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To: Carol Perkins
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Office of Research, Planning, and Performance
California State Water Resources Control Board

Re: Scientific Peer Review of the Scientific Basis of Proposed Revisions to the Total Maximum Daily Load of Methylmercury to the Sacramento-San Joaquin Delta Estuary

Based on my expertise and experience, I am reviewing the findings, assumptions, or conclusions I agreed I could review with confidence, as follows:

- Conclusion 1: The DMCP Review's proposed linkage model was determined by applying appropriate quantitative data analysis methods for pairing black bass mercury data with aqueous methylmercury data, finding the central tendency of data, and selecting regression models.

- Conclusion 2: The DMCP Review's proposed margin of safety sets an aqueous methylmercury implementation goal by accounting for the uncertainty in the linkage analysis data and modeling methods used to find the protective aqueous methylmercury concentration.

- Conclusion 4.a.: DMCP Review's proposed methylmercury load allocations and waste load allocations are achievable considering current technology, feasibility of controlling the sources, and recommended methylmercury allocation compliance calculations.

- Conclusion 4.b.: Achieving load allocations and waste load allocations for Delta regulated entities (e.g., municipal separate storm sewers (MS4s), public wastewater treatment facilities (WWTFs), irrigated agriculture) will result in measurable and statistically meaningful reductions in fish tissue mercury concentrations. This conclusion should be considered apart from whether other loads are achieved.

- Conclusion 4.c.: Achieving load allocations and waste load allocations for Delta regulated entities (e.g., MS4s, WWTFs, irrigated agriculture) will result in a measurable reduction in Delta aqueous methylmercury concentrations. This conclusion should be considered apart from whether other loads are achieved.

- Conclusion 4.d.: Measurable reductions of mercury in fish tissue will occur as all sources meet the proposed allocations, eventually attaining the proposed water quality objectives to protect human and wildlife health for consumption of trophic level 3 and 4 fish.

- Conclusion 5: The DMCP Review’s proposed methylmercury source analysis, allocations, and compliance calculation methods reasonably account for climatic variability.

Conclusion 1.

Summary: The dataset considered for the linkage analysis originally included 1,203 black bass total mercury concentrations and 2,052 aqueous methylmercury concentrations, collected between 2000-2019 (Excel file Appendix A.1., Figure 1 this review). Data collected prior to 2000 were not included in the Excel file.

```
. tab data_for_bb_eval_subarea

          Subarea |      Freq.     Percent        Cum.
------------------+-----------------------------------
    Central Delta |        396       32.92       32.92
  Moke/Cos Rivers |        164       13.63       46.55
 Sacramento River |        267       22.19       68.74
San Joaquin River |        150       12.47       81.21
       West Delta |         98        8.15       89.36
         YB-North |          3        0.25       89.61
         YB-South |        125       10.39      100.00
------------------+-----------------------------------
            Total |      1,203      100.00

. tab linkage_analysis_aq_data_subarea

          Subarea |      Freq.     Percent        Cum.
------------------+-----------------------------------
    Central Delta |        351       17.11       17.11
      Marsh Creek |         30        1.46       18.57
  Moke/Cos Rivers |        104        5.07       23.64
 Sacramento River |        466       22.71       46.35
San Joaquin River |        146        7.12       53.46
       West Delta |        173        8.43       61.89
         YB-North |        187        9.11       71.00
         YB-South |        475       23.15       94.15
Yolo Bypass North |        120        5.85      100.00
------------------+-----------------------------------
            Total |      2,052      100.00
```

Figure 1. Output from STATA (version 17.0) for data collected between 2000-2019, including the number of black bass total mercury concentrations (top) and the number of aqueous methylmercury concentrations (bottom) for each subarea (data from Excel file, Appendix A.1).

For the linkage analysis, this dataset was collapsed to just 5 paired observations, representing the pooled median black bass total mercury concentration and the pooled median aqueous methylmercury concentration for 5 subareas (Central Delta, Moke/Cos Rivers, Sacramento River, San Joaquin River and West Delta). The time period was shortened from 2000-2019 to 2016-2019 because the standard error of the regression (SER) was minimized within this timeframe. The final linkage model (Figure 5.3) estimated the predicted aqueous methylmercury concentration when the black bass total mercury concentration was 0.258 mg/Kg for standardized length of 350 mm [the Recommended Fish Tissue Implementation Goal (Table 4.5)], i.e., 0.061 ng/L.

