Reviewer information

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Item under review

Staff Report for Scientific Peer Review – Delta Mercury Control Program Phase 1 Review of the Sacramento – San Joaquin Delta Estuary Total Maximum Daily Load for Methylmercury

Overall comments:

The data, documents and information are very extensive and carefully crafted, which are aimed at delivering a very important goal to reduce methylmercury (MeHg) levels in fish to protect wildlife and humans in the Central Valley and beyond. The original development of TMDL and the current revision appear to come along and definitely strengthen the scientific basis for the whole purpose. The amount and quality of data are good along with various reasonable assumptions, decisions, and adjustments made by the team. One of the most important conclusions is that it is the upstream tributaries, not local point sources, as the main contribution of MeHg to the Delta which is definitely a scientific accomplishment. However, such clear results also illustrate the difficulty in controlling mercury contamination through regulation of point sources.

Comments to specific conclusion:

Based on my expertise and experience, I am reviewing the findings, assumptions, or conclusions I agreed I could review with confidence on **Conclusion # 1: Concerning proposed linkage model applies appropriate quantitative data analysis methods.**

Under this conclusion, I agree with the exclusion of migratory fish species while the inclusion of three black bass species (largemouth bass, smallmouth bass, and spotted bass) would definitely help fill in data gaps in sites where largemouth bass were not caught or the number of samples was too small. However, it should be noted that these different black bass species (e.g. largemouth bass *vs.* smallmouth bass) can have somewhat different dietary preferences and potentially different methylmercury (MeHg) bioaccumulation patterns. You just cannot simply treat them the same.

For instance, a Lake Ontario study used stable isotope and molecular approaches, and showed that prey items for largemouth bass is much more diverse (3-4 times higher) than smallmouth bass (Nelson et al. 2017), while an earlier U.S.G.S. report found that the relationships between unfiltered MeHg and fish total Hg are much stronger for largemouth bass than smallmouth bass in a range of background aquatic habitats across the U.S. (Scudder et al. 2009). Thus, these results show an important aspect to be considered using different fish species across sites with caution. Another point should be noted that if one species is consistently absent in a subarea, it may imply that its prey items and other water conditions are very different from the others, and thus MeHg bioaccumulation and trophic transfer patterns may be potentially affected as well.

The selection of 2002-2019 data period would definitely maximize the range of fish mercury (Hg) data for black bass species and aqueous MeHg data. Regarding the size standardization, it is a commonly employed technique to examine fish tissue Hg levels across sites since it is well known that fish Hg levels generally increase with fish size because MeHg is very slowly eliminated from the fish body and fish with increasing size may consume higher trophic level prey items and this can accumulate more MeHg. The choice of total length of 350 mm seems appropriate because the fish length ranged from 150-600 mm from these monitoring efforts, which are often referred to as “standardized predator fish mercury concentrations”.

However, interpolation was used for most fish Hg data but for one site (i.e., Sacramento River in 2017) the fish length ranged only from 208-340 mm and extrapolation was used to estimate fish Hg levels in 350 mm, which seems fine but not ideal. In a published study, for example, the choice of the standardized length would be well justified by selecting a specific length near the mid-point among all fish samples examined, in which northern pike was standardized to 550 mm while walleye was standardized to 400 mm in this work at Minnesota (Monson, 2009). Figure below is derived from this work (for northern pike in one single year among sites) to illustrate this point:

