Peer Review of Hudson River PCBs Reassessment RI/FS Phase 2 Reports

Baseline Modeling Report

Premeeting Comments

Saratoga Springs, New York
March 27-28, 2000

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FOR PAGINATION PURPOSES.

Additional comments by Ellen Bentzen

<u>Principal study questions:</u>

P1. When will PCB levels in fish meet human health and ecological risk criteria under continued NO ACTION?

P2. Can remedies other than NO ACTION significantly shorten the time required to achieve acceptable risk levels?

P3. Could a flood scour sediments, exposing and redistributing buried contamination?

It is noted that question 2 is not under the domain of the BMR results.

<u>HUDTOX</u>:

Note: answers are offered for certain questions only for this section as my expertise lies with the bioaccumulation models. The approach taken with the HUDTOX model questions has emphasis towards its use ultimately for future decisions and application to contaminant concentrations in biota (question P1). Overall, HUDTOX is an impressive model given the difficulty of mapping and parameterizing all the processes an advective system. Nonetheless, there are still specific issues to be addressed before its use in any decision process for the Hudson River.

A1. *The HUDTOX model links components describing the mass balance of water, sediment, and PCBs in the Upper Hudson. Are the process representations of these three components compatible with one another, and appropriate and sufficient to help address the principal study questions?*

The mass balance model for PCBs in the Hudson must take into account the balance for water, including flow from the main river and tributaries, plus mixing; the balance for solids, which includes the important component of tributary loading (to a greater extent than water loading), and interaction between deposition to sediments and resupension from sediments; and the PCB mass balance which is influenced by the water and solids mass balances, and which includes chemical partitioning between dissolved and particulate phases where organic carbon plays a key role. Given the available data which was not all originally designed for the purpose of constructing the HUDTOX (or bioaccumulation) models, the processes defined for HUDTOX for these three components are compatible with one another and are appropriate for addressing the principal study questions. The fundamentals of these processes are approaching sufficiency. Two weak links (but not exclusive), include the lack of a broader range of temporal sediment data (see question 8 below) and treatment of the PCB partitioning (question 10). Also, further resolution to the issues raised in Question 11 must be considered.

Additional comments by Ellen Bentzen

A2. *The HUDTOX representation of the solids mass balance is derived from several sources, including long-term monitoring of tributary solids loads, short-term solids studies and the results of GE/QEA's SEDZL model. The finding of the solids balance for the Thompson Island Pool is that this reach is net depositional from 1977 to 1997. This finding also has been assumed to apply to the reaches below the TID. Is this assumption reasonable? Are the burial rates utilized appropriate and supported by the data? Is the solids balance for the Upper Hudson sufficiently constrained for the purposes of the Reassessment?*

The assumption of net deposition to reaches below TIP is probably reasonable despite the limited data. Support for this may also be seen in the PCB depth profiles- there is a substantial load of PCBs extending to 16 cm (or deeper) by 1977 (initial calibration year; Figure 6.52) from a 20 year history of contamination (from 1956). The estimated burial rates for the Upper Hudson are 0.24 to 1.5 cm/year in cohesive sediments (page 129 vol 1), which corresponds to depositions between 5 to 30 cm in 20 years. This is interesting to compare to other systems, such as a lake, where 20 years of sedimentation may result in about 5 cm of accumulation.

A3. *HUDTOX represents the Upper Hudson by segments of approximately 1000 m in length in the TIP, and by segments averaging over 4000 m (ranging from 1087 to 6597 m) below the TID. Is this spatial resolution appropriate given the available data? How does the spatial resolution of the model affect the quality of the model predictions?*

My interpretation considers that the spatial resolution is appropriate given the importance of TIP for the PCB dynamics to the lower river. Given the gradient that exists between Fort Edward and Federal Dam for all of the key parameters (water, solids and PCBs mass balances), the segmentation of the river as given appears logical and appropriate. The quality of the model predictions is the result of many factors, spatial resolution being but one. There probably would be little gained to have a finer spatial resolution given the variability in the various parameters. The model is calibrated to broad averages, which is reasonable, but the scale division of the river allows focussing of these averages for observed differences along the river. These also seem to be reasonable in terms of examining PCB distributions in water and sediment for consideration of biota exposures.

A4. *Is the model calibration adequate? Does the model do a reasonable job in reproducing the data during the hindcast (calibration) runs? Are the calibration targets appropriate for the purposes of the study?*

The model calibration appears quite adequate and does a reasonable job in reproducing the data during the hindcast runs. However, as noted in the bioaccumulation model questions, it must be noted that providing a good fit to the data used to develop the model does not ensure that the model has completely captured the mechanisms governing PCB distributions among the media. The intensive effort expended for the water and solids mass balances are more robustly based, even considering where data are lacking. It is more difficult for the PCB mass balance because of the assumptions governing the distribution of PCBs between dissolved and associated states (to dissolved organic carbon, DOC, and particulate organic carbon) are not as well characterized nor supported by empirical data (e.g. the partitioning to DOC; see below).

A5. *HUDTOX employs an empirical sediment-water transfer coefficient to account for PCBs loads that are otherwise not addressed by any of the mechanisms in the model. Is the approach taken reasonable for model calibrations? Comment on how this affects the uncertainty of forecast simulations, given that almost half of the PCB load to the water column may be attributable to this empirical coefficient.*

A6. *Are there factors not explicitly accounted for (e.g. bank erosion, scour by ice or other debris, temperature gradients between the water column and sediments, etc) that have the potential to change conclusions drawn from the models?*

In general, the most likely factors appear to be accounted for. There is obviously no forecasting future events outside the realm of the past observations, but one factor which could influence the various processes (including bioaccumulation pathways) would be possibly significant change in the nutrient water quality by either increased inputs (increased development in the watershed) or improved water quality (better sewage treatment, agricultural practices, etc). This could change solids loadings (inputs and sedimentation), temperature, and PCB partitioning (plus food web structure obviously the latter point for the bioaccumulation models) which may be outside the current boundaries examined in the model. Changes in *in situ* production may change sedimentation rates (as well feeding relationships and all the related effects). The sensitivity analysis indicates that substantial changes in solids loading have an impact on the model outcome. The model forecast is for a sufficiently long period that such changes are not impossible.

A7. *Using the model in a forecast mode requires a number of assumptions regarding future flows, sediment loads, and upstream boundary concentrations of PCBs. Are the assumptions for the forecast reasonable? Is the construct of the hydrograph for forecast predictions reasonable? Should such a hydrograph include larger events?*

The assumptions for the forecast are reasonable and well developed. I do not believe that the hydrograph should include larger events- the model is based upon averages which is a reasonable approach.

A8. *The 70-year model forecasts show substantial increases in PCB concentrations in surface sediments (top 4 cm) after several decades at some locations. These in turn lead to temporary increases in water-column PCB concentrations. The increases are due to relatively small amounts of predicted annual scour in specific model segments, and it is believed that these represent a real potential for scour to uncover peak PCB concentrations that are located from 4 to 10 cm below the initial sediment-water interface. Is this a reasonable conclusion in a system that is considered net depositional? After observing these results, the magnitude of the increases was reduced by using the 1991 GE sediment data for initial conditions for forecast runs. Is this appropriate? How do the peaks affect the ability of the models to help answer the Reassessment study questions?*

While I cannot comment on the aspect of the model development which predicts the scouring event to redistribute PCBs, it is reasonable in a dynamic system which can still be net depositional overall. There is obviously considerable movement of sedimentary material. Overall, the magnitude of the new PCB pulse does appear to be relatively small. The agreement by use of the GE data supports the observations but the change in the magnitude highlights the issue that sediment dynamics are one of the weak links in the forecast because of limited temporal data. Note for all reaches but TIP, sediment data exist for 3 years and the model underpredicts sediment concentrations in the 1990's. Although this is within a factor of 2 to 4, the real range can be predicted values around 5 mg/L vs observed 20+ mg/L. Given the importance of sediment loads both water concentrations by exchange and to fish concentrations, this could be a substantial error. Another question to consider is whether the observation would be different if a higher resolution for the sediment profiles were used. No trends can be established from the profiles shown in the BMR because of variable and thick core slice sections. Is there more information in the DEIR and LCR?

A9. *The timing of the long-term model response is dependent upon the rate of net deposition in cohesive and non-cohesive sediments, the rate and depth of vertical mixing in the cohesive and non-cohesive sediments and the empirical sediment-water exchange rate coefficient. Are these rates and coefficients sufficiently constrained for the purposes of the Reassessment?*

A10. *The HUDTOX model uses three-phase equilibrium partitioning to describe the environmental behaviour of PCBs. Is this representation appropriate? (Note that in a previous peer review on the DEIR and the LRC, the panel found that the data are insufficient to adequately estimate three-phase partition coefficients).*

HUDTOX considers three-phase equilibrium partitioning to describe the behaviour of PCBs in the water column. This is both an interesting and important question to address fully, because of the implications of deriving the bioavailable PCB concentration taken up by biota. The Hudson River has both high DOC concentrations (range 3 to 6 mg/L) and variable solids (2 to 100 mg/L). Partition coefficients were derived to characterize the distribution of PCBs among three phases in the water column: dissolved (= bioavailable), particulate-bound and DOC-bound. The partition coefficient for DOC, K_B, is set to equal 1.0 * $K_{DOC.}$ (Equation 5-11). This is based upon the statement that "dissolved organic materials are typically assumed to be composed entirely of organic carbon, f_{OC} = 1". This is a surprising statement, as organic matter by its nature has to have the other essential macro & micro- elements (P, N, O, S, etc).

Hence, K_B is related to K_{DOC} (probably incorrectly). K_{DOC} is reported as commonly estimated as "K_{POC} * a binding efficiency factor based on analysis of field data measurements of each chemical phase". What is the binding efficiency factor? Presumeably this is further developed in the DEIR, but insufficient information is given in the RBMR for adequate evaluation of this development (the BMR description is lacking in detail; for example, not all the terms are adequately defined. Note for example, that L in these equations must refer to volume but L is also used several pages before for length; notation should be consistent and defined throughout! What is L_W, for example; the next page uses L_{WATER}). The statement is made that there is considerable uncertainty in the determination of these 3-phase partition coefficients, but this is not clearly elaborated. The BMR states the result that the lightest PCB congeners are highly associated with DOC in the water (up to 50% of their total) but congeners comprising tri+ are only about 10% associated with DOC. Thus, the most soluble PCB congeners are largely bound to DOC? This contradicts the situation in the sediments where all congeners are approximately equal in their association with organic carbon.

Another observation which does not seem to be explained is the tremendous difference in estimated log K_{POC} and log K_{DOC} between GE and Phase 2 data, both which are given in Table 6-28. These are order of magnitude differences? Thus, theoretically this well may be an important approach because DOC is important in this river, and it may be that the average values derived for the partition coefficients are reasonable (except for equating all organic matter as carbon), but there is no way of adequately assessing this based upon the information provided in the BMR.

Overall, this is an important issue, but to what extent? The sensitivity analysis demonstrated that K_{POC} is an important parameter. Where no sensitivity analyses done for K_{DOC}? This must be clarified and/or further resolved. The comment above in the question that the reviewers for the DEIR considered there to be insufficient data to resolve this question is vague: the BMR suggests that there were data but specifics are not sufficiently identified.

Additional comments by Ellen Bentzen

A11. *HUDTOX considers the TIP to be net depositional, which suggests that burial would sequester PCBs in the sediment. However, the geochemical investigations in the LRC found that there was redistribution of PCBs out of the most highly contaminated areas (PCB inventories generally greater than 10 g/m²) in the TIP. Comment on whether these results suggest an inherent conflict between the modeling and the LRC conclusions, or whether the differences are attributable to the respective spatial scales of the two analyes.*

A12. *The model forecasts that a 100-year flood event will not have a major impact on the long-term trends in PCB exposure concentrations in the Upper Hudson. Is this conclusion adequately supported by the modeling?*

Miscellaneous:
p. 86, section 6.5.4. ..."flow increases by only a factor of 1.2 and 1.5 percent"... percent is not meant here (see p. 73), but changes the value significantly!

Table 6-44: either I am misreading this, or how can the concentrations for BZ#4 exceed total PCBs for these pore waters?

p. 138, first paragraph. There is an incorrect reference to Figure 7-30 which should read 7-22.

p. 90: discussion of detection limits for PCBs in water. These are high (10 ng/L), presumeably because of small volumes of water extracted for analysis? (not identified in the BMR). But note that lower values are reported in Table 6-19 (0.8 to 2.1 ng/L). Presumeably again, due to extraction of larger water volumes for these? Clarify details (summary table would be helpful, as done for sediments, Table 6-1).

p. 99: reference to sediment grab samples from river mile 189.2 were dropped because high. This is not well justified in the BMR. Explain.

Recommendations:

Overall: the HUDTOX model is a significant product to be used for an incredible system. PCBs in the Hudson are an impressive problem, with such high concentrations observed in water, sediments and biota. Even without using the model forecasts but considering the past trends for PCBs, they are declining at but a modest rate of less than 10% per year. The model is useful in examining rates of change under different loading scenarios and is ready to be used in the event of changes to some of the identified key parameters in the river. The sensitivity analyses are important for this latter point. Models are made to fit the data they are derived from but this does not guarantee that they have captured the appropriate mechanisms. As discussed above, for example, if the derivations used for the three-phase partitioning are flawed and organic carbon concentrations significantly change in the river at some point in the future, will the model be able to predict the consequence of those changes?

My recommendation is to accept the model with appropriate revisions. But, this must be tempered by the ultimate use for the model. If any action other than NO ACTION is considered, then the models should be thoroughly and comprehensively reviewed again. By thorough and comprehensive, I recommend that several independent reviewers be retained to review not just the BMR, but hand in hand with the DEIR, LRC, all previous review comments, and the GE reports. This would effectively constitute an audit. Sufficient time has to be allocated to these auditors, with opportunity to meet and question the people who have put such tremendous effort into analysing the data and developing these models. The auditor/reviewers would be in a strong position, however, to objectively assess the entire process. This peer review process will have been a useful contribution but probably has been hampered by both having insufficient time (note that while we were enlisted in the fall of 1999, documents were delivered only two months prior to the Review meeting, at the end of January 2000) and by not having all the information in hand (e.g. the DEIR and LRC). To address the scope of some of the questions requires information not provided in the BMR.

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Note: *Premeeting comment materials have been reproduced as received.*

Hudson River PCBs Site Reassessment RI/FS
Baseline Modeling Report
Peer Review 3

Charge for Peer Review 3

This is the third in a series of four peer reviews being conducted on scientific work products prepared for the Reassessment Remedial Investigation and Feasibility Study (Reassessment) for the Hudson River PCBs site. Previous peer reviews were conducted on the modeling approach and the Data Evaluation and Interpretation Report and Low Resolution Sediment Coring Report. Subsequent to this peer review the Human Health and Ecological Risk Assessments will be peer reviewed.

Members of this peer review are asked to determine whether the baseline modeling effort presented in the Revised Baseline Modeling Report (Revised BMR) is credible and whether the conclusions of the Revised BMR are valid. The reviewers are asked to determine whether the modeling work is technically adequate, competently performed, properly documented, satisfies established quality requirements, and yields scientifically credible conclusions. The peer reviewers are not being asked whether they would have conducted the work in a similar manner. In addition, the reviewers are asked to determine whether the models and the associated findings are appropriate to help answer the following three principal study questions that EPA will consider in its decision-making process for the site:

1. When will PCB levels in fish meet human health and ecological risk criteria under continued No Action? (1)

2. Can remedies other than No Action significantly shorten the time required to achieve acceptable risk levels? (2)

3. Could a flood scour sediments, exposing and redistributing buried contamination?

(1) Appropriate levels to meet human health and ecological risk criteria will be evaluated in the upcoming Feasibility Study.

(2) The Revised BMR represents a baseline modeling effort, and therefore does not include an evaluation of potential remedial scenarios. The modeling work presented in the Revised BMR will be used to develop potential remedial options in the Feasibility Study for the Reassessment.

The following documents were provided to the peer reviewers:

Primary
Revised Baseline Modeling Report (Jan. 2000)

Responsiveness Summary to the Baseline Modeling Report (Jan. 2000)

Reference
Baseline Modeling Report (May 1999)
QEA/GE - PCBs in the Upper Hudson River (May 1999, amended July 1999)
Suggested charge questions from the public (Dec. 1999)
Hudson River Reassessment Database (August 1998)
Executive Summaries for other EPA Reassessment Reports
Peer Review Reports from first two peer reviews

The peer reviewers should base their assessments primarily on the Revised BMR, and on EPA's Responsiveness Summary for the Baseline Modeling Report, in which EPA responded to significant public comments received by the Agency on the May 1999 Baseline Modeling Report. These two documents are currently in preparation, and will be issued to the peer reviewers by the end of January 2000. The reference documents listed above are being provided to the reviewers as background information, and may be read at the discretion of the reviewers, as time allows, although the reviewers are not being asked to conduct a review of any of the background information. It should be noted that the Revised BMR to be issued in January 2000 will supercede the May 1999 Baseline Modeling Report.

For additional background information, please visit USEPA's web site on the Hudson River PCBs site, www.epa.gov/hudson.

Specific Questions

Fate and Transport (HUDTOX)

1. The HUDTOX model links components describing the mass balance of water, sediment, and PCBs in the Upper Hudson. Are the process representations of these three components compatible with one another, and appropriate and sufficient to help address the principal study questions?

2. The HUDTOX representation of the solids mass balance is derived from several sources, including long-term monitoring of tributary solids loads, short-term solids studies and the results of GE/QEA's SEDZL model. The finding of the solids balance for the Thompson Island Pool is that this reach is net depositional from 1977 to 1997. This finding has also been assumed to

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apply to the reaches below the Thompson Island Dam. Is this assumption reasonable? Are the burial rates utilized appropriate and supported by the data? Is the solids balance for the Upper Hudson sufficiently constrained for the purposes of the Reassessment?

3. HUDTOX represents the Upper Hudson River by segments of approximately 1000 meters in length in the Thompson Island Pool, and by segments averaging over 4000 meters (ranging from 1087 to 6597 meters) below the Thompson Island Dam. Is this spatial resolution appropriate given the available data? How does the spatial resolution of the model affect the quality of model predictions?

4. Is the model calibration adequate? Does the model do a reasonable job in reproducing the data during the hindcast (calibration) runs? Are the calibration targets appropriate for the purposes of the study?

5. HUDTOX employs an empirical sediment/water transfer coefficient to account for PCBs loads that are otherwise not addressed by any of the mechanisms in the model. Is the approach taken reasonable for model calibration? Comment on how this affects the uncertainty of forecast simulations, given that almost half of the PCB load to the water column may be attributable to this empirical coefficient.

6. Are there factors not explicitly accounted for (*e.g.*, bank erosion, scour by ice or other debris, temperature gradients between the water column and sediments, etc.) that have the potential to change conclusions drawn from the models?

7. Using the model in a forecast mode requires a number of assumptions regarding future flows, sediment loads, and upstream boundary concentrations of PCBs. Are the assumptions for the forecast reasonable? Is the construct of the hydrograph for forecast predictions reasonable? Should such a hydrograph include larger events?

8. The 70-year model forecasts show substantial increases in PCB concentrations in surface sediments (top 4 cm) after several decades at some locations. These in turn lead to temporary increases in water-column PCB concentrations. The increases are due to relatively small amounts of predicted annual scour in specific model segments, and it is believed that these represent a real potential for scour to uncover peak PCB concentrations that are located from 4 to 10 cm below the initial sediment-water interface. Is this a reasonable conclusion in a system that is considered net depositional? After observing these results, the magnitude of the

increases was reduced by using the 1991 GE sediment data for initial conditions for forecast runs. Is this appropriate? How do the peaks affect the ability of the models to help answer the Reassessment study questions?

9. The timing of the long-term model response is dependent upon the rate of net deposition in cohesive and non-cohesive sediments, the rate and depth of vertical mixing in the cohesive and non-cohesive sediments and the empirical sediment-water exchange rate coefficient. Are these rates and coefficients sufficiently constrained for the purposes of the Reassessment?

10. The HUDTOX model uses three-phase equilibrium partitioning to describe the environmental behavior of PCBs. Is this representation appropriate? (Note that in a previous peer review on the Data Evaluation and Interpretation Report and the Low Resolution Sediment Coring Report, the panel found that the data are insufficient to adequately estimate three-phase partition coefficients.)

11. HUDTOX considers the Thompson Island Pool to be net depositional, which suggests that burial would sequester PCBs in the sediment. However, the geochemical investigations in the Low Resolution Sediment Coring Report (LRC) found that there was redistribution of PCBs out of the most highly contaminated areas (PCB inventories generally greater than 10 g/m^2) in the Thompson Island Pool. Comment on whether these results suggest an inherent conflict between the modeling and the LRC conclusions, or whether the differences are attributable to the respective spatial scales of the two analyses.

12. The model forecasts that a 100-year flood event will not have a major impact on the long-term trends in PCB exposure concentrations in the Upper Hudson. Is this conclusion adequately supported by the modeling?

Bioaccumulation Models

1. Does the FISHRAND model capture important processes to reasonably predict long term trends in fish body burdens in response to changes in sediment and water exposure concentrations? Are the assumptions of input distributions incorporated in the FISHRAND model reasonable? Are the spatial and temporal scales adequate to help address the principal study questions?

2. Was the FISHRAND calibration procedure appropriately conducted? Are the calibration targets appropriate to the purposes of the study?

3. In addition to providing results for FISHRAND, the Revised BMR provides results for two simpler analyses of bioaccumulation (a bivariate BAF model and an empirical probabilistic food chain model). Do the results of these models support or conflict with the FISHRAND results? Would any discrepancies among the three models suggest that there may be potential problems with the FISHRAND results, or inversely, that the more mechanistic model is taking into account variables that the empirical models do not?

4. Sediment exposure was estimated assuming that fish spend 75% of the time exposed to cohesive sediment and 25% to non-cohesive sediment for the duration of the hindcasting period. The FISHRAND model was calibrated by optimizing three key parameters and assuming the sediment and water exposure concentrations as given, rather than calibrating the model on the basis of what sediment averaging would have been required to optimize the fit between predicted and observed. Is the estimate of sediment exposures reasonable?

5. The FISHRAND model focuses on the fish populations of interest (*e.g.*, adult largemouth bass, juvenile pumpkinseed, etc.) which encompass several age-classes but for which key assumptions are the same (*e.g.*, all largemouth bass above a certain age will display the same foraging behavior). This was done primarily because it reflects the fish data available for the site. Is this a reasonable approach?

<u>General Questions</u>

1. What is the level of temporal accuracy that can be achieved by the models in predicting the time required for average tissue concentrations in a given species and river reach to recover to a specified value?

2. How well have the uncertainties in the models been addressed? How important are the model uncertainties to the ability of the models to help answer the principal study questions? How important are the model uncertainties to the use of model outputs as inputs to the human health and ecological risk assessments?

3. It is easy to get caught up with modeling details and miss the overall message of the models. Do you believe that the report appropriately captures the "big picture" from the information synthesized and generated by the models?

4. Please provide any other comments or concerns with the Revised Baseline Modeling Report not covered by the charge questions, above.

Recommendations

Based on your review of the information provided, please identify and submit an explanation of your overall recommendation for each (separately) the fate and transport and bioaccumulation models.

1. Acceptable as is
2. Acceptable with minor revision (as indicated)
3. Acceptable with major revision (as outlined)
4. Not acceptable (under any circumstance)

Dr. Ellen Bentzen

ELLEN BENTZEN

Ellen Bentzen has a Ph.D. (1990) and an M.Sc. (1986) in aquatic ecology from the University of Waterloo and a B.Sc. (1982) in limnology from McGill University. She has worked as an applied aquatic ecologist/environmental toxicologist Research Associate at Trent University, Peterborough, ON. Her initial research project at Trent was a study of how aquatic food web structure influences the concentration of persistent organic pollutants (POPs) in lake trout from Ontario lakes. This work instigated a number of related projects ranging from field studies of POPs in the lower part of aquatic food webs and food web structure to development of contaminant bioaccumulation models (ongoing research). She also has examined the role of food web structure and dissolved organic carbon in lake water on bioaccumulation of mercury in lake trout and other fish species.

Ellen Bentzen is associated both with the Environmental Modelling Centre at Trent University, Peterborough, ON, working with Dr. Don Mackay, and with the St. Lawrence River Institute, Cornwall, ON (affiliated with the University of Ottawa, Ottawa, ON) working with Dr. David Lean. Both the Environmental Modelling Centre and the St. Lawrence River Institute have associations with industry and government agencies. She was a peer reviewer for Preliminary Baseline Modelling Report for the Hudson River Superfund project in 1998. She recently published a review paper on POPs in Lake Ontario biota in *Environmental Reviews.* This paper includes temporal data for a number of organisms from Lake Ontario and an assessment of recent trends in contaminant concentrations. She also has been collaborating on the development of contaminant bioaccumulation models both for benthic invertebrates and for lake trout residing in different aquatic food webs. She is currently examining food web effects on contaminant bioaccumulation in biota in subarctic lakes (Yukon Territory, Canada). Results from her research have been presented at SETAC (Society for Environmental Toxicology and Chemistry), IAGLR (International Association for Great Lakes Research) and ASLO (American Society of Limnology and Oceanography). Recent research papers include:

Bentzen, E., D. Mackay, B.E. Hickie and D.R.S. Lean. 1999. Temporal trends of polychlorinated biphenyls (PCBs) in Lake Ontario fish and invertebrates. Environ. Rev. 7: 203-223.

Mackay, D. and E. Bentzen. 1997. The role of atmosphere in Great Lakes contamination. Atmospheric Environment 31:4045.

Bentzen, E., D.R.S. Lean, W.D. Taylor and D.Mackay. 1996. Role of food web structure on lipid and bioaccumulation of organic contaminants by lake trout (Salvelinus namaycush). Can. J. Fish. Aquatic Sci. 53:2397.

Almond, M.J., E. Bentzen and W.D. Taylor. 1996. Size-structure and species composition of plankton communities in deep Ontario lakes with and without Mysis relicta and planktivorous fish. Can. J. Fish. Aquatic Sci. 53: 315-325.

Bioaccumulation Models:

B1. *Does the FISHRAND model capture important processes to reasonably predict the long term trends in fish body burdens in response to changes in sediment and water exposure concentrations? Are the assumptions of input distributions incorporated in the FISHRAND model reasonable? Are the spatial and temporal scales adequate to help address the principal study questions?*

The FISHRAND model appears to capture many important processes which may predict long term trends in fish body burdens in response to changes in sediment and water exposure concentrations. But, these type of models can give apparently correct outcomes without necessarily being mechanistically correct because the models ultimately are calibrated to optimize predicted vs observed fish PCBs under a particular set of conditions. Because water and sediment PCBs are high in the Hudson River, there are strong relationships between biota and media PCBs (see further elaborations under question 3), and these may mask actual underlying mechanistic processes. FISHRAND is developed from the Gobas 1993 model, in which critical equations developed for uptake and depuration (k_1 & k_2) were derived in Gobas & Mackay (1987) based upon very limited data sets. Gobas (1993) acknowledges this and states that due to insufficient data, the relationship for Q_L cannot be derived and is set at approximately 100 times smaller than Q_w (c.f Equations 3.8 to 3.11). FISHRAND did include the sensitivity analysis on the constant C_3 = 100, but it is not clear by how much this was varied? For example, Campfens and Mackay (1997) used a value of 1000 in their food web model for PCB bioaccumulation. Hendriks (1995) used an extensive data base to derive estimates for k_2 based upon K_{ow} and fish size, and the predicted values differ considerably from those in the Gobas model. Along the same lines, similar recent work on dietary uptake efficiency suggests revision of this part of the model may also be warranted (Fisk et al. 1998).

Thus, the estimation of k_1 and k_2 may be rather crude and these have ultimate importance in establishing the relative contribution of PCB uptake across gills vs diet. The contribution of uptake from water was established to be 1 to 15% for Hudson River fish, with the lowest water contributions to the piscivores.

The BMR briefly comments on the model comparison by Burkhard (1998) who reported that model outcome is sensitive to the sediment to water partitioning normalized to organic carbon (this is equivalent to the sediment to water fugacity ratio). Because HUDTOX predicted sediment concentrations were used along with average water concentrations, these parameters had no uncertainty nor were variations in the sediment to water fugacity ratio on biota PCB examined. This should be done.

