

Copper Antifouling Paint Sub-Workgroup 3/08/07 Meeting Notes

In-Person Participants:

Anderson, Colin – International Paint
Blossom, Neal – American Chemet
Breninger, Dave - RBOC
Cohen, Sahrye - BCDC
Ely, Terri - DBW
Johnson, David - DBW
Lang, Valetti - DTSC
Little, Dan – RWQCB 5
Moran, Kelly – TDC Environmental
Rentz, Mark – DPR
Salinas, Melissa – DTSC
Singhasemanon, Nan – DPR
Sniderman, Lisa – CCC
Stewart, Noel – Stewart Marine
Susman, Stan – Interlux Paint
Yee, Betty – RWQCB 5

Phone Participants:

Brown, Paul – Port of San Diego
Candelaria, Linda - RWQCB 8
Early, Pat – U.S. Navy SPAWAR
Gonzalez, Jamie – UC Sea Grant Extension Program
Holman, Karen – Port of San Diego
Johnson, Leigh – UC Sea Grant Extension Program
Jones-Lee, Anne – G. Fred Lee & Associates
Jordan, Dan – Contra Costa County
Lee, Fred – G. Fred Lee & Associates
Matuk, Vivian – CCC
Merck, David – Port of San Diego
Opper, Richard, Kona Kai Marina
Panell, Debra, SIYB
Riviera, Ignacio – U.S. Navy SPAWAR
Schottle, Rolf – AMEC
von Langen, Peter – RWQCB 3
Wolf, Katy - Institute for Research and Technical Assistance

These meeting notes contain highlights of announcements, discussion topics, and pending action items. Pending action items are tasks that require some type of follow up. These are denoted as “**Action Item**”. A contact information list that contains participants’ agency names, email addresses, and telephone numbers usually accompanies these meeting notes in a separate Adobe file. Special notes from the author occur as italicized text.

Introductions/Agenda Review:

- Thirty-three individuals (16 in person and 17 by phone) participated in the eleventh meeting of the Copper Sub-Group. Nan welcomed the participants and reminded the group to try its best to adhere to conference call etiquettes in light of the large group participating today. There were no changes to the agenda.

News, Activities, and Developments:

- **Update of Federal Copper Oxide Ecological Risk Assessment, and Reregistration Eligibility Decision – Nan Singhasemanon, DPR** – Nan recounted his recent interactions with U.S. Environmental Protection Agency (EPA) about two weeks prior to the meeting. He had discussions with representatives from the U.S. EPA’s Office of Pesticide Programs’ Antimicrobial Division about monitoring and biological effects data that should be available from California in the near-term. Since U.S.EPA is working on its ecological risk assessment (ERA) for copper oxide, they are very much interested in ambient water levels of copper and any associated toxicity data.

During this discussion, U.S. EPA also revealed that the release dates for its copper oxide ERA and registration eligibility decision (RED) will again be pushed back. At the November 2006 Copper Sub-Group meeting, the workgroup heard that the ERA was going to be ready in March 2007 and the RED was going to be ready in April 2007. Now, U.S. EPA is currently working with the Copper Reregistration Task Force (CRTF) and the ERA and RED will likely be released in 2008. This has some significant

implications for DPR, since we had planned to evaluate data that we would have accumulated up to the summer of 2007 and determine our course of action on copper AFPs by September 2007. DPR and the State Water Resources Control Board (State Board) agreed that DPR would have the opportunity to take appropriate scientific and/or regulatory actions to address water quality concerns associated with copper AFPs by September 2007. If the State Board finds DPR and U.S. EPA actions to be inadequate, then it will work with the San Diego Regional Water Quality Control Board (Regional Board) and other coastal Regional Boards to develop a state policy for control of this water quality impairment. A 2008 release date for the ERA and RED means that DPR and the State and Regional Boards will have to develop regulatory or mitigation actions without the benefit of seeing a scientific assessment of the environmental risk for copper oxide. Moreover, risk management decisions made toward the formulation of the RED will also not be available for consideration.

U.S. EPA also mentioned that it is working on other copper ERAs and REDs, namely copper naphthenate salts and copper-8-quinolate, which has the current release date around September 2007. DPR is working to identify any monitoring data that may be useful to U.S. EPA on these compounds.