Comments:
The linkage model from the DMCP Review (in Figure 5.3) is reproduced below with data from Table 5.1 (pg. 53), where *y* is the median aqueous methylmercury concentration, and *x* is the natural log of the median total mercury concentration for black bass. The regression equation in Figure 5.3 is: $y = 0.109 + 0.0351 * \ln(x)$, SER = 0.0195. The regression equation in this review is: $y = 0.108 + 0.0349 * \ln(x)$, SER = 0.0196. Slight differences may be due to roundoff error in Table 5.1.

```
. regress median_aqueous_mehg ln_median_bb

      Source |       SS           df       MS      Number of obs   =         5
-------------+----------------------------------   F(1, 3)         =      3.97
       Model |  .001525474         1  .001525474   Prob > F        =    0.1402
    Residual |  .001151326         3  .000383775   R-squared       =    0.5699
-------------+----------------------------------   Adj R-squared   =    0.4265
       Total |    .0026768         4    .0006692   Root MSE        =    .01959

------------------------------------------------------------------------------
median_aqu~g | Coefficient  Std. err.      t    P>|t|     [95% conf. interval]
-------------+----------------------------------------------------------------
ln_median_bb |    .0349491   .0175296     1.99   0.140    -.0208379    .0907362
       _cons |     .108479   .0131978     8.22   0.004     .0664777    .1504803
------------------------------------------------------------------------------
```

Figure 2. Output from STATA replicating the results in the DMCP Review (Figure 5.3). The variable "median_aqueous_mehg" is the median aqueous methylmercury concentrations (dependent) and "ln_median_bb" is the natural log of the median total mercury concentrations in black bass (independent) (n=5 observations).

The main strength of this TMDL is the rich data set, which spans 20 years (2000-2019) and includes fish tissue and aqueous samples collected throughout the subareas. By collapsing this data set to just 5 paired observations, much of the information relating black bass total mercury concentrations and aqueous methylmercury concentrations was lost. More sophisticated statistical models, which account for both spatial and temporal autocorrelation, would better reflect the environmental risks due to methylmercury contamination and efficient biomagnification in fish tissue.

Moreover, certain subareas (e.g., Yolo Bypass- South) were entirely excluded from the linkage analysis because the hydrology differed (Section 5.2). It is important to retain these subareas in the linkage analysis in order to more accurately predict the impacts of reducing methylmercury loads to the Delta.

With just 5 paired samples, the study is no longer sufficiently powered to assess the associations between concentrations of aqueous methylmercury and black bass total mercury. Note that the 95% confidence intervals for black bass total mercury concentrations are wide and include the null (95% confidence interval: -0.021, 0.091) (Figure 2 in this review). See comments below for Conclusions 4.b and 4.d.

Throughout the DMCP Review, the standard error of the regression (SER) (i.e., the root mean squared error, also called the residual standard error) was used as the sole measure of the goodness of fit of a model. For linear regression models (including the linkage model in Figure 5.3), assumptions for the residuals include: mean = 0 and homoskedastic (or constant) variance. If the model assumptions are not met (as is the case for the linkage analysis), the model is not valid, regardless of the SER.

Note that the linkage analysis in the DMCP Review (Figure 5.3) reversed the independent and dependent variables, compared to the 2010 Report. It would make more sense if the black bass total mercury concentration was the dependent variable.

Conclusion 2.

Summary: To obtain the margin of safety, the DMCP Review re-ran the linkage analysis, utilizing random subsets of the black bass total mercury data and random subsets of aqueous methylmercury data. For black bass total mercury concentrations, a random number of samples was selected (without replacement) ranging from 7 to the total number of samples, while 12 aqueous methylmercury concentrations were randomly selected with replacement for a randomly selected year. Data were regressed using various models; Figure 5.4 includes a histogram of the predicted aqueous methylmercury concentrations obtained after 10,000 iterations. The DMCP Review selected 0.059 ng/L (corresponding to the 5th percentile) as the implementation goal. This value represented a 3.3% reduction (margin of safety) from 0.061 ng/L.

Comments:

The DMCP Review did not explain why the 10% explicit margin of safety (utilized in the 2010 Report) was not used here. The 10% margin of safety seems reasonable and is comparable to values selected for other Mercury TMDLs in California, including the Sulphur Creek TMDL for Mercury (Cooke and Stanish, 2007) and the Cache Creek, Bear Creek and Harley Gulch TMDL for Mercury (Cooke et al., 2004).

