**

Quality Control review will initially be performed on results. Individual sample results will then be used to compare with results from similar studies, established water quality standards (i.e., CTR standards for dissolved copper and dissolved zinc), criteria (i.e., U.S. EPA's proposed updated aquatic life criteria for copper, NOAA's sediment quality criteria), guidelines, and other ecologically relevant values (e.g., LC<sub>50</sub>, EC<sub>50</sub>). Sample means and standard deviations will be calculated for use in subsequent statistical analysis. Various statistical tests will be used to determine differences between means for results from different water types and for results from marina samples and local reference site samples. Water quality results will be used in the Biotic Ligand Model (BLM) to estimate bioavailability and predicted toxicity.

### **VIII. TIMETABLE**

Site Visit/Selection:	April 2006 – June 2006
Field Sampling:	July 2006 - October, 2006
Chemical analysis:	July 2006 - April, 2007
Draft Report:	October 30, 2007
Final Report:	November 30, 2007

**IX. BUDGET (estimated)**

	Number of Analyses	Cost per Analysis	Cost
<b>Samples</b>			
<b>Water Analysis</b>			
Dissolved Copper	625	\$7.65	\$4,781.25
Dissolved Zinc	625	\$6.65	\$4,156.25
Soluble salts (Ca, Mg, K, Na)	625	\$14.60	\$9,125.00
Salinity (Cl)	625	\$6.65	\$4,156.25
Sulfate	625	\$6.65	\$4,156.25
Alkalinity	625	\$6.65	\$4,156.25
Total Copper	625	\$9.80	\$6,125.00
		<b>Water Analysis Subtotal</b>	\$36,656.25
		<b>Water QC cost @ 20%</b>	\$7,331.25
Total Suspended Solids (TSS)	625	\$13.20	\$8,250.00
		<b>Water Analysis Total</b>	\$52,237.50
<b>Sediment Analysis</b>			
Total Copper	232	\$13.85	\$3,213.20
Total Zinc	232	\$13.85	\$3,213.20
		<b>Sediment Analysis Subtotal</b>	\$6,426.40
		<b>Sediment QC cost @ 20%</b>	\$1,285.28
Grinding charge/sample	232	\$4.14	\$960.48
		<b>Sediment Analysis Total</b>	\$8,672.16
		<b>Total Analysis Cost</b>	<b>\$60,909.66</b>
<b>Validation</b>			
	Saltwater/ Freshwater	<b>Total cost validation/matrix</b>	
<b>Water Analysis</b>			
Dissolved Copper	2	\$100.00	\$200.00
Dissolved Zinc	2	\$100.00	\$200.00
Total Copper	2	\$100.00	\$200.00
Soluble salts (CA, Mg, K, Na)	2	\$100.00	\$200.00
Salinity (Cl)	2	\$100.00	\$200.00
Sulfate	2	\$100.00	\$200.00
Alkalinity	2	\$100.00	\$200.00
<b>Sediment Analysis</b>			
Total Copper	1	\$100.00	\$100.00
Total Zinc	1	\$100.00	\$100.00
		<b>Total Validation Cost</b>	\$1,600.00
		<b>Total Lab Cost</b>	<b>\$62,510.00</b>

\* All costs include 25% overhead charge.



	Units	Unit Cost	Cost
<b>Equipment and Supplies</b>			
Van Veen sediment sampler w/cable	1	\$3,600	\$3,600
Peristaltic pump	1	\$1,000	\$1,000
250ml plastic bottles	2360	\$1.89/bottle	\$4,455
250ml pre-cleaned plastic bottles	580	\$1.66/bottle	\$960
1/2 pint pre-cleaned plastic jars	176	\$3.55/jar	\$624
Filters	580	\$13.79/filter	\$8,000
1 L pre-cleaned glass bottles	24	\$2.08/bottle	\$50
125 ml pre-cleaned glass jars	12	\$4.17/jar	\$50
<b>Equipment &amp; Supplies Total</b>			<b>\$18,739</b>

	Units	Unit Cost	Cost
<b>Lodging</b>			
Assuming 3 staff persons/trip	108	\$100/night	<b>Total Lodging Cost</b>
			<b>\$10,800</b>
<b>Per diem</b>			
Assuming 3 staff persons/trip	135	\$40/day	<b>Total Per diem Cost</b>
			<b>\$5,400</b>
<b>Total Project Cost</b>			<b>\$97,449</b>

## X. REFERENCES

Arnold, W.R., R.C. Santore, J. S. Cotsifas. 2005. Predicting copper toxicity in estuarine and marine waters using the Biotic Ligand Model. *Marine Pollution Bulletin* 50:1634-1640.

