Department of Pesticide Regulation

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MEMORANDUM

Edmund G. Brown Jr.
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TO: David Duncan, Branch Chief
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FROM: Xuyang Zhang, Ph.D.
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Environmental Monitoring Branch

DATE: July 19, 2016

SUBJECT: **Response to the External Scientific Peer Review Comments on DPR's Determination of the Maximum Allowable Leach Rate for Copper Antifouling Products**

In October 2013, Assembly Bill (AB) 425 (Atkins) was signed into law which states, "No later than February 1, 2014, the Department of Pesticide Regulation (DPR) shall determine a leach rate for copper-based antifouling paint (AFP) 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."

In January 2014, DPR scientists determined the maximum allowable leach rates with a reverse modeling approach using the "Marine Antifoulant Model to Predict Environmental Concentrations" (MAM-PEC) model. The study was documented in a DPR report entitled "Modeling to determine the maximum allowable leach rate for copper-based antifouling products in California marinas" (Zhang and Singhasemanon 2014) hereafter referred to as "the study report." In January 2016, DPR sent the technical documents to the State Water Resources Control Board (SWRCB) for external scientific review. The technical documents highlighted DPR's approaches and hypotheses for review. They are listed as below:

1. DPR focused on the salt and brackish water marinas for copper mitigation based on the finding that high copper concentrations were found mainly in salt and brackish water marinas.
2. DPR used the MAM-PEC model for predicting concentrations of dissolved copper (DCu) within marinas.
3. DPR derived the maximum allowable leach rates using a reverse modeling procedure
4. DPR developed marina scenarios, representing marinas subjected to varying magnitude of copper contamination, using data collected from 20 California salt/brackish marinas.
5. DPR estimated underwater area of vessels using the best approach available at the time of investigation.

6. DPR considered the effects of elevated DCu concentration as a result of underwater hull cleaning
7. DPR compared the MAM-PEC derived leach rates to the leach rates of currently registered AFP products and estimated the portion of products that would have to be reformulated to potentially meet a maximum allowable leach rate limit or face cancellation of registration.
8. DPR concluded that to ensure that DCu concentrations not exceed the California Toxics Rule (CTR) of 3.1 µg/L in the marinas within the five scenarios, the AFP products used should be below the corresponding leach rates as listed in Table 6 of the study report.

Reviewers were selected with expertise in the following areas, in order of importance:

a) Marine ecotoxicology/environmental toxicology – with an emphasis on fate and transport of heavy metals affecting aquatic life, with a preference for individuals with expertise and/or proficient knowledge and training in the MAM-PEC modeling.
b) Environmental chemistry – with an emphasis in toxicology and/or chemistry, ecology, and/or MAM-PEC

Reviewers were asked to determine whether the scientific work product is "based upon sound scientific knowledge, methods, and practices." In June 2016, SWRCB transmitted the review comments back to DPR. This document addresses these review comments.

DPR appreciates the thorough reviews that the independent reviewers have provided. In general, reviewers are supportive of DPR's methodology and commented that DPR's approaches "are in line with accepted approaches and expert judgement and in most cases based on sound scientific knowledge and practices." We believe the review process and comments have further validated the scientific basis of the approaches that DPR has taken in determining the leach rate for protecting aquatic environment from copper exposure. Since most of the comments are positive, we are only responding to the critical ones and suggestions that need to be addressed in this document.

Comments by reviewer 1: Dr. Bert van Hattum

Critical Comment 1: Regarding DPR's approach No. 5 as listed above, on page 3 of the review document, Dr. Hattum stated "In the study report (Zhang and Singhasemanon 2014) most of the uncertainties mentioned above are properly acknowledged. I will address uncertainties related to the emission estimations further under topic No. 5 ."

DPR Response: The uncertainties associated with estimation of the underwater surface area for emission estimations have been addressed in the study report (Zhang and Singhasemanon, 2014). The authors have also acknowledged that estimating under-water area of vessels was the largest uncertainty in the modeling processes. Please refer to paragraph 3 on page 9 of the study report.