Otherwise, most of the assumptions of input distributions incorporated into FISHRAND seem reasonable; clearly a significant effort was put into this. However, one possibly alarming exception was the distribution and mean used for water column invertebrates percent lipid, set at 0 to 0.8%, mean 0.2% (Table 6.1). Overall, the whole treatment of water column invertebrates was very inadequately handled. The descriptions of what these were (e.g. biota composition) were unclear, as were sampling protocol. Note that in general, it would be very useful to have one or two tables outlining brief descriptions of the samples used; descriptions between the various biota were inconsistent in terms of details provided. It is recognized that details are provided in the Data Report, but which was not at hand, nor was the objective to evaluate the data per se, nonetheless, it would be good to have some more information than was offered. For example, when (years), where, how many, species identified, analyses done, etc. Wainman et al. (1993) report lipid content for zooplankton from a set of freshwater systems, and consider values less than about 1% would indicate virtual starvation in zooplankton. Certainly zero percent is not biologically possible! Also, a value around 1% organic carbon for phytoplankton seems to be much too low. This could have ramifications in estimating bioaccumulation in the lower part of the food web. It is worthwhile to note that the Gobas (1993) model also performs poorly at the base of the food web, although this has been somewhat better addressed in the later models (e.g. Morrison et al. 1997, 1999). Model outcomes are generally evaluated in terms of estimated fish contaminant concentrations based upon the same data set used to develop the model, but it is worthwhile to consider that if the model does not capture the base of the food web, how sensitive might the model be to track changes in water (and sediment) concentrations which directly affect plankton concentrations (assuming steady-state)? This may be very difficult to study in such systems as the Great Lakes (the data for which many models are developed) where water concentrations are at or well below detection limits, around 0.5 ng/L or less but could be very important in the Hudson with concentrations of PCBs in the water orders of magnitude higher (and predicted to remain high for a while but diminishing).

A better job could be thus done in comparing the values used to literature values. A statement on page 79 is made to the effect that distribution values (Table 6.1) compare reasonably to the literature, but no actual values or data are reported, thus not substantiated.

The spatial and temporal scales are reasonable based upon the system and available data. The 4 river segments seem to capture the general range from high in Thompson Island Pool (TIP) to the lows in the lower river.

B2. *Was the FISHRAND calibration procedure appropriately conducted? Are the calibration targets appropriate to the purposes of the study?*

The explanations for the sensitivity analyses are reasonably detailed and the effort is commendable. It would be useful to have a list of every single parameter that was examined; it is unclear and hence cannot be verified if some key parameter has not been examined. The table on page 74, book 3, only lists those found to have greatest impact on the outcome. Fish weight is listed in this table, but it is unclear if it was tested further in the calibration (not listed as such in the text below). Insofar as calibrating to the Gobas 1993 model, this seems to have been well done (but note the comments in question 1 above).

B3. *In addition to providing results for FISHRAND, the Revised BMR provides results for two simpler analyses of bioaccumulation (a bivariate BAF model and an empirical probabilistic food chain model). Do the results of these models support or conflict with the FISHRAND results? Would any discrepencies among the three models suggest that there may be potential problems with the FISHRAND results, or inversely, that the more mechanistic model is taking into account variables that the empirical models do not?*

Theoretically, the rationale behind the bivariate BAF (bBAF) and empirical probabilistic models are reasonable- to an extent. A goal behind the bBAF is to examine the potential relative contributions of sediment vs water sources to fish PCB burdens by direct regression comparisons. Regressions were run between lipid-normalized fish PCBs and water or sediment concentrations, water on a whole volume basis, and sediment normalized to organic carbon. Because of limited sediment data as well as spatial heterogeneity in sediment PCBs, the sediment data were obtained from the HUDTOX predictions whereas the water data were observed mean values for each of the four segments of the river. Data for the years of sampling from 1975 to 1998 were included. The BMR considers that the relative importance of sediment or water sources to the fish PCBs can be approximately evaluated based upon the goodness of fit of these regressions. This approach was developed in the PCMR but based upon a more limited data set and was criticized by several of the Peer reviewers. First, because sediment data are predicted but water are observed means, there is a possible inherent bias in comparing fits against fish PCBs between these two variables- the sediment data have no variability while the water data do (see Figure 1 below).

One such criticism is the employment of both variables, sediment and water, in a multiple regression for predicting fish PCBs because sediment and water concentrations are not independent of one another (an important assumption of multiple regression models). The response in the BMR considers that because of the nature of the river system, PCBs in water and sediments are not in equilibrium with one another, and hence it is justified to include both in a multiple regression (statistical procedures do not "care" about equilibrium). This is not a justification and is statistically invalid. This was also criticised in the Responsiveness summary (page 86/87); the response was the best fit (i.e. higher r^2) was obtained when both variables are included in the model. A scatter plot of sediment vs water concentrations was included suggesting a weak relationship. However, examination of the data show strong site differences in both sediment and water concentrations, which must then be taken into account when examining the water to sediment PCB relationship. A plot of log-10 transformed water PCBs against sediment PCBs shows that 67% of the variability in water may be explained or related to sediment concentrations when differences among the 4 segments are taken into account using analysis-of-covariance (ANCOVA; see Figure 2 below).

Using ANCOVA, there is found to be a significant difference in the relative concentration of water to sediment among the three of the 4 study segments of the river (segments 2 and 3 are similar). The ANCOVA results demonstrate that the slope is the same among the segments. (Note this may be an artifact of how the sediment concentrations are generated by the HUDTOX model, to decline at a similar rate relative to water concentrations among all reaches of the river over time; this needs to be examined.) Absolute concentrations are higher in TIP, but the intercept is lower, indicating a lower relative proportion of PCBs in water relative to sediment than downstream. If the reciprocal relationship is considered, this would mean that the ratio of the fugacities of PCBs in sediments relative to water are highest at TIP (actual ratio cannot be determined here because the water data are not expressed as freely dissolved PCBs normalized to organic carbon), similar in segments 2 and 3, and lowest at the reach below Federal Dam. A sediment to water fugacity ratio greater than one will indicate the net flux of PCBs will be out of the sediments into the water.

What these data clearly indicate is that sediment and water PCB concentrations are NOT INDEPENDENT of one another. It does not matter if the two media are not in equilibrium. There are several statements in the BMR which uses this latter point, and several others, to justify using these 2 variables together in a bivariate regression, but this is neither statistically nor logically valid, nor can the data be used to identify relative importance of sediment and water pathways to the biota. Also, as stated above, because the sediment data have no inherent variability in them, but the water data do, this also makes it impossible to establish the relative contribution of either media to biota PCB burdens. Nonetheless, as the following graphs will demonstrate, water and/or sediment are important driving factors behind biota PCB burdens and the relative importance of either may be less critical when concentrations are so high. Establishing water or sediment as the important source may be more important in a situation such as Lake Ontario, for example, where water concentrations are very low and a high sediment to water fugacity results in PCBs moving from sediments into the water column.

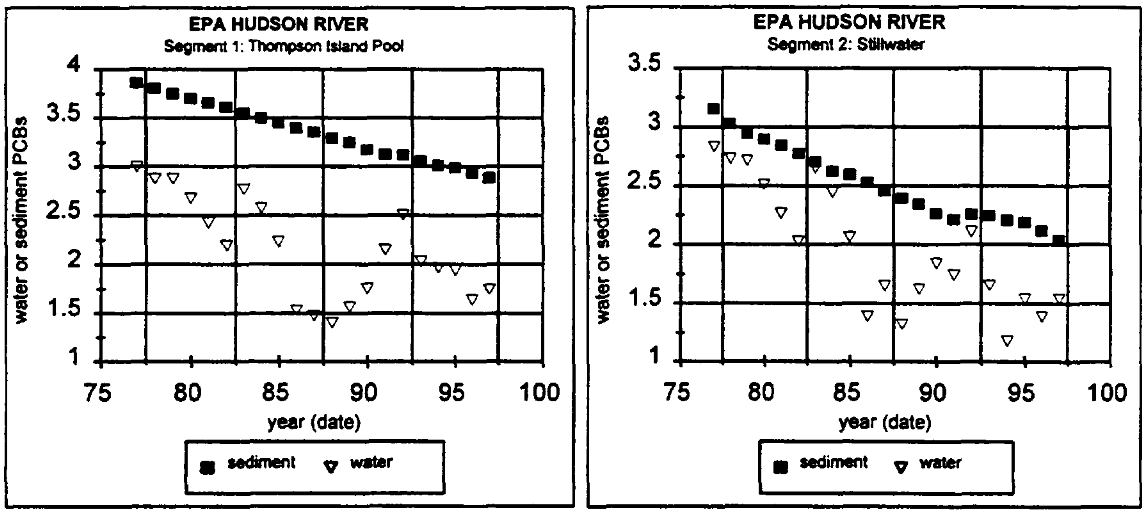

Figure 1. (Illustrative) Annual HUDTOX predicted sediment and averaged water concentrations for 2 segments of the Hudson. Note that because sediment values have no variability but the water values are variable, any comparison between water and sediment as sources of PCBs will be biased towards the sediment values on the basis of goodness-of-fit (r^2, etc). Nonetheless, the strong and significant relationships between both sediment and water concentrations and PCB concentrations in biota is extremely important and indicates a very strong driving force in the system.

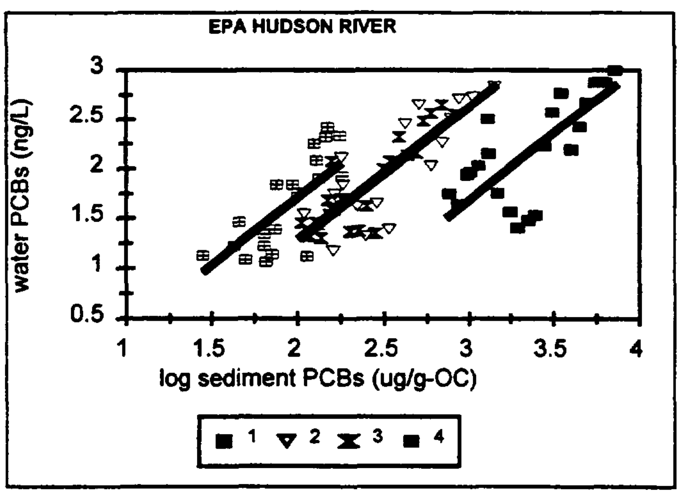

Figure 2. Water concentrations are strongly related to sediment PCB concentrations on a log-10 transformed basis, based upon data used in the Bivariate BAF model (r^2= 0.67). Note segment one is Thompson Island Pool (TIP).

Comments on the Bivariate BAF analysis.

Table 1. Summary of regression statistics for Hudson River fish lipid-normalized PCBs vs water and sediment PCBs. Statistics performed with SYSTAT.

species	X variable(s)	n	intercept	slope	r^2 (adj)	ANCOVA interaction prob	prob
brown bullhead	water	45	258.6	2.054	0.36		0.0000
log bullhead	log water	45	1.58	0.509	0.30		0.0001
	log water, segment	45			0.64	0.008	0.0000 0.0000
largemouth bass	water	40	469.3	4.73	0.61		0.0000
log LM bass	log water	40	1.94	0.515	0.48		0.0000
	log water, segment	40			0.69	0.58	0.0000 0.0004
yellow perch	water	19	265.3	4.15	0.46		0.0008
log y perch	log water	19	0.777	0.971	0.69		0.0008
	log water, segment	19			0.86	0.35	0.0000 0.013
log bullhead	log sediment	45	0.81	0.695	0.68		0.0000
	log sediment, segment	45			0.79	0.38	0.0000 0.0002
log LM bass	log sediment	40	1.403	0.587	0.75		0.0000
	log sediment, segment	40			0.88	0.06	
log y perch	log sediment	19	1.12	0.66	0.37		0.0034
	log sediment, segment	19			0.68	0.003	0.0006 0.030

Only a subset of the regressions were examined here. Several important points. The first is a puzzling discrepency between the regression results calculated here based upon the data from the BMR Tables 4.5, 4.7 and 4.8. For example, the intercept (constant) for brown bullhead was listed in Table 4.9 as 80.5 and the r^2 of 0.42, which differs from these results. Differences were noted for the other species as well. The BMR does not state which program was used to compute

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the statistics. I recently was given a very alarming reference to a study which demonstrates that statistics performed with **Excel are NOT TO BE TRUSTED and are extremely faulty** (McCullough and Wilson 1999). The BMR does state that Excel was used as a spreadsheet; if this is the case for the statistics, they must be recomputed with a "real" statistics program.

Second, the data were not examined for homogeneity of variance, except for one reference comment on page 54 of Book 3, BMR, that examination of a scatter plot (Fig. 4.4) does not reveal heteroscedasticity. This has to be tested on the data, not eyeballed. I performed Bartlett's test for homogeneity of variance on brown bullhead, largemouth bass and yellow perch (these 3 species were selected as examples from the 3 trophic positions for fish) and found that for the first two species, the data were heteroscedastic until log-10 transformed, thus at least for those it is most appropriate to perform statistical analyses on log transformed data. Yellow perch could be done either way, but for consistency of handling, I ran regressions on log transformed data (using Systat).

Next, the data should be considered in light of differences among the 3 segments in terms of water and sediment concentrations, and how these affect the relationships between the fish and the media PCB concentrations. This is done by ANCOVA, as shown in Figure 2 for the sediment and water data. The results are very interesting. Substantially more variability is explained in the fish PCB and water relationship when the River segment is taken into account for all three species. All regressions are highly significant. Note that in the BMR, page 54, section 4.2, the discussion pertaining to the single factor species-media regressions makes a weak, qualitative statement "despite increase in r^2, the quality of fit remains weak". This is rather subjective; comparing regression results uses more than just the r^2, which pertains to degree of variance explained by the model. The probabilities must also be reported. As shown in the table above, the results are highly significant. But the strengths of these relationships cannot be used to justify relative contribution of either sediment or water to fish PCBs. For example, the ANCOVA r^2 for largemouth bass is 0.69 for water&segment compared to 0.88 for sediment&segment. Using the rationale of the BMR, this would suggest that sediment is more important as a source of PCBs to largemouth than water but the opposite would be true for yellow perch. This is trying to explain too much with these data. Note in the table above, significant probabilities for the ANCOVA interaction term are significant for brown bullhead with water&segment and yellow perch (and marginally largemouth) with sediment&segment, indicating that the slope of the fish-PCB to media relationship varies among segments. Analyses can be done to detect which segments are different (although this may be due to variable samples of fish in each segment, as for yellow perch with only 2 to 4 fish in two of the segments; have to be careful not to overinterpret the data).

Relationships between fish lipid-normalized PCBs and water or sediment PCBs are shown for two segments.

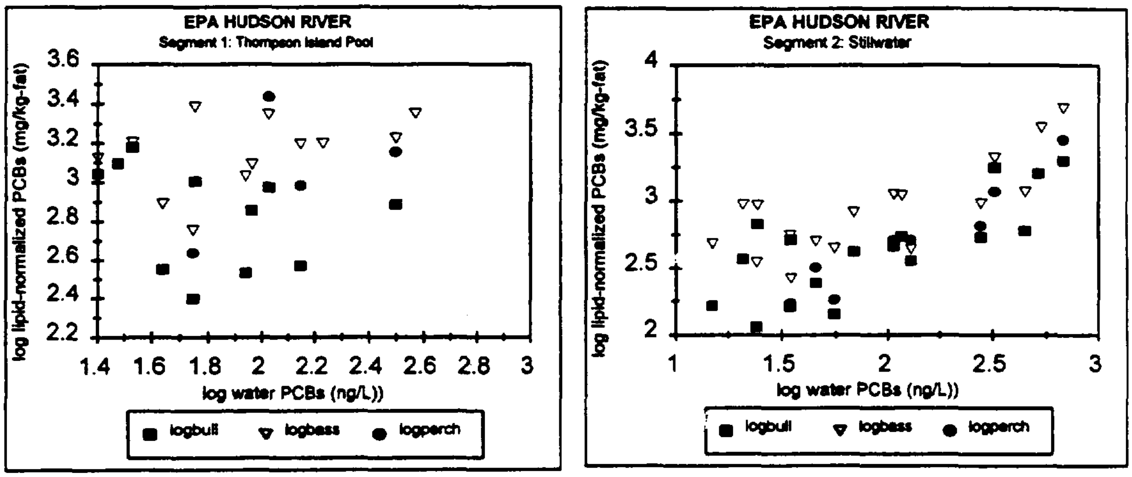
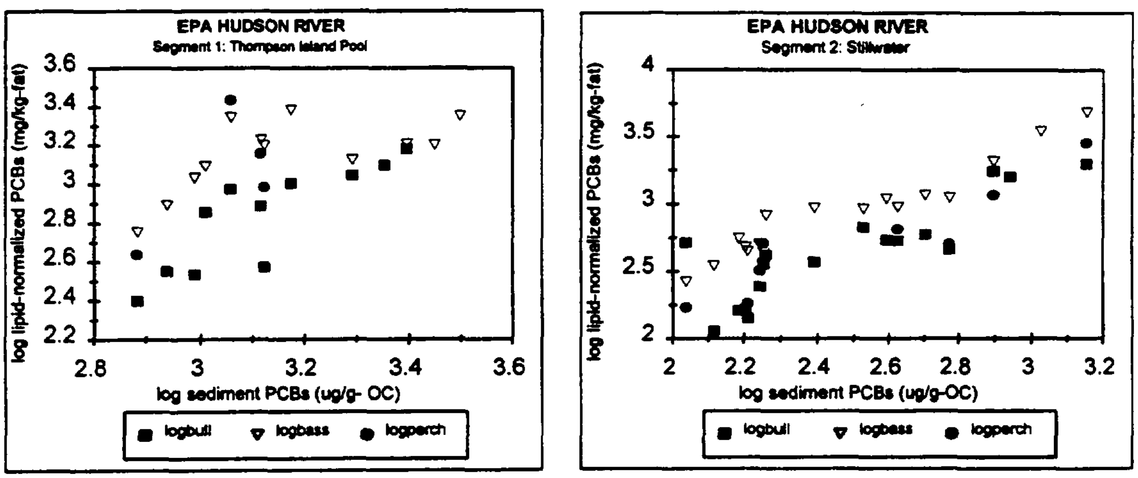


Figure 3. Lipid-normalized PCBs in three fish species in the first two river segments used in the



bioaccumulation models.

Figure 4. Lipid-normalized PCBs in three fish species relative to sediment PCBs in the first two River segments used in the BMR bioaccumulation model analyses.

Table 2: statistical analyses for data in Figures 3 & 4. Variables are log-10 transformed.

parameters (Y)	independent variables (X)	n	r^2	probability	ANCOVA interaction p
Segment 1: TIP					
fish PCBs	water, species	27	0.31	0.62 0.023	0.21
	sediment, species	27	0.62	0.0002 0.002	0.11
Segment 2: Stillwater					
fish PCBs	water, species	42	0.67	0.00000 0.0008	0.24
	sediment, species	42	0.85	0.00000 0.00001	0.99

These results demonstrate that it is harder to establish a relationship between fish PCBs and water in Thompson Island Pool because of the variability in the measurements (and likely real). This does not mean that water is less important than in other segments, it is just harder to establish trends based upon variable data. But the strengths of these relationships in general are astonishing, due to the very high water and sediment PCB concentrations. Many food web models, including the Gobas models, have been constructed based upon Great Lakes food webs and contaminant distributions. Following the ban in use of PCBs in the mid 1970's, fish PCBs plummeted rapidly from the 1970s when monitoring programs were first implemented, but by the 1980's concentrations in biota have declined only slowly (e.g. Bentzen et al. 1999; DeVault et al. 1996). Unfortunately, very little to no water data were collected in the early years but hindcasting analyses suggest that the initial rapid decline would be attributable to changes in water concentrations of the hydrophobic chemicals down to levels less than about 1 ng/L (PCBs in Lake Ontario water are probably now less than 0.5 ng/L). In these systems, food chain biomagnification is the main force behind PCB concentrations in biota at higher trophic positions, and contribution directly from water is minimal, but it shows how sensitive the system is to water concentrations. There is an underlying belief in the PMR that uptake from food is the most important for the piscivores, but this may not have been adequately examined, as discussed above in question 1. The difference among the three species illustrated in the above analyses does support trophic level differences contribute to their PCB concentrations (although the effect of age and size cannot be accounted for here). The FISHRAND model could be used to test this more fully. Results look pretty good simply because of the strong driving force of water and sediments (which are obviously linked) for all biota.

This is further illustrated by examining plots of lipid-normalized PCBs among pairs of biota. The relationships are very clear even between pairs of fish which are not closely related to one another in the trophic food web, such as brown bullhead and largemouth bass (Figure 5). Of the 4 fish pairs shown in Figure 5, these two had the least variable relationship with an $r^2 = 0.77$. This identifies that an external driving force operates on both species independent of food web structure. It is also useful to compare the BAFs derived here to literature values. This will be discussed under the probabilistic model.

Note that it is also useful to examine PCB congener profiles in sediment, water, and the biota (invertebrates as well as fish), for example as in Metcalfe and Metcalfe (1997). The use of Tri+PCBs in the models is well justified, but the congener data from the 1990's sampling should be included in the examination of sediment vs water PCB sources to biota.

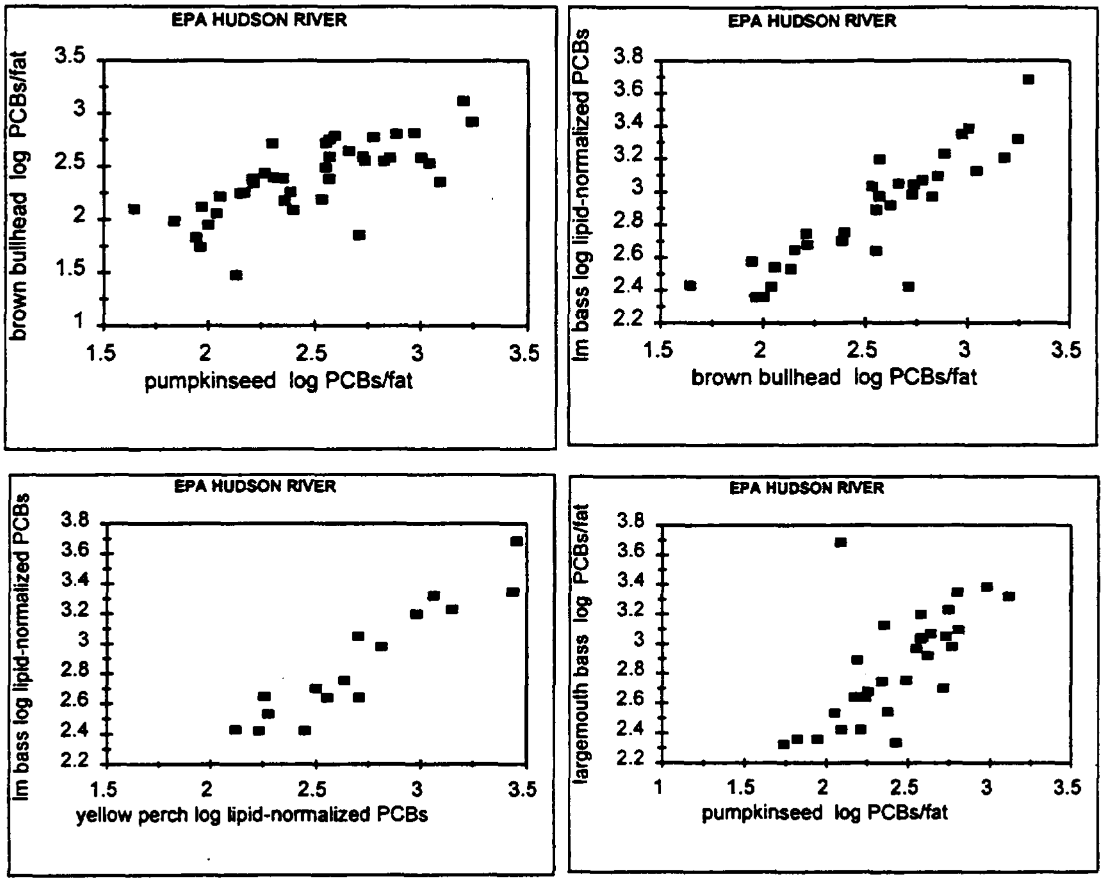


Figure 5. Examples of relationships for lipid-normalized PCBs between pairs of Hudson River fish.

log (pumpkin) = 0.29 + 0.96 (log bullhead) $n = 32, r^2 = 0.69$
log (lm bass) = 1.08 + 0.71 (log bullhead) $n = 33, r^2 = 0.77$
log (lm bass) = 0.92 + 0.72 (log y perch) $n = 18, r^2 = 0.73$
log (lm bass) = 1.16 + 0.71 (log pumpkin) $n = 30, r^2 = 0.66$

Empirical Probabilistic Food Chain Model:

The data and calibrations used in the probabilistic model are not entirely clear. The model covers three reaches (river miles 189, 168, 154) but the benthic invertebrate data shown in Figure 5.2 are from around TIP and below Federal Dam. As stated previously, it would be useful to have tables outlining sample sources, years, species, locations, etc. And while contaminant analyses may be done only for some limited samples, biotic descriptions for benthic creature distributions must be available and could be briefly described, to highlight that the ones used for PCB analyses in these models are representative of the river, etc. The water column invertebrates are especially poorly described/documented in the BMR. As elsewhere, in section 5.1.4, mention is made of comparison to literature values but nowhere are any of these summarized. It is noteworthy that mention is made at several points that the Hudson River is unique and thus it is difficult to compare any results to other systems. It is valid to consider that the flow and general physical dynamics of the river are unique, and hence the HUDTOX model is developed for this system. But this does not necessarily follow for consideration of bioaccumulation models, which are driven by biotic relationships and characteristics of the species. In general, it would be very useful to compare results and observations from the Hudson to other systems, specifically concentrations and derived BAFs.

The BAFs here for biota to water are not easily compared to other data nor to the sediment or biota to biota BAFs because water is not expressed relative to organic carbon. Understandably, data are not available for the temporal patterns, but FISHRAND nonetheless makes assumptions to estimate freely dissolved PCBs and water column organic carbon. It is not clearly justified why this could not be done for these BAFs, as well. The assumption is made that water column invertebrates are at steady state with water PCBs, hence the invertebrate data could be used to generate a possible distribution of what the freely dissolved PCBs normalized to carbon values might be. A value of 13.2 for water column invertebrates is assigned; this seems to be rather high and out of line with the other data, and with published values (error?).

The BAFs are not interpreted to any great extent; the sole purpose was to use them in a predictive capacity (which is not that appropriate; FISHRAND does this and can be used to generate the BAFs as well, using population averages or midpoints, etc.). A BAF around one for sediment invertebrates is used to demonstrate steady state conditions between them and sediments. The BAF for planktivores is just 1.7 (based upon 50th percentile, but not what was used, which was stated at 1.08- not sure why, either). Either value, especially the lower one, suggests little to no biomagnification of PCBs between planktivorous fish and invertebrates, equivalent to equilibrium directly with water. The BAF for the piscivores relative to planktivores is 2.5, closer to the approximate suggested value of 3 between trophic levels indicating biomagnification (Gobas

1993). Note that a recent paper by Morrison et al. (1999) offers estimated BAFs for a number of hydrophobic chemicals in the Lake Ontario food web.

Note that while it is standard protocol to organic carbon normalize sediment data, Landrum and Robbins (1990) point out that this could be misleading at times, dependent upon the contribution of other fine clays, sediment lipid material, etc, could also bind to organic contaminants. This could be a factor behind some of the observed BSAF variability.

In summary, the bivariate BAF "model" needs to be revised with appropriate treatment of the statistics and fuller interpretation of the data. Given the predicted declines in water and sediment concentrations over time, these simple equations actually can be used to generate average estimates of fish concentrations, but based upon the assumption that the relationship between water and sediment concentrations is adequately modelled as shown. The probabilistic model can be used in an equally simple manner to estimate contaminants in other biota that are not treated by the simple time data, but it would be preferable to express the water concentrations on an equivalent basis to the other BAF estimates. Note that this was done by Webster et al. (1999) who described a synoptic indicator, equating all biota and physical compartments (air, water and sediment) in terms of lipid partitioning (equilibrium lipid partitioning). This is based upon fugacity relationships, but describes what are essentially BAF's on an equivalent basis. Incorporating distribution functions for the parameters makes it more broadly descriptive. The FISHRAND model is obviously more complex, and as such incorporates many more assumptions and parameters which are not all well determined. But the advantage of the model is that it does allow examining more specific factors which may regulate PCB partitioning and retention into biota, hence a more mechanistic approach. However, because of the uncertainties of several quantities, it can be used as a tool for testing specific questions about these various factors. For example, if there are significant shifts in predator-prey dynamics in the river, due to species invasions or catastrophic losses in some age classes of particular fish species, the model can be refined to predict what changes in partitioning of PCBs may result. The Campfens and Mackay (1997) food web bioaccumulation model was developed for this type of flexibility (using a food web matrix rather than a set of fixed feeding parameters).

B4. *Sediment exposure was estimated assuming that fish spend 75% of the time exposed to cohesive sediments and 25% to non-cohesive sediment for the duration of the hindcasting period. The FISHRAND model was calibrated by optimizing three key parameters and assuming the sediment and water exposure concentrations as given, rather than calibrating the model on the basis of what sediment averaging would have been required to optimize the fit between predicted and observed. Is the estimate of sediment exposures reasonable?*

The estimate of sediment exposures is likely reasonable. Despite the heterogeneity of the sediments, fish are mobile and hence will be exposed to sediments. Using an average is thus reasonable. However, as discussed in question 1, it would be useful to use FISHRAND to examine what possible variations in sediment to water fugacity ratios might have on fish PCBs. This is a useful application of the model. This isn't needed to use for optimizing fit, but for predicting the consequences of other changes (changes in sediment characteristics, for example, from increased sewage discharge or other activities, which might thus change the bioavailability of PCBs in the sediments differently from what is predicted based upon current conditions).