California Department of Pesticide Regulation. 2005. Product/Label Database [Online]. Summary report output: indexed by product, chemical, and site data. Available at <http://www.cdpr.ca.gov/docs/label/labelque.htm> (Verified June 2006).

Dietrich, H. 2005. Procedure for determining soil particle size using the hydrometer method. Standard Operating Procedure METH004.00. Environmental Monitoring Branch. California Department of Pesticide Regulation, Sacramento, CA. (Available online at <http://www.cdpr.ca.gov/docs/empm/pubs/sops/meth004.pdf>) (Verified June 2006.)

Grunnet, K. and I. Dahllof. 2005. Environmental fate of the antifouling compound zinc pyrithione in seawater. *Environmental Chemistry* 24(12): 3001-3006.

Gunasekara, A. 2006. Instructions for calibration and use of total organic carbon (CD-85A) instrument. Standard Operating Procedure METH005.00. Environmental Monitoring Branch, California Department of Pesticide Regulation, Sacramento, CA. (Available online at [http://www.cdpr.ca.gov/docs/empm/pubs/sops/meth005\\_00.pdf](http://www.cdpr.ca.gov/docs/empm/pubs/sops/meth005_00.pdf)) (Verified June 2006.)

Hall, L. and P. Gardinali. 2004. Ecological risk assessment for Irgarol 1051 and its major metabolite in United States surface waters. *Human and Ecological Risk Assessment* 10(3): 525-542.

Los Angeles Regional Water Quality Control Board. 2005. Total maximum daily loads for toxic pollutants in Marina del Rey Harbor. Draft Report. LARWQCB, Los Angeles, CA.

Pap, R. 2004. San Francisco Bay marina water quality project. Prepared for the San Francisco Bay Conservation and Development Commission, San Francisco, CA.

San Diego Regional Water Quality Control Board. 2005. Total maximum daily load for dissolved copper in Shelter Island Yacht Basin, San Diego Bay. Resolution No. R9-2005-0019, Basin Plan Amendment and Technical Report. San Diego, CA

Schiff, K., J. Brown, and D. Diehl. 2006. Extent and magnitude of copper contamination in marinas of the San Diego region, California. Technical Report. Southern California Coastal Water Research Project, Westminster, CA.

Singhasemanon, N. 2005. California copper monitoring studies with potential relevance to the evaluation of copper antifouling paint pollution. Staff Draft, First Version. California Department of Pesticide Regulation, Sacramento, CA. (Available online at <http://www.cdpr.ca.gov/docs/sw/caps/custudies.pdf>) (Verified June 2006.)

Thomas, K.V., M. McHugh, and M. Waldock. 2002. Antifouling paint booster biocides in UK coastal waters: inputs, occurrence, and environmental fate. *Science of Total Environment* 293:117-127.

U.S. Environmental Protection Agency. 1983. Methods for chemical analysis of water and wastes. EPA/600/4-79/020. National Exposure Research Laboratory, Cincinnati, OH.

U.S. Environmental Protection Agency. 1993. Methods for the determination of inorganic substances in environmental samples. EPA/600/R-93/100. Environmental Monitoring Systems Laboratory, Cincinnati, OH.

U.S. Environmental Protection Agency. 1994. Methods for the determination of metals in environmental samples, Supplement I. EPA-600/R-94/111. U.S. Environmental Monitoring Systems Laboratory, Cincinnati, OH.

U.S. Environmental Protection Agency. 1995. Short term methods for estimating chronic toxicity of effluents and receiving water to West Coast marine and estuarine organisms. EPA/600/R-96/054. National Exposure Research Laboratory, Cincinnati, OH.

U.S. Environmental Protection Agency. 1996a. Sampling ambient water for trace metals at EPA water quality criteria levels. EPA/821/R-96/011. Engineering and Services Division, Office of Water, Washington, D.C.

