REVIEW OF DRAFT PLAN FOR DEVELOPING SELENIUM TMDLs FOR THE NEWPORT BAY WATERSHED

submitted by Dirk Wallschläger, Ph.D.
April 26th 2017

I was asked to provide a review of the scientific assumptions, findings and conclusions, specifically the four points listed below, in the proposed rule relating to the development of Total Maximum Daily Loads (TMDLs) for selenium (Se) in the Newport Bay watershed. Before I do, I would like to point out that this is a very complex problem, and that, as always in such situations, one concludes that more could/should have been done, provided that more time and resources had been available. Notwithstanding my following points of criticism, I think that the SWRCB staff and their collaborators have done a respectable job of producing a scientifically-defensible report, which provides valuable guidance for managing Se in this watershed. While there are many things that were done well/right in my opinion, I will largely ignore those in the interest of time/space, and focus mostly on things that could be improved, given the availability of time and resources.

Point # 7: Linkage Analysis – Representativeness of modelling simulations, input parameters and assumptions for the three subwatersheds modelled

In response to this point, I will limit myself to discussing the treatment of the water-phytoplankton bioaccumulation step in the modelling process, since the subsequent trophic transfer steps are relatively inconsequential (by comparison) for the overall result, and are treated appropriately in accordance with the papers by Luoma and Presser, as far as I can tell.

Based on the provided information, the Se bioaccumulation model developed by Presser & Luoma (Appendix N) uses only total Se concentrations for calculating K_d values. The authors point out in the introduction that Se speciation in the water plays a crucial role in determining the magnitude of K_d, yet aqueous Se speciation is not explicitly incorporated into the bioaccumulation model. This approach has been used in subsequent work by Dr. Luoma, and is probably superior in predicting Se tissue concentrations. Provided that reliable Se speciation data are used (see my comments below), and provided that time and financial resources do not prevent any further refinement of the modelling exercise in this project, I would recommend expanding the model to include aqueous Se speciation information, and repeating the linkage analysis.

I understand that aqueous Se speciation was indirectly taken into consideration by assuming certain K_d values that may be reflective of different Se speciation scenarios in the studied waters. However, I have some concerns about the quality of some of the Se speciation data reported in Appendix F, and consequently their usefulness for estimating K_d values. Generally speaking, Se speciation results should only be used if they were generated by HPLC-ICP-MS methods. The HG-based operational Se speciation approaches (based on Cutter's work) are prone to interferences that may lead to biased results for Se(VI) and "organic" Se, so those results (Meixner et al., 2004; Hibbs et al., 2008) should not be used in the modelling process.

Furthermore, it is unclear from the provided description if the OCPW data were all generated by Weck (which is only explicitly mentioned in the legend of Table F.5), and whether Weck used HPLC or not, since US EPA method 200.8 is only for total/dissolved trace elements, so I also ignored those data for my considerations.

Also, the developed Se bioaccumulation model was only (out of the three water bodies discussed here) explicitly applied to San Diego Creek (SDC) in appendix K. I have assumed (since I didn't find any explicit evidence in the report) that it was correspondingly applied to model Se bioaccumulation in the Santa Ana-Delhi Channel (SADC) and in Big Canyon Wash (BCW).

For the SADC, only 3 Se speciation data points exist. After eliminating the Meixner et al. (2004) data point for the reasons discussed above, only 2 data points remain. Obviously, no sensible assessment of a "representative" Se speciation pattern can be made from this, and I strongly recommend generating more Se speciation data points in the future, using the appropriate HPLC-ICP-MS methods, to allow a refinement of the K_d values used for this system.

However, this very limited data set allows me to illustrate the problems potentially associated with incorporating Se speciation data into the Se bioaccumulation considerations. Using the average K_d values presented by Presser & Luoma (Appendix N, p. 1389: 317 for Se(VI), 1,760 for Se(IV) and 24,249 for SeMet), if one takes the average of the 2 results presented for organic Se in Table F.11. (p. 1043), a low fraction of organic Se of 0.36% is obtained, which results in a K_d of **421**, compared to K_d = 361 when ignoring organic Se altogether. For clarification, this value represents <u>discrete</u> organic Se species determined by HPLC-ICP-MS, and while it is not reported which particular organic Se species were found in these samples, even in the worst case (= all selenomethionine with K_d = 24,249), the K_d values assumed in the SDC modelling exercise (200 or 400) appear appropriate for SADC. On the other hand, if one assumes that all of the Se in a water sample that is neither Se(IV) nor Se(VI) is organic Se (of unknown chemical identity), then one obtains an organic Se fraction of 7.48% for SADC, and a K_d value of **2,148**, which would then not fit with the values assumed for SDC. In this scenario, most of the "organic" Se would be assumed to have <u>no discrete molecular structure</u> (e.g., it could be associated with NOM), and therefore have no known K_d value, but may have a significant impact on Se bioaccumulation in the system. The point of all this is that it cannot be ascertained from the limited existing data if the K_d values for SDC are appropriate for describing Se bioaccumulation in SADC, and thus more data are needed to evaluate this question.