B5. *The FISHRAND model focuses on the fish populations of interest, e.g. adult largemouth bass, juvenile pumpkinseed, etc, which encompasses several age-classes but for which key assumptions are the same, e.g. all lm bass above a certain age will display the same foraging behaviour. This was done primarily because it reflects the fish data available for the site. Is this a reasonable approach?*

This is a reasonable and fairly standard approach. The goal is to predict the possible range of PCB concentrations in the fish population, not individuals, as a function of changing sediment and water concentrations over time.

General questions:

G1. *What is the level of temporal accuracy that can be achieved by the models in predicting the time required for average tissue concentrations in a given species and river reach to recover to a specified value?*

They can be no better than the temporal resolution of the water and sediment data. Elimination rate constants estimated from FISHRAND can indicate temporal resolution.

G2. *How well have the uncertainties in the models been addressed? How important are the model uncertainties to the ability of the models to help answer the principal study questions? How important are the model uncertainties to the use of model outputs as inputs to the human health and ecological risk assessments?*

The uncertainties have been reasonably well addressed in the bioaccumulation models. These are obviously important in the FISHRAND model because of the number of parameters with unknown precision, and the discussion in Chapter 8 reasonably well laid out. However, the justification of using the Gobas 1993 model "because it has been validated for a number of sites" is somewhat misleading and philosophically flawed. The reference to Burkhard (1998) in 8.1.2.2 as an example of such is incorrect because he compared two models for assessing important parameters using the same Lake Ontario data (Oliver and Niimi 1988) which has been used by several modellers in the development of their models, including Gobas (1993). Some of the parameters have been updated in subsequent versions or other models (eg later Gobas, Morrison et al. 1999), as discussed in question 1 above. The other cited reference to Morrison et al. (1997) is based upon an alternate site, western Lake Erie, which is very different from Lake Ontario, and her model was further modified in her latest application on Lake Ontario. It is critical to review and summarize these various efforts to as great extent as possible before using ANY model for regulatory decisions. This underscores a characteristic which is severely lacking in the BMR in general, which is a deficiency of examining results from other sites which may be used to help interpret the Hudson River observations. As stated previously, in terms of bioaccumulation models, fish are physiologically similar among widespread temperate locations and data from other sites may be used in the Hudson, i.e. respiration, uptake efficiencies, role of lipid in k_2, etc. All these parameters which influence uptake and retention of PCBs by fish are fairly ubiquitous. It is not clear how well any of these were used in the BMR sensitivity analyses but the issue is of importance for application to human health and risk assessments.

G3. *It is easy to get caught up with modeling details and miss the overall message of the models. Do you believe that the report appropriately captures the "big picture" from the information synthesized and generated by the models?*

As discussed above, both the bivariate BAF and empirical probabilistic models stop short of some useful observations, the first because of flawed statistical analyses, the second because of inconsistent calculations of BAF which are not all comparable (i.e. the use of whole water concentrations; note this is not an issue for the bivariate BAF which examines trend relationships.) Discussion of results and implications there of tend to be brief in all the sections. As discussed in the previous question, this also pertains to the lack of comparison to outside observations and data. There is a wealth of information and observations to be compared to in the Great Lakes, where many bioaccumulation models have been developed (often on the same data set) and a more recent set of papers which have examined related issues. These include the development of the standardized approach for comparing the distribution of PCBs among the biota and physical media (ELP, for equilibrium partitioning; Webster et al. 1999) which is useful because it allows us to predict how changes in one compartment will affect PCB concentrations in the others. Various studies have considered what the half life of PCBs are in biota in order to estimate how long it will take the fish to reach acceptable target concentrations (International Joint Commission sets a target of 100 ng/g ww for protection of wildlife). For example, an average PCB half life for all biota in Lake Ontario is found to be approximately 12 years and it will take 3 to 4 half lives to reach the IJC target (Bentzen et al. 1999). It certainly is interesting to note that lipid-normalized PCBs in comparable fish species in Lake Ontario, for example yellow perch, were at their measured maximum of 125 mg/kg ww in the mid 1970's which is lower than yellow perch PCB concentrations in the Hudson River in the 1990's.

Nonetheless, the "big picture" is available for the bioaccumulation models, but is presented in a fragmented manner (partly a nature of the report style) and would be enhanced by a more thorough treatment of the results in a broader context.

G4. *Other comments or concerns with the Revised Baseline Modeling Report.*

Some errors are noted (not in any particular order) plus some general recommendations:

p. 4, reference to Sloan et al. 1984 is not consistent with the references (1985 given).

p. 5, top paragraph: "Connolly et al. predicted levels in Hudson River striped bass..." is an example of a vague statement. What type of levels and to what degree of accuracy?

p. 61, reference to section 3.5 should read 3.5 (both on 2nd and 4th lines).

p. 93, "Buckhard" should read Burkhard.

Figure 3.3: use consistent units for concentrations.

Delete Fishpath results since these are not used.

The species Pontoreia does not exist; presumeably mean Pontoporeia, however it should be noted that the classification of Pontoporiea was changed about a decade ago to Diporeia.

p. 31, it is confusing to use C for the constants when it is also used for concentration.

p. 75, need to elaborate on the nature of the water column invertebrates. What about algae? Identify the basic protocol used to collect samples, and when, etc (commented on in more detail above).

References

Bentzen, E., D. Mackay, B.E. Hickie, and D.R.S. Lean. 1999. Temporal trends of polychlorinated biphenyls (PCBs) in Lake Ontario fish and invertebrates. Environ. Rev. 7: 203-223.

Campfens, J. and D. Mackay. 1997. Fugacity-based model of PCB bioaccumulation in complex aquatic food webs. Environ. Sci. Technol. 31: 577-583.

DeVault, D.S., R. Hesselberg, R.W. Rodgers, and T.J. Feist. 1996. Contaminant trends in lake trout and walleye from the Laurentian Great Lakes. J. Great Lakes Res. 22: 884-895.

Fisk, A.T., R.J. Norstrom, C.D. Cymbalisty and D.C.G. Muir. 1998. Dietary accumulation and depuration of hydrophobic organochlorines: bioaccumulation parameters and their relationship with the octanol/water partition coefficient. Environ. Toxicol. Chem. 17: 951-961.

Hendriks, A.J. 1995. Modelling non-equilibrium concentrations of microcontaminants in organisms: comparative kinetics as a function of species size and octanol-water partitioning. Chemosphere 30: 265-292.

Hoff, R.M., et al. 1996. Atmospheric deposition of toxic chemicals to the Great Lakes: a review of data through 1994. Atmosph. Environ. 30: 3505-3537.

Landrum, P.F. and J. A Robbins. 1990. Bioavailability of sediment-associated contaminants to benthic invertebrates. Chapter 8, Sediments: Chemistry and toxicity of in-place pollutants. R. Baudo, J. Giesy and H. Muntau, eds. p 237-263. Lewis Pub., Michigan.

McCaullough, B.D. and B. Wilson. 1999. On the accuracy of statistical procedures in Microsoft Excel 97. J. Computational Stat. Data Analysis. 31 (July).

Metcalfe, T.L. and C.D. Metcalfe. 1997. The trophodynamics of PCBs, including mono- and non-ortho congeners, in the food web of North-Central Lake Ontario. Sci. Total Environ. 201: 245-272.

Morrison, H.A., D.M. Whittle, C.D.Metcalfe, and A.J. Niimi. 1999. Application of a food web bioaccumulation model for the prediction of polychlorinated biphenyl, dioxin, and furan congener concentrations in Lake Ontario aquatic biota. Can. J. Fish. Aquat. Sci. 56: 1389-1400.

Thompson, S., M. Macleod, and D. Mackay. 2000. A modelling strategy for planning the virtual elimination of persistent toxic chemicals from the Great Lakes: an illustration of four contaminants in Lake Ontario. J. Great Lakes Res. in press.

Wainman, B.C., D.J. McQueen, D.R.S. Lean. 1993. Lipid content of freshwater zooplankton. J. Plankton Res. 15: 1319-1332.

Webster, E., D. Mackay, and K. Qiang. 1999. Equilibrium lipid partitioning concentrations as a multi-media synoptic indicator of contaminant levels and trends in aquatic ecosystems. J. Great Lakes Res. 25: 318-329.

note: further comments are forthcoming (section one).

Recommendations: Bioaccumulation models

Accept with minor revisions as indicated.

Dr. Steven Eisenreich

Biography not available at time of print

Hudson River PCBs Site Reassessment RI/F S
Baseline Modeling Report
Peer Review 3
Comments by Steven J. Eisenreich

Fate and Transport (HUDTOX)

1. The HUDTOX model links components describing the mass balance of water, sediment, and PCBs in the Upper Hudson. Are the process representations of these three components compatible with one another, and appropriate and sufficient to help address the principal study objectives?

The process representations in the mass balance of water, solids and PCBs in the Upper Hudson River seem appropriate. The key processes in the PCB mass balance in HUDTOX and acting as inputs to the Bioaccumulation models are (1-1) PCB mobilization from contaminated sediments in the reaches of the river upstream of Fort Edward by sediment resuspension and sediment-water transfer, (1-2) tributary solids loads, (1-3) air-water exchange or *net* volatilization, (1-4) net sediment accumulation of mass and PCBs, and (1-5) the three-phase partitioning model.
(1-1)The data suggest that sediment-water transport of PCBs under low flow (2x average flow) non-scouring conditions from cohesive sediments dominates PCB inputs to the water column. This is inferred from PCB congener profiles (particulate-like) in the water column and higher concentrations than foreseen based on upstream transport. The importance of this component relies on effective sediment-water mass transfer coefficients (relatively uncertain) and surficial sediment PCB concentrations (measured and modeled). If the mechanistic pathway is not as described in the report and inferred from water column PCB data, then the model formulation is incorrect even if hindcasts and forecasts seem appropriate. Much of this is based on knowing PCB concentrations in the water over the Upper Hudson River over time when water and sediment sampling techniques as well as PCB analytical procedures have changed considerably. Although the EPA has gone to great length to interrogate and evaluate packed-column GC vs capillary column GC techniques, this still results in a considerable uncertainty in the data upon which inferences on sediment-water release are based.
(1-2) The report concludes that tributary solids loads dominate sediment loads in the upper HR; this must be so given the mass balance modeling of various reaches. The sediment load was evaluated on a small fraction of the tributaries and the tributary PCB load was not determined effectively on any of the tributaries. The EPA report does a good job of estimating non-monitored tributary loads but the result retains considerable uncertainty. Also, regressions relating TSS and flow in the Hudson River all show that TSS varies over a factor of ten for each flow at each site for the reported data. Was the uncertainty of this aspect incorporated into the model calibration and uncertainty?
(1-3) See below.
(1-4) This representation of the processes by the model seems very appropriate.
(1-5) See below
The model representations, with exceptions noted, are appropriate and sufficient to help address the principal study objectives.

2. The HUDTOX representation of the solids mass balance is derived from several sources, including long-term monitoring of tributary solids loads, short-term solids studies and the results of

GE/QEA's SEDZL model. The finding of the solids mass balance for the Thompson Island Pool is that this reach is net depositional from 1977 to 1997. This finding has also been assumed to apply to the reaches below the Thompson Island Dam. Is this assumption reasonable? Are the burial rates utilized appropriate and supported by the data? Is the solids balance for the Upper Hudson sufficiently constrained for the purposes of the Reassessment?

The conclusion reached in the RBMR that the TIP reach is net depositional is well supported in the report and is reasonable given the generation of solids upstream and in tributaries, and the bathymetry and water flows in the TIP. The assumption that the reaches below the TID are also net depositional is reasonably well supported by data (sediment PCB concentrations) and/or modeling.

3. HUDTOX represents the Upper Hudson River by segments of approximately 1000 meters in length in the Thompson Island Pool, and by segments averaging over 4000 meters (ranging from 1087 to 6597 m) below the Thompson Island Dam. Is this spatial resolution appropriate given the available data? How does the spatial resolution of the model affect the quality of model predictions?

The spatial resolution of the model is dependent, in part, on the dimensions of the study area and the availability of sufficient data at the necessary resolution. Given the availability of sediment and water data in the Upper Hudson River over time and space, and the scarcity of tributary solids loading over much of the area of interest, the spatial resolution of the model seems appropriate.

4. Is the model calibration adequate? Does the model do a reasonable job in reproducing the data during the hindcast (calibration) year? Are the calibration targets appropriate for the purposes of the study?

The model calibration is adequate and does a reasonable job in reproducing the data during the hindcast (calibration) year.

5. HUDTOX employs an empirical sediment/water transfer coefficient to account for PCBs loads that are otherwise not addressed by any of the mechanisms in the model. Is the approach taken reasonable for model calibration? Comment on how this affects the uncertainty of forecast simulations, given that almost half of the PCB load to the water column may be attributable to this empirical coefficient?

The report specifies that release of PCBs from primarily cohesive sediments under low flow conditions (2x average flow) is an important feature of the PCB mass balance accounting for the majority of inputs in the Upper Hudson River. The PCB congener profile in the water column and sediment is similar suggesting a clear linkage.

A factor that may be important in influencing sediment-water transfer of apparent particulate PCBs (same congener profile) - read, sedimentary colloidal OM, is groundwater recharge in the near shore sediments or in the sediments of the main channel. This seems to be the only remaining plausible mechanism whereby cohesive sediments contaminated with PCBs under largely low-flow conditions (i.e., < 2x average flows) contribute the majority of the PCBs to the water column in the overall PCB mass balance. If this is true, perhaps the irrigation of the sediments by recharge water under low flow conditions advects both dissolved but more importantly colloidal OM and associated PCBs into the water column. To incorporate this in a clear mechanistic approach based on GW flows along the miles of the Upper Hudson River would probably confound the modeling framework. The EPA has incorporated this feature empirically in the sense that they adjust sediment-water transfer coefficients to account for somewhat unusual observations as stated above. Is there any other conceivable source of the PCBs in these sections not accounted for in the model (e.e., higher tributary loads of PCBs)? It is uncomfortable as a scientist to acknowledge a contaminant input or mobilization pathway that cannot be described or mechanistically understood, especially as it appears so important in the mass balance model.

6. Are there factors not explicitly accounted for (e.g., bank erosion, scour by ice or other debris, temperature gradients between the water column and sediments, etc.) that have the potential to change conclusions drawn from the model?

The factors mentioned here (bank erosion, scour by ice or other debris, temperature gradients between the water column and sediments) are likely not to have any significant potential to change conclusions drawn from the model. Temperature gradients between the water column and sediments will not influence partitioning processes (not very temperature sensitive) or sediment mass transport to any significant extent. Bank erosion will often, of course, provide coarse sediment to the water column under erosional conditions. From a mass balance of solids or PCBs, this is already accounted for by adjusting apparent tributary loads of solids between monitoring sites. Scour by ice, as pointed out in the RBMR, will not have any major influence in changing conclusions of the model output.

7. Using the model in a forecast mode requires a number of assumptions regarding future flows, sediment loads, and upstream boundary concentrations of PCBs. Are the assumptions for the forecast reasonable? Is the construct of the hydrograph for forecast predictions reasonable? Should such as hydrograph include larger events?

The model forecast incorporates numerous informed and scientific assumptions. They appear to be justified and appropriate given the availability of data, the quality of the model calibration and the questions placed before EPA. I cannot judge whether the hydrograph used in the forecast is appropriate except that it adequately addresses known hydrological variables. It is of major concern to many that large scale episodic events equivalent to 200 or 300 year floods may mobilize substantial amounts of sediment and associated PCBs. W. Lick (U of CA-Santa Barbara) has often said that episodic large scale events such as floods, hurricanes, anomalous snow accumulation and melt, and dam failures are the dominant features driving long-term ecosystem responses. However it does not seem justified to introduce even greater uncertainty into the model forecast.

8. The 70-year model forecasts show substantial increases in PCB concentrations in surface sediments (top 4 cm) after several decades at some locations. These in turn lead to temporary increases in water-column PCB concentrations. The increases are due to relatively small amounts of predicted annual scour in specific model segments, and it is believed that these represent a real potential for scour to uncover peak PCB concentrations that are located from 4 to 10 cm below the initial sediment-water interface. Is this a reasonable conclusion in a system that is considered net depositional? After observing these results, the magnitude of the increases was reduced by using the

1991 GE sediment data to initialize conditions for forecast runs. Is this appropriate? How do the peaks affect the ability of the models to help answer the Reassessment study questions?

This is an entirely reasonable conclusion that is considered net depositional since both sediment delivery and resuspension occurs. The Upper Hudson River system from the measurement of the solids inputs and sediment accumulation rates and the modeling, the Upper Hudson river system must be *net* depositional. After reviewing the implications of finding that some surficial sediments must increase in concentration over some reaches and time periods, better data was used to initiate the model calculation. The phenomenon did not disappear but rather diminished in importance. This was a reasonable approach and appropriate. The peaks (vague term) should have no substantial impact on the ability of the Reassessment to answer the study questions.

9. The timing of the long-term model response is dependent upon the rate of net deposition in cohesive and non-cohesive sediments, the rate and depth of vertical mixing in the cohesive and non-cohesive sediments and the empirical sediment-water exchange rate coefficient. Are these rates and coefficients sufficiently constrained for the purposes of the Reassessment?

Net mass deposition (i.e., accumulation) is reasonably constrained given the magnitude the mass balance models. The rate and depth of vertical mixing and the sediment-water exchange coefficients are much less constrained in that they are modeled/calibrated coefficients to fit an observation that is not mechanistically described or understood. That is, what process actually describes the apparent sediment-water release of dominant amounts of PCBs from cohesive sediments under low flow conditions?

10. The HUDTOX model uses the three-phase equilibrium partitioning model to describe the environmental behavior of PCBs. Is this representation appropriate? (Note that in a previous peer review on the Data Evaluation and Interpretation Report and the Low Resolution Sediment Coring Report, the panel found that the data are insufficient to adequately estimate three-phase partition coefficients.)

The three-phase model of PCB partitioning assumes that equilibrium is achieved between the truly dissolved phase and both the DOC (generating the K_{DOC}) and the POC (generating the K_{POC}). The DOC is assumed to be colloidal organic matter (COM) that is insufficiently separated from the dissolved phase by standard field separation techniques (filtration, centrifugation). It is well known that some colloidal OM passes typically-used 0.5 to 1.0 um pore size glass-fibre and membrane filters. If so and the colloidal OM contains sorbed PCB, then the apparent dissolved phase (water passing the filter - filtrate) has contributions from the truly dissolved and colloidal phases, thus overestimating the dissolved concentration and subsequent organisms exposure and volatilization.

In early studies, the importance of colloidal OM was linked to 'sampling artifacts' whereby the Kp or Koc decreased with increasing TSM concentrations. Although some interpreted this as a particle-interaction phenomenon, most viewed it as a result of sampling artifacts. The presence of an important colloidal or third phase for partitioning was detected by either the observation of decreasing Kp with increasing TSM, or a slope significantly less than 1.0 in a plot of log Kp or log

Koc vs log Kow. Many field results from lakes, rivers, estuaries and oceans yield slopes from 0.2 to 0.85. The values of slope less than 0.6 are generally taken to indicate the presence of an important third phase (colloidal OM with sorbed PCBs) and/or a lack of equilibrium. The RBMR states that evidence exists in the Upper Hudson that equilibrium is achieved (I assume this means a slope on the log Kp or Koc vs log Kow plot of close to 1.0). So if equilibrium is achieved (as stated), then what evidence exists that a third phase is present and important? At DOC concentrations in river water of 2-6 mg OC/L, TSM values of 2-100 mg/L and foc of 0.01 to 0.04, can the fraction of colloidal or DOC-bound PCB be important? The assumption was made that DOC is a surrogate of colloidal OM; is this a good assumption? The assumption was made that foc in DOC is equal to 1.0 (i.e, 'dissolved organic materials are typically assumed to be composed entirely of organic carbon'), when it almost certainly cannot be greater than 0.5 or 0.6 given the O, H, N and S content of aquatic natural organic matter. What implications do the above have for speciation calculations of PCBs since the amount in the particulate and dissolved phase is so critical to sedimentation, water-air exchange and organism exposure?

As for the estimation of three-phase partition coefficients, log Kocs can be calculated with reasonable accuracy given the bountiful literature on this topic. The relationship between Koc and Kdoc is less clear with literature values suggesting that Kdoc ~ 0.1x to 0.5x Koc. Selection of a value of 0.1 and applying it uniformly in the modeling framework introduces uncertainty into speciation calculations and the ultimate importance of each relevant pathway. Given the determination of a previous panel of experts that insufficient information exists to apply a three-phase speciation model for PCBs in the Hudson even though adequate POC and DOC data exist, and the apparent and assumed equilibrium status of sorption, what then is the justification for the application of the three-phase model?

Table 6-33 presents typical low and high flow partitioning behavior during cold weather and warm weather periods. The fraction of PCB (depending on state variable) in the colloidal-DOC fraction is typically 0.02 to 0.06, whereas for BZ#4, it is between 0.3 to 0.6. Although the anomaly is presented and discussed in the text, it is difficult to imagine any situation where so large a fraction of a low MW PCB is in the DOC phase when other more hydrophobic PCB congeners are not. I suggest that the concentration data upon which this determination was based are inconsistent with any reasonable mechanism and pathway known, and thus the field data driving this determination for this congener only are substandard at best and wrong at the worst.

In Section 6.9.2.8, the statement is made that "Results suggest that with accurate representation of temperature, foc and DOC, it is possible to predict phase distributions of individual congeners to within 45% for the Upper Hudson River upstream of TID and to within 33% below the TID." It is not clear what the predictions are being compared to since field and laboratory speciation studies are unavailable for complete speciation.

11. HUDTOX considers the Thompson Island Pool to be net depositional, which suggests that burial would sequester PCBs in the sediment. However geochemical investigations in the Low Resolution Sediment Coring Report (LRC) found that there was redistribution of PCBs out of the most highly contaminated areas (PCB inventories generally greater than 10 g/m^2) in the Thompson Island Pool. Comment on the whether these results suggest an inherent conflict between the modeling and the

LRC conclusions, or whether the differences are attributable to the respective spatial scales of the two analyses.

It is difficult to conclude that an inherent conflict exists. What is apparent is that the TIP is net depositional for PCBS while some local (but perhaps important processes) are not 'captured' in the model. It is important to recognize that net depositional for the TIP does not necessarily mean that no redistribution of PCBS in the sediments occurs. The model may not capture the redistribution due to scale or temporal and even sediment concentration constraints.

12. The model forecasts that a 100-year flood event will not have a major impact on the long-term trends in PCB exposure concentrations in the Upper Hudson. Is this conclusion adequately supported by the modeling?

This conclusion is adequately supported by the modeling, and it is reasonable from an intuitive point of view given the past known signals of solids and PCB mass under different flow regimes.

Bioaccumulation Models

1. Does the FISHRAND model capture important processes to reasonably predict long-term trends in fish body burdens in response to changes in sediment and water exposure concentrations? Are the assumptions of input distributions incorporated in the FISHRAND model reasonable? Are the spatial and temporal scales adequate to help address the principal study questions?

The FISHRAND model appears to capture important processes to reasonably predict long-term trends in fish body burdens in response to changes in sediment and water exposure concentrations.

The assumptions of input distributions incorporated in the FISHRAND model appear reasonable.

The spatial and temporal scales appear adequate to help address the principal study questions. This means that dissolved PCB concentrations in the water on a monthly basis and the surficial sediment PCB concentrations on an annual basis provided by the HUDTOX fate and transport model must be accurate and constrained.

It is a general conclusion that direct uptake of truly dissolved PCBs across the gill membrane is most often a small component of the total PCB burden because of the importance of dietary uptake. The experience from the Great Lakes and small lakes as well and apparently some European rivers, is that the rate of change in the PCB concentration in fish decreases occurs at the rate at which the dissolved concentrations change. Or put another way, the time rate of change in fish and water concentrations evaluated on an annual scale are about the same. Given that it may be assumed that surficial sediments, suspended sediments and water are at or near equilibrium (thus phytoplankton and bacteria as well), the rate of change in the PCB fish burdens should mimic the decrease in water column concentrations, which are supported by sediment-water release. Thus the PCB fish burden is controlled by the dissolved PCB exposures (through either gill uptake or dietary uptake) and will change at approximately the same rate evaluated on the annual time scale.

2. Was the FISHRAND calibration procedure appropriately conducted? Are the calibration targets appropriate for the purposes of the study?

3. In addition to providing results for FISHRAND, the Revised BMR provides results for two simpler analyses of bioacumulation (a bivariate BAF model and an empirical probabilistic food chain model). Do the results of these models support or conflict with the FISHRAND results? Would any discrepancies among the three models suggest that there may be potential problems with the FISHRAND results, or inversely, that the more mechanistic model is taking into account variables that the empirical models do not?

4. Sediment exposure was estimated assuming that fish spend 75% of the time exposed to cohesive sediment and 25% to non-cohesive sediment for the duration of the hindcasting period. The FISHRAND model was calibrated by optimizing three key parameters and assuming the sediment and water exposure concentrations as given, rather than calibrating the model on the basis of what sediment averaging would have been required to optimize the fit between predicted and observed. Is the estimate of sediment exposures reasonable?

The sediment exposure pathway is obviously an important one for most fish species of the Upper Hudson River. The sediment exposure pathway was indeed estimated by assuming that fish spend 75% of the time exposed to cohesive sediments (higher PCB concentration areas). Although the RBMR is silent on this point, I trust that fish biologists have been consulted on what habitat is occupied by different species of fish and for what fractiion of the time. This is not the kind of input parameter that should be used as a calibration parameter, however. It is much more scientifically-defendable to make the best assumptions based on the expert opinion of those who should know. Thus the estimate of sediment exposures is reasonable if the sediment surficial concentrations of PCBs over time and space are constrained.

5. The FISHRAND model focuses on the fish populations of interest (e.g., adult largemouth bass, juvenile pumpkinseed, etc.) which encompasses several age-classes but for which key assumptions are the same (e.g., all largemouth bass above a certain age will display the same foraging behavior). This was done primarily because it reflects the fish data available for the site. Is this a reasonable approach?

This is a reasonable approach given what is known about relevant fish species on foraging. To do otherwise would introduce significant uncertainty since such detailed data as age-dependent foraging behavior (other than young and adult) are not known even for these areas of major interest.

General Questions

1. What is the level of temporal accuracy that can be achieved by the models in predicting the time required for average tissue concentrations in a given species and River reach to recover to a specified

value?

The apparent temporal accuracy is not certainly less than one year and not greater than 10 years. Based on the apparent temporal resolution provided in the Fate and Transport model and the variability in a natural population of fish, then 1-5 years appears reasonable.

2. How well have the uncertainties in the models been addressed? How important are the model uncertainties to the ability of the models to help answer the principal study questions? How important are the model uncertainties to the use of model outputs as inputs to the human health and ecological risk assessments?

3. It is easy to get caught up with modeling details and miss the overall message of the models. Do you believe that the report appropriately captures the "big picture" from the information synthesized and generated by the models?

The RBMR is a comprehensive scientific report on the assessment of PCB mobilization, transport and exposure in the Upper Hudson River. It captures the minute picture, the intermediate picture and the 'big' picture. The model design and model final output are conceptually clear and the implications apparent.

4. Please provide any other comments or concerns with the Revised Baseline Modeling Report not covered by the charge questions, above.

4-1. <u>HLC</u>: Any factor influencing the concentration of PCBs in the water column and their speciation (i.e., truly dissolved, particulate (with solid OC), and colloidal (with DOC)) is important in air-water exchange. Thus the absolute concentration in the truly dissolved phase is critical in determining volatilization fluxes. Inherent in the estimation of volatilization fluxes is the role of Henry's law constant as a function of temperature in determining the magnitude of flux through the magnitude of the concentration or fugacity gradient, and the magnitude of the overall mass transfer coefficient. The representation of air-water exchange processes seems very appropriate to the task but the magnitude of HLC and its temperature function are known with greater accuracy based on the document as appended (Bamford, Leister and Baker, 2000). Given the magnitude of the HLC and the temperature function, even greater volatilization fluxes, especially at cold temperatures, are likely to occur. I strongly encourage that the new HLCs and their temperature dependence be incorporated into a revision of the PCB mass balance calculations. A protocol will have to be developed that estimates the HLC(T) for PCB congeners not measured, Tri+, and total PCBS.

