Development of an Ecological Risk Assessment Methodology for Assessing Wildlife Exposure Risk Associated with Mercury-Contaminated Sediments in Lake and River Systems

Part 1: Essential Data Requirements
Part 2: SERAFM - - Spreadsheet-based Ecological Risk Assessment for the Fate of Mercury (A Screening Model)

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(A Screening-level Model)

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NOTICE

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ABSTRACT

Mercury is an important environmental contaminant with a complex chemistry cycle. The form of mercury entering an ecosystem from anthropogenic and natural sources is generally inorganic, while the environmentally relevant form is in the organic form, methylmercury. Therefore, the risk assessor is presented with several challenges in developing remediation strategies for a mercury contaminated river, lake, or pond. To assist with ecological risk assessments for mercury in these systems, a screening level tool was developed. First, the data requirements needed to develop such an assessment and to generally implement a fate and exposure model were specified and are provided herein. Second, a process-based, steady-state risk-assessment model, SERAFM (Spreadsheet-based Ecological Risk Assessment for the Fate of Mercury) was developed and is presented herein also. The SERAFM model ("SERAFM") incorporates the chemical, physical, and biological processes governing mercury transport and fate in a surface water body including: atmospheric deposition; watershed mercury transport, transformations, and loadings; solid transport and cycling within the water body; and water body mercury fate and transport processes. SERAFM is comprised of a series of sub-modules that are linked together in series, so that each part is viewed as a building block within the general modeling framework. SERAFM estimates exposure mercury concentrations in the sediment, water column, and food web, and calculates hazard indices for exposed wildlife and humans. Because mercury risk assessments are complicated due to the different source types, that is, from historical loadings of mercury from current atmospheric deposition and watershed loadings, SERAFM simultaneously calculates exposure conditions for three different scenarios at any given site. These are: 1) the historical case of mercury-contaminated sediments; 2) suggested clean-up levels necessary to protect the most sensitive species, if possible; and 3) background conditions that would be present if there were no historical contamination. The sub-modules within SERAFM include: mercury loading (watershed and atmospheric deposition); abiotic and biotic solids balance (soil erosion, settling, burial, and resuspension); equilibrium partitioning; water body mercury transformation and transport processes; and wildlife risk calculations. The spreadsheet structure of SERAFM permits dismantling and reassembling of specific sub-modules to allow model flexibility and to maintain model transparency.

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EXECUTIVE SUMMARY

Mercury is of increasing environmental concern due to both its suspected toxicity and its tendency to bioaccumulate and biomagnify in food webs. The United States Environmental Protection Agency (US EPA) evaluated the mercury issue in 1997 in its Mercury Study Report to Congress and targeted mercury as a primary area of research interest. In 2003, the Ecosystems Research Division (ERD) of the National Exposure Research Laboratory (NERL) in Athens, Georgia received Assistance Request Number 10 from the Ecological Risk Assessment Support Center (ERASC). This request was designed specifically to target the question: How can we develop a remediation goal for mercury in sediment when the concentration of mercury in sediment may be a poor predictor of mercury exposure to biota? Additionally, this request also asked the related questions: 1) What are the best ways to estimate mercury transfer (as methylmercury) from sediment to the water column and/or the aquatic food chain, including birds and mammals feeding upon fish and aquatic invertebrates? and 2) Should remediation goals for mercury in sediment be developed for methylmercury only or, perhaps, total mercury normalized for factors associated with methylation?

In an effort to address these questions, ERD developed a methodology that would assist a regulator in deriving a remediation goal for sediments historically contaminated by mercury in lake and river ecosystems. In this report, the process used to develop remediation goals, including necessary data requirements, are described, and a tool is provided to facilitate calculations of a remediation goal to protect fish and wildlife. This

methodology is composed of two parts: Part One: essential data requirements; and Part Two: screening-level mercury ecological risk assessment modeling framework. The purpose of part one is to specifically provide a description of the essential data that a risk project manager would need to obtain to establish a remediation goal for mercury in sediments, as well as any other data that would be additionally useful. Part Two of this project involves a description of the transport and fate processes required to derive the remediation goal, and the creation of a modeling tool to aid in this endeavor.

In Part One, a progression of different types of data requirements is presented in three tiers. The first tier presents the minimally essential data, the second tier presents useful data that would increase the strength of the assessment, and the third tier presents the most rigorous and most accurate approach for an assessment. The data requirements specified herein include mercury measurements; ancillary measurements; number of samples, including temporal, spatial and replication variability; fish tissue mercury sampling; additional food web analysis measurements; and water body characteristics.

