Review of ‘Amendment to the Water Quality Control Plan for Inland Surface Waters, Enclosed Bays, and Estuaries of California—Mercury Water Quality Objectives and Program of Implementation’

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Summary

In a regulatory framework, the current standards for protection of water quality and fish from Hg contamination have been found to be inadequate given the scale of the pollution problem in California and the risks to humans and wildlife. Thus, an Amendment has been proposed to strengthen the regulation of Hg contamination and its monitoring. Below I evaluate and comment specifically on items 5-8 (Attachment 2) regarding the scientific soundness of the proposed rules. Note: I combine my discussion for the related topics of 5-7, given they are interrelated. Subsequently I provide more detailed and considered comments on broader aspects of the proposed rule as stipulated in a and b in Attachment 2. Specifically, I provide contextual information and even some suggestions for how particular options may be improved and where potentially important data and/or theoretical gaps exist. I mostly limit my discussion to matters that are within my main areas of expertise, but do provide a professional (non-expert) opinion in some cases. My comments are keyed to specific sections/issues listed in the Staff Report. Overall, I am generally supportive of the science that lies behind the amendment. I believe the report represents deep consideration of the relevant issues in light of the contamination risks to wildlife and humans across the state.

Addressing the Science

5. A water column concentration of 12 ng/L total mercury in rivers is generally consistent with meeting the Sport Fish Water Quality Objective (0.2 mg/kg methylmercury in fish tissue) in rivers based on bioaccumulation factors...

6. Consideration of a more protective water column concentration than 12 ng/L total mercury is warranted as the effluent limitation for municipal wastewater and industrial discharges to waters that are slower flowing than rivers and streams, since these waters are likely to experience higher rates of mercury methylation and bioaccumulation.

7. A more protective water column concentration than 12 ng/L total mercury is warranted as the effluent limitation for municipal wastewater and industrial discharges to waters where more stringent water quality objectives apply for subsistence fishing or tribal subsistence fishing.

[Section 6.1 (Issue A)] I support Option 2 (the fish tissue objective). Water concentrations of total and methylmercury tend to be low and are often diluted over large areas by the mixing of highly concentrated water with the disproportionately common low concentration water. Given the apparently low risk of Hg contamination by skin contact and/or by drinking water with low levels of MeHg (or even total Hg), I agree with a more modern standard of measuring MeHg in fish tissues. However, fish sampling is obviously a destructive procedure, so the monitoring efforts of such concentrations over
large areas may be complicated. Nevertheless, this is the most logical standard to implement since it is the primary pathway of contamination to humans and to wildlife in areas that are not designated impaired under the Clean Water Act. In the latter cases, the local TDML standards (including those for sediment) should still supersede this objective. I see the complication of not being able to regulate industrial/mining discharges, but perhaps a hybrid of Options 2 and 3 is possible, where Option 3 (only for discharged water, rather than the water column of the receiving water course) can hold. If not, selection of Option 2 will obviate regulation (at the state level) of Hg-laden discharges, except in cases that are (or become) classified as ‘impaired’. If the designated concentration for Option 3 were elevated for discharges only (as I have conceived of it here), this may alleviate the concerns of industry about the infeasibility of implementation. I don’t totally agree with the supposition in Option 4 that anoxic sediments are the primary sources MeHg production. This has not been shown at the landscape scale and may instead reflect biases in sampling (of lowland wetlands, estuaries, etc). We DO know that a drop in oxygen levels is required to activate anaerobic bacteria, but this can also occur within sediments that are not classified as anoxic, but are instead subjected to anoxic or even suboxic conditions temporarily (Briggs et al., 2015; Singer et al., 2016). These flood pulses have been suggested by others to induce MeHg production in hyporheic zones along streams (Bradley et al., 2012; Hinkle et al., 2014). While it may be true that atmospheric deposition of Hg is a primary source in other regions, this is not likely to be the case in most of the California water bodies (see above). This statement needs to be clarified. It is encouraging that the Water Board is working on a separate set of Hg objectives for sediment that would sit alongside the fish tissue objectives recommended (if adopted). Presumably the same parallel objective approach could be adopted for wastewater and industrial discharges to ensure this pollution source is regulated, but at a feasible/appropriate level? Option 5 is not viable. In environmental science/management, we need quantitative standards to ensure regulation is consistently applied and achieves its objectives.