4-2. <u>Air Concentrations</u> Part of the driver of *net* air-water exchange fluxes (here *net* volatilization) is the atmospheric concentration of gaseous PCBS. The data applied in the RBMR are the excellent air concentration data generated at Point Petre, on Lake Ontario as part of the Integrated Atmospheric Deposition Network (Hoff et al., 1996) for the period of 1992-94. These report an annual average PCB concentration of 170 ± 86 pg/m^3 with concentrations peaking in summer and reaching minima in the cold winter. It should be noted that they measured all congeners and homologues applicable to the Upper Hudson River study. Thus no estimation or interpolation procedure needs to be applied to the data to determine how each congener varies as a function of season and temperature. In addition, PCB concentrations were consistently higher when winds are off the lake suggesting that volatilization from the water drives a significant part of the signal. We also know that PCB air concentrations over the water of the Great Lakes of Superior, Michigan and Ontario plus Green Bay are higher than at comparable sites on shore sampled simultaneously. In the lower Hudson River Estuary/Raritan Bay where total PCB water concentrations are consistently 1 to 4 ng/L, air concentrations range from 500 to 3500 pg/m^3 and exceed air concentrations measured on shore simultaneously (data from Brunciak, Eisenreich, et al. Draft manuscript). The message is that air concentrations over and near the Upper Hudson River (necessary to estimate *net* volatilization fluxes) are likely considerably higher than applied in the model as described in Section 6.10.2.3, and perhaps as high as 10,000 to 50,000 pg/m^3 over the water. In addition, background concentrations of PCBs in air in the period 1977-1991 anywhere near the Upper Hudson River are likely to have been greater than those applied in the model. Given that few data are available to document ambient much less over-water PCB concentrations, it is not clear how to handle this question. If the fugacity gradient is very large in any case, perhaps volatilization vastly exceeds absorption and the air side PCB absorption can be neglected.

Recommendation

Based on your review of the information provided, please identify and submit an explanation of your overall recommendation for each (separately) the fate and transport models and bioaccumution models.

Fate and Transport Models

Acceptable

With major revisions (as outlined)

Bioaccumulation Models

Acceptable

with minor revision (as indicated)

Henry's Law Constants of Polychlorinated Biphenyl Congeners and Their Variation with Temperature

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Abstract

The Henry's law constants of 26 polychlorinated biphenyl congeners were measured using a gas-stripping apparatus at five environmentally relevant temperatures between 4 and 31 °C. The Henry's law constants ranged between 0.09 Pa m^3/mol ± 0.06 Pa m^3/mol for 2,2',3,3',4,4',5,6-octachlorobiphenyl (BZ congener #195) at 4 °C and 294 Pa m^3/mol ± 28 Pa m^3/mol for 2,2',3,3',4,,5,5'6'-octachlorobiphenyl (BZ congener #201) at 31 °C. The temperature dependence of each PCB congener's Henry's law constant was modeled using the van't Hoff equation to calculate the enthalpy and entropy of phase change between the gaseous and dissolved phases. For many PCB congeners, this study reports the first experimentally-measured temperature variations of their Henry's law constant. The enthalpies of phase change ranged between 14.6 kJ/mol ± 1.8 kJ/mol for 2,2',4,6,6'-pentachlorobiphenyl (BZ congener #104) and 163 kJ/mol ± 7 kJ/mol for 2,2',3,3',4,4',5-heptachlorobiphenyl (BZ congener #170). These data can be used to predict PCB congener Henry's law values within the experimental temperature range within a relative standard error < 15 %.

Citation: Bamford, H.A., Poster, D.L., Baker, J.E. Henry's law constants of polychlorinated biphenyl congeners and their variation with temperature. to be submitted to *J. of Chem. Eng. Data.*

Table 1. Literature and measured Henry's law constants at different temperatures in the range between 4 °C to 31 °C[a]

(HLC in Pa m^3/mol)

Congener[b]	4 °C	11 °C	18 °C	25 °C	31 °C	Literature 25 °C [Reference]
1	5.28 (4.29, 6.51)	8.52 (7.39, 9.82)	13.4 (12.0, 15.0)	20.8 (18.1, 23.8)	29.7 (24.7, 35.7)	28.9(B) 30.2(D92)
8	6.08 (5.36, 6.89)	9.94 (9.13,10.8)	15.9 (14.9, 17.0)	24.9 (22.9, 27.0)	35.9 (32.2, 40.1)	20.3(M83) 24.9(B) 30.7(D92)
18	8.20 (7.03, 9.55)	12.2 (11.0, 13.5)	17.8 (16.4, 19.3)	25.5 (23.1, 28.2)	34.3 (30.0, 39.3)	20.3(M83) 58.1(B) 38.5(D88) 32.0(D92)
28	13.2 (12.1, 14.4)	19.2 (18.0, 20.3)	27.4 (26.1, 28.8)	38.6 (36.3, 41.1)	51.1 (47.0, 55.5)	22.8(B) 32.0(D88) 29.0(D92)
29	12.2 (10.9, 13.7)	18.2 (16.9, 19.7)	26.6 (25.0, 28.3)	38.2 (35.3, 41.3)	51.4 (46.2, 57.1)	25.3(B) 30.0(D92)
44	11.9 (11.2, 12.6)	16.0 (15.4, 16.7)	21.4 (20.6, 22.1)	28.1 (26.9, 29.4)	35.2 (33.2, 37.3)	24.3(M83) 32.8(B) 23.3(D92)
50	29.0 (24.5, 34.5)	38.2 (34.0, 42.9)	49.6 (45.2, 54.4)	63.6 (56.8, 71.2)	78.1 (67.2, 90.8)	138(B) 61.8(D92)
52	11.5 (9.91, 13.3)	16.1 (14.6, 17.8)	22.3 (20.6, 24.1)	30.4 (27.6, 33.5)	39.2 (34.5, 44.6)	22.3(M83) 53.2(B) 34.7(D88) 32.3(D92)
66	14.0 (12.3, 15.9)	19.7 (18.0, 21.4)	27.2 (25.3, 29.2)	37.0 (33.9, 40.5)	47.8 (42.4, 53.8)	84.2(M83) 13.7(B) 20.5(D92)
77	4.47 (3.19, 6.28)	7.06 (5.59, 8.92)	10.9 (9.03, 13.2)	16.5 (13.1, 20.7)	23.2 (17.2, 31.3)	4.37(B) 9.52(D88) 10.4(D92)
87	12.8 (10.5, 15.5)	18.7 (16.4, 21.3)	26.9 (24.3, 29.9)	38.1 (33.6, 43.3)	50.8 (42.9, 60.2)	33.4(M83) 19.9(B) 18.6(D92)
101	15.7 (13.5, 18.3)	22.2 (20.0, 24.6)	30.8 (28.4, 33.4)	42.2 (38.2, 46.6)	54.6 (47.7, 62.4)	32.7(B) 25.4(D88) 24.9(D92)
104	39.7 (35.8, 44.1)	47.6 (44.4, 51.1)	56.6 (53.5, 59.8)	66.8 (62.4, 71.5)	76.5 (69.8, 83.8)	185(B) 90.9(D88) 75.1(D92)
105	3.04 (1.89, 4.89)	7.04 (5.10, 9.73)	15.7 (12.2, 20.3)	33.7 (24.6, 46.1)	63.1 (41.5, 95.9)	10.1(D92)
118	7.25 (5.27, 9.99)	12.7 (10.3, 15.8)	21.8 (18.3, 25.9)	36.3 (29.4, 44.8)	55.3 (41.7, 73.3)	40.5(M83) 12.7(D92)
126	1.00 (.660, 1.52)	2.74 (2.07, 3.64)	7.16 (5.72, 8.97)	17.9 (13.6, 23.5)	37.9 (26.8, 54.8)	8.29(D92)
128	.940 (.590,1.49)	3.35 (2.45, 4.58)	11.2 (8.77, 14.4)	35.5 (26.3, 48.1)	91.5 (61.0, 137)	50.7(M83) 6.85(B) 3.04(D88) 10.5(D92)
138	2.84 (1.82, 4.43)	7.52 (5.56, 10.2)	19.0 (15.0, 24.2)	46.1 (34.4, 61.7)	95.2 (64.3, 141)	48.6(M83) 11.0(B) 13.2(D92)
153	27.1 (16.2, 45.5)	35.7 (25.0, 51.2)	46.5 (34.9, 62.0)	59.8 (42.3, 84.5)	73.5 (46.5, 116)	35.5(M83) 17.9(B) 13.4(D88) 16.7(D92)
154	17.6 (15.3, 20.4)	27.6 (24.9, 30.5)	42.1 (38.9, 45.7)	63.2 (57.4, 69.9)	88.2 (77.6, 100)	72.1(D92)

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Table 1. Literature and measured Henry's law constants at different temperatures in the range between 4 °C to 31 °C[a]

(HLC in Pa m^3/mol)

Congener[b]	4 °C	11 °C	18 °C	25 °C	31 °C	Literature 25 °C [Reference]
170	.130 (.090, .200)	.790 (.590, 1.05)	4.24 (3.39, 5.31)	21.1 (16.1, 27.8)	78.7 (54.6, 114)	19.3(B) 8.85(D92)
180	.440 (.310. .650)	2.07 (1.61, 2.67)	8.98 (7.34, 11.0)	36.3 (28.4, 46.5)	114 (82.2, 159)	30.4(B) 10.9(D92)
187	2.98 (2.03, 4.38)	8.67 (6.67, 11.3)	23.9 (19.5, 29.4)	63.1 (49.0, 81.3)	140 (100, 196)	42.2(B) 20.5(D92)
188	16.0 (12.6, 20.4)	31.7 (26.9, 37.4)	60.9 (53.5, 69.4)	114 (96.7, 133)	189 (153, 234)	44.9(D92)
195	.090 (.050, .160)	.530 (.360, .790)	2.92 (2.15, 3.98)	14.8 (10.1, 21.6)	56.1 (33.8, 92.9)	12.0(D92)
201	1.10 (.770, 1.58)	5.18 (4.05, 6.63)	22.7 (18.7, 27.5)	92.6 (73.0, 117)	294 (214, 404)	13.2(D92)

[a]Predicted Henry's law constants from the linear regression analysis of ln H vs. the reciprocal temperature (n = 11). 95 % confidence intervals presented in parentheses.
[b]Compounds are listed in order of IUPAC number.

B: Burkhard, L.P., Armstrong, D.E. and Andren, A.W. Henry's Law constants for the PCBs. *Environ. Sci. Technol.* **1985**, 19, 590-596.

D88: Dunnivant, F.M., Coates, J.T. and Elzerman, A.W. Experimentally determined Henry's Law constants for 17 PCBs. *Environ. Sci. Technol.* **1988**, 22: 448-453.

D92: Dunnivant, F.M., Elzerman, A.W., P.C., J. and Mohamed, N.H. Quantitative structure-property relationships for aqueous solubilities and Henry's law constants of polychlorinated biphenyls. *Environ. Sci. Technol.* **1992**, 26(8): 1567-1572.

M83: Murphy, T.J., Pokojowczyk, J.C., and Mullin, M.D. Vapor exchange of PCBs with Lake Michigan: the atmosphere as a sink for PCBs. In *Physical Behavior of PCBs in the Great Lakes*, Mackay, D., Paterson, S., Eisenreich, S.J., and Simmons, M.S., Eds., Ann Arbor Science, Ann Arbor, MI, 49-58.

Table 2. Measured enthalpy and entropy of HLC, along with enthalpy of HLC, vaporization, and the enthalpy associated with the transition from octanol solution to air, taken from the literature.

$$HLC' = \exp(-\Delta H_{HLC} / R\,T + \Delta S_{HLC} / R)^{a}$$

Congener	r^2	ΔH_{HLC} [b] (KJ/mol) this study	ΔS_{HLC} [c] (KJ/mol K) this study	ΔH_{HLC} (KJ/mol K) [References]	ΔH_{VAP} (KJ/mol K) [References]	$\Delta H_{O/A}$ (KJ/mol K) [References]
1	0.94	42.4 ± 3.7	.102 ± .013			
8	0.98	43.7± 2.2	.108 ± .008			
18	0.95	34.7 ± 2.7	.078 ± .009		75 [K&M, 97]	80 [K&M, 97]
28	0.98	32.7 ± 1.6	.075 ± .005	50 ± 6 [TH, 92]		
29	0.97	34.8± 2.0	.082 ± .007		76.7 [H&B, 96]	72.6 [F&B, 94]
44	0.99	25.8 ± 1.1	.049 ± .004		81 [K&M, 97]	86 [K&M, 97]
50	0.87	23.2 ± 3.0	.048 ± .010			
52	0.94	29.5 ± 2.6	.062 ± 0.009	52 ± 5 [TH, 92]	81 [K&M, 97]	86 [K&M, 97]
66	0.96	29.4 ± 2.3	.064 ± 0.008		83.3 [H&B, 96]	73.3 [F&B, 94]
77	0.86	40.2 ± 5.8	.093 ± 0.020		87.2 [H&B, 96]	73.3 [F&B, 94]
87	0.91	33.4 ± 3.4	.077 ± 0.012			
101	0.93	29.9 ± 2.7	.067 ± 0.009		86.4 [H&B, 96]	73.5 [F&B, 94]
104	0.88	14.6 ± 1.8	.019 ± .006			
105	0.90	76.3 ± 8.4	.220 ± .029		89.8 [H&B, 96]	89.6 [F&B, 94]
118	0.90	50.3 ± 5.7	.134 ± .019		89.3 [H&B, 96]	89.9 [F&B, 94]
126	0.93	91.8 ± 10	.267 ± .035		94.9 [H&B, 96]	93.3 [F&B, 94]
128	0.96	116 ± 8.1	.355 ± .028			
138	0.93	88.6 ± 7.9	.264 ± .027		91.9 [H&B, 96]	87.8 [F&B, 94]
153	0.95	65.3 ± 5.1	.187 ± .017		91.4 [H&B, 96]	89.9 [F&B, 94]
154	0.96	39.3 ± 3.5	.101 ± .012			
170	0.98	163 ± 7.4	.507 ± .025			
180	0.98	142 ± 6.6	.440 ± .023		96.5 [H&B, 96]	86.8 [F&B, 94]
187	0.96	97.3 ± 6.8	.296 ± .023		94 [K&M, 97]	89 [K&M, 97]
188	0.96	61.7 ± 4.3	.181 ± .015			
195	0.97	165 ± 10	.510 ± .035			
201	0.98	143 ± 6.4	.451 ± .022			

[a] This equation, along with ΔH_{HLC} and ΔS_{HLC} values from this table can be used to calculate HLC′ for each compound at any temperature within the experimental temperature range

[b] ± standard error of the slope.

[c] ± standard error of the intercept.

K&M: Komp, P. and McLachlan, M.S. Octanol/air partitioning of polychlorinated biphenyls. *Environ. Tox. and Chem.*. **1997**, 16(12): 2433-2437.

H&B: Harner, T. and Bidleman, T.F. Measurements of octanol-air partition coefficients for polychlorinated biphenyls. *J. Chem. Eng. Data.* **1996**, 41: 895-899.

F&B: Falconer, R.L. and Bidleman, T.F. Vapor pressures and predicted particle/gas distributions of polychlorinated biphenyls congeners as a function of temperature and ortho-chlorine substitution. *Atmos. Environ.* **1994**, 28: 547-554.

TH: ten Hulscher, T.E.M., van der Velde, L.E. and Bruggeman, W.A. Temperature dependence of Henry's law constants for selected chlorobenzenes, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons. *Environ. Tox. and Chem.*. 1992, 11: 1595-1603.

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Biography not available at time of print

Hudson River Site Reassessment RI/FS. Baseline modelling Report, Peer Review 3.

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Fate and transport (HUDTOX)

1. The HUDTOX model links component describing the mass balance of water, sediment, and PCBs in Upper Hudson. In my view, this is the only way to model the fate of PCBs in the river. In river systems, the main governing variable for mass transfer of substances is the water discharge. The principal questions of the study, the modelling of PCB transport (the load, e.g. g/day) and PCB concentrations (of main concern for bioavailability, e.g. ng/L) can be addressed by using these components. There are, however, several other components that are needed and also included in the model (see further below), and at least one variable that possibly would have lead to improvements of the model if better focussed, i.e. the water temperature.

   The model (empirical mass balance over time) divide water discharge into two major categories; low flow (<10 000 cfs, non-scouring conditions) and high flow (>10 000 cfs, scouring conditions). I agree that this division is a pedagogic good way to represent the results, and also scientifically sound as movement of sediment will start to increase at a certain water discharge (although at a somewhat more gilding scale than precisely 10 000 cfs), determined by the baseline flow of the river. The major PCB transport occurs at low flow conditions, that is a major surprise to anybody working with mass transport of substances in rivers; the highest transport of substances often (always) occur at high flows. I find it surprising that PCB transport is not governed by water discharge, but I have not been working in highly contaminated systems like the Hudson River that may differ from less contaminated ones (Larsson et al. 1990, Bremle and Larsson 1997, Berglund et al. 1997). On the other hand, PCB concentration in the water has been shown to be inversely correlated to water discharge; a phenomenon coupled to internal sources of rivers (like contaminated sediment) resulting in PCB release. This release (see further below) is positively temperature dependent and mainly occurring at high water temperatures in the summer, when water discharge is low.

   The finding can thus, possibly, be explained by the "behaviour" of the major source of PCBs; the sediment of Thomson Island Pool (TIP) and nearby downstream locations. In the summer, at high water temperatures, the highly contaminated sediment releases PCB, by processes such as desorption, bioturbation and gas ebolition (not studied in the present investigation). These processes seem to dominate over sediment resuspension at high flow, thereby explaining the surprising result that transport of PCBs is higher at low flow. This has nothing to do with high or low water discharge, and these terms should be avoided when discussing the transport. The "non scouring" processes that transfer PCB across the sediment water interface are at work from low to high water discharges, but is positively affected by water temperature (higher in the summer). It's confusing that the transport is defined by high and low flows – despite the fact that discharge has nothing to do with the processes. I would like to have seen a correlation approach of water temperature and PCB transport at Thomson Island Dam. I suspect that the water discharge and the water temperature at Thomson Island Dam are negatively correlated, resulting in an apparent "low flow" transport.

2. The solid mass balance study indicate that TIP and reaches below are net depositional from 1977 to 1997, and the results are used for burial rates of PCBs. I agree that TIP and reaches below are net depositional, otherwise we would not have a problem with PCB in these areas, the sedimentation of PCBs would have occurred in other reaches of the river. The solid mass balance in relation to hydrological conditions and water transport rates are indeed penetrated in the report, explaining scouring- and non-scouring areas of sediment, main stream and tributary inputs of solids. I find this part of the study so thoroughly discussed that the focus of the investigation, PCB concentration and transport almost is over shadowed. The data are in some case small in numbers, and on the boarder-line in using for a broader context. I do not find that this is essential for the outcome of the model; the essential part is transport from sediment to water in TIP (temperature dependent transport) and in downstream reaches and the load of PCB from upstream sources (Fort Edwards). However, if solid transport from the upstream reaches would have been high – the outcome would have been another (and, consequently, justifying the present approach).

3. I think that the spatial resolution of the HUDTOX is quite satisfactory. TIP is the major source for PCBs in the river and the 1000-m segment is, therefore, justified in comparison with 4000-m segment downstream. I cannot find that spatial resolution would affect model predictions substantially, the outcome of the model (e.g. predictions for the future) is mainly affected by other variables, like year to year measurement (from 1977-1997) of PCB at different locations.

4. Is the model calibration adequate? Does the model do a reasonable job in reproducing the data during the hindcast (calibration) runs? Are the calibration targets appropriate for the purposes of the study? I see this question as a key to hindcast and forecast predictions of the PCB fate in the Hudson River. Any prediction (hindcast or forecast) depend on the data set used in order to describe the behaviour of the system for the actual time the measurements were carried out. In this case, data exist for the period of 1977 to 1997. The most important data for describing the PCB fate in the system are PCB concentrations in the water. This is the important outcome from all processes, that ultimately also control PCB uptake in fish. Other variables, like PCB concentration in the sediment, water discharges, sediment scouring, etc. may help us to understand the dynamics of PCB in the system in order to do predictions. It is in my view possible to predict PCB concentrations in the water using other variables, but this should be done with care and depending on the aim of the calculations. I find that the database on PCBs from the upper Hudson is quite satisfactory for describing PCB behaviour during the study period, as effects of water flow, the importance of TIP as a source, the effects of sediment resuspension etc. When it comes to predictions over long time periods, I have some comments that need to be addressed.

a) When examining the data set of PCB concentrations in water over time (Table 6.15) the first three years of measurements group together (1977-1979, e.g. Fig. 6.25) and show considerably higher PCB concentration than the following 17 years. These 3 years will have a major impact on any time trend analysis; any hindcast or forecast prediction since these years are the basis for the later PCB decline. If data from these three years were excluded, it would affect PCB decline time trend over the years substantially; despite if the approach were a time trend analysis or an empirical mass balance model as HUDTOX. Let us examine the data of the three years, ignoring the contributing study. The measurements at TIP are not started until 1991, so the major source area has to be estimated. For Fort Edwards, 3 measurements are carried out in 1977, 35 in 1978, and 53 in 1979. PCB concentration (that is converted to loads in Fig 6.25) is not that high compared to the rest of the data set at this location. However, the load is very high at Schulerville, Stillwater, and Waterford during these three years, approximately 3-5 times higher than the following years. At these three stations, yearly measurements during 1977-1979 are 12 to 52, a quite satisfactory yearly number. Yet compared to the total measurements over the years, these three years represent 60/426 measurements at Schulerville (14%), 102/607 at Stillwater (17%) and 120/815 at Waterford (15%). If these measurements are biased in any way, the predicted long-term (70 year) decrease rate will be overestimated. I feel that this is the case, I don't think that the decrease in PCB load will occur as fast as the authors predict. As time trend analysis of PCB has been under debate for biota in the Great Lakes (e.g. Stow et al. 1994) as well as for biota in the Baltic Sea (Bignert et al. 1995) with the same problem as in the present study (a few, early years of high contamination), I would have like to seen a strict statistical analysis of the data to add to the overall picture of the HUDTOX model. Stow et al. (1994) has suggested a good approach to such an analysis.

b) I have a problem with the model assumptions (calibration?). As far as I understand, the underlying data to take the overall model approach is generated at Fort Edwards, simply because this station has the largest data bank. I want to point out that the sources for PCBs at Fort Edward may well differ substantially from the source contribution of TIP. The sediment contamination at the pool will possibly result in other conclusions of, for example, relationships with water discharge and water temperature as found for data at Fort Edwards. Being a major source, the TIP data could be examined more thoroughly, although the measurements start at a more recent point in time (in 1991).

5. The empirical coefficient for sediment to water transport is from my point of view derived correctly (by simply calculating the difference between PCB concentrations of outgoing water from e.g. TIP to that of incoming water and compensate for time, sediment area and water discharge. I agree that the mechanisms underlying the transport is not fully understood and therefore cannot be modelled mechanistically. I don't find it important for the approach of PCB fate in the upper Hudson. I can, however, think that it is important for predictions of PCB fate in the future. I want to stress that the PCB transport from sediment to water seems to be temperature dependent in TIP and nearby downstream areas, yet this variable has not been enough examined. To forecast PCB concentration in the future, not knowing the mechanisms for the major sediment to water load, is not without objections. It creates an uncertainty of the long-term predictions.

6. I think that the majority of factors important for the PCB fate in the upper Hudson have been accounted for. No model can account for all factors. I have already pointed out that I think that water temperature is important and it has also been indirectly accounted for in the model by seasonal changes in PCB concentration and transport.

7. Using the model in a forecast of 70 years indeed requires a number of assumptions regarding important variables. I think that the hydrograph forecast is quite reasonable, and I would like to answer the question of larger events to the following question of the 100-year flood event. I have above explained what I think is important in a future forecast. I don't object to predictions of variables examined within the model (as future water flows, sediment loads, and upstream boundaries of PCBs). My objections are mainly focussing on time – is the observation pattern over the 20 years of study enough to predict a 70-year future scenario? I would say yes if the database had included a larger number of yearly measurements when PCB load was high (now represented by the years 1977-1979). I would say no, if the database don't, as is the present situation. This does not mean that I find the present model work carried out erroneously, it's simply not possible to make a 70-year prediction without high uncertainty. The predictions of seasonal oscillations that decrease on a long term is sound, but the point in time when the oscillation approach upstream PCB concentrations (modelled at 0, 10 and 30 ng/L) is uncertain. I understand that the predicted scenarios have a pedagogic strength, but I find several objections to state that the PCB concentration will reach background in 30 years. Such a statement is coupled with high uncertainty (that often is missing when the statement is referred in, for example, media). The model is sound for describing the PCB fate in the upper Hudson during the 20 years of study, it can well be used for hindcast of PCB concentrations at locations that lack data, it can be used to predict that PCB concentration will decrease in the future according to seasonal patterns, but I think it is going too far to state details in that decrease.

8. I would like to answer this question in a broader context. We have today in the upper Hudson and nearby downstream reaches a high contamination of PCB in the sediment. In a long-term scenario, this contaminated sediment will spread downstream according to a "pulse". The pulse will broaden from a relative small stretch of the river, the sediment of TIP and nearby downstream reaches, to include a longer part of river sediment, depending on the time that has passed. The longer the time that has passed, the longer the stretch containing PCB contaminated sediment. As the sediment are redistributed downstream the river, concentration of PCB will decrease as a result of dilution by less contaminated solids. This will result in decreased concentration of PCB in the water. As the Hudson River is regulated, no natural meandering will occur, and consequently, no contaminated sediment will be deactivated in riverbanks as a result of a changing water channel. I have no problems in understanding that some sediment areas will show decrease in PCB concentrations, some sediment areas downstream will show substantial increase in PCB concentration and a subsequent higher transport to the water. Processes such as long-time sediment scouring will reveal lower sediment layers of higher PCB concentration, even if the area is net depositional. As a forecast do change according to initial data input

(whether it's GE data or not) in it's details, the overall conclusions remain the same (which for me is the important issue).

9. From a model point of view, the distinction between cohesive and non-cohesive sediment areas is a good approach. I further agree to that the average speed of the water current will affect bottom-material in the non-cohesive areas in a way that an "armour" layer will develop; a surface layer containing similar sized particles (coarse particles). I find no objections to the model assumptions of net depositions; in fact I find the reasoning interesting and valid. The extent of the vertical mixing will differ substantially within and between areas and again I find that the authors have properly addressed this problem. As for the empirical sediment-water exchange coefficient I agree to the proposed underlying mechanisms, however, these mechanisms have not been investigated. In the long-term response of the model, or when the model is used for future predictions, it is not satisfactory that the most important coefficient (the transfer of PCBs from the sediment of TIP and nearby sediment areas) is just empirical. A substantial change in any of the proposed mechanisms; as the number of macroinvertebrates (bioturbation), redox-conditions (gas ebolition) or a mechanisms that is important but not recognised (e.g. microbial mineralisation of organic matte, desorption) may influence future transport. Empirical coefficients that are composed of several mechanisms (rates) are not good predictors, as the behaviour is unknown but linked to other variables (as water temperature).

10. I have dealt with the three-phase equilibrium partitioning in the previous review report. As stated then, I find that the approach is too sophisticated and the data insufficient (e.g. organic carbon in water) to be used. I also think that it is unnecessary.

11. I think this question is connected to question 8. I have no problem to understand that TIP is net-depositional under a long-term perspective that would lead to a sequestering-process of PCB in the sediment. Under some conditions particle redistribution will occur within the pool that may transfer PCBs to some areas and deposit PCBs in other. TIP is situated within a river, and is not an accumulation area of a lake. Looking at transport of PCBs within TIP or out from the pool, the extent of the transport is of the magnitude that cannot solely be explained by diffusive transfer over the sediment water/interface. The transport is in my view, connected with particle resuspension. If I speculate, I can imagine that PCB contaminated particles are transported slowly just above the sediment surface, being deposited and again redistributed in a cycle, that result in very slow movement downstream (bed-load transport, Allan 1995). Such a transport may well not be recognised in a program of water sampling of PCBs. So for me there is no conflict in the results, but it is possible that there are processes within Hudson River that have not been accounted for.

12. The 100–year flood was estimated to be 47 330 cfs (1280 m^3/s). At Fort Edward (1977 – 1997) discharge reach over 30 000 cfs (810 m^3/s) in some years. Consequently, the 100-year flood increases water discharges with about 50% of the flow under "normal" years. If so, I agree to the conclusions drawn; that the 100-year flow will not have a major impact on the long-term trends of PCB in the upper Hudson. The effect will be limited to a comparably short period, and

transient in nature. Hudson River is regulated, and I cannot conclude if the 100-year discharge scenario is realistic or not (I would suggest it is, in thought of the expertise involved).

Bioaccumulation models

1. I think the FISHRAND model captures a major part of the processes that are important to understand PCB uptake in fish of the upper Hudson River. The uptake is driven by concentrations of PCB in the sediment and, consequently, in the water. The general approach to divide factors in non species-specific (abiotic factors would maybe have been better) and species-specific ones is good, and makes the reader understand what is important. I also like the build-up of the reasoning, with a statistical approach first (the bivariate BAF model), followed by a more advanced "probabilistic "food chain model and finally the FISHRAND model. There are some observations that are not accounted for (or explained) as the sharp decline in PCB levels for fish from the period 1977-79 to 1980 (see general question 4 below). How can levels decrease that fast in a long-lived population of fish as large-mouth bass? There are also limitations in the fish pollutant data-base that in my view is serious as: i) data gaps for the early years for fish in TIP and gaps in data from other locations ii) age and sex of fish were not determined. When making long-term predictions, you understand how important "background" contamination is, i.e. the upstream concentrations of PCB in the water (0 ng/L, 10 ng/L and 30 ng/L). In the forecast, the key question is when the exposure of the sediment sources of TIP and downstream areas have decreased in a way that background (upstream conditions) are approached. For me, this is a very complicated question, that make the time-scenario more complex than just a few PCB scenarios of 0 ng/L, 10 ng/L and 30 ng/L. I do, however, recognise the pedagogic strength of the reasoning.