In Part Two, a spreadsheet modeling framework is presented that can be used as a risk assessment tool for mercury contaminated surface water ecosystems. This model is the **SERAFM** model ("SERAFM"), the **S**preadsheet-based **E**cological **R**isk **A**ssessment for the **F**ate of **M**ercury. In this tool, aprocess-based understanding of mercury is incorporated into a steady-state modeling framework to assist with a wildlife risk assessment.

A spreadsheet modeling environment was chosen for a few important reasons. A spreadsheet provides a transparent and flexible working environment. The transparency of the model is evident in that all the equations used for all calculations are easily viewed. There are no hidden calculations. All manipulations that the model performs can be easily reviewed and can readily be adapted or updated as needed. Similarly, a spreadsheet can act as an inherent database to maintain all data and parameters. Therefore, all parameters used and the values assigned to these parameters are presented in a simple manner so that these can be changed or updated as needed. The modules contained within the model itself are separated distinctly into individual worksheets. Cross-referencing is performed across worksheets so that using the formula auditing tool bar, all parameters can be simply traced back to their precedents and dependents. The transparency of the model is enhanced by the flexibility it provides the user. The user can change what is needed or let the default characteristics be used. This is a powerful feature because the framework of this model can be used on a general, screening level application or a more detailed and described system to investigate research questions.

The model was designed to simulate a watershed and associated water body that receives atmospheric deposition of mercury and has had historical loadings of mercury to the sediments, such as one associated with a facility of some kind that historically released mercury to the watershed and/or water body. The SERAFM model runs its calculations assuming steady-state and using process-based mathematical governing equations to describe the fate and transport of mercury within the ecosystem. The SERAFM model specifically calculates the mercury concentrations (HgII, MeHg, Hg0) in the water

column (dissolved and total), in the food web (plankton, zooplankton, benthic invertebrates, and trophic level 3 and 4 fish), and the hazard indices of exposed wildlife and humans. The SERAFM model starts by calculating exposure concentrations for the historical scenario, and from this case the most sensitive species (the species with the highest hazard index) is identified. SERAFM then calculates exposure concentrations and hazard indices for a scenario using only the effective background conditions, defined as the conditions that the ecosystem would currently be under if it had never had historical mercury loading. This scenario is particularly important to simulate because ecosystems that are not receiving direct loadings of mercury still receive mercury loading from the watershed and atmospheric deposition. Therefore, this scenario represents the "best case" if all mercury from possible discharges or disposal practices had been negated, and only current background conditions are influencing the system. Then, by using the most sensitive species, the model does a simple linear approximation of what the required sediment concentration would have to be to reduce the hazard index of the most sensitive species to 1, and thus effectively protect all species associated with this water body from mercury exposure. It is quite possible that because of the level of mercury present in the current conditions that no level of remediation will recover the system to sufficiently protect the most sensitive species. That is, current background atmospheric and watershed loading of mercury to the water body is high enough to put the most sensitive species at risk and until these inputs are reduced, the site will remain above risk. All three scenarios are calculated instantaneously as parameters are changed.

This report is structured so that the user may take what he or she needs from it without having to read it in its entirety. Each section presents a specific topic and can be used as a reference. The background of the technical assistance request is presented in Section 1: Introduction. The data requirements are presented in Section 2: Essential Data. The structure and rationale of the model are presented in Section 3: Model Structure. In this section, the reader will understand the compartmental structure of the model and how each worksheet within the spreadsheet model interacts. A general overview of the governing mercury transport and fate processes included in SERAFM and how the model fits together is presented in Section 4: Overview of SERAFM. Section 5: SERAFM Modules and Equations describes the general modules that fit together to comprise the overall SERAFM modeling framework. In this section, the mathematical governing equations are presented. The user primarily interacts with the "Input&Output" worksheet that is described in Section 6: Model Interface Layout. This section also gives brief details of the other worksheets. In Section 7: Model Implementation, details are provided on how to use the model as a risk assessment tool. In this section, the user is walked through a method of progressive calibration of the model. Since the model is structured in module compartments, it is important to calibrate the model in a series of steps on each level according to the module. Section 8: References lists all references used in this work. The appendix provides a literature review of reported rate constants for mercury transformation processes.