The margin of safety should account for uncertainty in the linkage analysis and modeling methods. Instead, the methods described in Section 5.3 add to the uncertainty, for example, 1) by pairing multiple years of black bass total mercury concentrations with a randomly selected year of aqueous methylmercury data, 2) by inconsistently resampling, i.e., with replacement (for aqueous methylmercury) and without replacement (for black bass total mercury data), and 3) by choosing a different regression model for each of the 10,000 iterations [e.g., linear, power, exponential, non-linear least squares (NLS), generalized additive models (GAM), or logarithmic models], depending on the SER, rather than use the same model as in Figure 5.3.

The range of values presented in Figure 5.4 (approximately 0.05-0.09 ng/L) is evidence against this approach for determining the margin of safety. More than 90% of the aqueous methylmercury concentrations are actually greater than the original value (0.061 ng/L), i.e., less protective, and hence do not provide a margin of safety.

One way to account for the uncertainty in the model, is to utilize the 95% confidence interval for the beta coefficient. Because the confidence interval contains 0, the result is unachievable.

Conclusion 4.a.
Summary: This section considers whether waste load allocations (for point sources) and load allocations (for nonpoint sources) are achievable, given the current technology, feasibility of controlling the sources, and compliance calculations.

Comments:
My comments are focused on the methylmercury compliance calculations. In Section 8.1.4.1, the DMCP Review recommended using a five-year median annual load for all waste load allocations and load allocations for compliance. The median load is calculated from at least 2 aqueous samples collected annually during the dry/wet seasons, and the median flow volumes. This differed from the 2010 TMDL report, in which the average- not the median- was used for both variables. In addition, in the 2010 TMDL report, WWTFs used a one-year average, not a five-year rolling average to assess compliance. For the DMCP Review, although compliance is potentially achievable, using the median methylmercury load over a 5-year period will likely mask decreasing trends. It is recommended to use the mean or geometric mean.

In the same section (Section 8.1.4.1), an example was provided to assess compliance, including 10 aqueous methylmercury concentrations and 5 flow volumes from 5 consecutive years. One of the aqueous methylmercury concentrations was nondetectable. For samples below the detection level, half the minimum detection level should be used rather than 0 ng/L, as proposed in the DMCP Review. This difference will be important if using the mean or geometric mean.

Compliance will be most challenging for load allocations, including Tributary Inflows, Agricultural Returns and Open Water Sediment Flux, which comprise 57%, 18% and 9.0% of methylmercury gross loads, respectively (2,460 g/year, 771 g/year, and 391 g/year, respectively, from Tables 8.3-8.9), i.e., 84%. These methylmercury loads are much higher compared to NPDES WWTFs and MS4s (i.e., point sources), which contribute just 1% of methylmercury gross loads (44 g/year, Tables 8.3-8.9). There are few details regarding compliance for Tributary Inflows, Agricultural Returns and Open Water Sediment Flux (in Sections 8.1.4.7, 8.1.4.2, and 8.1.4.4, respectively). Hence, it is uncertain whether the load allocations are achievable. If compliance goals are not met, what measures are proposed to offset these significant sources of methylmercury loads?

In Table 8.21, the percent allocations or the methylmercury allocations may be incorrect. For example, for the Cache Creek Settling Basin, the percent allocation is 6.79%; however, the median annual methylmercury load did not differ from the methylmercury allocation (69.931 g/year), i.e., no reduction, therefore the percent allocation should be 100%. The percent allocation for Cache Creek (above the settling basin) is 6.79%; however, this should be 1.535 g/year (not 4.981 g/year). Also, the methylmercury allocations for the tributaries Ridge Cut Slough, Willow Slough, Upper Lindsey, and Ulatis Creek are incorrect. For example, the methylmercury allocation for Ridge Cut Slough and Willow Slough are 8.447 g/year and 0.168 g/year, respectively; however, these should be 8.005 g/year and 0.667 g/year, respectively (for 6.79% allocation). Please check the calculations and update other tables if needed.

Conclusion 4b.
Summary: In the section, I was asked to consider whether the load allocations and waste load allocations for regulated entities will result in measurable and statistically meaningful reductions in fish tissue total mercury concentrations.