For the BCW system, there are sufficient Se speciation data for surface waters presented in Table F.13, and they are were all generated with appropriate analytical methods, therefore allowing a calculation of speciation-based K_d values, as outlined in the previous paragraph. When ignoring the presence of organic Se species, the resulting K_d is **649**. This value is higher than the estimates for SDC, and could be adjusted to produce a more realistic estimate of K_d for BCW, similar to what was suggested for the UCI wetlands (K_d = 800) in the Presser & Luoma report (Appendix N).

There are some issues with the presentation of the data for organic Se in the BCW system, since there are several data points where a significant fraction (in the low % range) of organic Se is reported when all discrete organic Se species are below the detection limit. Therefore, I could

only perform a worst case analysis where I assumed that any Se that is neither Se(IV) nor Se(VI) was organic Se (with the K_d for SeMet). This yields an average organic Se fraction of 11.2%, and a K_d of **3,297**. This organic Se fraction may be a little high, but for those samples where discrete organic Se species were measured, the organic Se fraction ranged from 0.9 to 10.4%, indicating that there can indeed be a significant organic Se fraction in these samples. Also, when discrete organic Se species were reported, usually methylseleninic acid, MeSe(IV), was the predominant species, and while it's K_d is unknown, it is likely to be lower than that of SeMet, which would reduce the total K_d somewhat. Still, it appears that K_d for BCW is probably higher than the values used to model Se bioaccumulation in SDC, and this should be reflected in some additional model simulations, because it may impact the water quality targets significantly.

Finally, the analysis of the Se speciation data for SDC is complicated. For my analysis, I used the data in Table F.6 and disqualified the Meixner et al. (2004), Hibbs et al. (2008), and OCPW 2012 data for the reasons outlined above. The remaining data yield K_d = **430**, when the presence of organic Se is ignored, which is in line with the 75th percentile suggested by Presser & Luoma (Appendix N). Again, since no discrete organic Se species concentrations were shown, I decided to ignore the organic Se fractions listed in Table F.6, and calculated the worst case scenarios described above, which yield 22.1% organic Se and K_d = **5,907**. I believe that this estimate of the organic Se fraction is high, although several samples show very high organic Se fractions. It is noteworthy that all of those samples are from the IRWD wetlands inlet, and were analyzed by IRWD, while the samples from the other locations within the SDC system were analyzed by ASC and showed low organic Se fractions. I would recommend a detailed re-analysis of those data sets to determine if there is really such a high organic Se fraction in the IRWD samples, because that has a significant impact on the interpretation of the Se speciation data with respect to their influence on K_d.

In summary, I suggest that the K_d values used in the modelling project may be lower than one would expect based on the apparent Se speciation, and that a careful re-examination of some of the Se speciation data might shed some light on this discrepancy. Subsequently, I would also recommend a couple of additional model simulations with higher K_d values to assess the impact of substantial organic Se fractions in SDC and BCW on the water quality targets, if those organic Se fractions prove to be real. Additionally, some more Se speciation analyses in the SADC system are required before one can even contemplate if the K_d values used by Presser & Luoma are appropriate there.

Finally, I want to point out that sulfate concentrations in waters influence (inversely) K_d for Se(VI), yet there is no mention of sulfate concentrations in any part of the report (as far as I can tell). I'm assuming that sulfate is high in these waters, and therefore, K_d for Se(VI) may be at the low end of the range suggested by Presser & Luoma (maybe in the 150 range?), and would therefore have the opposite effect on the water quality targets than the uncertainty of the organic Se fraction discussed above. I wonder if a simple correlation analysis of K_d values for Se(VI) reported in previous literature as a function of sulfate concentration could yield more site-specific K_d values for the studied water bodies.

Point # 8: Linkage Analysis – Appropriateness of modelled water column concentrations and model validation procedure

The wording of this point is misleading. It is pointless to ask if the range in water column Se concentrations derived from the different modelling scenarios is "appropriate", because depending on how the model is run, and what assumptions are made in each model run, you can obtain pretty much any water column concentration you like. The question of "appropriateness" is more one of risk assessment, and in that sense, the model seems to produce water quality targets for Se that can be assumed to be protective of the wildlife species in question, under the assumption that the parameters put into the model and optimized during the calibration process do hold true for prediction of future developments. However, there will never be a range of concentrations that's "appropriate"; there will just be one upper threshold value that is considered protective under the given set of biogeochemical assumptions. Also, while this is a nitpicky point, it is not the data that are being calibrated, but the model itself.