1   BACKGROUND

Mercury has been recognized as an important environmental pollutant by the United States Environmental Protection Agency (USEPA) because of its suspected neurotoxicity (USEPA, 1997). Mercury occurs naturally in the environment in its neutral, elemental state (Hg^0, Hg0) as well as its oxidized, divalent state (Hg^{2+}, HgII). Mercury also exists in the form of organometallics, such as the environmentally relevant compound methylmercury (CH_3Hg^+, MeHg). The USEPA, the United States Food and Drug Administration (FDA), and the European Food Safety Agency (EFSA) have recognized that methylmercury is a contaminant of concern in announcing consumer advisories for methylmercury concentrations in fish (USDHHS and USEPA, 2004; EFSA, 2004).

Methylmercury bioaccumulates (*i.e.*, increases in concentration in an organism during its period of exposure) and biomagnifies (*i.e.,* increases in concentration from trophic level to trophic level (*e.g.*, from phytoplankton to zooplankton, to prey fish, to predator fish) within a given food web. Methylmercury concentrations can increase orders of magnitude from the aqueous methylmercury concentrations in lake water to methylmercury tissue concentrations in higher trophic level organisms such as fish and piscivorous birds and animals. The ingestion of fish tissue contaminated with methylmercury is the predominant exposure pathway for humans and wildlife. Wildlife exposure to mercury can be of even greater concern than for humans because wildlife survival sometimes relies on the exclusive consumption of aquatic organisms. The 2003 National Listing of Fish and Wildlife Advisories (NLFWA) by the USEPA reported that there are 3,094 advisories for mercury in 48 states. These advisories represent 35% of the nation's total lake acreage and 24% of the nation's total river miles. Approximately

101,818 lakes, 14,195,187 lake acres, and 846,310 river miles in the US are under advisories. Additionally, 100% of the Great Lakes and their connecting waters are under advisory (USEPA, 2004).

Mercury exhibits a complicated chemical cycle (see Figure 1). Mercury first enters the global cycle through both anthropogenic and natural sources. Anthropogenic point sources of mercury consist of combustion (*e.g.*, utility boilers, municipal waste combustors, commercial/industrial boilers, medical waste incinerators) and manufacturing sources (*e.g.*, chlor-alkali, cement, pulp and paper manufacturing) (USEPA, 1997). Natural sources of mercury arise from geothermic emissions such as crustal degassing in the deep ocean and volcanoes as well as dissolution of mercury from geologic sources (Rasmussen, 1994). Because mercury has a residence time of approximately one year in the atmosphere, emitted mercury can travel long distances before depositing. Remote lakes that are otherwise not exposed to direct loadings of mercury, such as those in eastern Canada, northeast and north central US, and Scandinavia, have been reported to have high levels of mercury in both the water bodies and fish (see Fitzgerald et al., 1998).

When mercury travels long distances through the atmosphere, it then deposits via wet and dry deposition onto watersheds and water bodies. Deposited mercury can undergo oxidation and reduction reactions that transform mercury from its divalent state (HgII) to its elemental state (Hg0) and vice-versa. Additionally, bacteria can transform mercury into the bioaccumulative and toxic form, MeHg. Once transformed, MeHg can accumulate in aquatic vegetation and phytoplankton. Zooplankton then graze and bioaccumulate the MeHg, which is subsequently transferred up the food chain to prey and

predator fish. These fish are then consumed by humans and wildlife, resulting in accumulation of methylmercury in their tissue, which can result in toxic levels of mercury. With each step up the food chain, mercury undergoes biomagnification, resulting in higher and higher concentrations of mercury in each higher level organism.

Clearly, it is advantageous to understand the processes governing mercury cycling so that we can adequately understand the level of risk to wildlife and humans exposed to mercury from a given water body under various loading scenarios. There is a vast body of literature describing the many different mercury transport and fate processes, and recent research has furthered our understanding of the aggregate impact of watershed loadings in addition to direct atmospheric loading. Patterns and correlations have been investigated relating mercury concentrations in water to mercury concentrations in fish. The USGS performed a national study investigating correlations between concentrations of different species of mercury in a variety of media and the corresponding concentrations of mercury in fish tissue. They found that bioaccumulation was strongly correlated with MeHg concentration in water, but only moderately correlated with MeHg concentration in sediment or total Hg concentration in water (Brumbaugh, 2001). These observations provide a challenge to establish a basis adequately predicting fish mercury concentrations. First, methylation of mercury is believed to occur predominately in the sediments, and second, sites that have undergone direct inputs of mercury contamination may have sediments contaminated well above background levels. The challenge then arises as to how to handle exposure and risk assessments for aquatic ecosystems that have had direct inputs of mercury to the water body and/or sediments. This is the crux of the work presented in this report.

