Update on NY-NJ Mercury Model Enhancement (March 2011)

The review of the mercury model enhancements have been completed.

The Modeling Evaluation Group (MEG) prepared a memo supporting the use of the model and providing additional suggestions for work to further understand the model's behavior. (***Pgs. 2-3***)

HydroQual reviewed this memo and prepared a response to their comments. At this point, EPA feels that HydroQual has addressed the MEG's comments and we can move forward with the mercury model. (***Pgs. 4-7***)

Also included in this file is an e-mail to the MEG indicating that EPA will be moving forward with using the enhanced mercury model for TMDL development. The MEG did not raise any objections to this approach. Thus, EPA has contracted with HydroQual to complete a mercury matrix using the enhanced model. (***Pg. 8***)

November 18, 2010

To: Susy King, NEIWPCC

From: Joe DePinto (Senior Scientist, LimnoTech) and Chad Hammerschmidt (Assistant Professor, Wright State University)

Re: Recommendation on enhanced mercury model for the development of TMDLs

We have reviewed the enhanced CARP mercury model that has been revised for New York/New Jersey Harbor TMDL development purposes. This review was conducted through our reading of the "Technical Memorandum Report Refining the CARP Mercury Model" document and via interactive conference call with HydroQual on 20 Oct 2010.

The CARP mercury model for the Harbor was revised by HydroQual based on comments from a Model Evaluation Group in 2007. A major model revision was a change in the estimation of the Hg methylation and methylmercury (MeHg) demethylation rates. The MeHg demethylation process in the aerobic layer of sediments was reformulated to be a function of the model-computed sediment oxygen demand, where it is shown that the sediment oxygen demand is a good surrogate for microbial activity. The method used to estimate gross Hg methylation rate and gross MeHg demethylation rate seems reasonable, given the data available for net MeHg production rate. Importantly, modeled net MeHg production rates compare well with measured rates at several stations in the Harbor where the modeled and empirical data were contrasted.

The revised model does a much better job of simulating the Hg(II) and MeHg levels and fluxes in the system than the previous version of the model, including both absolute comparisons with empirical data and the comparison of probability distributions in the system. Compared to empirical results for particular locations in the Harbor, the revised model predicts sediment particulate MeHg very well and particulate Hg(II) within a factor of about two, but it under-predicts pore water MeHg and over-predicts pore water Hg(II). However, sediment-water fluxes of MeHg from the revised model compare well with measured fluxes and appear to capture seasonal variations. The revised model appears to do a good job in predicting water-column Hg(II) and MeHg, although it under-predicts water column Hg(II) and MeHg in the North River area where model results are compared to the Heyes et al. (2004) data. Discrepancies in this region of the system may result from Heyes and colleagues intentionally sampling in the turbidity maximum. Nevertheless, the model calibration overall is quite good and seems like it is ready for application.

However, before the model is applied to the TMDL calculation, we would like to see a few more sensitivity and diagnostic runs to evaluate the model's behavior relative to its use for the TMDL:

1) Compare model computed distribution coefficients for Hg(II) and MeHg in the water column and sediments to those that have been measured. This might provide some insight on a critical condition for the TMDL.

2) Run a series of sensitivity analyses with the model to assess its response to i) variations of organic carbon loads (both external and internal), and ii) variations of Hg methylation rates and MeHg demethylation rates with the uncertainty of the model relationship for their determination (maybe this has been done already). This sensitivity analysis may provide useful information for establishing a TMDL margin of safety.

3) Run the model to steady state with respect to the average Hg loadings during the calibration period to determine how far the system is from steady state with respect to the loadings. The TMDL determination should be made at steady state, especially if the system is not now close to steady state.

MEMORANDUM

TO: ANTONY TSENG
ROSELLA O'CONNOR

DATE: JANUARY 2011

RE: MERCURY TMDL MODEL MEG REVIEW COMMENTS RESPONSE

FROM: R. L. MILLER
JAMES WANDS

FILE: RTIN.003.001.3G

Technical Memorandum Report
Refining the CARP Mercury Model
Response to Model Evaluation Group (MEG) Comments

Task 3G
U.S. EPA Contract EP-C-08-003
Task Order 2008-01 Modification 4
Awarded to RTI International and HydroQual, Inc.

Previously, the CARP mercury model was revised by HydroQual for NY/NJ Harbor TMDL development purposes. The revisions were summarized by HydroQual in a March 22, 2010 technical memorandum report and during a conference call with an EPA appointed Model Evaluation Group (MEG) on October 20, 2010. The MEG members include Joe DePinto (Senior Scientist, LimnoTech) and Chad Hammerschmidt (assistant Professor, Wright State University).

The major enhancement was a change to the CARP model methylation and demethylation rates based on site specific measurements conducted by independent academic researchers subsequent to CARP. The major result of the revision is an improvement in model and data comparisons for water column and sediment methylmercury concentrations. This improvement is important because, although the TMDL calculations will be based on existing State water quality standards for total and dissolved mercury, it must be demonstrated that the final TMDL determined also meets the federal criterion for methylmercury in fish.