2. I think the calibration of the model was properly addressed. There is a more important question, though, and that is the verification of the model. On page 73-74, a sensitivity analysis is described and summarised in a table. I would like to have seen some practical examples here, if you substantially change some variables as growth rate, percent lipid in fish or uptake efficiency what will happen to the outcome of the model? I understand that the "sign of derivative" has some information value in this respect – but I would have liked to see some scenarios of this kind. Further, it would have been nice to have seen a data set from another river (an independent data set) put into the model and runned.

3. As stated in the beginning, I like the approach with a statistical approach first (the bivariate BAF model), followed by a more advanced "probabilistic "food chain model and finally the FISHRAND model. I think the results supports the FISHRAND model, although the different approaches all have some limitations. I don't find any principal problem with FISHRAND. I don't think that FISHRAND is a pure mechanistic model, however, since it in some respects relies on empirical findings (like the sediment and water concentrations and relationships between them, like the effect of temperature, fish lipids and distributions, etc.)

4. The assumption of 75/25 fish distribution over cohesive and non-cohesive sediment is in my opinion not important. If the model outcome is sensitive to this

relationship, and would come to a completely different outcome assuming a 60/40 distribution, I would be very cautious in any interpretation.

5. I would say that you have to make assumptions about "principal" fish foraging in different year classes (size-distributions). It's a very narrow, scientific question (interesting, though) to address if e.g. large-mouth bass >20 cm can be a specialist in foraging behaviour (say feeding mainly on crayfish versus feeding solely on small fish). If so, such relationship may help to explain why concentrations of persistent pollutants in an age-class of predatory specie vary up to one order of magnitude. However, for the purpose of this study this is out of focus and the approach therefore reasonable.

General Questions

1. The level of temporal accuracy in the models, in predicting the time required for a given species to reach a certain concentration of PCB (in a certain river stretch) is my major concern of the two studies. There are several factors that affect the judgement of how accurate predictions over a long time scenario can be, such as: a) Rivers are far less studied than lakes in the respect of persistent pollutants in biota b) Time trends for persistent pollutants in biota is a matter of debate c) The strength of the governing sources of persistent pollutants (internal or external) to aquatic ecosystems does not change systematically over time. I do not object to the models themselves, but I would be careful when addressing long-time scenarios. To state that "asymptote is approached in roughly 2039" (page 100, summary and conclusions, volume 4D) may be a correct outcome from the model. However, can "roughly" be combined by a certain year as 2039? Is the year interval 5 years around 2039, or 10? I think that the authors are well aware of the uncertainties in such a statement, but it may easily be interpreted erroneously by a non-specialist.

2. The uncertainties of the models have been continuously addressed in the reports. When coming to the summary sections, however, uncertainties are not focussed. I can understand why; when major findings are reported you don't want to constrain these findings by using words as "may", "under the options of", "this forecast is only valid under...", "the year when concentration in water reach an asymptote should only be seen as approximate....", "the data-base on yellow perch is far less than for large-mouth-bass and, therefore,...". It's a delicate matter to write summary sections, not to become vague but at the same time showing the reader that the results may suffer from uncertainties. In my view models help people to understand how the system is functioning, how the overall processes are interacting, and how this information can be used in predictions. There are always uncertainties connected to models (that affect the outcome), and this should be clarified for the non-specialist (more a pedagogic problem).

3. I think that the models capture the big picture of PCB fate in the upper Hudson River. Levels will decline over time as forecasted principally by the model. It could possibly be stressed that decline in one area of the river mean an increase of PCB in another, downstream reach of the Hudson. The upper parts are not isolated from the rest of the river, and this need to be considered in the "big picture". If the polychlorinated biphenyls are not broken down, a decrease in the

sediment of TIP means a downstream transport or volatilisation, that will mean an export of pollutants from the system – not a total disappearance.

4. When examining the data (from water and sediment and from fish) underlying the approach of modelling and predictions, there is a striking difference between the years 1977-79, and the following years. This can be exemplified by the PCB data from fish (several species), where the decrease from 1977-79 to 1980-82 is a factor 3-4 (e.g. from ca 1800 to 600 for brown bullhead, from 4500 to 1000 for large-mouth bass). How can concentrations of PCB decrease that sharp in a population of fish that are rather long-lived? Some of the more heavily exposed fishes must survive to the "next" capture year? The phenomenon can also be seen for PCB load (river water) measured at three stations in the upper Hudson. PCB load is substantially higher in 1977-79 compared to the following years. This is not, however, reflected at the uppermost station at Fort Edward where the PCB load has decreased to a lesser degree and at a more steadily over time. To me, this suggests two scenarios, one valid for the upper Hudson until 1979, and another from 1980 and onward. Suggesting that the sediment of TIP is the major source for PCB during the 20 year period; I cannot understand the sudden decrease from 1979 to 1980. The more steady decrease from 1980 and onward seems logic to me, as sediment and PCB in the water are transported from TIP and downstream.

Recommendations

I find the two reports acceptable with minor revision as indicated above.

References

Allan, J.D. 1995. Stream Ecology. Structure and function of running waters. Chapman and Hall, London 388 pp.

Berglund, O., Larsson, P., Brönmark, C., Greenberg, L., Eklöf, A. and Okla, L. 1997. Factors influencing organochlorine uptake in age-0 brown trout (*Salmo trutta*) in lotic environments. Canadian Journal of Fisheries and Aquatic Sciences 54, 2767-2774.

Bignert, A., Litzén, K., Odsjö, T., Olsson, M., Persson, W. & Reutergårdh, L. 1995. Time related factors influence the concentrations of sDDT, PCBs and shell parameters in eggs of Baltic Guillemot (*Uria aalge*), 1861-1989. Environmental Pollution, 89:27-36.

Bremle; G. and Larsson, P. 1997. Long-term variation of PCB in the water of a river in relation to precipitation and internal sources. Environmental Science and Technology 31, 3232-3237.

Larsson, P., Okla, L., Ryding, S.-O. and Westöö, B. 1990. Contaminated sediment as a source of PCBs in a river system. Canadian Journal of Fisheries and Aquatic Sciences 47, 746-754.

Stow, C.A., Carpenter, S.R. and Amrhein, J.F. 1994. PCB concentration trends in Lake Michigan Coho (*Onchorhynchus kisuth*) and Chinook salmon (*O. tchawytscha*). Canadian Journal of Fisheries and Aquatic Sciences 50, 1384-1390.

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BIOGRAPHY

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Peer Review Report
Hudson River PCBs Reassessment RI/FS
Phase 2 Report
Volume 2D – Revised Baseline Modeling Report

Prepared by

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Fate and Transport (HUDTOX)

1. **The HUDTOX model links components describing the mass balance of water, sediment, and PCBs in the Upper Hudson. Are the process representations of these three components compatible with one another, and appropriate and sufficient to help address the principal study questions?**

The processes represented by the main components of HUDTOX are as follows:

(a) Mass Balance of Water: continuity, advection, gravity, bed friction (shear), and turbulent exchange.
(b) Mass Balance of Sediment Solids: settling, flow-driven resuspension, sediment bed particle mixing, scour and burial.
(c) Mass Balance of PCBs in water column: advection, dispersion, upstream and tributary loading, settling, re-suspension, equilibrium sorption (particulate and DOC-bound), volatilization, and sediment-water diffusion (truly dissolved and DOC-bound).
(d) Mass Balance of PCBs in sediments: settling, re-suspension, sediment-water diffusion (truly dissolved and DOC bound), equilibrium sorption (particulate and DOC-bound), de-chlorination, particle mixing, and surface-subsurface sediment diffusion (truly dissolved and DOC bound).

The process representations of these components are compatible with each other, in terms of the level of details and theoretical basis. In my opinion, HUDTOX forms a comprehensive framework for the representation of the most significant processes affecting the PCB distribution in the Upper Hudson River, and is adequate to address the principal questions of the study.

2. **The HUDTOX representation of the solids mass balance is derived from several sources, including long-term monitoring of tributary solids loads, short-term solids studies and the results of GE/QEA's SEDZL model. The finding of the solids balance for the Thompson Island Pool is that this reach is net depositional from 1977 to 1997. This finding has also been assumed to apply to the reaches**

below the Thompson Island Dam. Is this assumption reasonable? Are the burial rates utilized appropriate and supported by the data? Is the solids balance for the Upper Hudson sufficiently constrained for the purposes of the Reassessment?

<u>On the Solids Balance</u>

In developing the long-term solids balance for HUDTOX, daily average TSS concentrations from the upstream at Fort Edward and from all tributary inputs are to be supplied for the entire calibration period (1977-1997). Unfortunately, only the following very limited data was available:

(a) 11% of data at Fort Edward;
(b) Less than 2% of data for tributaries.

As a result, estimates of the data must be supplied, and they were mainly provided for from rating curves. The Fort Edward's sediment rating curve was found to be flow and time-stratified (Fig. 6-14) and the data available for the two time periods (1977-90 and 1991-97) was substantial. However, the data for the tributaries was so scarce that basically all calculations were performed with the information from three so-called "reference" tributaries:

(a) Moses Kill - for tributaries between Fort Edward and Stillwater;
(b) Rattan Kill - for the tributary Fish Creek;
(c) Hoosic River – for tributaries between Stillwater and Waterford.

This approach did not result in a sediment balance for the period from 1977 to 1997, and so some artificial adjustment was performed to force the balance. With these input, the mainstem sediment passing Stillwater and Waterford were used as model calibration targets.

There are two major problems with the approach:

1. Whereas flow only increases by 1.5% between Fort Edward and Waterford, the solids load increases by a factor of 5.7. This indicates that a lot of the TSS actually entered from the tributaries. Unfortunately, the amount and location from which they enter were all estimated from very frivolous relations. The cumulative effect of these assumptions was only checked against the TSS at the two calibration locations, with no information provided in the reaches in between. This does not allow for an adequate description of the 470% increase in sediments for the Upper Hudson River.

2. PCB is a hydrophobic substance with a high tendency of partitioning to sediments. The ultimate concentrations of PCB in the water and sediments depend heavily on the exact amounts of TSS for each study segment. With the amount of uncertainty in the TSS values, the spatial resolution of PCB calculations is not supported.

On the Net Depositional Issue

The net depositional conclusion for the Thompson Island Pool is accurate. From the data, the burial rates for cohesive (0.24 - 1.50 cm/yr) and non-cohesive (0.04 – 0.10 cm/yr) sediments are very reasonable estimates for the Upper Hudson River. The values for the Thompson Island Pool (0.65 and 0.07 cm/yr for cohesive and non-cohesive sediments respectively) also compare reasonably well with the independent SEDZL calibration values (of 0.81 and 0.03 cm/yr).

3. **HUDTOX represents the Upper Hudson River by segments of approximately 1000 meters in length in the Thompson Island Pool, and by segments averaging over 4000 meters (ranging from 1087 to 6597 meters) below the Thompson Island Dam. Is this spatial resolution appropriate given the available data? How does the spatial resolution of the model affect the quality of model predictions?**

Both the TSS and PCB concentrations were monitored at only five locations on the mainstem of the Upper Hudson: Fort Edward, Thompson Island Dam, Schuylerville, Stillwater and Waterford (Figs. 6-9 and 6-19). In light of this, the spatial resolution used in HUDTOX is appropriate. In addition, the segment sizes were judiciously selected with consideration of the locations of tributaries, locks, dams, and USGS gaging stations. In the problematic Thompson Island Pool area, a two-dimensional segmentation was used to differentiate between areas with cohesive and non-cohesive sediments. Furthermore, each segment contains a water column and 13 layers of 2-cm sediment layers. These are all important considerations that would help to ensure accurate model predictions.

4. **Is the model calibration adequate? Does the model do a reasonable job in reproducing the data during the hindcast (calibration) runs? Are the calibration targets appropriate for the purposes of the study?**

For the Model Calibration (1977-1997)

The model was simultaneously calibrated for the period of 1977-1997 against the following target data sets:

(a) Tri+ surface sediment concentration;
(b) Measured solids burial rates from dated sediment cores;
(c) Computed solids burial rates from a sediment transport model;
(d) In-river solids and Tri+ mass transport at high and low flows;
(e) Solids and Tri+ water column concentrations.

Only four model parameters were adjusted during calibration: gross settling velocities into cohesive and non-cohesive sediment areas; re-suspension rates from non-cohesive sediment areas; depth of particle mixing in the sediment bed; and the magnitude of the sediment particle mixing.

In my opinion, the calibration was very thorough and conservative, and should be deemed adequate for the model. The calibration targets when assessed with a weight-of-evidence approach do provide a good picture of the different elements of the model performance, and is extremely suitable for the nature of the study.

For the Model Hindcast (1991-1997)

To obtain simultaneous good comparison with data for all the five congeners and total PCBs at TID, two adjustments were required in the model hindcast runs:

(a) Sediment partition coefficients were computed from the GE 1991 sediment core composite data (USEPA, 1997). This improved the model fit greatly for BZ#4.
(b) Separate particle and porewater-based sediment-water mass transfer coefficients were used. This improved performance of the BZ#4 and total PCBs while showing reasonable results for other congeners.

The results after these two adjustments, as given in Fig. 7-66, were very good for all congeners.

Other comparisons performed (and the observations) included:
(a) Comparison for other downstream locations (Schuylerville, Stillwater, and Waterford) for the period 1991-1993 (satisfactory).
(b) Comparison to GE summer 1996, 1997 float data collected from TIP down-river, for RM 194.5 to RM 188.5 (very good).
(c) Comparison to GE data of (BZ#28/BZ#52) at Fort Edward, Thompson Island Dam, Schuylerville, Stillwater and Waterford, for summer and non-summer conditions, as well as high and low flows (acceptable, but with model over-estimating frequently).

The hindcast runs were instrumental in discovering new insights concerning partition and mass transfer coefficients for different congeners. It also demonstrated the wide range of application of HUDTOX on different congeners. For the congeners with environmental behavior different but similar to Tri+ (i.e. BZ#28 and BZ#52), the excellent results from the hindcast provides added confidence on the model performance. In essence, the hindcast runs are quite thorough and have done a good job at reproducing the data.

5. **HUDTOX employs an empirical sediment/water transfer coefficient to account for PCBs loads that are otherwise not addressed by any of the mechanisms in the model. Is the approach taken reasonable for model calibration? Comment on how this affects the uncertainty of forecast simulations, given that almost half of the PCB load to the water column may be attributable to this empirical coefficient.**

The empirical sediment/water mass transfer coefficient was based on a simple one-step mass balance of the PCB gain across the TIP, by treating the entire TIP as a black box, according to Eq.6-25, on p.119. The values of the mass transfer rate, k_f, were then calculated for pairs of data from 1993-1997 and plotted against the days of Julian year.

This premise is flawed in that it assumed implicitly that of all the processes affecting the PCB gain in the water column across the pool, the sediment/water mass transfer always plays a similar role at around the same time of year. An inspection of the transfer mechanisms for dissolved phase (5 in total) and particulate phase (4 in total) on p.115-6 of the report indicates that the premise is too simplistic. As a result, the data produce a widely scattered plot on Fig. 6-55, for which one can easily fit another trend with the same statistical performance.

Furthermore, the entire time series of annual k_f-values produced from the fit was applied for the 1977-1997 calibration, and then again repeated for the 70-year forecast simulation. If the process is so significant as to contribute 50% of the total PCB concentrations of the water column, the approach should warrant more research.

In conclusion, I have serious doubt over the validity of the approach, and the net effect of 50% from this single process to the water column PCB load also seems highly unrealistic.

6. **Are there factors not explicitly accounted for (e.g., bank erosion, scour by ice or other debris, temperature gradients between the water column and sediments, etc.) that have the potential to change conclusions drawn from the models?**

No, in my opinion all the important processes have been explicitly modeled. As a matter of fact, some of these other processes mentioned are too localized and random in occurrence, to be formulated within the time and spatial framework of the model. To me, the inclusion of too many "frivolous" processes will add unnecessary uncertainties in the model, and may even obscure the implications of significant processes from the model output.

7. **Using the model in a forecast mode requires a number of assumptions regarding future flows, sediment loads, and upstream boundary concentrations of PCBs. Are the assumptions for the forecast reasonable? Is the construct of the hydrograph for forecast predictions reasonable? Should such a hydrograph include larger events?**

Nobody can predict the future accurately, and the formation of the hydrograph from a time series of randomly selected annual hydrographs from record, and repeating the simulations for four different series, is very reasonable. Solids load assumption of a similar pattern to recent record (1991-1997) is also a sound one. Upstream boundary concentrations of PCBs of 0, 10, and 30 ng/L were used in the simulations. However, the values from GE data for 1997 and 1998 were 9.9 and 30.4 ng/L (see p.158, Book 1 of RBMR), respectively, and those were the "better" years in recent history according to Fig. 8-3! Therefore, the upper bound value of the simulations is under-estimated and a bigger range of say 0 to 50 ng/L may prove to be more realistic.

8. (Note : separate answer are provided to the two parts of this question)

(a) The 70-year model forecasts show substantial increases in PCB concentrations in surface sediments (top 4 cm) after several decades at some location. These in turn lead to temporary increases in water-column PCB concentrations. The increases are due to relatively small amounts of predicted annual scour in specific model segments, and it is believed that these represent a real potential for scour to uncover peak PCB concentrations that are located from 4 to 10 cm below the initial sediment-water interface. Is this a reasonable conclusion in a system that is considered net depositional?

Given the relatively long time frame of the forecast, this is a reasonable and logical conclusion. Even though the river was in general net depositional, local scour will occur at locations where the shear stress is high. When this is considered in light of the information from the sediment cores, the cumulative effects of the scour could possible result in exposure of deeper PCB reserves in the system.

(b) After observing these results, the magnitude of the increases was reduced by using the 1991 GE sediment data for initial conditions for forecast runs. Is this appropriate? How do the peaks affect the ability of the models to help answer the Reassessment study questions?

I agree with the comment from the report, on p.160 of Book 1, concerning these increases: that the magnitude is very small when compared in the context of historical observations. Therefore, the peaks should not have any significant effects on the ability of the model to answer the Reassessment study questions.

Concerning the initial conditions for the sediment data, the end results of the 1991-1997 model hindcast were used as input for the initial conditions. In effect, this corresponds to initializing the forecast simulations with measured conditions in 1991, so that the first period (1991-1997) of the "forecast" may be validated by real data. This approach utilizes the most recent and reliable dataset to begin the model forecasts, and seems to be an excellent choice.

9. The timing of the long-term model response is dependent upon the rate of the net deposition in cohesive and non-cohesive sediments, the rate and depth of vertical mixing in the cohesive and non-cohesive sediments and the empirical sediment-water exchange rate coefficient. Are these rates and coefficients sufficiently constrained for the purposes of the Reassessment?

<u>On the Rate of Net Deposition</u>

The rates of net deposition in cohesive and non-cohesive sediments were obtained from the 1977-1997 long-term model calibration. In general, the computed burial rates for cohesive sediments (0.24-1.50 cm/yr) are an order of magnitude larger than that of non-cohesive sediments (0.04-0.10 cm/yr). These values compare favorably with the SEDZL model results, and are sufficiently constrained for the Reassessment.

On the Vertical Mixing

Vertical mixing rates were determined for cohesive and non-cohesive sediments, for the TIP and downstream (TIP to Federal Dam) reaches, based on core depth profiles, expected biological activities, and calibration of sediment Tri+ concentration temporal trajectories. Individual values of these rates were summarized in Table 7-1.

The mixing depths were computed from long-term calibration as:

- 10 cm in cohesive sediments in all reaches;
- 6 cm in non-cohesive sediments in TIP;
- 4 cm in non-cohesive sediments downstream of TID.

These values seem appropriate, and are sufficiently constrained for the purpose of the Reassessment.

On The Sediment-Water Exchange Coefficient

Please refer to comments for Question 5.

10. The HUDTOX model uses three-phase equilibrium partitioning to describe the environmental behavior of PCBs. Is this representation appropriate? (Note that in a previous peer review on the Data Evaluation and Interpretation Report and the Low Resolution Sediment Coring Report, the panel found that the data are insufficient to adequately estimate three-phase partition coefficients.)

The equilibrium partitioning of PCBs into the three phases: particulate, DOC-bound, and truly dissolved, is an appropriate and even necessary approach in the current application for two reasons.

Firstly, the model was applied to Tri+ PCB, total PCB, and five other congeners. Whereas the partition to the DOC-bound phase is small (<10%) for the heavier congeners (mostly Tri+) in the water column, it is quite significant (up to 50%) for the mono- and di-chlorinated congeners. Therefore, the framework of HUDTOX must be comprehensive and general enough to allow for the predictions of all the congeners being investigated.

Secondly, in the first Reassessment question, the bioaccumulation of PCBs in the fish population is of interest. The two most significant pathways by which PCBs enter into fish bodies are from contaminated diet and water (during respiration intake). Since truly dissolved PCBs are usually more readily bioavailable than those sorbed to DOC, the three-phase approach will allow for a more accurate representation of PCB accumulation to biota across different trophic levels. When the PCBs representation in the lower trophic level organisms (mostly preys) are accurate, the predictions for top-predator fish will be greatly enhanced. I feel that the use of a two-phase partition model (with the omission of the DOC-bound phase) will probably produce a cumulative effect resulting in an under-estimation of PCBs in the higher level fish. In addition, the results from the three-phase partition may be converted conveniently to that of two-phase, with dissolved concentration being the sum of DOC-bound and truly dissolved concentrations. The same will not apply to the opposite direction.

11. HUDTOX considers the Thompson Island Pool to be net depositional, which suggests that burial would sequester PCBs in the sediment. However, the geochemical investigations in the Low Resolution Sediment Coring Report (LRC) found that there was redistribution of PCBs out of the most highly contaminated areas (PCB inventories generally greater than 10 g/m^2) in the Thompson Island Pool. Comment on whether these results suggest an inherent conflict between the modeling and the LRC conclusions, or whether the differences are attributable to the respective spatial scales of the two analyses.

The Thompson Island Pool is net depositional according to HUDTOX, which implies that overall the sediment settling is more than the re-suspension on a pool-wide scale. Even so, local scouring may occur when the shear stress is high enough, and this was corroborated by the independent SEDZL sediment transport model and the LRC geochemical data. Therefore, I do not see any conflict between the modeling and the LRC conclusions.

12. The model forecasts that a 100-year flood event will not have a major impact on the long-term trends in PCB exposure concentrations in the Upper Hudson. Is this conclusion adequately supported by the modeling?

In the modeling, the effect of the 100-year flood was simulated with the replacement of one of the events with the 100-year peak flow, during the spring of the first year when PCB concentrations are at its worst. The conclusions drawn form this run, which shows that the impact is short-lived and minimal, were supported by the modeling results. There are, however, two potential problems with the approach:

(a) The spring flow in the first year was scaled up approximately 4 times (Q_p increases from 21,339 to 47,330 cfs at Fort Edward) to represent the peak flow of the 100-year event, but the duration of the storm was kept constant. The merit of this approach is questionable, in that most bigger floods do not have only higher peaks, but longer duration and higher flow volumes than smaller ones.

(b) Sediment core data indicate that much of the PCB reserves in the sediments are buried at deeper locations. Should the 100-year flood have occurred at a later time, when localized scour has brought the reserves closer to the surface, then the effect may be much more pronounced than currently predicted. This scenario was not considered in answering the Reassessment question 3, but should definitely be included because potential problems may be significant.

Bioaccumulation Models

1. Does the FISHRAND model capture important processes to reasonably predict long term trends in fish body burdens in response to changes in sediment and water exposure concentrations? Are the assumptions of input distribution incorporated in the FISHRAND model reasonable? Are the spatial and temporal scales adequate to help address the principal study questions?

The main processes represented in FISHRAND affecting the concentration of PCBs in fish bodies are:

(a) gill uptake from water column
(b) dietary uptake (both sediment and water-based)
(c) gill elimination (respiration)
(d) fecal egestion
(e) growth rate-related dilution

These should be sufficient to describe the long-term trends in fish body burdens in response to changes in sediment and water exposure concentrations.

The model was run for transects at River Miles 189, 168, and 155, with water and sediment concentration input directly adopted from forecasts of HUDTOX. This spatial scale, which corresponds to the Thompson Island Pool, Stillwater, and Waterford respectively, allows the effects of PCBs on the fish at the most contaminated area (TIP) as well as reaches downstream be studied. The simulation was performed with a time interval of a month, with mean monthly dissolved water concentrations and annual average sediment concentrations. Even though these spatial and temporal scales are not very aggressive, they are adequate to describe the typically slow response of fish body burdens to environmental changes.

2. Was the FISHRAND calibration procedure appropriately conducted? Are the calibration targets appropriate to the purposes of the study?

The first step of calibration for FISHRAND involved a sensitivity analysis, from which it was determined that the most significant parameters to be used for calibration are: TOC, K_{OW} (which affects uptake efficiency, PCB partitioning, and excretion rate), growth rate coefficient, and percent lipid in fish. This was followed by preparation of estimates of the central tendency and distributions for each of the input parameters. The last step was the formal calibration by application of the Bayesian updating procedure to obtain posterior estimates of distributions. The model results are compared to Tri+ concentrations in fish tissues for comparison.

As for location, FISHRAND was calibrated for Stillwater (RM 168) and then applied to the other two locations. For the downstream location at Waterford (RM 155) the parameters were found to be acceptable, but "adjustment" (see p. 73, Book 3 of RBMR) had to be made to the TIP (RM 189) to reflect changes in some environmental factors. Unfortunately, the exact nature of the adjustment and reasoning were not given. This is a significant oversight as the most problematic area in the Upper Hudson also happens to be at TIP.

The calibration target was to produce a set of environmental parameters (common), and fish parameters (species-specific), that give a good match to measured data. Judging from the overall scheme, I think that the calibration approach was adequate. However, I should add that some of the procedures were not explained too clearly in the calibration, and therefore I do not feel confident to suggest that a proper calibration was performed and documented.

3. **In addition to providing results for FISHRAND, the Revised BMR provides results for two simpler analysis of bioaccumulation (a bivariate BAF model and an empirical probabilistic food chain model). Do the results of these models support or conflict with the FISHRAND results? Would any discrepancies among the three models suggest that there may be potential problems with the FISHRAND results, or inversely, that the more mechanistic model is taking into account variables that the empirical models do not?**

The bivariate BAF model is a very crude statistically-based attempt at correlating the fish PCBs concentrations to those of water and sediments. I really do not see very much value in the exercise. Firstly, it did not provide us with much in terms of new insight. The analysis on data for six fish species resulted in these finding:

(a) For Brown Bullheads, which typically has a larger sediment-derived food component, the PCBs in the fish depends strongly on sediment concentrations;
(b) For Pumpkinseed, White Perch and Yellow Perch, whose diet composed of a large fraction of water-borne Epiphytes, their PCBs levels are more strongly related to water column concentrations;
(c) For Largemouth Bass, which has a more mixed diet, the PCBs in the fish depends on both water and sediment concentrations.

Secondly and more important, it does not allow for the effect of the biomagnification process through diet uptake, a process which has been widely accepted as the most significant for prediction of fish body burdens. Therefore, if any statistical correlation are to be performed, the diet's contamination pattern should definitely be included as an independent variable.

As for the empirical probabilistic food chain model, distributions for the bioaccumulation factors between the model compartments were obtained from mean summer-averaged data. It was stated repeatedly in the report that the application should be reserved strictly for long-term quasi-steady state conditions – and never be applied for short-term forecast to fluctuating water column and sediment concentrations. Therefore, it is not an amenable study tool with the HUDTOX's daily forecasts. Even when all the averaging on PCB concentrations are performed from HUDTOX output, the final forecast as given in Figure 5-9 is not doing too well a job with predicting the long-term trends.

In conclusion, I feel that the mechanistic approach in FISHRAND is much more realistic in its representation of the most significant processes affecting bioaccumulation in fish. Both of the other approaches do not add very much to the final conclusions of the study. This is especially true when the modeling framework for data, processes, food-chain compartments, PCB congeners, species etc., are all inconsistent among the three methods. In fact, I am doubtful if any meaningful comparison of the results is even feasible.

4. **Sediment exposure was estimated assuming that fish spend 75% of the time exposed to cohesive sediment and 25% to non-cohesive sediment for the duration of the hindcasting period. The FISHRAND model was calibrated by optimizing three key parameters and assuming the sediment and water exposure concentrations as given, rather than calibrating the model on the basis of what sediment averaging would have been required to optimize the fit between predicted and observed. Is the estimate of sediment exposures reasonable?**

The 75-25 division of exposure among cohesive and non-cohesive sediments is a very questionable approach. There is no evidence in the report that indicates that this was a well-researched and/or widely accepted value. It was simply stated on p.28 of book 3 that fish (except for white perch), on the average, spend 75% of time over cohesive sediments. In sharp contrast to these numbers, according to section 4.3.1.1 on p. 33 of Book 1 of the RBMR report, the actual area of non-cohesive sediments in TIP is approximately three times that of cohesive sediments. Certainly this should somehow affect the exposure ratio, but apparently it was overlooked. With this "75-25 assumption", all the sediment concentrations were calculated from HUDTOX forecasts as weighted averages between the two types of sediments.