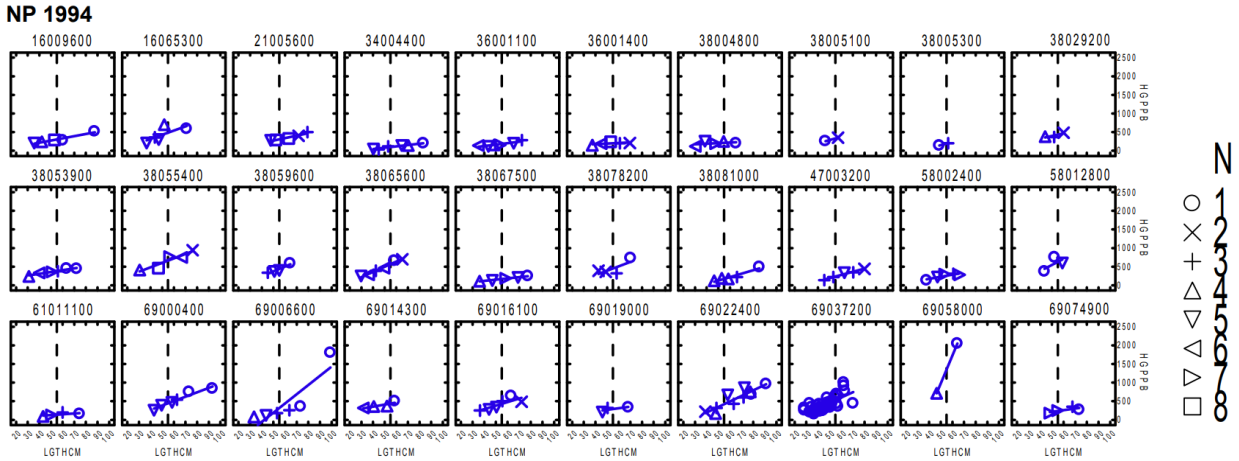

Figure caption: Fish Length (cm) versus Fillet Mercury Concentration (ng/g) by Species, Year, and Lake ID Number. The vertical dashed line is standard length (55 cm for northern pike, NP). Line connecting points are for reference only and were not used to calculate the standard-length mercury concentration. Adapted and modified from Monson (2009).

The regression models (with the lowest SER chosen) seem to provide a logical way to relate Hg in other TLG with TL4 fish (150-500mm) but as shown in Fig. 4.2 of the Staff Report the regression for all TL3 fish (C, D, E) showed non-linear relationships among the seven subareas. I suggest that nonlinearity would imply very different food web structures and/or prey items among these systems, and the “forced” fit of the relationships may just simply generalize the complicated relationships that we do not understand completely. Furthermore, the wide range of Hg contamination (as reflected

in MeHg content in fish) and potentially other pollution may also imply that these sites can have different ecosystem structures that are not known currently, which may compromise the simple comparison of the fish Hg data across sites. Nevertheless, I offer no suggestion to handle this particular situation. The final selection of 0.258 mg/kg in 350 mm black bass would compare well to the 0.3 mg/kg of EPA guideline, and as described it can provide adequate protection to humans and wildlife in the Delta. However, as shown in Table 4.4 the Hg content in the great majority of fish samples 350 mm well exceeded 0.258 mg/kg, as commented below, it will definitely be a big challenge for long-term fish Hg reduction in the Delta.

Regarding the linkage analysis between aqueous unfiltered MeHg and fish Hg concentrations, the selection of aqueous and black bass data from 2016 to 2019 seem to be sufficient and more relevant to the current situations (referring to 2024-2025). I support the provision of four seasonal years of aqueous MeHg data to match the lifespan of the sampled black bass fish. As noted above, the inclusion of smallmouth bass and spotted bass may add some uncertainty in interpreting the fish tissue Hg data, but this may be currently the only way to handle the situation. The use of median, rather than the mean, seems to make more sense since environmental data in these systems tend to be skewed quite a bit, using median can provide a more robust comparison.

The proposed linkage model (Fig. 5.2), however, is non-linear and seems to be different from the literature data. The issue may be less of a concern because board staff mainly focused on the lower end of the curve (x=0.258 and y=0.061), generating values at the low end of the non-linear regression curve between aqueous MeHg and 350 mm black bass Hg data. However, the use of unfiltered MeHg concentrations actually have some inherent problems and I want to elaborate this point below.