[Section 6.5 (Issue E)] I support the establishment of quantitative (numeric) guidelines for MeHg in fish tissue for subsistence and tribal subsistence use. However, given the large variations MeHg concentrations for different sites, I actually support Option 5, which would enable further study to determine more precisely what standards are required for different sites. The option would also be less controversial to water dischargers, which might limit legal challenges. Overall, without some clear metric, it would be impossible to evaluate and/or enforce water quality standards. This is not my area of expertise, but a strong case is made that quantitative standards will ultimately be necessary, so it seems that now is the time to create them.

[Section 6.11 (Issue K)] I support Option 1. Option 2 is not logical because fish can be contaminated by Hg from various sources, so this limitation would be draconian, in that it is assumes only the discharge from wastewater treatment or industry is responsible. Clearly there are legacy sources of Hg contamination in food webs of California that are not associated with these activities. In spite of the challenges in quantifying bioaccumulation factors, I still think it is preferable to use a water column concentration in the effluent. This makes monitoring and regulation more feasible.

[Section 6.12 (Issue L)] I am not very familiar with the analysis of bioaccumulation factors (BAFs), but it is clearly an analysis of limited utility because it is based on so few studies, incomplete science, and the variability in the resulting metric is so high (note the log scale on Figure I-1 in the Water Column Appendix). I cannot reasonably evaluate what would constitute an appropriate water column limit for effluent, nor can I imagine that anyone can. However, another environmental scientist is probably in a
much better position to evaluate this than I am. I do recognize that the limit must be higher than the current average water column concentration of 4.7 ng/L for California waters (as mentioned in the draft report). Another consideration is how and when the monitoring should proceed. The issue mentions quarterly sampling, but this may not fit with the timings of maximum concentration and/or maximum discharge. Perhaps the schedule of sampling for a particular discharge should be designed on an adaptive basis that could be determined from past discharge records of each company? Again, this is clearly not my area of expertise.

8. Since mercury is often bound to sediment, the use of sediment controls will effectively reduce the transport of mercury into waters, for discharges that can contain large amounts of sediment.

[Section 6.8 (Issue H)] I generally agree with the recommendation for Option 2. However, I have concerns that may require more thought and revision before this option can be adopted in the Amendment. I am particularly concerned about the specific (and singular) emphasis on erosion control. I acknowledge that sediment-adsorbed Hg is the dominant source of Hg contamination of water bodies and food webs, that former mines are important contributors, and that erosion of mine tailing can move significant quantities of Hg-laden sediment to downstream locations (Singer et al., 2013). Thus, limiting erosion of Hg-laden sediment from Hg and gold mines (especially abandoned ones) is potentially important. However, this focus on future erosion does not acknowledge that most of the landscape downstream from large and/or important Hg-contributing mines (e.g., within Yuba R, Cache Cr basins, etc) is ALREADY contaminated with Hg-laden sediment over broad areas and to deep depths (e.g., (Bouse et al., 2010; Donovan et al., 2016a, b; Donovan et al., 2013; Marvin-DiPasquale et al., 2009; Singer et al., 2013)), so controlling erosion from these mines (which in and of itself may be infeasible in many locations) may only have a minor contribution in limiting further contamination to these water courses. In fact, the infrequent flooding regime that inundates previously contaminated sediments for long periods, may thus enable in situ MeHg production (in the absence of further erosion), which could drain back into rivers and become available to food webs. We have documented widespread contamination of sediment throughout the Sacramento Valley, so even though it might be helpful to control the erosion of sediment from abandoned mines, the non-point Hg source problem may be of greater concern. I would like to see this risk reflected in the language on Issue H (and others). This would put less blame/focus on owners of abandoned mines (including government agencies) and treat the problem as a legacy of former mining gone amok. This nonpoint upland contamination source is not explicitly included in Issue I.