It should be pointed out that there are major implications of these calculations. Since the cohesive sediments are in general a lot more contaminated than the non-cohesive ones, the final values of sediment concentration will vary over quite a range depending on the choice of this division. Therefore it should be treated as one of the highly suspicious but important parameters, and be subject to more investigation, careful calibration and even sensitivity analysis.

5. **The FISHRAND model focuses on the fish populations of interest (e.g. adult largemouth bass, juvenile pumpkinseed, etc.) which encompass several age-classes but for which key assumptions are the same (e.g., all largemouth bass above a certain age will display the same foraging behavior). This was done primarily because it reflects the fish data available for the site. Is this a reasonable approach?**

According to Fig. 6-5, which summarizes the distribution of fish size of the samples for each species, there is quite a variation of the sizes among the fish data. As an example, the following lists the ranges of the 90% confidence interval as read off from the figure for a few species:

Largemouth Bass =	250 – 1,550 g
Brown Bullhead =	200 – 750 g
Pumpkinseed =	8 – 27 g

Therefore, to model these species as a single population of interest is a highly debatable approach. The claim in the report (p. 93) that "virtually all the data available for the Hudson River are for fish falling a particular grouping of age-classes" is also an inaccurate one. On the contrary, during the analysis quite a few fish sample data were discarded from the data set because they do not fall within the broad range of the size definitions. This seems like a very wasteful approach to me. The work-intensive procedure involved in obtaining fish sample dictates its scarcity in general, however the database available for the Upper Hudson River is still considerably more extensive than most other. Altogether some over 10,000 samples across all species were collected (p.38), certainly then this should allow for some broadband age-class analysis for at least some of the species.

General Questions

1. **What is the level of temporal accuracy that can be achieved by the models in predicting the time required for averaging tissue concentrations in a given species and river reach to recover to a specified value?**

My personal estimation would be +/- five years.

2. **How well have the uncertainties in the models been addressed? How important are the model uncertainties to the ability of the models to help answer the principal study questions? How important are the model uncertainties to the use of model outputs as inputs to the human health and ecological risk assessments?**

Most of the uncertainties in the models have been fairly well addressed, many of the questionable parameters were investigated with literature review and sensitivity analyses. Ultimately, much of the final estimates were provided in the form of statistical distributions. The models do a good job in general to interpret the large pool of data collection. In the absence of any other solution, the models do provide some solid forecasts upon which decisions may be made. Therefore, as long as decision makers are working within the premise of what models can reasonably provide, they are instrumental tools to help answer the principal study questions.

3. **It is easy to get caught up with modeling details and miss the overall message of the models. Do you believe that the report appropriately captures the "big picture" from the information synthesized and generated by the models?**

In spite of all the technical details of the models, the report manages to stay very focused on providing answers for the principal study questions, and the conclusions drawn have appropriately capture the essence of the implications from the model results and is a fair representation of the "big picture".

4. **Please provide any other comments or concerns with the Revised Baseline Modeling Report not covered by the charge questions, above.**

The following comments apply to the **Hydrodynamic Model,** described in Chapter 3 of Book 1 of the RBMR report:

(a) The calibration of the hydrodynamic model consisted of varying the value for Manning's 'n', so that the predicted upstream elevations match those from rating curve measurements for Q = 30,000 cfs. As a check on the approach, the same 'n' was applied for lower flows of 10,000 and 20,000 cfs, and the results, as given in Table 3-3, were shown in National Geodetic Vertical Datum (NGVD) levels. According to the report, p. 21 of Book 1, model results are "slightly higher than the rating curve for small flows. This presentation of information is misleading in that the NGVD values are typically very high, and so difference in predictions are not as obvious. If, however, the absolute difference between upstream and downstream elevations are shown, they would be as follows :

Flows, cfs	Modeled Difference in water elevation, ft	Rating Curve (Measured) Difference in water elevation, ft	Percent difference from model
10,000	121.5-120.6 = 0.9	121.2-120.6 = 0.6	+ 50%
20,000	123.8-122.2 = 1.6	123.6-122.2 = 1.4	+ 14.3%

These are NOT minor over-estimations! More importantly, most of the flows from past record are at values much lower than the calibration target of 30,000 cfs, which implies that the hydrodynamic model will not be producing accurate results most of the times.

(b) Another indication that there might be some problems with the values of the Manning's 'n' from calibration, is when they are compared to published values:

	Model baseline value	Recommendations from Zimme, 1985	Recommedations from FEMA, 1982
Main channel 'n'	0.02	0.027	0.028-0.035
Flood plain 'n'	0.06	0.065	0.075

Had the model been calibrated to match the water profiles at lower flows, the 'n' values would be higher, and more consistent with suggestions from other sources.

(c) The entire chapter 3 has no indication anywhere for the values of river depth, h. Instead, only surface elevations, z, were used. However, when refer back to the original continuity equation, the flow depth is one of the three state variables. Without any reference to the river bed bottom elevations, the NGVD elevations are almost useless to the reader.

Recommendations

The following are my recommendations on the two models based on the review of the information provided:

1. The Fate and Transport Models

Recommendation: Acceptable with Minor Revision

Explanation:

The Fate and Transport Models Report was very well-presented and thorough. The concepts underlying the major components of hydrodynamic, depth-of-scour, and HUDTOX are all well documented. The model calibration and hindcast were both performed very well. Except for some minor revision, I find the report acceptable in its theoretical basis and technical approach. Suggestions on the report include some refinement with the solids balancing, the improvement on the analysis of the sediment-water mass transfer, and an extension of the 100-year flood study with various scenarios.

2. The Bioaccumulation Models

Recommendation: Acceptable with Major Revision

Explanation:

The report for the bioaccumulation models is in general of poor quality, with quite a few editorial errors. In a few instances, the review work was hampered because of the obscure presentation. In particular, the first two methods (the bivariate BAF model and the empirical probabilistic food chain model) are presented to provide complementary views of PCB uptake, but with the very different frameworks really did nothing much to elucidate the problem. Furthermore, they were never used for any forecast simulations, and therefore do not provide much in terms of addressing the study objectives. The same goes with FISHPATH, which was presented partially but never applied. More effort should be expended on the preparation of an improved analysis from the FISHRAND, which in theory is an excellent tool to utilize the HUDTOX results to provide answers to the Reassessment questions. Some major revisions are necessary for the report, and these include the utilization of the three-phase partition results, age-class study for the upper species, more thorough lipid analyses, and the improvement of model performance on the lipid-normalized concentrations.

Dr. Wu-Seng Lung

Biography

Wu-Seng Lung

Wu-Seng Lung has a B.S. in Civil Engineering from National Cheng Kung University, Taiwan, a M.S. in Civil Engineering from the University of Minnesota and a Ph.D. in Civil Engineering (Water Resources) from the University of Michigan. He has over 25 years of experience in modeling natural water systems.

Between 1975 and 1983, he worked at three consulting firms applying modeling to various water quality studies for regulatory agencies, industries, and law firms. Dr. Lung joined the Civil Engineering Department at the University of Virginia in 1983 and is now a Professor. He has published a book entitled, Water Quality Modeling: Application to Estuaries, by CRC Press. Dr. Lung served as Associate Editor for *Journal of Environmental Engineering* from 1994 to 1998 and is now the Editor-in-Chief of *Water Quality and Ecosystem Modelling*. He is a member of the EPA Science Advisory Board, serving on the Environmental Modeling Committee.

Comments on Hudson River PCBs Reassessment Baseline Modeling Report

The following comments are prepared based on my review of the following documents:

1. Revised Baseline Modeling Report (January 2000) by Limno Tech, Inc.
2. Responsiveness Summary to the Baseline Modeling Report (February 2000)
3. Final Report of the Hudson River PCBs Site Modeling Approach Peer Review (November 1998)
4. Final Report on the Peer Review of the Data Evaluation and Interpretation Report and Low Resolution Sediment Coring Report for the Hudson River PCBs Superfund Site (June 1999)

To gain a broader perspective of the modeling study, I also reviewed the reports by Quantitative Environmental Analysis (QEA). This write-up represents my comments to date. Additional comments may be presented at the meeting on March 27-28.

1. *The HUDTOX model links components describing the mass balance of water, sediment, and PCBs in the Upper Hudson. Are the process representations of these three components compatible with on another, and appropriate and sufficient to help address the principal study questions?*

The HUDTOX modeling framework consists of a hydrodynamic model and a fate and transport model of PCBs for the Upper Hudson River from Ft. Edward to the Federal Dam for a distance of approximately 40 miles. The hydrodynamic processes and water column kinetics are appropriate for representing the PCB concentrations in the system. The water quality constituents modeled are solids, total PCBs, Tri+ (PCB_{3+}) and five PCB congeners. The main focus is on the Tri+ species, which is the portion bioaccumulates in fish. The modeling approach presented in the revised Baseline Report is technically sound to address the principal study questions.

2. *The HUDTOX representation of the solids mass balance is derived from several sources, including long-term monitoring of tributary solids loads, short-term solids studies and the results of GE/QEA's SEDZL model. The finding of the solids balance for the Thompson Island Pool is that this reach is net depositional from 1977 to 1997. This finding has also been assumed to apply to the reaches below the Thompson Island Dam. Is this assumption reasonable? Are the burial rates utilized appropriate and supported by the data? Is the solids balance for the Upper Hudson sufficiently constrained for the purposes of the Reassessment?*

Having said that, however, there lacks a sediment transport model to track the movement of sediments at the riverbed. Instead, results from the sediment transport model, SEDZL, are utilized to assign sediment burial rates for the study area. This appears to be a weak link in the HUDTOX modeling framework as the sediment-water interaction for particles is the key process characterizing the fate and transport of the PCBs in the system, particularly in the Thompson Island Pool. While using the SEDZL results yields a reasonable representation of the solids balance, a full-scale sediment transport model that has the predictive capability for future conditions would minimize uncertainties associated with the sediment burial and deposition rates. Since the HUDTOX modeling framework already uses a fine resolution hydrodynamic model in the water column providing information on bottom shear stress, it is only logical to fully utilize this data in a sediment transport model, making a seamless integration of the three model components.

Regarding the burial rates, the LTI study uses 0.65 cm/yr and 0.07 cm/yr for cohesive and non-cohesive sediments, respectively, while the QEA study uses 0.81 cm/yr and 0.03 cm/yr respectively. To solids balance in the Upper Hudson is maintained by a net deposition rate, the difference between the absolute burial rate and resuspension rate. As long as the net rate is reasonable, the solids balance can be achieved. The difference in burial rates between the two modeling studies must be compensated for in the resuspension rates because results from both LTI and QEA studies give very good fit of solids with the data. Note that the LTI study shows the long-term solids results from 1977 to 1997 matching the general trend of the data. The QEA results focus primarily on the short-term storm events and their results mimic the data quite well.

It should be pointed out that the solids balance presents only part of the picture. While slight variations of burial and resuspension rates are tolerable in solids balance calculations (as displayed in the results from both modeling teams). For PCB modeling, accurate absolute burial and resuspension rates of solids are essential. The true test of the model comes in the PCB modeling.

3. *HUDTOX represents the Upper Hudson River by segments of approximately 1000 meters in length in the Thompson Island Pool, and by segments averaging over 4000 meters (ranging from 1087 to 6597 meters) below the Thompson Island Dam. Is this spatial resolution appropriate given the available data? How does the spatial resolution of the model affect the quality of model predictions?*

The Upper Hudson River below the Thompson Island Dam is represented in HUDTOX with a 1-D configuration in the water column (for a total of 19 segments) and 2-D in the sediment. In the Thompson Island Pool, it is configured as 2-D in the water column (for a total of 28 segments) and 3-

D in the sediment. Such a spatial resolution is considered appropriate in light of the data available. More importantly, this resolution is compatible with the longitudinal gradients of PCBs in the Upper Hudson River. The model developed by QEA has a comparable segmentation in the longitudinal direction. In general, where receiving water concentrations show or are expected to show a rapid rate of change of concentration, small segment lengths are selected to reproduce these gradients. In the box type models, accuracy of the calculated solution is a function of segment size. The term associated with accuracy based on segment size is called numerical error and can be thought of as an additional mixing or dispersion (in the longitudinal direction in this case) term. To minimize errors, this term should be on the order of, or less than, the actual dispersion coefficients. It appears that segment sizes in TIP and the river below TID have been selected to satisfy both criteria noted above and are consistent with the resolution found in many other riverine water quality models.

4. *Is the model calibration adequate? Does the model do a reasonable job in reproducing the data during the hindcast (calibration) runs? Are the calibration targets appropriate for the purposes of the study?*

The model calibration results look reasonable, particularly the long-term Tri+ concentration trends at various locations. Note that the QEA model results of PCB_{3+} are very similar to the HUDTOX results.

5. *HUDTOX employs an empirical sediment/water transfer coefficient to account for PCBs loads that are otherwise not addressed by any of the mechanisms in the model. Is the approach taken reasonable for model calibration? Comment on how this affects the uncertainty of forecast simulations, given that almost half of the PCB load to the water column may be attributable to this empirical coefficient.*

The HUDTOX model uses an empirical sediment-water transfer coefficient to account for non-hydrodynamically related PCB loads in the Thompson Island Pool. Such a scheme works for the model calibration analysis. The degree of empiricism has actually improved since the draft report in May 1999. At the present time, a constant temporal function is utilized throughout the simulation period for both cohesive and non-cohesive solids. This reduces the number of knobs in the model calibration. Note that the seasonally variable mass transfer coefficient, k_f, which is derived from data from 1993 to 1997, is noticeably higher than the value developed by QEA. [The k_f values derived by QEA are based on the water column and sediment data collected in 1998.] While this empirical approach is acceptable for model calibration, it is not clear whether k_f would change over time, particularly over a long period, which would have an impact on the long-term model simulation results. Essentially, the model uses a parameterization procedure to incorporate a not-too-well-understood process. Making the k_f rate for cohesive sediments twice as the k_f rate for non-cohesive sediments in the model sensitivity analysis do not change the results much and it may not address the issue. Perhaps some feedback from the water column PCB dynamics to this parameter may be incorporated into the model to further reduce the degree of empiricism.

As stated in the charge question, this process accounts for almost half of the PCB load to the water column in Thompson Island Pool. This appears to be one of the most significant uncertainties in the model.

6. *Are there factors not explicitly accounted for (e.g., bank erosion, scour by ice or other debris, temperature gradients between the water column and sediments, etc) that have the potential to change conclusions drawn from the models?*

The modeling framework represents the closest representation of the PCB fate and transport in the Upper Hudson given the extent of the available data. Many other processes may be included but must have data to support the parameterization of the processes in the model. On the other hand, the model can be used to explore any missing processes by analyzing individual processes currently in the model along with the model sensitivity runs to provide additional physical insights into the dynamics of the system.

7. *Using the model in a forecast model requires a number of assumptions regarding future flows, sediment loads, and upstream boundary concentrations of PCBs. Are the assumptions for the forecast reasonable? Is the construct of the hydrograph for forecast predictions reasonable? Should such a hydrograph include the larger events?*

While the upstream boundary concentrations of PCBs of 0, 10, and 30 ng/L provide a bound analysis for the forecast simulations, it is clear that the upstream concentration would reduce with time, particularly for the long-term simulation of 70 years. Perhaps a more reasonable upstream boundary concentration should include this feature. It would also be interesting to simply repeat the 20-yr hydrograph from 1977 to 1997 in sequence for the model simulation. That is, the model runs would recycle the 20-yr observed hydrograph continuously.

8. *The 70-year model forecasts show substantial increases in PCB concentrations in surface sediments (top 4 cm) after several decades at some locations. These in turn lead to temporary increases in water-column PCB concentrations. The increases are due to relatively small amounts of predicted annual scour in specific model segments, and it is believed that these represent a real potential for scour to uncover peak PCB concentrations that are located from 4 to 10 cm below the initial sediment-water interface. Is this a reasonable conclusion in a system*

that is considered net depositional? After observing these results, the magnitude of the increases was reduced by using the 1991 GE sediment data for initial conditions for forecast runs. Is this appropriate? How do the peaks affect the ability of the models to help answer the Reassessment study questions?

Before addressing this question, let me point out the following. The HUDTOX modeling report states that the sediments in the Upper Hudson River from Ft. Edward to Waterford is a sink for the solids from 1977 to 1997 (see Figure 7-14), which is expected. On the other hand, Figure 7-31 suggests that the sediments are a source for PCBs (Tri+). The sediment-water interaction of PCBs in the Upper Hudson River can be summarized in the following table. Results from the following table show that the sediment system is a major source of PCB to the water column from 1977 to 1997. It is still not clear to me how this small amount of annual scour in certain model segments is predicted. To help understand this, one may need to print out the time-series of the sediment-water interaction of PCBs (in fluxes) for these segments. Physical insights such as this are extremely important for us to understand the fate and transport of the PCBs in the Upper Hudson River and help managers to grasp the big picture.

Sediment-Water Interaction of PCBs in Upper Hudson River

River Portion	Settling (kg)	From Sediment (kg)	Difference (kg)
Thompson Island Pool	1,006	5,256	4,250
TID to Schuylerville	1.027	3,972	2,945
Schuylerville to Stillwater	4,027	4,725	698
Stillwater to Waterford	3,393	5,987	2,594
Total			10,487

A hypothetical long-term model run may recycle the 1977-1997 (known) hydrograph with continuing decreasing PCB concentrations at the upstream boundary to see if this small amount of scour is still predicted.

9. *The timing of the long-term model response is dependent upon the rate of net deposition in cohesive and non-cohesive sediments, the rate and depth of vertical mixing in the cohesive and non-cohesive sediments and the empirical sediment-water exchange rate coefficient. Are these rates and coefficients sufficiently constrained for the purposes of the Reassessment?*

As stated in the LTI report, the sediment mixed layer depth and particle-mixing rate are parameters for which direct measurements are not available. They may not be quite constrained as the model sensitivity results show.

10. *The HUDTOX model uses three-phase equilibrium partitioning to describe the environmental behavior of PCBs. Is this representation appropriate? (Note that in a previous peer review on the Data Evaluation and Interpretation Report and the Low Resolution Sediment Coring Report, the panel found that the data are insufficient to adequately estimate three-phase partition coefficients.)*

This three-phase equilibrium partitioning is first time considered for the PCB modeling of the Hudson River as previous modeling studies, e.g., by Thomann only consider the partitioning between the dissolved and sorbed PCBs. While non-equilibrium or slow partitioning may be observed, using instantaneous equilibrium is considered mathematically tractable. As stated in the LTI report, total PCB is used only for estimating total PCB transport and is not used for primary calibration of the HUDTOX model, uncertainty in total PCB partitioning behavior does not affect the calibration.

11. *HUDTOX considers the Thompson Island Pool to be net depositional, which suggests that burial would sequester PCBs in the sediment. However, the geochemical investigations in the Low Resolution Sediment Coring Report (LRC) found that there was redistribution of PCBs out of the most highly contaminated areas (PCB inventories generally greater than 10 g/m) in the Thompson Island Pool. Comment on whether these results suggest an inherent conflict between the modeling and the LRC conclusions, or whether the differences are attributable to the respective* spatial scales of the two analyses.

The table presented in the answer to Question 8 shows that Thompson Island Pool is a source of PCBs to the water column.

12. *The model forecasts that 100-year flood event will not have a major impact on the long-term trends in PCB exposure concentrations in the Upper Hudson. Is this conclusion adequately supported by the modeling?*

The DOSM model (applied to TIP only) was used to develop relationships between river flow and cohesive sediment resuspension for use in the HUDTOX model. The hydrodynamic model was run for a range of flow conditions spanning typical summer flows to the 100-year flow. The DOSM was used to estimate cohesive sediment resuspension for each of these flow conditions, thus producing a family of resuspension-flow relationships. The relationships were used as input to the HUDTOX model to represent cohesive sediment resuspension across all flow conditions in the Thompson Island Pool portion of the River (p. 10 of the LTI report). The answer to this question lies in the sediment transport model. Results from the model by QEA may be able to substantiate this finding, as there is a sediment transport model in that package.

Dr. Robert Nairn

Biography not available at time of print

Hudson River PCB's Site Reassessment RI/FS
Baseline Modeling Report
Peer Review 3

Charge Questions And Responses

R.B. Nairn, Ph.D., P.Eng.
W.F. Baird & Associates Ltd.

FATE AND TRANSPORT (HUDTOX)

1. The HUDTOX model links components describing the mass balance of water, sediment, and PCB's in the Upper Hudson. Are the process representations of these three components compatible with one another, and appropriate and sufficient to help address the principal study question?

My specific training, experience and expertise relate to hydrodynamic and sediment transport modeling. Therefore, throughout this review, including my response to the charge questions, I will focus on these aspects of the Revised Baseline Modeling Report. I have focused on Book 1 of Volume 2D and any references to page numbers or "the report" refer to this document.

With respect to Question 1, I have reviewed in detail the components of HUDTOX associated with mass balance of water and solids and will answer the three parts of Question 1 accordingly.

The process representations of the mass and sediment balances are compatible. However, this is only due to the fact that the hydrodynamic model (RMA2) has been applied in a steady state manner and that a very generalized flow routing has been developed to match the spatial resolution of the HUDTOX model segments. The RMA2 model was never applied in a true "hydrodynamic" sense and it is incorrect to state that a hydrodynamic model has been applied by LTI in these investigations. As will become apparent in answers to later questions, this is an important distinction.

I have concerns that the representations of water and sediment balances may not be appropriate nor sufficient to address the principal study questions. I am certain that Study Question 3 regarding the possibility of a flood scouring and redistributing sediments has not be addressed sufficiently due to the selected spatial and temporal scales of the HUDTOX model (or for that matter the linked RMA2-DOSM model). With respect to Study Question 1, my concern relates to the importance of the spikes in PCB concentrations that have been predicted by HUDTOX to occur in the future. It certainly appears that HUDTOX is capable of simulating the long term averaged decay of PCB concentrations in the water and sediment. However, I believe that the spatial and temporal representation of processes in HUDTOX related to the water and sediment balance are inappropriate to reliably predict the potential, magnitude and frequency of future spikes in PCB concentration. Whether this is a critical problem will depend on the assessment of the importance of these spikes by experts in bioaccumulation.

These points are elaborated at length in answers to other questions below.

2. **The HUDTOX representation of the solids mass balance is derived from several sources, including long-term monitoring of tributary solids loads, short-term solids studies and the results of GE/QEA's SEDZL model. The finding of the solids balance for the Thompson Island Pool is that this reach is net depositional from 1977 to 1997. This finding has also been assumed to apply to the reaches below the Thompson Island Dam. Is this assumption reasonable? Are the burial rates utilized appropriate and supported by the data? Is the solids balance for the Upper Hudson sufficiently constrained for the purposes of the Reassessment?**

It is my opinion that the statement that the TIP and lower reaches of the Upper Hudson are "net depositional" is not a finding, but an assumption. Furthermore, this assumption is based on relatively weak evidence and has a tremendous impact on the nature of future spikes in PCB concentration in the water and surface sediments, if not the long term trends. Pages 82 and 83 of Book 1 of Volume 2D explain that the system was assumed to be net depositional due to the fact that the Upper Hudson *"is an impounded system with six dams over the 40 miles between Fort Edward and Waterford"*. Additional supporting evidence for the net depositional assumption and to determine burial rates includes the SEDZL modeling by QEA (1999) and the information from the high resolution sediment cores (p. 128 of the report). On the same page, the report notes that *"there are limitations to the high-resolution sediment cores that preclude the direct use of these data as calibration inputs. The cores are few in number and not considered representative of average solids burial rates on the spatial scale of the HUDTOX model."* Therefore, the entire basis for assuming the system is net depositional relates to the opinion that this should be the case in an impounded river and to the SEDZL findings by QEA. The SEDZL findings are also later used to quantify sediment burial rates based on the trapping efficiency for different reaches of the SEDZL model.

In summary, the only evidence that the Upper Hudson is net depositional stems from the findings of the SEDZL model. I have only completed a preliminary review of QEA (1999) and cannot provide a fully informed opinion of the reliability of this finding by QEA at this time. However, QEA would be faced with the same dilemma of insufficient information to test validate the net deposition assumption (or the burial rate quantification).

The solids balance for the Upper Hudson has been constrained by the key assumption that the Upper Hudson is net depositional and the findings from SEDZL to quantify burial rates. These two pieces of information were used to complete a solids balance. To complete the balance, the tributary loadings (as determined by the available data, rating curves and indirectly the drainage area ratio (DAR) method for tributaries without discharge data) downstream of TID were increased significantly and arbitrarily to make up for a large deficit between incoming and outgoing sediment loads between Fort Edward and Stillwater and Stillwater and Waterford.

In addition to the arbitrary (i.e. without direct justification) increase to tributary loads in the solid balance, there are several other uncertainties associated with estimation of the in-river sediment loads as listed below:

- The different techniques used to determine TSS concentrations (see page 76 – USGS vs. GE methods) and the resulting development of total loads at the key boundaries for the solids balance (Fort Edward, Stillwater, etc.);
- The time stratification of the sediment load rating curves at Fort Edward (before and after 1991);
- Uncertainty related to determining a depth-averaged sediment load when variations in velocity and sediment load through the water column are considered - particularly for the GE data where TSS was sampled at three discrete depths;
- Tremendous scatter in discharge-TSS plots used to develop ratings curves;
- Use of the GE data only for the period after 1991 which leads to a decrease in incoming sediment loads at Fort Edward (p. 80);

Some but not all of these potential sources of uncertainty in constraining the solids balance have been addressed.

The greatest concern with the solids balance is the fact that tributary loadings were increased by a factor of 2.46 between TID and Stillwater and 1.91 between Stillwater and Waterford. The ultimate basis for these corrections relates in principle to the unproven "net depositional" assumption and in absolute terms to the trapping efficiencies estimated with SEDZL by QEA (1999).

The forecasts completed in Section 8 show that the spikes in future surface sediment and water PCB concentrations are very sensitive to tributary sediment loading assumptions, particularly downstream of TID.

An underlying problem is the lack of understanding of two key processes that have a large influence on the solids balance:

1. Runoff, soil erosion and in-tributary erosion for the tributary and adjacent

watersheds;
2. Morphodynamics and the related river bed evolution.

3. **HUDTOX represents the Upper Hudson River by segments of approximately 1000 meters in length in the Thompson Island Pool, and by segments averaging over 4000 meters (ranging from 1087 to 6597 meters) below the Thompson Island Dam. Is this spatial resolution appropriate given the available data? How does the spatial resolution of the model affect the quality of model predictions?**

A shortcoming of the RBMR (Volume 2D) is the lack of graphical information presented to describe the characteristics of the river such as bathymetry and detailed sediment bed maps. However, based on information provided in this report and in reports by others (e.g. QEA, 1999) it appears that a higher spatial resolution could be achieved with the available data. However, it seems that the decision by LTI to apply the selected resolution for HUDTOX was more related to taking a "long term" predictive philosophy to the modeling. This decision has served well the prediction of long terms trends in the decay of PCB's but is not well suited to shorter time scale and finer spatial scale issues such as the exposure of localized areas of highly contaminated sediments (and the resulting spikes in PCB concentrations) and the assessment of scour in a 100 year event.

As noted above, it is my opinion that the selected spatial and temporal resolutions are insufficient to appropriately assess the resuspension in a 100 year event and the magnitude and frequency of future spikes in PCB concentrations.

4. **Is the model calibration adequate? Does the model do a reasonable job in reproducing the data during the hindcast (calibration) runs? Are the calibration targets appropriate for the purposes of the study?**

With respect to the flow modeling, the calibration and validation were limited to the following exercises:

- Calibration was completed through adjustment of a single value of Manning's 'n' for the entire length of the main channel and for a flow of 30,000 cfs. The selected Manning's 'n' is within a range of appropriate values for 2D models.
- Validation of flow velocities against measurements from one location on a single day – detailed comparisons are not provided (p. 21).
- Validation through comparisons to the FEMA HEC-2 model water levels.

While these calibration and validation exercises may be sufficient to verify the ability of the model to provide accurate inputs at the spatial and temporal scale of HUDTOX, they are not sufficient for assessments at a more detailed scale as may be required for assessment of processes associated with shorter time scale and finer spatial resolution such as resuspension during the 100 year flood or the magnitude and frequency of spikes in future PCB concentrations.

With respect to the sediment dynamics, the calibration consisted of *"adjusting constant gross settling velocities for cohesive and non-cohesive areas, and resuspension rates from non-cohesive areas"* to agree with the target burial rates (p.127/128). The settling velocities were calibrated using the results of the SEDZL model simulations completed by QEA (1999). The report notes (p. 128) the "uncertainty" associated with the burial rates determined by SEDZL.