Many sites often require that site remediation goals be developed for the sediments instead of or in addition to those for the surface water. For these latter sites, it is believed that the sediments are acting as a secondary source of mercury or as an exposure medium for ecological receptors. For some contaminants, bioaccumulation factors based on sediment contamination (*e.g.*, BSAF: Biota-Sediment Accumulation Factor) have been successfully developed and used as a direct correlation between the sediment contaminant concentration and fish and/or wildlife contaminant concentrations. The issue, therefore, remains to develop a protective remediation goal for mercury in sediments, knowing that the concentration in the sediment may be a poor predictor of mercury exposure to fish and wildlife. To this end, a steady-state, process-based mercury cycling model has been created to assist a risk assessor or researcher to predict mercury concentrations in the sediment, water column and fish in a given water body for a specified watershed. The SERAFM, Spreadsheet-based Ecological Risk Assessment for the Fate of Mercury, model predicts mercury concentrations for the species Hg0, HgII, and MeHg. The model runs three simultaneous scenarios. One scenario is for historically contaminated sediment, where the total mercury concentration in the contaminated sediment is known. This scenario would be relevant, for example, for modeling a Superfund site where the contaminated sediment is acting as a loading source to the aquatic ecosystem. In this first scenario, the total mercury concentration in the sediment is entered into the model as a known parameter. The second scenario is a hypothetical background or reference condition, which is defined as the condition as if no historical loading of mercury had occurred at this site. Therefore, the mercury concentrations in both the water and sediment are calculated with no known mercury

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sediment concentration, but rather the total mercury concentration in the sediment is directly calculated by the model. Mercury loadings to the water body are only from direct atmospheric deposition to the water body and watershed, and subsequent erosion and runoff. In this scenario, the water body sediment acts as a sink rather than a possible source to the system. Using the calculated results of these two scenarios, a third scenario is run to develop a proposed, possible sediment clean-up goal. This scenario uses a linear extrapolation from the previous two scenarios to calculate the necessary sediment total mercury concentration to protect the identified most sensitive species. Then, from this information, the concentrations of mercury in the water body and fish tissue mercury concentrations and the wildlife and human hazard indices are calculated as done in the first scenario.

2   ESSENTIAL DATA

2.1   Mercury Measurements

There are three media of interest in these aquatic ecosystems: water column, sediment, and fish tissue.   The essential mercury data requirements in these media consist of measuring the total mercury and methylmercury concentrations in both the water and the sediment. For each of these measurements, both a filtered and unfiltered sample are required. These data are required for all tiers, but the amount and extent of samples vary tier by tier. Ancillary measurements are listed in Section 2.2. The details of the necessary samples are presented in Sections 2.3 and 2.4. Mercury concentration in fish tissue is also required, but this will be addressed further in Section 2.5. A summary of the types of samples and number of suggested samples required is presented in Table 1.

2.2 Ancillary Measurements

There are several ancillary measurements that are also required for the water column and the sediments. For tier one, the total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations must be measured in both the water and the sediment, as well as the total suspended solids concentration in the water and the bulk density of the sediments. For tier two, the particle size distributions in the water column and the sediments are needed. Additionally, in tier two, the water temperature is measured. For the third tier, water column dissolved oxygen (DO) and pH measurements are added.

2.3 Number of Measurements/Sampling Dates

The number of measurements taken affects the confidence in the measured value. The statistical significance is increased with more samples. In the first tier, there are three sampling dates: early, mid and late summer. The dates chosen coincide with the greatest activity within a lake. During the summer months, the temperature in a lake increases. This promotes faster fish growth and more bacterial activity (faster methylation rates). Therefore, if only a few samples can be taken, it is important to at least get samples during this most important summer time. If it is possible to take more samples, then the breadth of sampling time frame can be increased to cover late spring and early fall in tier two, and then early spring and late fall on into tier three. If the type of water body that is being studied is believed to have appreciable parametric temporal variations, then it may be important to increase the number of their measurements to capture this variability. The number of measurements suggested here is the minimum number of samples that would be required in our opinion.

2.4 Number of Replications

In addition to capturing the temporal variation in the sampling, there needs to be replication of the samples to increase the statistical significance of the measurements. There are two types of errors associated with these types of measurements. First, there is the spatial variability that occurs when sampling a heterogeneous media. Second, there is the sampling error associated with any sample. To help understand the level of error within each, it is prudent to independently account for both. To this end, we recommend sampling in a manner that will allow estimation of these errors.