The MEG provided a written review of the model enhancements on November 18, 2010. Overall the MEG provided positive feedback on the enhanced model:

> "A major model revision was a change in the estimation of the Hg methylation and methylmercury (MeHg) demethylation rates. The MeHg demethylation process in the aerobic layer of sediments was reformulated to be a function of the model-computed sediment oxygen demand, where it is shown that the sediment oxygen demand is a good surrogate for microbial activity. The method used to estimate

> gross Hg methylation rate and gross MeHg demethylation rate seems reasonable, given the data available for net MeHg production rate. Importantly, modeled net MeHg production rates compare well with measured rates at several stations in the Harbor where the modeled and empirical data were contrasted.
>
> The revised model does a much better job of simulating the Hg(II) and MeHg levels and fluxes in the system than the previous version of the model, including both absolute comparisons with empirical data and the comparison of probability distributions in the system. Compared to empirical results for particular locations in the Harbor, the revised model predicts sediment particulate MeHg very well and particulate Hg(II) within a factor of about two, but it under-predicts pore water MeHg and over-predicts pore water Hg(II). However, sediment-water fluxes of MeHg from the revised model compare well with measured fluxes and appear to capture seasonal variations. The revised model appears to do a good job in predicting water-column Hg(II) and MeHg, although it under-predicts water column Hg(II) and MeHg in the North River area where model results are compared to the Heyes et al. (2004) data. Discrepancies in this region of the system may result from Heyes and colleagues intentionally sampling in the turbidity maximum. Nevertheless, the model calibration overall is quite good and seems like it is ready for application."

The MEG also provided three suggestions for sensitivity/diagnostic model simulations to provide additional information on the behavior of the model. To assist in EPA's consideration of these suggestions, HydroQual's responses below provide further descriptions and discussion of model applications.

MEG Suggestion 1 – *Compare model computed distribution coefficients for Hg(II) and MeHg in the water column and sediments to those that have been measured. This might provide some insight on a critical condition for the TMDL.*

HydroQual Response for MEG Suggestion 1 – A time-variable, multi-year approach is planned for Harbor TMDL development for mercury, consistent with the adopted approach for other toxic contaminants of concern, nutrients/dissolved oxygen, and pathogens. A time-variable, multi-year approach provides a method for accounting for critical conditions that can vary across locations and Harbor sub-regions. In this sense, gaining insight on a critical condition for the mercury TMDL based on variations in implied distribution coefficients is not a necessary TMDL step. If undertaken, the information to develop the data-derived and model-derived distribution coefficients for comparison as suggested by the MEG is already largely presented in Attachments C and D and Table 2 of the March 22, 2010 technical memorandum report where dissolved and particulate phase mercury and methylmercury concentrations are shown. Calculations of distribution coefficients would be another way of presenting (i.e., as a ratio) this phase specific concentration information.

MEG Suggestion 2 – *Run a series of sensitivity analyses with the model to assess its response to i) variations of organic carbon loads (both external and internal), and ii) variations of Hg methylation rates and MeHg demethylation rates with the uncertainty of the model relationship for their determination (maybe this has been done already). This sensitivity analysis may provide useful information for establishing a TMDL margin of safety.*

HydroQual Response for MEG Suggestion 2 – The intended approach for all Harbor TMDLs (i.e., pathogens, nutrients/dissolved oxygen, hydrophobic organic contaminants) is to account for the margin of safety implicitly. Sensitivity analyses are one mechanism for developing part of the justification for the implicit margin of safety. The MEG suggested two different types of sensitivity analyses for margin of safety justification purposes. The first involves sensitivity to organic carbon loads.

Organic carbon loading, specifically the ambient dissolved organic carbon produced by the organic carbon loadings, has greater relevance for methylmercury concentrations than it does for total mercury and dissolved mercury concentrations which will drive the mercury TMDLs. Also, organic carbon considerations are not unique to methylmercury and impact the hydrophobic organic contaminants of concern. Sensitivity work on organic carbon loadings from tributary headwaters examining the impact of more refractory particulate organic carbon loading on strongly hydrophobic contaminants such as dioxin was previously performed and reported on for EPA in May 2010.