The calibrated gross settling velocity for cohesive sediments (4.15 m/year) is very low and not representative of actual settling velocities. In fact, this settling velocity corresponds to a condition where the product of concentration (in mg/l) and shear stress (in dynes/cm^2) is approximately 6, for example a concentration of 3 mg/l and a shear stress of 2 dynes/cm^2 (see Burban et al, 1990). Clearly, the calibrated gross settling velocity no longer represents the actual localized process of settling (as it is much too low) and is essentially a calibration parameter with little physical meaning. The same argument applies to the very low gross settling velocities calibrated for non-cohesive sediments (1.5 m/day) very low high-flow solids resuspension velocity of 3.6 to 16.4 mm/year. This approach to calibration where physical process representation is undermined at the expense of calibration may be sufficient to describe long term trends in PCB's, but again, is in appropriate to evaluate processes that are dependent on a finer spatial and temporal scale (such as the 100 year scour or the forecasted future PCB concentration spikes).

In a sense the development of tributary loadings discussed in Chapter 6 of the report was also a form of calibration, in that case against a notion of net deposition and the burial rates determined from SEDZL.

The reasonably good comparisons to suspended load are due to the calibration and adjustment of incoming sediment loads at the model external (Fort Edward) and internal boundaries (tributary loads). These comparisons may provide some level of confidence in the ability of HUDTOX to simulate long term sediment balance and PCB trends, but certainly not resuspension processes at a finer scale.

Therefore, the overall representation of sediment dynamics in HUDTOX is very heavily, if not entirely, dependent on the accuracy and reliability of the burial rates determined by QEA (1999) with SEDZL. In addition, while the representation appears to be sufficient to describe long term, large scale processes compatible with long term trends it is not compatible with shorter term processes (such as the 100 year scour or the forecasted future PCB concentration spikes).

In order to calibrate or validate a model to finer scale processes such as local erosion and deposition, it would be necessary to compare the model predictions to information on local velocities and local bed changes measured at a number of locations or transects (or averaged over discrete areas in the case of river bed change).

5. **HUDTOX employs an empirical sediment/water transfer coefficient to account for PCB's loads that are otherwise not addressed by any of the mechanisms in the model. Is the approach taken reasonable for model calibration? Comment on how this affects the uncertainty of forecast simulations, given that almost half of the PCB load to the water column may be attributable to this empirical coefficient.**

My background is not applicable to this question.

6. **Are there factors not explicitly accounted for (*e.g.*, bank erosion, scour by ice or other debris, temperature gradients between the water column and sediment, etc.) that have the potential to change conclusions drawn from the models?**

Factors such as bank erosion and scour by ice or other debris are certainly not important relative to the temporal and spatial scale of HUDTOX. In other words, they are probably not important with respect to long term trends, and even of they were, they have likely been captured by some facet of the solids balance calibration (i.e. adjustment of tributary loadings) or through the adjustment of the gross settling velocity and resuspension of non-cohesive sediments.

There are a range of key factors that have not been explicitly accounted or may have been considered incorrectly and these are described below.

There may be a key problem with the parameterization of the resuspension of cohesive sediments in the Depth of Scour Model (DOSM). The problem relates to the concept developed by Willy Lick that at a given shear stress erosion potential is achieved over approximately one hour. It is believed that a lag of flocs or larger grains forms during the erosion process to provide a protective layer over the underlying sediment. In a number of publications (including Galiani et al, 1991 and Lick et al, 1995 quoted in the report) it is clearly indicated that erosion is reactivated once the shear stress is increased (and the lag protection is removed by the higher flow velocities). Also, this understanding of the erosion process of cohesive sediments has largely been developed from Shaker test experiments that are only capable of simulating shear stresses of approximately 10 dynes/cm^2 or less. Under higher shear stresses that occur in the Hudson River during flood events (with shear stresses well in excess of 10 dynes/cm^2), it is possible that a protective layer may not even form (the critical shear stress for sand particles is less than 10 dynes/cm^2 and for fine gravel is in the range of 50 dynes/cm^2). The limitations of the Shaker test have been documented in detail by Lick et al (1995 – Measurements of the Resuspension and Erosion of Sediments in Rivers, UC-SB report).

On page 33 it is outlined that resuspension potential is limited to the maximum predicted erosion during one hour of the peak flow for the DOSM application. Therefore, the DOSM estimates of scour during the peak flow of a 100 year flood event are not meaningful as they only represent scour for a one hour period. The fact that erosion is reactivated throughout the rising limb of the flood hydrodgraph (with the removal of protective lag deposits) and that lag deposits may not develop at very high shear stresses have not been considered.

The approach to resuspension of cohesive sediments in the HUDTOX model is described on page 47 of the report. It is stated that: *"resuspension occurring over previous model time steps within an increasing hydrograph is tracked such that total cumulative erosion equals the amount computed using the maximum shear stress during that event ... The total amount of erosion is limited by the maximum predicted erosion associated with the peak flow"*. This description of resuspension approach in HUDTOX is confusing but would seem to imply that only one hour of erosion occurs (associated with the peak flow) during any given flood event simulated by HUDTOX. If this is the case, the model has been formulated incorrectly and resuspension will be significantly underpredicted both for the 100 year event and for all flood events simulated by HUDTOX.

The fact that a <u>steady state</u> flow model has been applied to a <u>very coarse</u> resolution grid will severely restrict the ability of the model to simulate erosion of both cohesive and non-cohesive sediments. Local values of high velocities in time and space are ignored. While these velocities may not be important with respect to long term trends, it is well accepted that erosion and scour processes are very episodic and local erosion and redistribution of sediment will simply not be represented by HUDTOX.

Finally, with respect to the overall evolution of the river bed in the TIP it was surprising that the bed changes associated with the removal of the Fort Edward Dam were only mentioned in passing on p. 79: *"Over the period between July 1973 and April 1976, following removal of the Fort Edward Dam in 1973, approximately 1.0 million cubic yards of PCB laden sediments were washed downstream into Thompson Island Pool."* This is a tremendous amount of sediment and equivalent to more than <u>twice</u> the sediment delivered to the TIP over <u>20 years</u> during the 1977 and 1997 calibration period. Where did this sediment end up? How did it influence the river bed dynamics in TIP? Almost certainly this resulted in a tremendous perturbation to the dynamics of the TIP river bed and is probably still influencing the resuspension and redistribution processes within the TIP.

7. **Using the model in a forecast mode requires a number of assumptions regarding future flows, sediment loads, and upstream boundary concentrations of PCBs. Are the assumptions for the forecast reasonable? Is the construct of the hydrograph for forecast predictions reasonable? Should such a hydrograph include larger events?**

I have been closely involved in a project over the last four years which is assessing the potential flooding and erosion rates along the entire shore of Lake Michigan over the next 50 years. The Great Lakes Environmental Research Lab (GLERL) in Ann Arbor has stochastically developed a sequence of possible net basin supplies to the Great Lakes to determine plausible future lake level scenarios over the next 50 years. Many of these scenarios featured periods of much higher lake levels (due to increased precipitation and decreased evaporation) and more frequent highs than have been experienced in the last 50 to 100 years. The predicted GLERL scenarios agreed well with paleo-lake level evidence (such as beach ridge and swash zone elevations) of much higher lake levels in the last several thousand years since the lakes stabilized near the existing levels. These scenarios did not consider the impact of global warming. It would seem prudent to assess the impact of plausible changes in future hydrology (such as increased occurrence of higher floods and/or higher extremes). The report only considers different sequencing of the existing record.

Another key uncertainty in the future (not to mention the past and present) relates to tributary discharge and loadings. Changes to land use practices could significantly alter tributary runoff characteristics which could lead to either an increase (e.g. with higher soil loss due to increased agricultural land use or increased flashiness due to urbanization and resulting bank erosion in the tributaries) or a decrease in sediment loading (e.g. due to improved agricultural practices or due to urbanization). In the model forecasts it has been demonstrated that the frequency and magnitude of future spikes in PCB concentrations are very sensitive to tributary loading.

8. **The 70-year model forecasts show substantial increases in PCB concentration in surface sediments (top 4 cm) after several decades at some locations. These in turn lead to temporary increases in water-column PCB concentrations. The increases are due to relatively small amounts of predicted annual scour in specific model segments, and it is believed that these represent a real potential for scour to uncover peak PCB concentrations that are located from 4 to 10 cm below the initial sediment-water interface. It is a reasonable conclusion in a system that is considered net depositional? After observing these results, the magnitude of the increases was reduced by using the 1991 GE sediment data for initial conditions for forecast runs. Is this appropriate? How do the peaks affect the ability of the models to help answer the Reassessment study questions?**

It is my opinion that the system has not been proven to be net depositional. A system cannot be net depositional indefinitely, particularly where dams consist of submerged weirs. An equilibrium bed condition will eventually be established in these cases. Nevertheless, even if the system were proven to be net depositional, the occurrence of long term erosion at some locations that will uncover once buried PCBs is entirely possible. This occurrence is an natural outcome of an evolving river bed where areas that were once depositional become erosional due to changes in the upstream river bed conditions, flows and sediment loadings (both locally and on a larger river system scale). From the information provided, the river bed of the TIP almost certainly is evolving. A large influence on this evolution will have been the perturbation to the system caused by the removal of the Fort Edward dam.

Whether it was appropriate to use the 1991 GE sediment data as initial conditions for the forecast conditions is not really the issue. The main issue is that the morphodynamics or river bed dynamics throughout the Upper Hudson are simply not adequately represented by the temporal and spatial scale of the HUDTOX model. Therefore, the prediction of the frequency and magnitude of the spikes in PCB concentrations (that are caused by local erosion) with HUDTOX are not expected to be reliable.

9. **The timing of the long-term model response is dependent upon the rate of net deposition in cohesive and non-cohesive sediments, the rate and depth of vertical mixing in the cohesive and non-cohesive sediments and the empirical sediment-water exchange rate coefficient. Are these rates and coefficients sufficiently constrained for the purposes of the Reassessment?**

My background and expertise allow me to comment on the first part of the question related to the rate of net deposition in cohesive and non-cohesive sediments. In the response to Question 4 on calibration, it was noted that the gross settling rates for cohesive and non-cohesive sediments are very low and not representative of true physical processes, at least at scale that these parameters are normally measured. These values may be better understood simply as calibration parameters to achieve a coarse resolution (in time and space) representation of sediment dynamics. The settling rates are essentially calibrated against the long term burial rates that in turn are determined from the results of the SEDZL modeling completed for the Upper Hudson by QEA (1999). A preliminary review of the QEA (1999) report demonstrates that the predicted burial rates appear to compare well to the limited field data available from the high resolution cores. However, in order to provide an answer to whether these rates are sufficiently constrained for the purposes of the Reassessment, the QEA (1999) report would have to be reviewed in detail.

10. **The HUDTOX model uses three-phase equilibrium partitioning to describe**

the environmental behavior of PCB's. Is this representation appropriate? (Note that in a previous peer review on the Data Evaluation and Interpretation Report and the Low Resolution Sediment Coring Report, the panel found that the data are insufficient to adequately estimate three-phase partition coefficients).

My background is not applicable to this question.

11. **HUDTOX considers the Thompson Island Pool to be net depositional, which suggests that burial would sequester PCBs in the sediment. However, the geochemical investigations in the Low Resolution Sediment Coring Report (LRC) found that there was redistribution of PCBs out of the most highly contaminated areas (PCB inventories generally greater than $10 g/m^2$) in the Thompson Island Pool. Comment on whether these results suggest an inherent conflict between the modeling and the LRC conclusions, or whether the differences are attributable to the respective spatial scales of the two analyses.**

My answer to this question is similar to my response to Question 8. The HUDTOX model provides a glimpse of the potential for the local erosion and exposure of contaminated sediments (through the spikes in PCB concentration) associated with the redistribution of sediment in a system that may be net depositional. In other words, if it is proven that the system is net depositional – this is a very slow and spatially averaged process. There will invariably be areas of the river bed that experience long term erosion and these areas might once of have been depositional zones. This process of complex river bed evolution will not be well represented by the spatial and temporal scale of the HUDTOX model. While the model was able to highlight the possibility of the occurrence of spikes in PCB concentrations the temporal and spatial scale of the model is not sufficient to reliably predict the frequency and magnitude of these spikes.

12. **The model forecasts that a 100-year flood event will not have a major impact on the long-term trends in PCB exposure concentrations in the Upper Hudson. Is this conclusion adequately supported by the modeling?**

No, this conclusion is not adequately supported by the modeling for the reasons explained in my response to Question 6 and summarized below:

- It would appear that the parameterization of resuspension for cohesive sediments may be incorrect due to what I understand to be a one hour limit to erosion for the 100 year event;
- A hydrodynamic simulation of the 100 year event has not been completed;
- The temporal and spatial scale of the HUDTOX model is far too coarse to

adequately represent erosion processes at a spatial scale compatible with the consideration of a single flood event.

BIOACCUMMULATION MODELS – N/A to expertise of R. Nairn

GENERAL QUESTIONS

1. **What is the level of temporal accuracy that can be achieved by the models in predicting the time required for average tissue concentrations in a given species and river reach too recover to a specified value?**

My background is not applicable to this question.

2. **How well have the uncertainties in the models been addressed? How important are the model uncertainties to the ability of the models to help answer the principal study questions? How important are the model uncertainties to the use of model outputs as inputs to the human health and ecological risk assessments?**

A principal model uncertainty relates to the ability of HUDTOX to predict the processes at a temporal and spatial scale necessary to describe erosion during a 100 year event and local erosion associated with the exposure of highly contaminated sediments in the future (leading to spikes in PCB concentrations). The HUDTOX model appears to be sufficient to represent the long term decay of the PCB concentrations in the water and surface sediments. However, if the potential for PCB concentration spikes in the future or exposure of contaminated sediment during a 100 year event are important to human health and ecological risk assessments, the HUDTOX model as presently formulated is not an appropriate tool to assess these processes.

In addition, there is considerable uncertainty related to the solids balance and specifically, the tributary loadings and the rate of net deposition. The full range of uncertainty in these variables was not investigated in the sensitivity tests associated with the model forecasting. Tributary loadings could change significantly in the future due to climate change or changes in land use.

Finally, it would be prudent to address the question of whether the trapping efficiency of the various reaches of the Upper Hudson will remain uniform in the future as assumed in the HUDTOX model (based on the SEDZL modeling of QEA, 1999). In other words, is it reasonable to expect that the rate of deposition in a river system will be uniform over a 70 year period (based on a 20 year calibration or test period)? How is the river bed evolving? How did/does the massive pulse of 1,000,000 cubic yards of sediment released to the TIP between 1973 and 1976 after the removal of the Fort Edward dam influence the river bed dynamics in the TIP? These questions have not been answered because the HUDTOX model spatial and temporal resolution are insufficient to answer these questions.

3. **It is easy to get caught up with modeling details and miss the overall message**

of the models. Do you believe that the report appropriately captures the "big picture" from the information synthesized and generated by the models?

As explained in my answer to Question 2, some key uncertainties and assumptions in the model have not been adequately addressed or tested to assess whether the model captures the "big picture" related to long term trends in PCB concentration decay. However, providing these uncertainties can be addressed, it would appear that the long term trends of PCB concentration predicted by HUDTOX will reflect the future trends reasonably well.

On the other hand, the HUDTOX model as presently formulated is unable to sufficiently represent the processes which may lead to PCB concentration spikes in the future (i.e. deviations from the long term trends), either due to large flood events or localized erosion (both of which relate to scales of finer resolution than the simulated in the current HUDTOX model). Therefore, to some extent, the acceptability of the current HUDTOX model will depend on the importance of PCB concentration spikes with respect to bioaccumulation and ecological and human health risk.

4. **Please provide any other comments or concerns with the Revised Baseline Modeling Report not covered by the charge questions, above.**

No additional comments.

RECOMMENDATIONS

Based on your review of the information provide, please identify and submit an explanation of your overall recommendation for each (separately) the fate and transport and bioaccumulation models.

1. Acceptable as is
2. Acceptable with minor revision (as indicated)
3. Acceptable with major revision (as outlined)
4. Not acceptable (under any circumstance)

Recommendation: Acceptable with revisions as outlined below:

1. Specifically address the issues raised in the answers to the charge questions.

2. The frequency and magnitude of future PCB concentration spikes (in addition to the impact of a 100 year flood) must be assessed in further detail. Ideally this should be completed with a more detailed hydrodynamic model integrated with a model of sediment dynamics (i.e. at a much finer spatial and temporal resolution than HUDTOX). It may be possible to complete additional assessment of this

issue without the use of a refined model by examining the amount of erosion that would need to occur to result in an unacceptable ecological or human health risk.

3. Check that the resuspension of cohesive sediments in the HUDTOX model considers that the one hour limit to erosion potential is reactivated after an increase in shear stress and that a lag may not develop at higher shear stresses.

4. Reformulate the erosion/deposition of non-cohesive sediments if an finer scale model is developed and implemented.

5. Review the long term evolution of the river bed either quantitatively, with a refined model and/or through an updated bathymetry survey and comparison to the 1991 and earlier surveys. The latter recommendation to complete bathymetric survey comparisons would also serve to better constrain the long term burial rates. This recommendation should also include an assessment of the influence of the reported 1,000,000 cubic yard pulse of sediment released to the TIP between 1973 and 1976 after the removal of the Fort Edward Dam.

6. In addition to an updated bathymetry survey (completed with high resolution multi-beam equipment), it would be very helpful to complete additional high resolution cores to confirm the assumed burial rates.

7. Consider the application of a watershed model to describe historic (and future) discharge and sediment loading (such as SWAT or AGNPS).

8. In lieu of recommendation 6 above, and at the very least, assess the influence of reduced tributary loadings reflecting a change in land use <u>in addition</u> to possible uncertainty in the solids balance (i.e. more than 50% reduction in loading considered in Chapter 8).

Dr. Ross Norstrom

Ross Norstrom Biography

Ross Norstrom has a B.Sc. (magna cum laude) and a Ph.D. in Chemistry from the University of Alberta, Canada. After postdoctoral fellowships in gas phase photochemistry at the University of Bonn and Cambridge University, he joined an interdisciplinary group at the National Research Council in Ottawa, and spent 4 years studying dynamics of mercury and PCBs in the Ottawa River ecosystem. During that period he developed the first bioenergetics-based model for bioaccumulation of contaminants in fish. In 1974, he took a position as a research scientist with the Canadian Wildlife Service, Environment Canada where he has made contributions in many areas of PCB and other organochlorine contaminants science, including analytical methods development, discovery of new contaminants, biological monitoring data interpretation, taxonomic SARS for bioaccumulation, modeling bioaccumulation in birds, metabolism and metabolites, and ecotoxicology. In September 1999, he received an honorary Ph.D. in Natural Sciences from the University of Stockholm, in recognition of, "great achievements in the application of advanced chemical methods in order to increase our understanding of how environmental pollutants affect the ecosystems in and around the Great Lakes...and in Arctic regions." He has been involved in PCB research for 30 years.

Ross Norstrom is presently a senior scientist with Environment Canada, where most of his research is focused on trends and effects of PCBs and other organochlorine compounds in polar bears. He is also adjunct professor in the Centre for Analytical and Environmental Chemistry, Carleton University, where he has research programs on the identification, environmental occurrence and toxicity of methylsulfone-PCBs, hydroxy-PCBs and naturally-occurring polychlorobromo aromatic hydrocarbons in wildlife and humans. He is also studying relationships among bioaccumulation of polychlorinated compounds, enantiomer fractions of chiral contaminants and C/N stable isotope signatures in an Arctic polynya ecosystem. He is conjunct professor in the Watershed Ecosystems Graduate Program, Trent University, where he is researching the mechanistic aspects of PCB uptake, distribution and excretion in birds, and developing a general bioenergetics-based deterministic model for bioaccumulation in birds. He has been involved in organizing Canada-Russia bilateral Arctic monitoring programs; participated in a peer review of the EPA Ecological Risk Assessment Program, contributed to a Swedish Council for Planning and Coordination of Research (FRN) study on state of ecotoxicology research in Sweden, was a member of an international peer review team for a Royal Swedish Academy of Sciences evaluation of Swedish environmental research, has consulted globally on dioxin and PCB issues, including Natural Resource Damage Assessments. He has authored or co-authored over 160 scientific publications.

Charge for Peer Review 3

Specific Questions

Fate and transport (HUDTOX)

1. *The HUDTOX model links components describing the mass balance of water, sediment, and PCBs in the Upper Hudson. Are the process representations of these three components compatible with one another, and appropriate and sufficient to help address the principal study questions?*

Given the overall success of the model in predicting Tri+ water concentrations, it would appear that the processes are a good representation of probable exposure of the organisms as input to the bioaccumulation models. The use of an archival stack of deep sediment layers provides some confidence that exposure of the water column to more contaminated deeply buried sediments will correctly modeled. Although HUDTOX appears quite capable of predicting congener profile changes over time based on parameterization of a number of important processes for individual congeners, it appears that this information is not used to any extent except to calculate Tri+ concentrations. I assume that there are some significant differences in congener patterns in various reaches of the river, although this information is not provided (at least I did not see it). If so, would there also not be differences in trends of patterns over time among areas? This could be important in spatial and temporal differences in toxicity of Tri+ concentrations, which will vary depending on congener makeup.

Although evidence appears convincing that dechlorination is unlikely to be important compared to sediment water exchange in declining inventory because it only occurs to a significant extent in the most contaminated sediments, has this been taken into account if some of these sediments are exposed by scouring events?

2. *The HUDTOX representation of the solids mass balance is derived from several sources, including long-term monitoring of tributary solids loads, short-term solids studies and the results of GE/QEA's SEDZL model. The finding of the solids balance for the Thompson Island Pool is that this reach is net depositional from*

1977 to 1997. This finding has also been assumed to apply to the reaches below the Thompson Island Dam. Is this assumption reasonable? Are the burial rates utilized appropriate and supported by the data? Is the solids balance for the Upper Hudson sufficiently constrained for the purposes of the Reassessment?

I am not qualified to comment on this question.

3. *HUDTOX represents the Upper Hudson River by segments of approximately 1000 meters in length in the Thompson Island Pool, and by segments averaging over 4000 meters (ranging from 1087 to 6597 meters) below the Thompson Island Dam. Is this spatial resolution appropriate given the available data? How does the spatial resolution of the model affect the quality of model predictions?*

The TIP segments are well chosen to represent mid-channel, as well as near-shore areas of varying cohesive and non-cohesive sediment, and should therefore be a good representation of sediment-water exchange. Below TID, the segments are simply lengths of the river. Given that the major PCB inventory is in TIP, this appears to be a reasonable level of spatial resolution. Uncertainty in predicting future trends is therefore likely to be higher below TID, especially for benthic fish such as the bullhead, which are not probably not spatially integrating to the same extent as species like large-mouth bass. Nevertheless, calibration of FISHRAND indicates good ability to predict trends both within and downstream from TIP for both bullheads and large-mouth bass.

4. *Is the model calibration adequate? Does the model do a reasonable job in reproducing the data during the hindcast (calibration) runs? Are the calibration targets appropriate for the purposes of the study?*

The calibration data shows that HUDTOX is very successful at reproducing the short-term, as well as the long-term, trends in water and sediment Tri+ concentrations. HUDTOX does an admirable job of following even the seasonal trends in water column concentrations of PCBs throughout the calibration period. The reliability of HUDTOX for forecasting this parameter is likely to be good because the important factors which govern not only short-term, but also long term behavior, are included. Addition of dynamic sediment stratigraphy to the model and greater spatial resolution (at least in

TIP) enhance the probability that time-dependent changes, such as uncovering of more contaminated deeper sediments by scouring, will not be missed. It should be remembered that calibration of the water concentrations is dominated by the lower chlorinated congeners, whereas the higher chlorinated congeners are more important in fish. Therefore the goodness of fit, even for Tri+ or 'total' PCB concentrations in water may not be completely representative of the bioaccumulated congener mix.

There are more recent data on long-term trends of gas phase PCB concentrations in the atmosphere (Hillery et al. 1997) than those used in deriving the boundary conditions for atmospheric loading to the river over time (Fig. 6-51, Book 2).

5. *HUDTOX employs an empirical sediment/water transfer coefficient to account for PCBs loads that are otherwise not addressed by any of the mechanisms in the model. Is the approach taken reasonable for model calibration? Comment on how this affects the uncertainty of forecast simulations, given that almost half of the PCB load to the water column may be attributable to this empirical coefficient.*

There are so many factors that may govern sediment-water mass transfer, e.g., pore water and water column DOC, colloids, bioturbation. In many cases it is difficult to even define what these are. For example, freely dissolved concentrations in water are an operational definition because no measurement technique is entirely free from the possibility of altering the natural state of the water. Under these conditions, I think it appropriate that an empirical, rather than a deterministic approach be taken. From the examples given (pg. 116-117, Book 1) theoretical approaches would considerably underestimate the mass-transfer rate. The approach taken, using a seasonally variable load gain through TIP, is reasonable. However, as the report points out, the applicability of k_f to lower reaches of the river is a source of uncertainty.

As Figure 6-56, Book 2, shows, the average 'total PCB' k_f value is a significant over-prediction for low chlorinated congeners, and under-prediction for more highly chlorinated congeners. How then are the predictions of water concentrations of most congeners in the short hindcast as accurate as they are (Figure 7-66, Book 2)? Use of the generic Tri+ mass-transfer coefficient for higher chlorinated congeners such as BZ#138 appears to give nearly as good predictions of water concentrations in the short hindcast as BZ#28, despite large differences in physical properties. Are there any assumptions or additional compensating parameter adjustments that were done to achieve a fit that might effect very long-term projections for highly chlorinated congeners? The statement on page 151, Book 1, that, "model performance in hindcast applications was strongest for BZ#28 and BZ#52, the congeners whose environmental behavior most resembles that of Tri+," begs the point . It will not be these two congeners that risk assessors will be interested in.

In general, I am concerned about the uncertainty resulting from the underlying assumption that congener makeup of Tri+ is unchaning over a long period of time than I am about uncertainty in Tri+ concentration predictions. Tri+ toxicity/unit concentration may also be changing over time. The comments at the top of page 122 in Book 1 about what was actually done concerning specific congeners are puzzling. What does, "This would allow simultaneous application of the Tri+ calibration to all congeners, varying only congener-specific chemical properties," really mean?

6. *Are there factors not explicitly accounted for (e.g., bank erosion, scour by ice or other debris, temperature gradients between the water column and sediments, etc.) that have the potential to change conclusions drawn from the models?*

I am not qualified to answer this question.

7. *Using the model in a forecast mode requires a number of assumptions regarding future flows, sediment loads, and upstream boundary concentrations of PCBs. Are the assumptions for the forecast reasonable? Is the construct of the hydrograph for forecast predictions reasonable? Should such a hydrograph include larger events?*

See comment above on atmospheric loading trends.

8. *The 70-year model forecasts show substantial increases in PCB concentrations in surface sediments (top 4 cm) after several decades at some locations. These in turn lead to temporary increases in water-column PCB concentrations. The increases are due to relatively small amounts of predicted annual scour in*

specific model segments, and it is believed that these represent a real potential for scour to uncover peak PCB concentrations that are located from 4 to 10 cm below the initial sediment-water interface. Is this a reasonable conclusion in a system that is considered net depositional? After observing these results, the magnitude of the increases was reduced by using the 1991 GE sediment data for initial conditions for forecast runs. Is this appropriate? How do the peaks affect the ability of the models to help answer the Reassessment study questions?

The effect of the two peaks due to scouring is predicted to last ca. 10 years from 2044 - 2054. The importance of this will depend to a large extent on whether the predicted levels due to the regular declines input from surface sediments produce concentrations that are near, or close to the action limit. I cannot comment on the validity of this prediction.

9. *The timing of the long-term model response is dependent upon the rate of net deposition in cohesive and non-cohesive sediments, the rate and depth of vertical mixing in the cohesive and non-cohesive sediments and the empirical sediment-water exchange rate coefficient. Are these rates and coefficients sufficiently constrained for the purposes of the Reassessment?*

I am not qualified to answer this.

10. *The HUDTOX model uses three-phase equilibrium partitioning to describe the environmental behavior of PCBs. Is this representation appropriate? (Note that in a previous peer review on the Data Evaluation and Interpretation Report and the Low Resolution Sediment Coring Report, the panel found that the data are insufficient to adequately estimate three-phase partition coefficients.)*

The consistency of the log k_{poc} and log k_{doc} values derived from water and sediment data (apart from BZ#4) gives confidence in these values. However, without the background information on how these are derived operationally, it is difficult to judge how accurate the values are.

11. *HUDTOX considers the Thompson Island Pool to be net depositional, which suggests that burial would sequester PCBs in the sediment. However, the geochemical investigations in the Low Resolution Sediment Coring Report (LRC) found that there was redistribution of PCBs out of the most highly contaminated areas (PCB inventories generally greater than 10 g/m2) in the Thompson Island Pool. Comment on whether these results suggest an inherent conflict between the modeling and the LRC conclusions, or whether the differences are attributable to the respective spatial scales of the two analyses.*

I will leave this up to the hydrodynamicists.

12. *The model forecasts that a 100-year flood event will not have a major impact on the long-term trends in PCB exposure concentrations in the Upper Hudson. Is this conclusion adequately supported by the modeling?*

Based on my limited understanding of hydrodynamic processes, the arguments that are put forward appear to be very reasonable and apparently supported by a separate GE analysis.