In another significant federal development, a Federal Register Notice was released on February 22, 2007 announcing the availability of the revised recommended aquatic life ambient freshwater quality criteria for copper. In the previous draft criteria notice, U.S. EPA proposed a move toward adopting the use of the Biotic Ligand Model (BLM) for fresh water. It also proposed to update (lower) the current salt water criteria chronic and acute values based on new data. However, in the February 2007 notice, U.S. EPA chose to only adopt the use of the BLM as the derivation procedure for fresh water systems. The other proposed changes did not occur. Note that in our November meeting, the workgroup had a discussion on the potential changes and impacts, if any, that changes to the federal criteria would have on the existing CTR standards that are currently applicable in California.

- **Preliminary Results from DPR/SWRCB Statewide AFP Monitoring Study - Nan S., DPR** – Nan provided a recap of DPR's statewide AFP monitoring study. He then mentioned that DPR is currently in a data accumulation and data management phase. Quality control analysis is being done as data are received from the lab. Since the primary analytical lab (i.e. ANR laboratory in Davis) struggled to keep up with the large number of samples and requested analysis, DPR had to amend the existing analytical lab contract to allow for more time. Both parties quickly approved the amendment.

In addition to the laboratory contract amendment, Nan said that he is also in the process of amending the reimbursement contract that DPR has with the State Board to help fund the monitoring study. There were several reasons for this although the delay in data generation was the most significant factor in necessitating a change in the deliverable due dates. An amendment to the contract was also necessary since DPR was not able to complete the sediment sampling and assessment portion of the contract work task. DPR, however, may still pursue sediment work for total copper and zinc on its own.

Nan then presented two PowerPoint slides that contained preliminary study results for the workgroup to see. The first slide shows a table with censored preliminary dissolved copper, Irgarol 1051, and toxicity results for all of the study marinas. Since Nan did not want to show individual results, he decided to summarize the data that was available so far to show mean marina concentrations and mean local reference concentrations. (*A PowerPoint slide with updated dissolved copper data will be included as a file with these meeting notes.*) Nan also cautioned that since new data were still coming in from the lab, people should expect most, if not all, of these numbers to change somewhat. He also pointed out that the laboratory quality control results that he had seen so far were excellent. Although there are many more constituents analyzed by various labs for this study, Nan only focused on key constituents that he believes folks would be most interested in (e.g., dissolved copper, toxicity, and Irgarol).

At first glance, it was apparent that the mean marina levels of dissolved copper varied greatly among the study marinas. Low copper levels (two lowest) were observed for the two freshwater lake marinas (Tahoe Keys and Folsom Lake marinas). However, the mean marina concentrations of the other two fresh water marinas (Sacramento and Village West marinas) placed them along the middle of the spectrum of the study marinas. The brackish water marinas were generally distributed around the mid-range of the list. The nine or ten marinas that had the highest marina means were marinas that were located in salt water areas. Some of the more surprising results were Loch Lomond Marina in San Rafael and Santa Barbara Harbor. Nan thought that high levels at Loch Lomond were unexpected since it was a fairly small recreational boat marina that appeared to be well-flushed. The results from Santa Barbara also seemed unusual to Nan since he thought that the marina area appeared to be well-flushed. The most striking results were from Marina del Rey's back and front basins. Mean dissolved copper levels in both of these areas were in the low and mid teens. Nan noted that some of the individual results that he had seen at Marina del Rey (MdR) were even higher than the values documented in Shelter Island Yacht Basin (SIYB) in San Diego Bay. Based on the SIYB TMDL, dissolved copper levels at SIYB were documented to be in the 5-12 µg/L range.

A participant asked what the California Toxics Rule (CTR) acute and chronic values were for comparison. Kelly Moran, however, cautioned that since the values being shown are mean values and not individual results, it would not be appropriate to compare the means to the CTR values (3.1 µg/L chronic and 4.8 µg/L acute). These values represent four-day averages (chronic) and one-hour averages (acute). Kelly also added that one can deduce that if these are mean values, about half of the data set will be higher than these values and so on. Linda Candelaria commented that a display of the standard deviations would be helpful in understanding the data set. Nan agrees that he should have included this statistical information on the slide. He will add this to future data summaries. Nan said that the variances for each marina were generally quite small with the local reference sites having even smaller variances.