First of all, unfiltered MeHg would technically include both dissolved and particulate phases of MeHg in surface water. Surface water samples in the Delta and its upstream tributaries (e.g., Cache Creek) are well known to have variable particulate contributions as a function of hydrology, season, and extreme events (e.g., heavy rainfall, drought, wildfires). I used a set of data from a U.S.G.S. study at Cache Creek flowing into the Cache Creek Settling Basin (CCSB) measuring both unfiltered and filtered/dissolved MeHg (Domagalski et al., 2004), which I plotted their data among particulate MeHg (i.e., unfiltered MeHg minus dissolved MeHg) *vs.* dissolved MeHg:

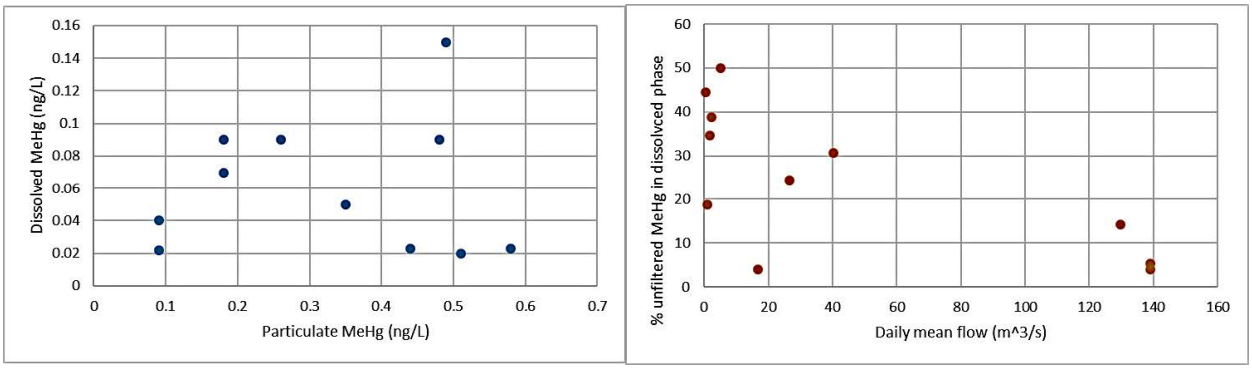

Figure caption: Left – A plot of particulate MeHg (i.e., unfiltered MeHg minus dissolved

MeHg) and dissolved MeHg in Cache Creek flowing into CCSB. Right – A plot of daily mean flow and percentage of unfiltered MeHg in dissolved phase in Cache Creek flowing into CCSB.

As shown in the above figure on the left, it is clear that increasing particulate MeHg in the water column (expressed as ng/L) may not necessarily translate into increasing dissolved MeHg pools. As shown in the figure on the right, it shows that the percentage of MeHg in each sample in the dissolved phase would be highly variable and in general decrease with increasing daily flow, implying that at high flow (e.g., wet season, winter) one may expect predominantly high TSS and high proportion of MeHg associated with the particulate phase.

Second, it is the most important after all and it is the potential difference of MeHg bioavailability among dissolved vs. particulate pools. Since fish take up MeHg predominantly from their diets such as smaller fish and/or invertebrates or detritus, and the lowest trophic levels such as phytoplankton and periphyton must take up MeHg in its dissolved phase only and it would be predominantly bound to dissolved organic matter in freshwater through thiol group (Seelen et al., 2024), and thus it is well regarded that dissolved MeHg should have a much higher relevance to fish Hg bioaccumulation, not the particulate phase. It is probable that some organisms such as filter-feeders can assimilate MeHg from the particulates while the MeHg on the particulates can desorb and dissolve in the water over time.

However, in the system under investigation, much of MeHg in surface water can be associated with particulates (except for periods of base flow), and thus by assessing only unfiltered MeHg we can mistakenly overestimate MeHg bioavailability. To illustrate this problem objectively, another U.S.G.S. study (published in peer-reviewed journal; Chasar et al. 2009) has demonstrated quantitatively that fish Hg correlated strongly and significantly with dissolved MeHg across sites, not particulate MeHg with predatory fish across streams. Thus, this evidence is in line with our understanding how MeHg moves up the food chain from the base of the food web largely through its dissolved pathway.

Based on my expertise and experience, I am reviewing the findings, assumptions, or conclusions I agreed I could review with confidence on **Conclusion # 2: Concerning proposed margin of safety**.

The derivation of 0.061 ng/L of unfiltered aqueous MeHg appears to be already at the low end of the aqueous MeHg data as shown in Fig. 5.4, being approximately 5-10th percentile. The deliberate selection of 5th percentile by the board staff would further reduce the desired aqueous MeHg to 0.059 ng/L which would definitely provide further protection. The reduction from 0.061 to 0.059 ng/L would result in 3.279% (or 3.3%) of margin of safety.