U.S. Environmental Protection Agency. 1996b. Toxicity identification evaluation procedures. EPA/600/R-96/054. National Exposure Research Laboratory, Cincinnati, OH.

U.S. Environmental Protection Agency. 2002. Total maximum daily loads for toxic

pollutants, San Diego Creek and Newport Bay, California. U.S. EPA Region IX, San Francisco, CA.

U.S. Environmental Protection Agency. 2003a. Irgarol: updated environmental risk assessment for antifoulant use. Memorandum from K. Montague and R. Petrie to D. Edwards through N. Cook, July 15, 2003. Antimicrobial Division, U.S. EPA Office of Pesticide Programs, Washington, D.C.

U.S. Environmental Protection Agency. 2003b. Draft update of ambient water quality criteria for copper. Report No. 822-R-03-026. Office of Science and Technology, Office of Water, Washington, D.C.

U.S. Environmental Protection Agency. 2005. Determination of total organic carbon and specific UV absorbance at 254 nm in source water and drinking water. EPA-600/R-05/055. National Exposure Research Laboratory, Cincinnati, OH.

**APPENDIX 1: AFP Monitoring Study: Sampling  
Location/Frequency Table**

**AFP Monitoring Study: Sampling Location/Frequency Table**

Sampling Location	Water Types*	Site ID	Round 1		Round 2		Round 3			
			Water		Water		Water		Sediment	
			Metals/ BLM**	Irgarol	Metals/ BLM**	Toxicity/ TIE	Metals/ BLM**	Irgarol	Tot. Zn/Cu, TOC, Grain Size	Irgarol
Folsom Lake Marina	F	FL1 to FL8	8		8		8		8	
Tahoe Keys Marina	F	TK1 to TK8	8		8		8		8	
Sacramento City Marina	F	SA1 to SA8	8		8		8		8	
Village West Marina	F	VW1 to VW8	8		8		8		8	
Antioch Marina	B	AM1 to AM8	8		8		8		8	
Benicia Marina	B	BM1 to BM8	8	2	8	4	8	2	8	1
Vallejo Municipal Marina	B	VM1 to VM8	8	2	8	4	8	2	8	1
Pittsburg Marina	B	PM1 to PM8	8	2	8	4	8	2	8	1
Clipper Yacht Harbor	S	CY1 to CY8	8		8		8		8	
San Francisco Marina	S	SF1 to SF8	8	2	8	4	8	2	8	1
South Beach Harbor	S	SH1 to SH8	8	2	8	4	8	2	8	1
City of Berkeley Marina	S	CB1 to CB8	8	2	8	4	8	2	8	1
Marina Bay Yacht Harbor	S	MB1 to MB8	8	2	8	4	8	2	8	1
Loch Lomond Marina	S	LL1 to LL8	8	2	8	4	8	2	8	1
San Leandro Marina	S	SL1 to SL8	8		8		8		8	
Ballena Isle Marina	S	BI1 to BI8	8	2	8	4	8	2	8	1
Coyote Point Marina	S	CP1 to CP8	8		8		8		8	
Santa Cruz Harbor	S	SC1 to SC8	8		8		8		8	
Monterey Harbor	S	MH1 to MH8	8		8		8		8	
Santa Barbara Harbor	S	SB1 to SB8	8		8		8		8	
MdR Basins D, E, F	S	RB1 to RB8	8	2	8	4	8	2	8	1
MdR Basins A, B, C, G, H	S	RF1 to RF8	8		8		8		8	
Alamitos Bay Marina	S	AB1 to AB8	8	2	8	4	8	2	8	1
Downtown/ Shoreline Marina	S	DS1 to DS8	8	2	8	4	8	2	8	1
<i>Total</i>			<i>192</i>	<i>24</i>	<i>192</i>	<i>48</i>	<i>192</i>	<i>24</i>	<i>192</i>	<i>12</i>

\* Sample Locations, F: Freshwater, B: Brackish Water, S: Saltwater

\*\* Metals and BLM parameters include: Dissolved Cu, Total Cu, Dissolved Zn, TSS, DOC, Cl ( Salinity), Sulfate, Alkalinity, Mg, Ca, Na, and K.