Critical Comment 2: Regarding the hydrodynamic settings in MAM-PEC modeling, on page 3 of the review document, Dr. Hattum stated "For the hydrodynamic exchange processes it is difficult to evaluate the realism of the predicted exchange for the 5 scenarios used in the study report. I recommend additional tracer studies to verify the exchange processes in a number of typical marinas, to provide further support to the chosen approach."

DPR Response: We agree with Dr. Hattum on the importance and the uncertainties associated with the hydrodynamic exchange processes. Due to the limited time and resources, tracer studies on marinas were not feasible under the project time frame. However, as Dr. Hattum also mentioned in his review, "MAMPEC simulation runs executed by International Paint (International Paint, 2010, cited in the study report) with the dimensions of the California marinas that were also used later in the study report, showed a reasonable match with measured concentrations in the survey of Singhasemanon et al. (2009)." This indicated that DPR's parameter settings on the hydrodynamic processes were able to capture the variations of California marinas reasonably well.

Critical Comment 3: On page 3 of the review document, Dr. Hattum stated "With respect to the chemical fate processes of Cu I recommend to use a Kd (sediment water or SPM water partitioning coefficient) value based on local measurements, possibly directly derived from the survey of (Singhasemanon et al. 2009). This could increase the accuracy of the predicted dissolved fraction.

DPR Response: In our MAM-PEC simulations, we set the sediment-water portioning coefficient (Kd) value to 30000 L/Kg (logKd = 4.5). According to Brown and Caldwell (2011), the typical range of logKd was 0.7–6.2 with a median value of 4.2. Measurements taken in Marina del Rey in Southern California showed a median logKd value of 5.4 with a range of 4.5–6 (Brown and Caldwell, 2011). Therefore, the use of 4.5 for logKd was within the range of local measurements and in good agreement with literature data. In addition, local studies have shown that the partitioning coefficient between water and sediment within the same marina or harbor could be highly variable (Bessinger *et al.*, 2006; Bucket *et al.*, 2007; Brown and Caldwell, 2011). Since we were working on the basis for a statewide regulation, we determined that the setting of Kd to 30000 L/Kg was appropriate.

Critical Comment 4: Regarding the spatial variation within marinas, the reviewer stated that "Another important aspect to consider is that in MAMPEC a worst-case approach is assumed for the spatial allocation of the emissions in a harbor or marina. Emissions from ships at berth are distributed over the last row of cells along the back side of the harbor (x2 in environment input screen). Especially for marinas this is not realistic and emissions usually are more equally dispersed over the whole harbor area. Model runs based on emissions dispersed over the whole harbor result in PECs that depending on the exchange conditions can be 40% lower than PECs derived the worst-case allocation of emissions. In MAMPEC v2.5 this can be simulated when the ships at berth entered as moving ships. As this may affect the final predicted leaching rates in Table 6 of the study report, I recommend repeating the model runs with emissions dispersed over the whole harbor area."

DPR Response: We agree with Dr. Hattum that the spatial allocation of the emission within a harbor was a worst-case approach not considering the flushing effects. However, for many marinas in California, especially the large ones, the flushing is poor inside the marina and even more so towards the back. For these marinas, MAMPEC's spatial allocation is not unrealistic for capturing peak concentrations.

Critical Comment 5: Regarding parameter settings in MAM-PEC modeling, the reviewer stated that "The settings provided in the study report may not be complete; estimates for exchange conditions (current in front of the harbor, flushing, wind exchange) were not reported. It is not clear if these parameters have been determined separately for each marina in the database, and that different percentile values were added to the scenarios. From the data provided in the study report (Table 2) it seems that only tidal exchange was addressed. It is not clear if the exchange settings from the applicant study (International Paint, 2010, cited in the study report) were applied. As this may affect the estimated maximum allowable leaching rates, I recommend reconsidering the chosen settings for the hydrodynamic exchange and to add these to the report and to evaluate if repeating the model runs is required."