Noel Stewart made the observation that it was difficult for him to soundly evaluate the data presented since the study design was not presented. The design may be biased or flawed. For example, Noel believed that some ships could have extensive copper plating that could be introducing a very large amount of dissolved copper into the marina or harbor water. Sample integrity may have also been jeopardized by other inputs.

Nan stated that most of the workgroup participants were fairly familiar with the study design since the sampling plan had been distributed to the workgroup over the last year and had been discussed at previous workgroup meetings. Nan added that several of the participants also provided technical input to the sampling plan. Confounding factors such as seasonality of sample collection, and location of sampling within and outside of the marina were certainly considered. A quality assurance project plan (QAPP) had to also be prepared before samples can be taken due to the involvement of State Board and U.S. EPA funds on the study. Nan invited participants who may not be familiar with the study to take a closer look at the monitoring plan and QAPP documents. But since a few folks might have been new to the group, Nan gave a quick overview of the design.

Toxicity and Irgarol samples were taken at a subset of locations. Since samples had to be analyzed quickly due to their short holding times, the ease of which the samples could be quickly shipped dictated the selection of these sites. Developmental toxicity to mussel embryo was statistically significant at two locations Berkeley Marina and MdR Back Basins. Toxicity at Berkeley, although statistically significant from control, translated to fairly low level of toxicity in terms of percent mortality. The toxicity at MdR, however, had a much higher percent mortality. Follow up Toxicity Identification Evaluation (TIE) confirmed that a metal (like copper) was responsible for the toxic effects in this sample.

Irgarol was detected in all of the study samples. Nan noted, however, that part of this was due to the very low detection limit used in the method. As presented in the slide, Irgarol results are presented in two columns. The first column contained the mean of the two samples taken from each marina in the first sampling round (July-August). The second column contained the analogous mean from the third sampling round (September-October). Again, this was done to summarize the data and to provide some level of censorship on the preliminary data. Irgarol results were mixed like the dissolved copper results. Several effective concentration (EC₅₀) values selected from literature are shown below the preliminary results table for comparative use. Nan mentioned that by looking at the mean values alone, one can deduce that some of the samples contained several hundred parts per trillion of Irgarol in them, which exceeded the sample values. This suggested that Irgarol levels were potentially having some effects on the phytoplankton and aquatic plant communities. U.S. EPA has had some concerns over Irgarol due to its ubiquitous nature in coastal waters worldwide occasionally at levels that could affect primary productivity and occasionally at levels that could be acutely toxic to marine eel grass. The highest individual result of Irgarol (higher than 700 ng/L) was observed at Loch Lomond Marina in San Rafael.

The Department of Boating and Waterways' Deputy Director David Johnson asked what the next steps were going to be for DPR. DPR's Deputy Director of Policy Coordination (Mark Rentz) used this opportunity to directly address DPR's current evaluation of AFP-related data and its future course of action. Mark stressed that DPR will not rely solely on the results of the statewide monitoring study to craft its action plan for AFPs. There are other relevant sources of information that DPR will consider such as other monitoring data as well as registrant-completed studies. The Copper Sub-Group has identified most - if not all - of these sources of data. Mark saw the completion of the statewide monitoring study not as an end to DPR's investigation, but rather as a beginning. Nan and the DPR water quality team will begin their evaluation of data from the statewide study. The team will then brief DPR's management and make recommendations on a course of action. Once DPR management decides on the final course of action, it will meet with State Board management to disclose DPR's intentions to them before making our plans public. All this is supposed to take place by September 2007 as is explicitly noted in the State Board resolution number 2005-0071.

Kelly stated that if DPR does not somehow adequately address the copper AFP pollution issue, the Regional Boards will probably have to continue dealing with each beneficial use impairments through TMDLs. Since TMDLs average about \$700,000 each to develop and site-specific objectives potentially costing millions to do, she is concerned as to how the Regional Boards will be able to absorb these expenses. Moreover, implementation of the TMDLs will cost stakeholders a lot as well.

Mark felt optimistic about DPR's ability to work out a more comprehensive solution. Nan added that DPR is also in a unique position in terms of being able to work with registrants and other AFP stakeholder groups to explore new coatings and alternative management strategies.