Nevertheless, on an analytical and technical basis for aqueous MeHg measurements, there is essentially “no difference” for 0.059 or 0.061 ng/L since aqueous MeHg

measurements are known to have much higher variability than its corresponding total Hg measurements, the variations are often up to 20% among replicate analyses, and thus a water sample reported to be exactly 0.059 ng/L can vary from as low as 0.047 ng/L to as high as 0.071 ng/L, on a theoretical basis. From another perspective, surface freshwater with an unfiltered MeHg level at 0.059 ng/L (even ±20%) is deemed to be among the background environments, and thus in many cases the fish (or black bass 350mm) should not exceed the threshold tissue concentration of 0.258 µg/g wet wt.

For the approaches employed by the board staff regarding resampling and the execution of modeling exercises for 5 years of data, I believe the approaches are appropriate. In the future, I would strongly recommend independent verification by collecting field samples (water and fish) and “plug” these new field samples into the constructed relationships to validate the models and approaches used here.

Based on my expertise and experience, I am reviewing the findings, assumptions, or conclusions I agreed I could review with confidence on **Conclusion # 3: Concerning proposed water balance and methylmercury mass balance**.
This section is definitely very challenging as it needs to account for all sources and losses of MeHg within the Delta. I do not think that any Hg scientist can cover all aspects of these processes!

The calculation of mass load (equation 6.1) would definitely increase the uncertainty as it includes both concentration and water volume, both terms subject to its own individual variations. Nevertheless, Table 6.4 provided a very comprehensive database (despite being subject to a large uncertainty), demonstrating the importance of tributaries in contributing MeHg to the Delta along with open water sediment flux, as opposed to the much minor contributions from point sources such as waster and urban runoff (combined for less than 1.5%). This is a very impressive exercise in showing their importance quantitatively, and setting up an objective basis for calculating the allocations that as long as the aqueous MeHg levels discharged from point sources do not exceed 0.059 ng/L they should not be a major concern. Fig. 6.4 further shows that the estimation for the importance of tributary inflows would be elevated to >70% while the importance of (nontidal) wetlands are much reduced from ~20% in 2010 TMDL Staff Report to less than 5% in DMCP Review, and I would think this may be not entirely correct, which would largely depend on the relative aerial coverage of wetlands within the Delta and other factors.

Regarding atmospheric deposition, wet deposition of MeHg has been demonstrated as MeHg can be (barely) detectable in rainfall and snowfall samples. For total Hg, dry deposition is now regarded as the dominant pathway over the wet deposition. For MeHg, I think dry deposition of MeHg can exist and serve as another source of MeHg such as those through foliar uptake and/or in-vivo methylation of inorganic Hg within the foliage which have been recently postulated and demonstrated (Tabatchnick et al. 2012; Stinson et al. 2024). In other whole ecosystem studies, for example, St. Louis et al. (2001) showed a significantly higher atmospheric deposition of MeHg in forested areas

than open areas in proximity since litterfall contributed about half of total deposition, illustrating the real existence of dry deposition pathways for MeHg but we cannot confirm the possibility of methylation within foliage and/or litter. I do not know the exact numbers in the Delta but this source may need to be considered in the future.

For the loss pathways of MeHg, it is interesting to note the stark differences between tidal and nontidal wetlands. While I agree that particle settling can be a major loss pathway of MeHg from the surface water, the MeHg buried in the sediments may not be actually lost and may stay within "the Delta" for a while. I agree with the importance of particle settling because much of the aqueous MeHg can be associated with particulates in these aquatic ecosystems.

However, for photodegradation I am not quite sure if it can account for 25% of MeHg loss annually, because if much of MeHg is bound to particulates, I wonder if they can really be photodegraded by sunlight (e.g., the high turbidity in waters may actually attenuate much of sunlight already). I am not aware if there are literature explicitly showing the photodegradation of MeHg associated with mineral particles but there is at least one study showing the potential sunlight-mediated degradation of intracellular tissue MeHg in marine phytoplankton species (Kritee et al. 2017). The study by Gill (2008c) suggested essentially no difference for photodegradation of MeHg among unfiltered and filtered samples. However, by assessing its Fig. 5, one can find that the rate of MeHg loss would be similar among these two sample types but my speculation is that the photodegradation still occurs predominantly through dissolved phase in the unfiltered sample, because the two slopes looked almost identical. In fact, the slope is even higher for filtered samples (-0.00348) compared to that of unfiltered samples (-0.00288), which I am not sure if the presence of particulates may reduce sunlight penetration and/or reduce MeHg photodegradation in the dissolved phase.