Specifically, for the NY/NJ Harbor Toxics TMDL purposes of addressing margin of safety, seasonal variation, and potential public comments, a CARP modeling sensitivity analysis of 2,3,7,8-TCDD concentrations in the NY/NJ Harbor to refractory organic carbon fraction in tributary headwaters was completed in May 2010. Two versions of sensitivity analysis were completed. The first version considers a hypothetical increase of the inert fraction of particulate organic carbon introduced by tributary headwaters. While this increases sediment organic carbon, the analysis assumed that the total contaminant mass in the bed initial condition would remain unchanged. The increase in inert fraction of particulate organic carbon introduced by tributary headwaters evaluated would be expected to change future water column concentrations of strongly particle bound contaminants, such as 2,3,7,8-TCDD, by -11.9% to +4.2%, with an overall average potential change in the water column concentration across HEP waters of -2.7%. There would be longer time horizons associated with the response of contaminant concentrations in the bed to contaminant loading changes. The second sensitivity analysis considered the potential increase in the inert fraction of particulate organic carbon introduced by tributary headwaters in an historical context whereby legacy contaminant mass in the sediment bed was also simultaneously increased (i.e., legacy measured contaminant per mass organic carbon sediment initial conditions were applied to a higher mass of organic carbon). The second sensitivity analysis conditions resulted in the calculation of an average increase in 2,3,7,8-TCDD water column concentration of 30.1% and range of 9.4% to 49.4% across the HEP waters. For TMDL calculations where the full removal of legacy contamination as a starting point is an assumption in the TMDL, the results of the first sensitivity analysis are more relevant. A hypothetical change in refractory organic carbon fraction in tributary headwaters would be acting on current loadings only.

It is also noted that mercury is known to complex with species other than dissolved organic carbon (e.g., sulfides, chlorides, hydroxides, etc.) and these species are also an element of the implicit margin of safety for mercury. If a new organic carbon loading sensitivity were to be authorized by EPA, it might be advisable to evaluate a single "post nutrient TMDL" reduced organic carbon loading condition for mercury as well as the other TMDL contaminants.

The second suggestion involves model sensitivity to methylation and demethylation rates. To a large degree this has already been completed. Along with the methylation/demethylation rates of the original CARP model, the process of developing the enhanced CARP model included evaluation of nineteen different methylation/demethylation rate conditions with marked improvement (i.e., high

sensitivity) between the original and enhanced calibrations. While not exactly a series of runs within the uncertainties of the calculation methods for methylation and demethylation rates as the MEG suggested, the completed work bounds the extremes.

MEG Suggestion 3 – *Run the model to steady state with respect to the average Hg loadings during the calibration period to determine how far the system is from steady state with respect to the loadings. The TMDL determination should be made at steady state, especially if the system is not now close to steady state.*

HydroQual Response for MEG Suggestion 3 - The planned approach for mercury TMDLs, similar to the approach already being followed for hydrophobic organochlorine contaminants and planned for PAH contaminants, is to base TMDL calculations on model simulations of conditions 29 to 32 years in the future after loading adjustments have been made. The rationale for basing the TMDLs on modeled conditions after a long term exposure to the reduced loadings is to allow for the system to come into steady state with the loadings changes. This approach already captures the MEG's intention that TMDL determinations should be made at steady state.

The model calibration includes four years of "spin-up" and four years of calibration. It is already known from work done on CARP that the calibration period is insufficient for reaching a steady state with respect to loadings changes and the calibration period will therefore not be used as the basis for TMDL calculations for mercury or any of the other toxic contaminants. If EPA authorizes that new model simulations will be performed to test for steady state with respect to loadings changes as the MEG has suggested, the simulations would be for the purpose of confirming the previous CARP finding from 100 year simulations that for most Harbor locations and contaminants, 29 to 32 years of simulation are needed to achieve steady state with respect to loadings changes. Performing new model testing simulations over multiple decades would be a significant effort.

NY-NJ Harbor Mercury Model Review

Rosella OConnor to: jdepinto, Chad Hammerschmidt 02/11/2011 04:04 PM
Cc: SKing, Robert Nyman, Antony Tseng, robin miller

Greetings Joe and Chad:

Thank you for your memo regarding the enhanced mercury model for NY-NJ Harbor. HydroQual has provided a response which is attached below. Your memo indicated that the model calibration was "quite good" and could be used to develop TMDLs. You also provided suggestions on additional work that could be performed to further understand the model's behavior. As HydroQual's memo indicates, a good portion of work has already been completed to address your concerns regarding the critical condition and sensitivity analyses. With regard to your suggestion for using a steady-state condition to the determine the TMDL, EPA agrees with this approach and has already applied the approach to TMDL calculations for hydrophobic organochlorine contaminants.

At this point, EPA has very limited funds available. It is EPA's goal to provide the states with a mercury matrix based on the enhanced mercury model and provide some assistance in completing the TMDLs. Therefore based upon your memo, we feel that we can proceed with TMDL development for mercury. While additional analyses would be helpful in further explaining the model's behavior, at this time, EPA does not have the resources to carry out this work. Once the TMDLs are established, it is EPA's view that additional data should be collected for all contaminants for the purpose of providing updated information on sources and receiving water quality and refining the CARP model, if needed. At this point, we would have an opportunity to consider additional analyses as indicated in your memo.

If you have alternate suggestions or analyses that you feel can be completed under our current funding constraints to support the usability of the enhanced mercury model for the NY-NJ Harbor, please feel free to forward them to me by **February 28, 2011**. As always if you have any additional concerns or questions, please do not hesitate to contact me.

Regards,
Rosella

Hydro Qual MEG memo Jan11 2010.pdf