That said, the general approach presented in Appendices N and O is appropriate. It is first tested how well different values for K_d, determined from the statistical spread of field data for paired water-solid samples, predict the observed tissue and egg Se concentrations, and then the "best fit" K_d value is used to inversely model the water Se concentrations required to meet certain tissue Se targets. There are a couple of problems with respect to the predictive power of some parts of the model (see in the following), but the calibration process adjusts for those to represent the existing data with as much accuracy as one would expect from a simple model for such a complex system. The big question in modelling is, as always, if the model also predicts future (= unknown) data equally well, but there is no other way of finding out than to continue this process for future sampling events.

There seems to be a trend of underestimating Se concentrations in sediment when mean or median Se water concentrations are used, which leads to a choice of 75^{th} or 85^{th} percentile K_d data during the model calibration. The same problem propagates into fish tissue concentrations accordingly. This observation suggests to me that a) K_d is generally underestimated by the approaches used for the initial modelling runs (which is in line with my comments on point 7 above), and that b) sediment may not be the optimal choice for determining and checking K_d values. I would recommend considering adding phytoplankton and suspended matter in future studies, particularly where this hasn't been done yet, to see if that yields better K_d values. This is supported by some data in the discussion of BCW K_d values in section 7 of Appendix O. I also note that while Se concentrations in invertebrates are usually predicted quite well, Se concentrations in bird eggs are typically overestimated significantly. This isn't my area of expertise, but it seems to suggest that the TTFs for invertebrate -> bird egg appear to be problematic.

The example of K_d selection for BCW illustrates a number of problems that should probably be addressed to ensure the future success of this project. It is shown (in Table 7-3, Appendix O, p. 1483) that very different K_d values can be obtained, depending on what type of "solid material" is used as the basis of comparison. First, the solution presented (finding the "best choice" K_d value) is complicated, and highly site-specific. While this highlights the flexibility of

the modelling process, and apparently leads to the "best fit" here, it also requires a lot of detail knowledge and experience to make that decision. Unfortunately, one has to assume that Dr. Luoma will not be available to support this effort indefinitely, so it would be good to develop a suite of internal and external experts who could perform such functions in the future, particularly if the Se bioaccumulation scenario changes significantly in one of the studied watersheds.

Second, this example points out the importance of collecting different types of data (here: sediment, SPM and algal samples) to get a sound estimate for this crucial K_d value. It is not inconceivable that future changes to a particular watershed may lead to a shift in receptor species or their diet, which may then in turn affect which type of K_d value is the "best choice". Therefore, I would advocate for continuing to collect these different sample types in the proposed monitoring program, rather than just focusing on one type of solid sample for K_d calculations (even if that may appear warranted at the moment).

And third, the mathematical component of the suggested process for selecting and calculating the "best" K_d value is getting increasingly complex as one tries to refine it more and more (e.g. by adding particle size normalization to any of the presented K_d options), which makes the process more prone to errors. To illustrate that point, I believe (after checking some of the calculations) that there are several errors in Table 7.4; for example, the "sediment + SPM" value in line 7 should be 2,024, if I understood the procedure correctly (and not 1,333, as listed). So, either I didn't understand the procedure properly, or there are indeed mistakes in that table; either way, such errors could be problematic when the numbers are used subsequently. The analysis of the statistical distribution of "best choice" vs. "sediment + SPM" K_d values shows that overall, this doesn't make a significant difference, but if one looks at individual sites, K_d differences can be up to a factor of 3, which makes a huge difference for the final calculations of water quality targets.

Finally, as pointed out under point 7 above (and acknowledged in the SWRCB staff report), the existing data set for SADC is very limited, and I would personally feel hesitant to derive any water quality targets for the water body from it at this time. If it is necessary to do so right now, I would at the very least recommend that many more data are generated for SADC soon after the inception of this TMDL program, and that the modelling exercise for SADC is repeated soon after those data become available to check, and adjust, if necessary, the target water concentrations for this water body.

Point # 9: TMDL and Allocations – Scientific justification of TMDL allocations, LAs and WLAs

Overall, the proposed TMDL approach with adaptive management aspects makes a lot of sense to me. I agree with the different approaches suggested for the three subwatersheds, as they seem to be most reflective of the specific situations (for SDC and BCW) and address the lack of data for SADC appropriately at this time. My only comments arise out of ignorance of critical biological parameters. For one, an averaging period of 6 months for TMDL allocations, LAs and WLAs appears long compared to the time during which egg formation and development (apparently) occurs in the receptor species. On page 7-3 of the staff report, it is acknowledged that these processes occur on the order of weeks, and even if not all fish and bird species may develop eggs at the same time, it still seems to me that shorter averaging periods (2 or 3 months) might be more appropriate for assessing the Se exposure of embryos. This is in line with discussions I've overheard for other Se impacted watersheds. I'm hoping that the temporal resolution of RMP activities is high enough that this averaging process would only be an after-the-fact mathematical exercise, aimed at developing the best predictors for receptor tissue Se concentrations, rather than result in additional monitoring activities.