If we only assume that MeHg photodegradation occurs mainly in the dissolved phase, then photodegradation of MeHg may actually occur much less extensively in the surface waters within the Delta due to high turbidity especially during high flow conditions. Another piece of evidence can come from the novel use of stable Hg isotope tools, in which the magnitude of mass-independent fractionation can help indicate the degree of surface water MeHg photodegradation (principally via dissolved pool). From the limited research in the region (e.g., San Francisco Bay by Gehrke et al. 2011 and upstream tributaries by Donovan et al. 2016), we can see that photodegradation is somewhat limited compared to other much clearer freshwater systems (e.g. Great Lakes).

The overall MeHg "budget" shown in Fig. 6.29 appears to be reasonable though there can be under-/over-estimation in various items, but I concur with the board staff's view that the dominance of tributary inflows (6.7 g/day) to the Delta and should be the main target to regulate for any substantial and meaningful MeHg reduction.

Based on my expertise and experience, I am reviewing the findings, assumptions, or conclusions I agreed I could review with confidence on **Conclusion # 4.a: Proposed**

load allocations and waste load allocations are achievable.
All the values for load allocations (LAs) and waste load allocations (WLAs) are reasonable and based on the numeric target of aqueous MeHg concentrations (0.059 ng/L; or 0.258 mg/kg in black bass 350 mm). Regarding whether they can be achievable, it would be hard to tell but we can look at each one, based on the summary in Table 8.22.

For LA, there is basically 100% allocation for atmospheric deposition, open water sediment flux, tidal wetlands, and Cache Creek settling basin (CCSB), and this is largely correct that these are mostly non-point sources and even natural sources of MeHg. As addressed in Appendix E.3., it is possible to reduce the inputs of Hg and MeHg from CCSB to the Delta by increasing the sediment trapping capacity. In a recent study examining Cache Creek and a small tributary of Putah Creek (Cold Creek), it was shown that the total Hg concentrations in the suspended sediment from Cache Creek (201–334 ng/g) would be roughly 4 times of those suspended sediments in Cold Creek (56–88 ng/g) (Ku et al. 2024), implying that trapping these suspended sediments from Hg point sources originated from upstream Cache Creek (e.g., Sulphur Creek), by CCSB, would be very crucial in preventing these high Hg materials flowing into the Delta, get methylated, and/or get further transported to downstream such as San Francisco Bay.

For other LAs, agricultural returns would need quite a “deep cut” in order to meet the allocated amounts (e.g., from 234.578 g/yr to 57.211 g/yr for Central Delta), and it would be quite difficult to achieve that unless there is a drastic change in agricultural practices in these sites (e.g., complete eradication of agricultural wetland habitats). Another one is tributary inflows and it is again very difficult to achieve that (e.g., from 449.444 g/yr to 30.523 g.yr for YB-N and S), and according to different suggestions, trapping of suspended sediments seem to be a viable option because much of the Hg and MeHg in water are associated with particulate in these systems especially during high flow conditions, which may be achieved by CCSB. However, for other tributaries, I am not sure how the Hg and MeHg can be removed when the stream is draining into the Delta, and as mentioned, there should be tributary mercury control programs in place especially those with high allocations such as Sacramento River.

Among WLAs, the largest contributions would be derived from dredging and they have been given 100% allocations for the current load. I think there can be ways to mitigate or reduce MeHg release or production upon sediment dredging. For other WLAs, their contributions are very minor, and the current allocations are appropriate considering also future population growth.

Based on my expertise and experience, I am reviewing the findings, assumptions, or conclusions I agreed I could review with confidence on **Conclusion # 4.b: Proposed load allocations and waste load allocations should result in concentration reductions in fish tissue**.