Comments:
My first concern is that the regulated entities (e.g., WWTFs, MS4s, and irrigated agriculture) comprise a small portion of the methylmercury load. As noted for Conclusion 4.a., the allocations for regulated entities comprised just 19% of gross methylmercury loading (Agricultural Returns = 18%, and the sum of WWTFs and MS4s = 1%) (Tables 8.3-8.9). Hence the corresponding reductions in black bass total mercury concentration are expected to be low.

My second- and more important- concern is that the association between aqueous methylmercury concentrations and black bass total mercury concentrations is not statistically significant (Figure 2 in this review). This is attributed mainly to the loss of data, from thousands of observations (see Figure 1 in this review) to just 5 paired observations. Also, certain subareas were omitted from the linkage analysis. With such a small data set, my confidence level is low that the waste load and load allocations for regulated entities will result in meaningful reductions in black bass total mercury concentrations.

Moreover, Marsh Creek, Yolo Bypass- North and Yolo-Bypass South subareas were omitted from the linkage model. The DMCP Review noted that Yolo Bypass areas differed from the other subareas, with high aqueous methylmercury levels and low fish tissue total mercury levels (Section 5.2, page 51). Given that these 3 areas were not included in the linkage analysis, it is uncertain the effect(s) of decreased methylmercury loading on fish tissue total mercury levels.

The timeframe for achieving the implementation goals was not provided.

Conclusion 4.c
Summary: In this section, I was asked to assess whether achieving load allocations and waste load allocations for regulated entities (WWTFs, MS4s, and irrigated agriculture) will result in a measurable reduction in Delta aqueous methylmercury concentrations.

Comments:
As methylmercury loads from regulated entities decline, Delta aqueous methylmercury concentrations will also likely decline.

My only reservation concerns the potential for *in situ* microbial methylation of legacy inorganic mercury, which may also be an important source of methylmercury to the Delta. *In situ* production of methylmercury may offset the declines in methylmercury loads from regulated entities. However, this potential source was not addressed in the DMCP Review- please clarify.

Conclusion 4.d.
Summary: In this section, I was asked to assess whether measurable reductions in fish tissue mercury levels will occur, including trophic level 3 and 4 fish, as all sources meet the proposed allocations.

Comments:
Similar to Conclusion 4.b., the linkage analysis indicated that the association between aqueous methylmercury concentrations and black bass total mercury concentrations was non-significant (Figure 2 in this review). Hence, my confidence level is low that measurable reductions in fish tissue mercury levels will occur as all sources meet the proposed allocations.

As noted above, the timeframe for achieving the implementation goals was not provided.

Conclusion 5.
Summary: Here, I was asked to assess whether the analyses in the DMCP Review reasonably account for climatic variability.

Climate change was addressed in 2 sections in the DMCP Review, including Section 6.1.13 (Future Conditions) and Section 6.4.1 (Climate Change). The DMCP Review indicated that "the effects of climate change will likely increase methylmercury loading in the Delta" (pg 221). However, the DMCP Review opted not to account for climate change in the margin of safety (pg 69), and noted there was too much uncertainty concerning the impacts of climate change to incorporate potential impacts into their models (pg 218). Instead the DMCP Review suggested several projects to study the effects of climate change on methylmercury mass balance, such as studies of extreme flooding, and studies of erosion and runoff from burned areas (pg 219-220). Moreover, the report cited the timeframe (WYs 2000-2019) for data collection, in which climate change impacts were observed, e.g., in 2015 (rise in sea level) and 2012-2016 drought) (pg 69). The report noted that "the inclusion of more recent years of methylmercury and flow data should account for some of the expected patterns in the next 100 years" (pg 224).

Comments:
The linkage analysis utilized a shorter timeframe (2016-2019), not 2000-2019, compared to the methylmercury source analysis. Because the allocations and compliance are based on the linkage analysis, it is not possible to affirm that these calculations adequately accounted for climatic variability. However, if the linkage analysis is revised utilizing all of the available data (2000-2019), then it is more likely that the calculations adequately account for climatic variability.

References

Cooke, J., Foe, C., Stanish, S., Morris, P. Cache Creek, Bear Creek, and Harley Gulch TMDL for Mercury, Staff Report. Regional Water Quality Control Board-Central Valley Region, 2004. Available: https://calisphere.org/item/ark:/86086/n2ng4qg5/.

Cooke, J., Stanish, S. Sulphur Creek TMDL for Mercury, Final Staff Report. Regional Water Quality Control Board-Central Valley Region, 2007. Available: https://calisphere.org/item/ark:/86086/n2c24w44/.