Bioaccumulation Models

1. *Does the FISHRAND model capture important processes to reasonably predict long term trends in fish body burdens in response to changes in sediment and water exposure concentrations? Are the assumptions of input distributions incorporated in the FISHRAND model reasonable? Are the spatial and temporal scales adequate to help address the principal study questions?*

On page 17 of the Reponsiveness Summary, comment BG-1.31 questions the 'reality' of FISHRAND. The answer to this question is less than revealing, apparently written by a lawyer (no offense to the profession) rather than a modelar. Development of FISHRAND was a direct response to the suggestion in PMCR that a 'mechanistic' model be developed. The implication, I suppose, is that mechanistic models are more real, and that real is better. Mechanistic models may masquerade as real, and empirical models may be better. There is no hard and fast rank order of excellence to these approaches. The utility of mechanistic models depends on whether the important processes determining the toxicokinetics are really understood and properly incorporated, and what certainty which can be placed on the parameters describing these processes. They seldom work on an *a priori* basis. As soon as you need to calibrate, you introduce some degree of empiricism. I believe that a good mechanistic model includes only the level of detail that is required to yield an output with the required degree of accuracy for the questions that will be asked of it.

Reality is relative. The important property of models of the kind we are dealing with here is whether they can accurately and reliably predict the endpoints of concern – concentrations in fish over time – incorporating as much as possible of our understanding of what processes are likely to change, whether that is done empirically or mechanistically. On page 92, Section 8.1.2.1, Book 3, it is stated that the probabilistic empirical model is limited in reliability of prediction because it does not capture the mechanistic processes. Yet, the probablisitic model generally did a better job of predicting largemouth bass concentrations than did the first cut FISHRAND model prior to Bayesian Monte Carlo simulation and updating of the distributions. Is the latter process real?

The Gobas mechanistic models on which FISHRAND is based begin with the assumption that uptake and elimination processes are driven by fugacity gradients. The fact that the models can be paramaterized, and are quite successful after suitable calibration does not prove that the underlying physical- chemical and physiological processes are the true ones. There are alternative mechanisms that will equally well explain the success of these models.

The big question boils down to this: If FISHRAND has good predictive capability in the past, is this capability preserved in the future? (Assuming that there is more uncertainty associated with the biological than the hydrological processes.)

pg. 14, Book 3 makes a good point that not nearly enough is known about habitat and feeding preferences to model uptake by invertebrates mechanistically. Gobas assumes the same, and uses BAFs for invertebrates. Monte Carlo simulation of feeding preferences in the Probabilistic and FISHRAND models is a valuable way of estimating the variance due to the many unknowns for invertebrates.

pg. 26, Book 3. The Gobas model uses experimental data for uptake from water *at one temperature*. This does not represent reality unless it is somehow calculated as the annual average uptake rate for a wild fish. It is odd that food uptake is related to mean temperature (eqn 3-14), whereas respiration is not. Since food uptake is likely to dominate, the net effect of this is probably not too important, except for lower chlorinated congeners where both uptake and clearance may be gill-dominated.

pg. 27, book 3. Eqn. 3-13 assumes that uptake efficiency is inversely proportion to K_{ow}. The experimental data on this are inconclusive, in my mind. For example, Fisk et al. (1998) did not observe a strong effect of K_{ow} on accumulation efficiency of PCBs (and other organochlorines) in rainbow trout, however the overall efficiency of uptake was rather low. Some of the experimental uptake studies may produce artifactual dependence on K_{ow} because the way the contaminant is incorporated into the diet does not mimic the natural diet.

pg. 27, Book 3. Eqn. 3-14 uses a body weight exponent of 0.85 for ingestion rate – why is it different than 0.6 in eqn. 3-9 (respiration rate)? The two are directly linked, and should be the same.

pg. 27, Book 3. Eqn. 3-15 indicates that fecal egestion rate is 20% of dietary uptake rate, which is allometrically scaled to $W^{0.85}$. The result of this assumption is that both net uptake and net excretion in the gut will decrease as $W^{0.85}$, which is equivalent to saying that 80% of the PCBs are accumulated the diet and never excreted through fecal egestion. While this may be consistent with a fugacity gradient model, depending on digestibility of the diet, fugacity capacity, etc., it is equally compatible with a lipid co-assimilation model.

Thus, in the model net excretion only occurs via the gills. According to eqn. 3-11, gill elimination rate is proportional to k_1 which is in turn inversely proportional to V_f. The net effect of eqns. 3-11 and 3-15 is therefore that whole body elimination is inversely proportional to body weight, and in a non-linear fashion to K_{ow}. Because respiration is not temperature dependent, which is not mechanistically correct, clearance rate via gills is presumably considered to be constant throughout the year, which is also unlikely to be correct. At what temperature were the Q_w and Q_l transport rates derived?

Fisk et al. (1998) determined clearance rates for a wide range of organochlorine compounds spanning log K_{ow} from 5.2 – 8.2 in small (10 g) juvenile rainbow trout. The rates were relatively independent of log K_{ow} between 6-7.5. They compared half lives vs. log K_{ow} with those for rainbow trout weighing 45 g and 1000 g from other studies. Clearance of compounds in 45 g trout had a log K_{ow} dependence similar to the 10 g trout, except that the maximum half-lives were longer. For 1000 g trout, the half-lives increased very rapidly between log K_{ow} = 5-6 and became unmeasurable (>1000 d) thereafter. If the half-lives for log K_{ow} = 6 (and perhaps at lower K_{ow}'s) are compared for the three sizes of trout, they scale almost perfectly to $W^{0.65}$, that is, clearance rates are proportional to $W^{-0.65}$, not $W^{-1.0}$. Direct extrapolation of the results for rainbow trout to another species may not be valid due to dependence on lipid content, etc. Nevertheless, these data suggest that clearance rates (sum of all processes) are likely proportional to metabolic rate, not body weight. This is, in fact, a more 'mechanistic' assumption. If true, clearance rates from large largemouth bass may actaully be underestimated in the model.

It is worthy of note that virtually all of the uptake and elimination studies in the literature are performed on small fish, and scaling clearance to body size is therefore not well understood. Clearance of PCBs with log K_{ow} > 6 in fish in the kg range is so slow that it is unknown what sort of dependence there is at high K_{ow} , for example, whether it falls off slightly around log K_{ow} 8, as has been observed for smaller fish. De Boer et al. (1996) studied clearance of PCBs from a naturally contaminated population of eels. BZ#44, 52, 49, 87, 97, 101, 149 151 had half-lives in the order of 380 d – 3,550 d. No measurable clearance of BZ#128, 138, 141, 153, 170, 180, 187, and 190 occurred over 8 years! While the high lipid content of these fish is a factor in slow clearance, it illustrates that many of the assumptions based on experiments with small laboratory fish cannot be scaled to the natural environment.

As pointed out in the development of the QEA model and by Fisk et al. (1998), one of the problems with short term experimental clearance studies in fish is the possible existence of a 'slow' compartment. The clearance experiments may only be measuring the 'fast' compartment, and therefore overestimate clearance rates over the lifetime of the fish in a natural environment. Gobas et al. (1999) showed that it took 45 days for equilibrium on a lipid wt. basis to be reached among tissues in rainbow trout exposed dietary 2,2',4,4',6,6'-HxCB. Note, however that the dietary concentration in this study was 900 mg/kg, which could seriously compromise the conclusions.

It may be that a combination of underestimation of clearance rates due to incorrect assumption of the body weight exponent cancels out the overestimation due to clearance from the slow compartment in the successful prediction of PCB concentrations in larger fish.

Note that I strongly disagree with the statement on pg. 93, Book 3, that metabolism plays an important part in the ability of fish to retain PCBs (at least most Tri+ congeners). There are numerous studies to refute this statement. Furthermore, the ability to 'reconstruct' congener profiles that are very similar to Aroclor mixtures, in the Hudson River and elsewhere, does not support any substantial metabolic capability in fish.

pg. 28, Book 3. The Gobas model assumes growth of fish occurs much faster above 10 degrees than below 10 degrees, and is related to $W^{-0.2}$. While I entirely agree that growth should not be assumed to be continuous, there is no particular justification given for using this generic approach to modeling growth. The QEA model apparently used growth rates for largemouth bass specific for the Hudson River (although on cursory inspection I could not see any information on this in their report). There are also published data on largemouth bass energetics, e.g., Niimi and Beamish (1974).

pg. 28, Book 3. I note that the growth rate coefficients adopted were the corrected values given by Burkhard (1998), rather than the ones used by Gobas (1993). This should be noted.

pg. 28, Book 3. I agree that there would be little to be gained using monthly average sediment concentrations.

2. *Was the FISHRAND calibration procedure appropriately conducted? Are the calibration targets appropriate to the purposes of the study?*

pg. 29-30, Book 3. FISHPATH is called a 'deterministic' steady state model based on Gobas, and was used in the development of FISHRAND. Deterministic is defined by virtue of use of generic parameters without site-specific data. The Initial validation was done by comparing actual, Gobas, FISHRAND (run as steady state) and FISHPATH (steady state by definition) for Oliver and Niimi's data. FISHPATH and FISHRAND produced *identical* results for all trophic levels. So what is different betweeen them? The correspondence between the Gobas and FISHRAND simulations was good, but I assume that largely the same parameters were used. Was this simply a validation of coding? Note that the Gobas model may have incorrect underlying assumptions (e.g., clearance rates, above) which may not affect the steady state situation for Lake Ontario, but be influential in the Hudson River, so it should not be considered a validation of the application.

The whole process of the Bayesian calibration and updating of assumed distribution of input parameters is difficult to comprehend, but its application is critical to calibration of the model. Distributed variables are lipid weight, dietary composition, TOC, log K_{ow}, annual sediment concentration, monthly water concentrations. Applying the Bayesian approach to determine posterior distributions of some of the parameters does not make a lot of sense to me. Presumably the 'empirical' lipid percentages of the fish, for example, are true values with a real distribution. Similarly, the mean K_{ow} of "Tri+" must be relatively stable, (assuming no changes in composition over time). Adjusting the distribution for K_{ow} and lipid weights is tantamount to empirical calibration, in my estimation. While it is true there is a distribution of values, this is not an uncertainty. Given the fact that Bayesian adjustment of K_{ow} distributions was a major factor in calibration of the model, this would appear to compromise some of FISHRAND's mechanistic character, although not necessarily its validity (for Tri+ concentrations).

It is stated that an attempt to calculate K_{ow} distributions based on congener profiles was 'infeasible', so a range was used, with a triangular distribution centered around log K_{ow} = 6.6. Why was this not feasible? Experimental data exist for most congeners, and can be estimated for the remainder. Is it reasonable to assume that log K_{ow} is more normally distributed K_{ow} itself? Has that been tested?

Comparison of Figure 5-9 with 6-6 shows that FISHRAND is much better than the probabilistic model in predicting bass concentrations. However, the fit prior to calibration (Bayesian updating) is actually worse than the probabilistic model. A clear statement as to the reasonableness of the adjustments to achieve this fit would help to understand what is going on.

There is a statement on pg. 81 that the deviation between predicted and actual Tri+ concentrations was typically around 16%, although there was 100% difference in 1991 and 48% in 1985. Regardless of the interpretation that is put on what is going on in the calibration process, this is probably as good a fit as can be expected in a dynamic system.

Fig. 6.11 and 6.12 show that ability of the model to predict variance in bass is worse than for other species. Does this have something to do with size ranges?

pg. 82, section 6.5 states that Figure 6-6 presents results for bass at river mile 155 using the calibration for river mile 168. This figure actually presents the before and after calibration at river mile 189. Where is the mile 155 result?

3. *In addition to providing results for FISHRAND, the Revised BMR provides results for two simpler analyses of bioaccumulation (a bivariate BAF model and an empirical probabilistic food chain model). Do the results of these models support or conflict with the FISHRAND results? Would any discrepancies among the three models suggest that there may be potential problems with the FISHRAND results, or inversely, that the more mechanistic model is taking into account variables that the empirical models do not?*

The data assembled in Appendix A appears to provide a good basis for the percent composition and source of the diet of the fish. I am surprised, however, that pelagic zooplankton do not seem to figure in the diet at all (See Fig. 3-2). Is this the case in the actual simulation?

The model correctly assumes that summer average concentrations should be used in the simulation because most feeding occurs at that time of year. This is an important seasonal feature which is frequently missing in bioaccumulation models. The modelers are to be commended for including this feature. However, the lack of seasonal (temperature) dependence on respiration may compromise estimates of clearance rates, and possibly uptake rates of less chlorinated congeners, via the gills.

Figure 5.1 provides a good demonstration of the stability of BSAF among 10 different invertebrate species. It is generally around 1-2. Bivalves are on the low side – possibly because of low lipid content?. Average BSAFs for all invertebrates are reasonably stable with river mile, apart from two locations. BAFs for water column invertebrates were ca. 10^6, and relatively stable with river mile (Figure 5.4) which is well within the range of other studies.

pg. 68, Book 3. Using estimated foraging habits, forage fish FFBAFs were calculated. Concentrations in TIP were much higher. There was a bimodal distribution in FFBAFs centered around 1.7 and 3.3. A clear explanation for this is not given.

Table 5.3 and Figure 5.9 show that the model does a much better job of predicting concentrations and trends in largemouth bass at mile 168 (Stillwater) than it does in TIP. There the model under-predicts by ca. a factor of 2 in many years. How much of this could be due to differences in sizes and age of fish? It is not clear from what I have read how fish weight enters into these models. Fig. 6.5 shows the distribution in bass weights to be very large – between ca. 100 g and 2500 g, with most in the 250 to 1500 g range. The large fish would not be suspected to be at equilibrium, or perhaps even show trends, which appears to be the case between 1982 and 1993 in TIP. However, the same results were found for pumkinseed (much better at mile 168 than 189), suggesting that this is not the reason, since they would not likely be subject to the same time lags.

4. *Sediment exposure was estimated assuming that fish spend 75% of the time exposed to cohesive sediment and 25% to non-cohesive sediment for the duration of the hindcasting period. The FISHRAND model was calibrated by optimizing three key parameters and assuming the sediment and water exposure concentrations as given, rather than calibrating the model on the basis of what sediment averaging would have been required to optimize the fit between predicted and observed. Is the estimate of sediment exposures reasonable?*

I assume that to some extent the relative importance of exposure to the two sediment types is reflected in dietary composition, and the assumption of 75%/25% exposure is compensated for in the optimization/calibration procedure, where dietary distribution is a distributed variable. Beyond this, I have no particular knowledge that would be applicable to answering this question.

5. *The FISHRAND model focuses on the fish populations of interest (e.g., adult largemouth bass, juvenile pumpkinseed, etc.) which encompass several age-classes but for which key assumptions are the same (e.g., all largemouth bass above a certain age will display the same foraging behavior). This was done primarily because it reflects the fish data available for the site. Is this a reasonable approach?*

Prey size preferences certainly change with size of predator. This is more likely to manifest itself in large fish like the largemouth bass. I am not sure whether there is specific information is available for this species. It appears that the transition to primary piscivory for largemouth bass was set at 50 mm. There are no fish listed in Table A-2 that are less than 172 mm, and the great majority are in the 300-500 mm range. Certainly a 50 mm fish is not able to eat the same size class of fish as a 500 mm fish. However, if the prey fish size range is relatively narrow, which may be the case if shiners and pumpkinseed are the main forage fish, then size preference may not be important.

congeners removes log K_{ow} as a distributed parameter, and provides a more rigorous test of the model.

The ecological risk assessment executive summary concludes that it will be after 2018 before levels in fish decrease below the adverse effect level. Was this based on FISHRAND results? TCDD TEQs are one of the endpoints. How are these going to be calculated from Tri+ concentrations? The summary states that for mammals and most birds, Toxicity Quotients for dioxin-like PCBs were greater than for total PCBs. Therefore, what may be most important to model is TEQ trends. While it may be possible to generate correlations between various endpoints such as TEQs and Tri+ PCBs in the short term, their validity in the long term depends on the stability of the congener makeup over time. The probability of congener changes over time is not adequately addressed in the present report.

Hebert et al. (1999) showed that there were gradual changes in congener composition in Lake Ontario and Lake Michigan herring gull eggs (after correction for a large decrease in point source loading of Aroclor 1242 to Lake Ontario) in the 1970s which were accountable as physical chemical processes that could be modeled by log K_{ow}. As expected, lighter congeners decreased faster than heavier congeners. Because Tri+ concentrations are heavily dominated by lower chlorinated congeners, at least in water, whereas most of the toxic congeners of concern are relatively highly chlorinated (e.g., BZ#105, 118, 126,169), the long term decrease in TEQ concentration may very well be slower than Tri+ concentrations.

My overall impression is that too much effort has been expended on explaining anomalies like the BZ#4 loadings in 1987 and 1993, when this congener (and other lower chlorinated congeners) are unlikely to figure very significantly in the risk assessment.

Apparently the role of dechlorination has been overemphasized in the past (See Chapter 6, Book 1), so not including dechlorination as an important factor in congener trends is justified.

A factor that *may* not be handled properly in the model is growth and recruitment to a size class. Do the fish 'grow' through the historical concentrations to reach concentrations at a particular level, or is there some assumption of quasi steady-state here? Is the distribution of fish sizes assumed to remain the same every year? Does this mean some of the larger fish 'die' every year and are replaced? There is a statement on pg. 92, that indicates the Gobas 1993 model, rather than the improved 1995 model, was the basis of FISHRAND. Also, "the later approaches (Gobas 1995) used an age-class model for each year of the fish's life rather than the growth dilution approach presented here." To some extent this is explained on pg. 93, where it says, "each individual fish grows, and... the volume of the population is assumed to be equilibrated by the processes of fish death and reaching the minimal size to be included in the population." What does this mean, in plain language?

One factor that is not explicitly brought out is what the size-concentration range is expected to be. This seems to me to be more important to know than 15, 50 and 95 percentiles describing variability (e.g., Figure 7-4, pg. 87, 10 ng/L boundary condition). Surely a lot of this distribution is size related. When it comes time to use the projections for risk analysis, it is important to know whether the fish above the 95th percentile, for example, are mostly above a certain size. Certainly, humans can be advised not eat fish above a certain size. Size will factor in the diet of wildlife as well. A bald eagle may prey on a 2.5 kg bass, but a mink probably will not.

4. *Please provide any other comments or concerns with the Revised Baseline Modeling Report not covered by the charge questions, above.*

One of the biggest challenges of this review is to enter it without the years of historical perspective that the various participants have had. While independence of opinion has its merits, it must be realized that in the short time frame available, it is not possible to absorb, much less analyze in any detail, all relevant aspects. The Charge indicates that this is not the primary purpose of the review. We have also been asked to refrain from advising how 'we would have done it'. Therefore, I have not attempted to do a detailed comparison of the relative merits of the QEA vs. EPA approaches to bioaccumulation modeling, although I have looked at both.

The primary strength in the QEA approach is that it takes a bioenergetics approach to contaminant uptake, that it is, it attempts to simulate actual respiration and food requirements for the species in question under a particular set of conditions, an admitted bias that I have. However, in my opinion, the toxicokinetics part of this model is unnecessarily complicated. While many of the arguments about slow and fast compartment clearance may be correct, there is a paucity of experimental data to verify this, much less apply it in a deterministic fashion. The derivation of clearance rates across the gill surfaces is a major potential source of error for this reason. The QEA model assumes gut clearance is negligible. Counter arguments could be made to this. Nevertheless, with suitable calibration, the model can undoubtedly be made to work. Note that the Gobas 1993 model apparently allows for clearance by both gill and gut, although making gut clearance proportional to food intake rate effectively eliminates gut clearance.

I generally agree with the EPA commentary in the Responsiveness Summary on the problems inherent in the application of the QEA model.

Recommendations

Based on your review of the information provided, please identify and submit an explanation of your overall recommendation for each (separately) the fate and transport and bioaccumulation models.

HUDTOX

2. Acceptable with minor revision (as indicated)

As outlined above under general comments, I would like to see a concerted attempt to produce a long-range forecast for a few representative congeners covering a range of physical properties bracketing those likely to figure in the risk assessment, in order to determine the probability of congener pattern changes over time, and therefore the suitability of using Tri+ concentrations for risk assessment.

FISHRAND

2. Acceptable with minor revision (as indicated)

Simulating individual congeners separately as suggested for HUDTOX automatically removes log K_{ow} as a distributed variable in FISHRAND. Assuming that distribution of fish lipid concentrations is reasonably well known and not highly variable temporally, I believe this should also be removed from the Bayesian optimization process. If it is truly uncertain and random, then perhaps it should remain in. This would provide a more rigorous test of whether the model could be calibrated and validated with the remaining distributed variables.

Further clarification of how fish size distributions and their relationship to bioaccumulation are handled in the model, and information on concentration vs. size relationships, as opposed to percentile distributions is required before final judgment on the suitability of this model for risk assessment can be made.

References

de Boer, J., F. van der valk, M.A.T. Kerkhoff, P. hagel and U.A.T. Brinkman. 1994. 8-year study on the elimination of PCBs and organochlorine compounds from eel, (*Anguila anguila*) under natural donditions, Environ. Sci. Technol. 28:2242-2248.

Fisk, A.T., R.J. Norstrom, D.C. Cymbalisty and D.C.G. Muir. 1998. Dietary accumulation and depuration of hydrophobic organochlorines. Bioaccumulation parameters and their relationship with the octanol/water partition coefficient. Environ. Toxicol. Chem. 17: 951-961.

Hebert, C.E., R.J. Norstrom, J. Zhu and C.R. Macdonald. 1999. Historical changes in PCB patterns in Lake Ontario and Lake Michigan, 1971-1982, from herring gull egg monitoring data. J. Great Lakes Res. 25:220-233

Hebert, C.W, J.L. Shutt and R.J. Norstrom. 1997. Dietary changes cause temporal fluctuations in polychlorinated biphenyl levels in herring gulls from Lake Ontario. Environ. Sci. Technol. 31:1012-1017.

Hillery, B.R., Basu, I., Seet, C.W., and Hites, R.A. 1997. Temporal and spatial trends in a long term study of gas phase PCB concentrations near the Great Lakes. Environ. Sci. Technol. 31:1811-1816.

Niimi, A.J. and F.W.H. Beamish. 1974. Bioenergetics and growth of largemouth bass (*Micropterus salmoides*) in relation to body weight and temperature. Can. J. Zool. 52:447-456.

Rasmussen, J.B., D.J. Rowan, D.R.S. Lean and J.H. Carey. 1990. Food chain structure in Ontario lakes determines PCB levels in lake trout (*Salvelinus namaycush*) and other pelagic fish. Can. J. Fish. Aquat. Sci. 47:2030-2038.

of fish are consistent with known feeding habits, and provide a good means of estimating the overall dietary preferences in initializing FISHRAND.

EMPIRICAL PROBABILISTIC MODEL

pg. 19, Book3. In the bivariate probabilistic model, it is assumed that mean seasonal exposure changes slowly relative to species uptake and depuration kinetics. For large fish, the depuration kinetics may indeed be similar relative to exposure changes, e.g., half lives of > 1000 days. See comments above.

pg. 21, Book 3. I am not a statistician, but I do not see why it should be so 'operationally difficult to truly separate' heterogeneity from measurement uncertainty in dealing with distributions of PCB concentrations in invertebrates, unless this statement is referring to the changes in methodology that occurred over time, e.g., from Aroclors to sum of congeners. Variance due analytical uncertainty within a method is measurable, usually quite normally distributed, and should not be difficult to factor into an ANOVA. With some experimental intercalibration of methods, even uncertainty due to changes in methodology could probably be determined.

pg. 21, Book 3. The assumption that fish are expected to obtain most of their PCBs from food is a reasonable one for this type of model.

pg. 23, Book 3. The fact that the relative sorption to particles vs. truly dissolved 'average out to some extent when evaluating a mixture' comes back to the criticism that modeling Tri+ concentrations is a confounding factor in risk analysis. It is the actual congener composition that is important.

pg. 23, Book 3. A statement is made that forage fish diet is on average 67% water column, and 35% sediment invertebrates. This does not appear to what was used in FISHRAND. In Fig. 3-2, pumpkinseed are 80%/20%, and spottail shiners 70%/25%, water column vs. sediment, with 5% phytoplankton. I assume this because feeding preferences are more accurately reflected (or optimized by the Bayesian calibration) in FISHRAND?

BIVARIATE BAF ANALYSIS

pg. 16, Book 3. A statement is made that while statistical models may capture historic conditions, they are not guaranteed to predict the future, particularly if the characteristics of the PCB source change over time. This statement is directed at the physical system (scouring, for example). However, changes in PCB composition over time are something that none of the models appear to address adequately.

pg. 41-44, Book 3. A lot of effort is put into translating historical packed column analytical data based on a very inconsistent array of Aroclor standards, to predict Tri+ concentrations. But how did the exact makeup of the congener composition change over time? Unless Tri+ composition is constant over time, having accurate knowledge of the concentration is a confounding factor in risk assessment.

pg. 45-46, Book 3. Interlaboratory comparison shows the potential for factors of 1.4-1.5 difference among laboratories supplying data. There is an admission that the Aroclor based data 'appears to be consistently higher than GE's sum of congeners', but no actual data are given, presumably because the 'data are not yet ready to be released'. However, this may be critical to validation of the model.

pg. 47, Book 3. It is not clear to me what congener-specific data were used in the regression, and over what period of time. This could introduce a bias – see previous comment.

pg. 55, Book 3. The comment on carryover of body burden from previous years is an important one. Depending on the relative rates of decline in concentrations in the ecosystem to clearance of the compounds from fish, there could be a time-lag. That is, however, likely to be a less serious problem in the future as declines approach an asymptotic value.

The conclusions resulting from fitting the model to mean data appear quite sound, especially that water and sediment are not at equilibrium. The three different statistical methods for analyzing the relative contribution of the two sources in the various species

Another indeterminate factor may be changes in climatological factors, especially the influence of unusually hot or cold years. For example, Hebert et al. (1997) showed that much of the "noise" in the long-term exponential decline in PCB concentrations in Lake Ontario herring gull eggs was due to exceptionally cold winters.

I highly recommend that continuing fish monitoring programs include $\delta^{15}N$ measurements in order to build up a data base on long-term stability of the ecosystem.

3. *It is easy to get caught up with modeling details and miss the overall message of the models. Do you believe that the report appropriately captures the "big picture" from the information synthesized and generated by the models?*

The concerns of the Peer Review team for the Preliminary Model Calibration Report have been carefully assessed, and the problems and shortcoming raised by this team appear to have been adequately addressed, as outlined in the Response to this report. The formulation and parameterization of the models has been well thought out, calibrated and validated. Overall, the combined HUDTOX and FISHRAND models do an excellent job of predicting water and fish concentrations historically. Provided there are no unforeseen changes in the ecosystem or hydrodynamics, forecast Tri+ concentrations are likely to be as good as could be expected in any modeling exercise.

However, I strongly believe that there is too much emphasis on modeling Tri+ versus individual congeners. This needs to be addressed in order for the models to be useful in answering the first study question: *When will fish meet the human health and ecological risk criteria under No Action?* I assume that the risk assessment will not be based on a parameter as vague as Tri+, unless it can be shown that projected congener makeup is unlikely to change over time. HUDTOX was applied to the hindcast of 5 congeners for 1991-1997. This information was apparently not used to produce a forecast for use in the FISHRAND, although there is a hint that this will be done in the future. While I understand that the accuracy of such a prediction may not be as good as Tri+ concentrations, it can and should be done. Furthermore, simulating individual

General Questions

1. *What is the level of temporal accuracy that can be achieved by the models in predicting the time required for average tissue concentrations in a given species and river reach to recover to a specified value?*

I do not believe this to be a fully answerable question. Despite the wealth of information (or perhaps because of it), quantitation of the uncertainty of forecasts over the very long time period apparently required is not something that can be achieved in a short and necessarily somewhat superficial peer review. Furthermore, it would be necessary to have a reasonably accurate prediction of the long term boundary conditions for water concentrations, which is apparently not possible with the present information. The *required* accuracy will probably also depend on what the specified tissue concentrations are. Short-term predictions are by their very nature likely to be more accurate. This question should be addressed in the context of the human and ecotoxicology assessments.

2. *How well have the uncertainties in the models been addressed? How important are the model uncertainties to the ability of the models to help answer the principal study questions? How important are the model uncertainties to the use of model outputs as inputs to the human health and ecological risk assessments?*

I am not qualified to address the statistical approaches to quantifying uncertainties. However, apart from these, there are unquantifiable uncertainties which may be even more important in long-term predictions.

The possibility of biological community structure changes may be one of the biggest sources of uncertainty in the forecasts. For example, invasion of exotic species, (zebra mussels, blunt-nosed goby) and other unpredictable changes to the river ecosystem could alter the ecosystem such that the model structure is no longer valid. Introduction or removal of a trophic level in the food chain could create a factor 5 higher or lower in concentrations in fish (Rasmussen, et a., 1990). Is there any indication that benthic or fish community structure has changed substantially due to the continuing decline in PCB concentrations?