- **Copper AFP Registrants Reregistration Task Force Presentation "EU Monitoring and Bioavailability Studies" & Discussion - Neal Blossom, American Chemet and Colin Anderson, International Paint** – Neal and Colin introduced themselves to the workgroup. Neal stressed that the intent of their presentations today was not to convince the group that there is no copper problem. Instead, the task force wanted to have its research be a part of the solution and hopefully one that incorporates risk-benefit perspective and approach.

Neal actually made a presentation that a colleague of his (Mike Waldock) would normally makes. Neal said that he would try to answer every question to the best of his ability, but warned that he may not be fully able to respond to all the questions. *The task force presentations were previously sent out in an email to the workgroup distribution list on 3/5/07.*

The first presentation was titled, “How Harmful is Copper”. This presentation suggested that it may be inappropriate to evaluate environmental risks by simply comparing total dissolved copper concentrations in natural waters to copper toxicity thresholds (i.e. LC50 or EC50 values) that have been determined under laboratory conditions using water that contains little or no natural complexing agents. (*Note that dissolved copper is being referred to in this section as “total dissolved copper” since the presenter and presentation used this term; however they both refer to the same measured quantity of copper in a filtered water sample.*) Therefore, a certain non-complexed or labile fraction of total dissolved copper is responsible for the toxicity to non-target aquatic organisms and is the key component in water samples that needs to be quantified. Neal presented toxicity data that showed how higher levels of total dissolved copper are needed to effect the test organisms as humic acid and dissolved organic carbon levels increase. Researcher also developed an analytical method to measure this fraction of labile copper. Neal presented monitoring results from the United Kingdom and Finland and showed how the labile and non-labile fractions compared. Both comparisons showed that approximately 20% of the total dissolved copper is labile copper with a tendency of higher proportion of the toxic labile form closer to the source. Risk quotients calculated for both European studies using labile copper data were less than 1 while those using total dissolved copper data were more than 1.

Conclusions from this presentation were:

- Labile copper controls toxicity in the environment not total dissolved copper
- Bivalves and seaweed are tolerant to higher copper concentrations in the real world than previously thought
- Greater focus should be placed on labile copper and actual measured toxicity in harbours, marinas and estuaries
- There is still a need to control inputs of waste paint to stop the build up of copper in sediments

Kelly noted that similar types of data are used to support the development of site-specific objectives (SSO) in San Francisco Bay. Water effects ratios (WERs) used in SSOs recognize that different waters have different ligands; however, WERs may be too expensive and impractical for industry to help fund on a multiple water body basis. SSOs may not be appropriate in many cases. Even with current CTR standards, there are concerns from the Services (Fish and Wildlife Service and the National Marine Fisheries Service) due to documented sub-lethal effects of copper on salmonids.

Linda Candelaria asked if Neal could provide some references to some of the studies that formed the basis of his (Mike Waldo) talk. *A list of references provided Neal is provided as an attachment with the meeting notes.*

Colin Anderson gave an overview on leaching rates and in-water hull cleaning properties of different AFP types. There are three main AFP types used on yachts: hard, ablative, and self-polishing copolymers (SPC), each of which has different mechanisms for biocide release. There are two main “soluble acids” or acid resins used to enable biocide release in sea water – rosins and SPC acrylics. The release of biocides is controlled by the type and amount of the acid resin, and not by the quantity of biocide in the paint. SPC and ablative AFPs exhibit a thinner leached layer than do the hard AFPs. A thin leached layer gives a more efficient release of biocides than does a thick leached layer.

Conclusions from this presentation were:

- High copper content does not always mean high performance.

- Ablative paints generally show better performance compared to hard paints, and do not need to be in-water cleaned.
- In-water cleaning removes the leached layer and leads to increased copper release.
- In-water cleaning is not needed if the correct AFP is used.

Colin and Neal also noted that the copper industry and its task forces have been heavily involved in key regulatory activities that include U.S. EPA reregistration, U.S. EPA/Navy Uniform National Discharge Standards (UNDS), the European Union (EU) Biocide Products Directive, and specific interactions with EU countries on copper AFP issues.