DPR Response: For the hydrodynamic settings, the tidal period and tidal range were assigned using the measured sample dataset provided in International Paint study (International Paint, 2010). Like the other chosen parameters, different values for these parameters were assigned to the 5 scenarios using the percentile values. For the other exchange settings, site specific measurements were not available and the default values in the standard "marina" scenario in the MAM-PEC model were used. The same values were used for all 5 scenarios. The five scenarios were created with the intention of capturing the variability in copper exposure for California coastal marinas not to represent particular marinas. A complete dataset measuring all the model input parameters were not available. Therefore, the most influential parameters were used to define the scenarios.

Comments by reviewer 2: Dr. Gretchen K. Bielmyer-Fraser

Critical Comment 1: Regarding the sample data set, the reviewer stated that "My concern is that the sample data set in Appendix 1 is missing some key information (e.g. data for total suspended sediment (TSS) and dissolved organic carbon (DOC)) for some of the marinas. As stated above (#2), DOC and TSS largely affect the bioavailability of copper and thus the toxicity. Additionally, TSS was one of the key parameters for scenario development. The breadth of the dataset will influence the quality/accuracy of the marine scenarios and is therefore pertinent.

DPR Response: The measured data from the 20 marinas were used to capture the variations of the important parameters within California marinas. For TSS and DOC, although measurements were missing for seven of the marinas, the median and range for the remaining 13 marinas were in line with those measured in Singhasemanon *et al.* (2009).

Critical Comment 2: Regarding the listed ship length grouping in table 4 and table 5 of the study report, the reviewer stated that “My only issue is in the calculation of the five scenarios, which used the number of vessels within each length of vessel category (Table 4 in the study report). In the “Length of vessel” category in Table 4, there is redundancy across categories. For example, 16 ft. vessels are counted twice (e.g. 8-16 ft., 16-19 ft.). I have the same comment for Table 5. Are these typos?”

DPR Response: This is a good point. We were not being clear about inclusion and exclusion of the breaking points for the length categories. We will modify tables 4 and 5 as follows with the square brackets denoting inclusion of the value and parentheses indicating exclusion of the value:

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

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

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

Length of vessel (ft)	Average length (ft)	Estimated beam (ft)	Underwater area (ft2)	Underwater area (m2)
[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

Critical Comment 3: Regarding the final choice of the maximum allowable leach rate, the reviewer stated that "Given the stated uncertainties of the model, I would suggest using the model-derived leach rates without the adjustments for BMP practices and less frequent (monthly) hull cleaning as a more conservative and thus more protective measure for aquatic life."

DPR Response: We appreciate this suggestion and understand the logic behind a conservative approach. However, we have already integrated a number of conservative assumptions elsewhere in our methodology. For example, the use of DCu as opposed to labile copper assuming that all dissolved copper is bioavailable; the assumption that all the ships in a marina were painted with copper paints (application factor =100); and that all the ships are at berth. Note that the product of DPR's modeling approach is a matrix of possible maximum allowable leach rate values that will be further subjected to risk-management considerations before a final decision is reached. Additional degrees of conservatism may be imparted during that stage. Moreover, as part of the overall mitigation scheme, DPR generated a list of recommended actions designed to be implemented with the setting of a maximum allowable leach rate. DPR believes that successful implementation of these actions by various parties will be just as important as building in additional conservatism in the maximum leach rate values.

Comments by reviewer 3: Dr. Gijsbert D. Breedveld

Critical Comment 1: Regarding documentation of the modeling process, the reviewer stated that "The reverse modelling is hampered by a clear documentation of the exact input parameters for each scenario and the applied correction factors that lead to the exact numbers presented in table 6."

DPR Response: The Zhang and Singhasemanon (2014) report listed the values of the key input parameters in tables 1, 2 and 5. The correction factors of 0.57 for BMP and 0.41 for non-BMP cleaning have also been listed in the report. The rest of the parameters were set using average measured or model default values. To avoid making the technical document longer than necessary, we decided to exclude all the summary files for model inputs and outputs. The exact model input and output values for each of the scenario runs are available upon request.

Critical Comment 2: Regarding DPR's choice of the MAM-PEC model, the reviewer stated that "I am explicitly missing a discussing of the applied Cu speciation model. MAMPEC 3.0 offers two ways of approaching Cu speciation/complexation: a 3-ligand model or an external run Biotic Ligand Model (BLM) input. Speciation has a significant influence on the dissolved Cu concentration. A BLM approach would give a more sound scientific basis for evaluating Cu-speciation and I therefore recommended Even if the version for the marine environment has not officially been released as far as I am aware, a discussion on the consequences of the applied speciation model for the outcome of the calculated leaching rates is warranted."