[Section 6.9 (Issue I)] In this section, the terminology is a bit challenging to interpret. Nonpoint Hg sources include riparian zones as listed, but the discussion seems to be focused only on the lowland environment (e.g., emphasizing permanent wetlands and agricultural lands). To my mind, this is too narrowly focused and ignores the potential production and delivery to the food web of MeHg in nonpoint source areas that are only seasonally wet. I generally support Option 2 here, but with a few caveats. The language here is focused on total Hg concentrations in sediment as an indicator of MeHg risk to water bodies (and the food web). There is not necessarily a direct link, even if this is logical to first order. Lower concentrations of total Hg (below 1 ppm), but well above background, may still provide important sources of MeHg to aquatic ecosystems. There should be acknowledgement here that we
need to link the hydrologic (flooding) regime to the risk of MeHg production, since even highly contaminated dry sediments won’t contribute Hg to food webs. The two risks are inundation that decreases oxygen levels in contaminated sediments and enables microbial methylation, and the erosion of Hg-laden sediment for delivery to downstream areas where methylation is likely (higher risk of inundation). Second, the spatial distribution of total Hg is not well established for most areas. We don’t know the vertical distribution of Hg contamination in areas downstream of former mines, nor do we know how far this contamination extends laterally away from river courses (but is still susceptible to inundation during large floods). These aspects represent an important data gap that the Alpers study is unlikely to fill at the level of detail required to understand the nonpoint source risk of MeHg contamination.

a. In reading the Draft Staff Report and proposed rule, are there any additional scientific findings, assumptions, or conclusions that are part of the scientific basis of the proposed rule not described above?

b. Taken as a whole, is the scientific portion of the proposed rule based upon sound scientific knowledge, methods, and practices?

Hg poses a long-term problem for the State of California. In addition to low-level global inputs of Hg through atmospheric deposition (pollution source: global anthropogenic emissions), California has a long history of Hg mining and its use for (most dramatically) industrial-scale gold mining. These historical processes and activities, combined with industrial activities and the subsequent redistribution of Hg attached to sediment and dissolved in water, have created pollution over landscapes and regions. Due to its historical legacy of gold and Hg mining (and to a lesser extent the industrial legacy in the estuary as well), the largest region of Hg pollution in California waterways is in the northern half of the state (e.g., San Francisco Bay region including the Bay-Delta estuary and many of its contributing streams). Some of these areas have already been designated as ‘impaired waters’ under the Clean Water Act, yet others are less well-regulated or monitored. It is likely that the problem of Hg contamination will persist well into the future because the Hg pollution in waters and sediments is so widespread that clean-up efforts are challenging if not intractable. Most of the historic Hg attached to sediment and in waters is in an inorganic form, and therefore not particularly dangerous to biota because it cannot be incorporated into tissues and the bloodstream. However, at many locations throughout the landscape methylmercury (MeHg), the toxic form of Hg that affects biota (including humans) may be produced by methylating bacteria in conditions of low oxygen. Unfortunately, the Hg pollution of California waters has indeed led to the production of MeHg and the subsequent contamination of food webs that depend on these waters, and the problem is compounded with higher trophic organisms such as fish. This raises a major challenge in California because fish form the basis of the diet of many forms of wildlife (waterfowl along the Pacific Flyway and migratory anadromids). Fish that are potentially contaminated with MeHg are also an important component of the diet of many California residents, and especially that of subsistence communities including tribes that have depended on this food source (and associated waters) for their entire cultural history.

Below I provide specific responses/impressions to aspects of the Staff Report (again keyed to the relevant sections of the report).
Section 4.1 There is evidence that iron-reducing bacteria (FeRB) may also play an important role in methylating Hg in some systems (Alpers et al., 2014; Gilmour et al., 2013), so it may be that conventional assumptions about where and how Hg is methylated are outdated. In particular, since sulfate-reducing bacteria (SRB) have been primarily implicated in MeHg production and sulfate is limiting in most of large basins (e.g., apart from wetlands), it is often assumed that wetlands comprise the only important loci for methylation. However, it is possible that FeRB play an important role, especially in locations where iron is high supply compared to sulfate (i.e., upland locations that are not permanently inundated).

Section 4.2 There is evidence that biofilms and algae also play an important role in providing MeHg at the base of food webs (Tsui et al., 2012). This is indicated elsewhere but missing here.

Section 4.4 I suggest that there is too much emphasis on wetlands and reservoirs as the primary sources of MeHg production. It may not be the case, which really opens up a much larger regulatory question. Just because fish MeHg is higher in these environments (which is not universally the case—see below), it does not follow that all or most MeHg production occurs in wetlands. Resident fish in permanent wetlands have longer exposure times to MeHg locally produced. However, the rates of MeHg production may not be higher (especially after accounting for in situ demethylation).