I think I should have answered the question in Conclusion 4.c. first because in order to achieve the LAs and WLAs we should first significantly reduce aqueous MeHg concentrations (but still not sure if we can arrive at the proposed goal of 0.059 ng/L) before any meaningful reduction of fish Hg levels. The LAs and WLAs, if achieved, should significantly reduce aqueous total Hg and potentially MeHg, and thus based on that I agree that it will result in measurable and significant reductions in fish Hg levels.

Based on my expertise and experience, I am reviewing the findings, assumptions, or conclusions I agreed I could review with confidence on **Conclusion # 4.c: Proposed load allocations and waste load allocations should result in aqueous concentration reductions**.

Compared to the question from Conclusion 4.b. above, this seems to be a more straightforward one to deal with. With all the LAs and WLAs achieved, there are definitely reductions of aqueous MeHg in the Delta. Based on Table 8.11, there must be a very significant reduction to achieve the proposed goal of 0.059 ng/L. Because most of our controls would be on total (inorganic) Hg, not MeHg directly, and thus the final outcomes are still highly variable. For example, you can have low total Hg in a system but relatively high MeHg if the conditions are highly favorable for Hg methylation and not favorable for degradation of MeHg (e.g., dense canopy blocking sunlight into the streams). Nevertheless, my prediction is that achieving these allocations will result in a measurable decline of aqueous MeHg.

Based on my expertise and experience, I am reviewing the findings, assumptions, or conclusions I agreed I could review with confidence on **Conclusion # 4.d: Proposed water quality objectives are attainable**.

I believe this is the most important question after all if these efforts and Hg control can translate into meaningful results, i.e., reduction of fish Hg to a safe and acceptable level !!! As explained in my comments above, I believe that the consideration of unfiltered MeHg is not the most accurate way to reflect the bioavailable pools of MeHg in the water for the food webs (and thus fish uptake). However, if this is true here, then say there is more than 50% of MeHg in the surface water associated with suspended particulates, then the bioavailability and its potential risk should be even lower than just glanced from the number, and thus achieving the allocations should likely result in a significant reduction of fish Hg content.

While I am not doubting the reduction of fish Hg levels upon decreasing aqueous MeHg (filtered and particulates), I am actually more concerned whether we would see similar degree of reduction of fish Hg content among the subareas because the fish and aqueous MeHg relationships are NOT linear among sites, but in the real world within each ecosystem I think fish Hg would respond in its own way with aqueous MeHg if the food web structures in site are relatively stable over time. To complicate the situation, by achieving the allocated amounts, you are reducing total (inorganic) Hg and other

conditions (e.g., sulfate, organic matter) may not be changed correspondingly, and thus whether you can reduce MeHg and thus fish Hg at the same degree or not, it is really hard to predict (but is a great scientific question to work on). Thus, I question whether there would be the same amount of beneficial outcomes (i.e., fish Hg reduction) per unit decrease of aqueous MeHg across sites within the Delta.

Based on my expertise and experience, I am reviewing the findings, assumptions, or conclusions I agreed I could review with confidence on **Conclusion # 5: Proposed source analysis, allocations, and compliance calculation methods reasonably account for climatic variability**.

Climatic variability would be more difficult to predict than those of fish Hg-aq MeHg-allocation relationships because I think our knowledge on climatic variability and how Hg cycling is impacted by climatic changes are still limited at the moment. For example, wildfires (common in California) can drive extremely high particulate Hg (Ku et al. 2024) and may enhance downstream MeHg bioaccumulation in some invertebrates (Baldwin et al., 2024) as food webs have been shown to be restructured following wildfire events (Kelly et al. 2006) which as we know can significantly influence MeHg trophic transfer pathways and fish Hg levels. As Hg cycling and MeHg formation are heavily impacted by hydrology, the consideration of the dry and wet seasons is very important. The current calculation methods already accounted for wet and dry years as depicted in Fig. 6.2 and Fig. 6.3 that there have been extreme wet and dry years in these water years. Therefore, I think the current calculation methods can reasonably account for climatic variability but may not capture all potential/extreme consequences leading to unknown Hg cycling processes in the future under a changing climate.

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