DPR Response: We considered the BLM during the model selection process. Given that our objective was to develop a copper leach rate for statewide regulation, not to meet or develop site-specific water quality criteria, we decided that the MAM-PEC approach using the 3-ligand model was more appropriate.

Critical Comment 3: Regarding the estimation of a ship's underwater area, the reviewer stated that "The underwater area is a very critical parameter since MAM-PEC estimates emissions using the area and leach rate per m2….. Since this parameter is so critical it would be recommended to have a closer look at the sensitivity of the MAM-PEC outcome for the equation that is used to estimate the surface area and underpin the choice used in this study."

DPR response: The sensitivity of the underwater area to the PEC of dissolved copper has been highlighted in the "uncertainty" section of the report. As the report has stated, "doubling the values of underwater area would almost double the PECs of dissolved copper."

Critical Comment 4: Regarding DPR's use of the factor of 2.9 to convert the product leach rates, which were derived using the ISO10890:2010, such that they could be comparable to the environmental leach rates derived by the MAM-PEC approach, the reviewer stated that "After a closer review of the references I conclude the following:

- ISO leach rate data in appendix II refer to calculations according to ISO 10890:2010.
- The correction factor of 2.9 is based on Finnie (2006) that compared the CEPE (2003) mass balance calculation method with data from the "Dome" method.
- The mass balance calculation according to CEPE (2003) is not identical to ISO10890:2010.

This leads me to the conclusion that the use of a correction factor of 2.9 to convert the ISO data in appendix II to estimate the "actual" leach rates, is not sufficiently documented."

DPR response: We agree with the reviewer and those stated in Van Hattum et al. (2014) that the ISO 10890:2010 is a more robust mass balance calculation method than CEPE (2003) and should be considered as the most appropriate mass balance method as it: "does not make any a priori assumptions about the way in which the biocide is released." That is why we used the ISO 10890:2010 method to derive the product leach rates.

The ISO 10890:2010 method was developed to improve the CEPE method. Thus these two methods are very similar. The European Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology has stated that "The results (from ISO 10890:2010) are numerically consistent with those of the earlier CEPE calculation method and the use of similar default correction factors is recommended to allow the most reliable estimates of biocide release to the environment to be made." (Environment Directorate Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology, 2012). This correction factor was further confirmed by a recent study by Finnie (2014), which found that the difference between ISO 10890 and CEPE "is never more than 2.8% and that the same conservative default correction factor of 2.9 is equally applicable to both methods". Therefore, our use of the correction factor of 2.9 was sufficiently justified given the availability of the current knowledge on these two methods.

Critical Comment 5: Regarding the number of significant digits in table 6, the reviewer pointed out that "Given the general variation in the input data and estimated correction factors for the various maintenance regimes, the use of 4 (or 3) significant figures in table 6 seems not to be warranted."

DPR response: This is a good suggestion. We have rounded the numbers on table 6 and revised the table accordingly as follows:

Table 6: Leach rates from modeling (LR0) adjusted leach rates accounting for cleaning effects (LR1: current cleaning schedule using BMP method; LR2: current cleaning schedule using non-BMP method; LR3: monthly cleaning using BMP method; LR4: monthly cleaning using non-BMP method)

Scenario	LR0 (µg/cm^2/day)	LR1 (µg/cm^2/day)	LR2 (µg/cm^2/day)	LR3 (µg/cm^2/day)	LR4 (µg/cm^2/day)
1	24.6	14.0	10.1	17.5	11.0
2	13.4	7.6	5.5	9.5	6.0
3	8.6	4.9	3.5	6.1	3.9
4	2.9	1.7	1.2	2.1	1.3
5	1.1	0.6	0.5	0.8	0.5

cc: Dr. Kean Goh, Environmental Program Manager I
Mr. Nan Singhasemanon, Senior Environmental Scientist (Supervisor)

References

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