Discussions ensued over leaching rates and contributions of hull-cleaning and passive leaching to copper in the water column and sediment. Ignacio Rivera said that he could provide the reference for a SCCWRP study that generated information on emissions. (*Ignacio's SCCWRP reference: Schiff, Kenneth, D. Diehl and A. Valkirs. 2004. Copper emissions from antifouling paint on recreational vessels. Marine Pollution Bulletin 48:371-377.*) Nan pointed out that there had been several studies (mainly conducted in San Diego Bay) that looked that leaching and emissions from hull cleaning.

Summaries and references for these studies can be found in:

- The SIYB Copper TMDL
http://www.swrcb.ca.gov/rwqcb9/tmdls/tmdl_files/shelter%20island/SIYB%20TMDL%20Tech%20Rept%2010-14-04%20rev1.pdf
 - DPR's Copper AFP Sub-Workgroup webpage:
http://www.cdpr.ca.gov/docs/sw/caps/04biblio_draft.pdf
 - SCCWRP publication website: <http://www.sccwrp.org/pubs/techrpt.htm>
- **Update on the Feasibility Study of Alternative Coatings & Management Practices – Melissa Salinas, Department of Toxic Substances Control** – Melissa provided a recap of discussions between the Department of Toxic Substances Control, DPR, and the Port of San Diego on the potential partnership on a feasibility study of alternative AFPs and hull fouling management practices. Funding has been earmarked at each agency and recent talks have focused on how exactly to fund the work. DTSC began drafting up a multi-party contract. DTSC and DPR would fund the Port of San Diego to develop a Request For Proposal process from which a sub-contractor would be selected. Melissa also met with Nan to discuss the tasks in the draft contract's scope of work.

Nan asked Melissa whether she was aware of very recent developments with the Port of San Diego. Nan said that he was not able to confirm this yet, but had heard that the Port may have decided to procure an alternate funding source instead since there may be some administrative roadblock in accepting payments from the State. Nan asked Karen Holman from the Port if she can confirm this, but Karen was not able to verify since she has only been reassign to deal with Port AFP issues. **Action Item:** Nan suggested that he and Melissa follow up on this and report back to the workgroup at the next meeting.

- **Other AFP-Related Updates & Announcements – Group & Nan S.**

Richard Opper from the Kona Kai Marina in SIYB mentioned that elevated detections of dissolved copper from the San Diego Regional Board's 2003 and 2004 San Diego Bay marina surveys appeared on the 2006 final CWA 303(d) impaired water bodies list.

Leigh Johnson from UC Sea Grant noted that a recent, informal collection of fouling growth from hulls of two boats in the San Diego area found that 4 of 5 species were invasive or cryptogenic (non-native of unknown origin). This finding mirrors results of formal studies in San Francisco Bay and Australia. Together, these results raised concerns over the extent of the spread of aquatic invasive species as well as the effectiveness of currently popular copper AFPs.

Pat Early from U.S. Navy's SPAWAR office mentioned that the Navy and U.S. EPA are still working to complete UNDS regulations.

Linda Candelaria from the Santa Ana Regional Board reported that she is currently analyzing data from her Lower Newport Bay metals study. A report should be ready within the next few months.

Peter von Langen from the Central Coast Regional Board shared that his region is interested in sediment levels of copper in Santa Barbara Harbor. Nan said that he had water column data for this harbor; however, he had no sediment results since sediment sampling for the statewide study had to be postponed.

Nan announced that a public hearing would be held in Oakland on May 9 and June 13, 2007 to consider the adoption of site-specific copper water quality objective for the San Francisco Bay north of Dumbarton Bridge into the San Francisco Bay Regional Board's Basin Plan. Kelly Moran added that comments could be submitted up until April 16, 2007. The Regional Board will receive oral public testimony at the May hearing and in response to the comments received at this hearing, may direct staff to make changes to the proposed amendment. The Regional Board will consider the adoption of the proposed amendment at the conclusion of the June hearing. *More information can be obtained online from the Region 2 homepage: <http://www.waterboards.ca.gov/sanfranciscobay/>.*

Other Items/Next Meeting/Adjourn:

- The next Copper Sub-Group meetings will be held on Thursday, May 17, 2007. Although the next scheduled meeting is supposed to be on May 10th, Nan will be unavailable to conduct the workgroup meeting that week. Please stay tuned for the agenda in early May.

Meeting notes prepared by: Nan Singhasemanon (DPR)