Finally, I'm not sure I follow the logic of the repeated statement that "all of the results [*derived from the biodynamic model*] are deemed equally valid for predictive purposes". As far as I understand, once one has selected the appropriate endpoint for a specific subwatershed (e.g. fish tissue or bird egg), then the Se bioaccumulation model will predict the appropriate water concentration that is considered protective, based on all of the assumptions that have gone into the modeling process (including safety margins, I assume). Habitat heterogeneity along a subwatershed does not seem like a confounding factor to me in this consideration, since I assume that the critical biological species are able to migrate within a subwatershed on the spatial scale investigated here. Therefore, it appears (to me) to be most protective to pick the lowest water concentration derived for any part of the subwatershed, and apply it to the whole subwatershed, as if the receptor biological species spent the entire critical period (of egg development) in that part of the watershed.

Point # 10: Monitoring – Appropriateness of the proposed RMP

Overall, the proposed monitoring program is sensible, and will probably provide much of the desired information needed in future project supervision and decision making. Generally, I question the generation and use of total Se data on top of dissolved Se data. While I understand that regulations are always based on total element concentrations, we know that there is typically not a significant particulate Se fraction in freshwaters. To support this argument, it was shown previously for this study area (Appendix O, Table 1-1, p. 1436) that there is no significant difference between total and dissolved Se concentrations. Additionally, the analytical methods typically used for total Se determination do generally not feature a complete digestion of particulate matter, and are thus a) arbitrary (i.e. strongly dependent on the methods used by specific laboratories) and b) meaningless (because they only capture an unspecified fraction of the particulate Se). The cost of the water component of the monitoring program could thus be cut in half without losing any significant information.

Although Se speciation analyses are mentioned under "other considerations", I would suggest that their scientific value is not emphasized enough in the RMP design. As discussed above (for points 7 and 8), reliable Se speciation information is scarce for the studied watersheds, especially SADC. Due to its key role in determining K_d, and the apparent underestimation of bioaccumulation by median K_d values, I think the bioaccumulation model would benefit from the addition of more Se speciation information, possibly even directly into the algorithm. We know that most Se treatment processes change the relative speciation of Se significantly, so Se speciation monitoring would make a lot of sense as part of the BMP Effectiveness monitoring program, because you're ultimately not interested in reducing Se loads, but Se bioaccumulation potential, and there are demonstrated cases where a reduction in total Se accompanied by a change in Se speciation did not necessarily result in reduced Se bioaccumulation. I would personally advocate adding Se speciation monitoring to the other components of the RMP as well, because the presented results indicate that Se speciation can change across a watershed, due to biogeochemical transformation processes, but I understand that this leads to a significant cost increase. At the very least, I would suggest adding Se speciation analyses to monitoring activities in the short- to medium-term in areas where information is lacking (especially SADC) and when and where biological populations are most at risk (i.e. before/during the breeding season) to see how that refines the understanding of the bioaccumulation process. Within one watershed, Se speciation might also be an interesting and relevant aspect of a trading program, if one source emits a different species of Se than another one, so that the impact of a 1-for-1 trade (in term of total Se concentrations or loads) would not be net neutral in terms of Se bioaccumulation potential.

Related, it would also be a good idea to add a biological community monitoring component to the RMP. My concern would be that in a few years, as a result of change in a subwatershed, for example due to climate change or reduction in Se emissions, the structure of certain aquatic food chains might change to the point where the current Se bioaccumulation model is no longer appropriate. I'm not a biologist, so I'm not sure of the appropriate frequency and extent of such monitoring programs, but I suspect that it may be adequate to conduct such an effort every

couple of years, or when the Se tissue concentrations in key receptors do not respond as predicted.

In addition to the proposed monitoring activities, I would strongly recommend to accompany the generation of more data with continued modelling efforts, in order to test and refine, if necessary, the Se bioaccumulation model and its underlying assumptions. The model is a key component in the derivation of the water quality targets for the watersheds, and (as discussed above for points 7 and 8) there are many aspects of it (such as the selection of appropriate K_d values) that are based on limited data sets and have been numerically optimized rather than being based on a sound fundamental understanding of the underlying biogeochemical processes. Therefore, it is advisable to test continuously if the water quality developments in the watersheds, e.g. after BMP implementation, fall in line with the model predictions that their target values are based on.