It is unreasonable to assume, in heavily Hg-contaminated environments of California (gold mining regions), that atmospheric deposition of Hg plays an important role in delivering MeHg to the food web. Recent work has shown that the isotopic signature of MeHg in food webs of Coast Ranges, Yolo Bypass, and Yuba/Feather Rivers, for example, is similar to that of the Hg stored in sediments deposited during the historical mining period (Donovan et al., 2016a, b; Gehrke et al., 2011). Also, what is the evidence that Hg from wet deposition is ‘more readily methylated’, particularly in the California setting? This seems like speculation and is perhaps based on an outdated notion (citations from 2002 and 2003), especially when applied at the landscape scale. I’m also unconvinced of the relevance of the statement supported by the Fleck reference. I don’t understand how this establishes the importance of a wet deposition MeHg source to food webs.

Another important potential impact of climate change is increasing frequency and duration of inundation, which may enable higher net MeHg production in areas that are seasonally dry, but which contain high Hg inventories over multiple meters of depth (Singer et al., 2016). We now have good evidence that such areas may be important loci of MeHg production and uptake into food webs (Donovan et al., 2016a, b).

Section 4.5 It seems that this monitoring effort is probably unnecessary. Efforts could be better targeted on sampling loci that we might be expect to be disproportionately contributing to MeHg loads. In other words, we continue to operate sampling over broad spatial scales, yet mixing of highly concentrated water with water of low concentrations will tend to systematically dilute the signal and the timing of sampling is of particular importance. Similarly, the location within the water column should prioritize locations where benthic organisms, etc. might take up MeHg (at the base of the food web). Also, there appear to be major geographic biases in sampling efforts, where particularly contaminated streams are not being consistently sampled for water and/or fish (e.g., Yuba R, Cache Cr). See example from Fig. 8 in (Singer et al., 2016) below, where forage fish MeHg concentrations in the Yuba and Feather Rivers equate to an average of 0.083 mg/kg wet weight, higher than most values shown in Figs. 4-8 and 4-9:
Other fish data from Cache Cr exhibit even higher MeHg concentrations. By contrast, the average MeHg concentrations for prey fish we analyzed from Yolo Bypass (a lowland wetland site expected to have much higher MeHg contamination) were 0.05 mg/kg. Note: the proposed MeHg limits for prey fish are 0.05 mg/kg for 50-150mm and 0.03 mg/kg for <50mm fish. Given that these fish provide a likely food source for higher trophic organisms, we may be missing important upstream sampling/monitoring locations that could better guide management and water quality control efforts. Given the migratory habits of many fish species, upland river sites represent an important data gap for understanding the regional picture of MeHg contamination, whether or not upstream reservoirs are providing a downstream MeHg supply.

Figures 4-3 and 4-4 seem to contradict the notion that fish of 150-500mm are the most relevant to regulate for MeHg. The all sizes category on these plots is consistently higher (for both trophic levels 3 and 4). Was this designed because that is the size threshold allowed for fishing or what is typically eaten? If so, this was not made clear.

Section 4.5.5 This section is very incomplete. There are numerous studies documenting total Hg across various parts of the SF Bay Region (including contributing watersheds). Why is the information not included here? Some relevant papers include, but not an exhaustive list: (Bouse et al., 2010; Domagalski, 2001; Domagalski et al., 2004; Donovan et al., 2016a, b; Donovan et al., 2013; Singer et al., 2013). Several of these papers clearly documented that the threshold for background total Hg in various parts of the basin is ~0.08 ppm (similar to the results presented for Cache Cr). Furthermore, these studies document that concentrations an order of magnitude higher are common in many locations (including river floodplains, bypasses, and Bay-Delta bottom sediments) with some loci that are 2 or more orders of magnitude higher in total Hg. For example, our group has documented concentrations of 3-10 ppm in Yuba River sediments and up to ~200 ppm in sediments draining Hg mines in the Cache Cr basin.

Section 4.8 I’m not convinced about the research on selenium and Hg. The interactions may be well understood in laboratory conditions and there may be negative correlations between Se and MeHg concentrations, but that does not clarify the process by which Se modulates methylation processes.
Perhaps I’m just not familiar with the relevant literature on this, but I am not convinced by the references provided. Quite frankly, I’m not sure why this whole section is included in this draft report. It seems out of place because the evidence is not convincing that Se amendments would provide any benefit (and could potentially be harmful, as indicated) to ameliorate MeHg production/uptake. It is also not followed up in the development of objectives.

References