In Table 1, the column associated with the required/suggested data, the number of replications suggested is presented as a number plus a number (*i.e., m+n*). The first number, *m*, represents the number of different locations that should be sampled. The second number, *n*, represents the number of replications suggested at any given location. Therefore, for example, for a second tier study parameter measurement, this column would show "5+3" samples. This designation yields a total of 7 unique samples; five different locations are to be chosen and at four of these locations, only one sample would be taken for each of the mercury and ancillary measurements, but at one location, a total of three different samples would be taken, upon which the measurements will be made. The five location samples are to assess spatial variability and the three co-located samples provide information on the variability at any given sampling point. This scheme helps one to determine if the range of each measured parameters is attributable to sampling/measurement error or spatial variability. These various uncertainty factors can then be incorporated in the model via Monte Carlo or other similar techniques

The "Replication" numbers presented in Table 1 for each of the three tiers are to be perceived as suggested minimums. The more samples that can be taken will clearly

provide more information and confidence in quantifying the variability at any given site and in the model predictions. Ultimately, selection of the number of samples must balance the scientific integrity of the project results with the economic feasibility and cost of the project.

2.5   *Biota: Fish*

Fish tissue is the medium by which the transfer of mercury to wildlife occurs. Therefore, to fully understand the overall transfer of mercury from the water and the sediments, the fish tissue mercury concentration must be measured. As stated previously, mercury bioaccumulates and species and biomagnifies with each transfer from lower trophic level organisms to higher trophic level organisms. In this category of data requirements, there are two types of fish species (two trophic levels) for which the mercury concentrations need to be determined, the piscivores and the mixed feeders. A piscivore is a species of fish that feeds primarily on other fish. A mixed feeder fish feeds on fish but also on invertebrates.

For each species of fish type sampled, five different measurements of mercury concentration in the fish tissue must be made. Tier one, the simplest level, requires one species of each type of fish (*i.e.*, piscivores and mixed feeder) be measured. For tier two, 2 - 3 species of each type is suggested; for tier three, 3 - 5 (or more) species of each type is suggested (Table 1). Selecting more species of each type of fish will give a more rounded perspective of the food web and trophic transfer of mercury within the food web itself.

An additional complication for measuring mercury in fish tissue is that there is a direct correlation of the mercury concentration in fish with length, weight and age of the

fish. Therefore, in addition to the fish tissue mercury concentration measurement, the sampled fish's weights and lengths for each species from each type of fish used must also be measured. If possible, it would be quite useful if the age of the individual fishes sampled could be determined as well. The modeler would then be able to account for the variability of the measured mercury concentration due to fish weight, length, and/or age.

2.6 Food Web

The level of food web dynamics and the complications associated with it are an important issue and concern in mercury modeling. Therefore, an increasingly more rigorous system of modeling mercury transfer within the food web is used depending on the assessment tier. In the first tier, correlations between the fish tissue mercury concentration and the water and sediment concentrations are used. This is similar to a more simplistic bioaccumulation factor approach. The bioaccumulation factor is to be determined using site-specific data, and not simply literature data. In the second tier, a trophic level mercury accumulation model is used. This model requires that the lower trophic levels be modeled, and thus the mercury concentrations in the macro-benthos are needed. For a third tier level assessment, a more rigorous food web model is used that incorporates food web dynamics and the growth rates of fish and other biota. This approach will require calibration to the water body and ecosystem being investigated.

2.7 Water Body Characteristics

In addition to the herein specified mercury and ancillary measurements, it would be most helpful if the parameters describing the water body were also provided. These parameters mainly deal with the physical structure of the water body and its surrounding environment. One important piece of information is the geometry of the water body, such

as the width and length of a reach of river, or the surface area and depth of a lake or pond. Additionally, the flow rate of a river and the lake/pond flushing rate (or hydraulic residence time) will allow for mass balance calculations within the system. Watershed loadings (as estimated from the size, land use, and wetland percentage) and upstream mercury concentrations further assist in understanding the ecological impact of changes in the studied/modeled water body sediment mercury concentration.

3 MODEL STRUCTURE

The model presented here is steady state and process based, incorporating a series of modules such that each module fits into a scheme to simulate a comprehensive picture of mercury exposure and risk. The model is written using Microsoft© Excel 2003 (Microsoft, Inc., 2003); it is implemented using a spreadsheet program for several reasons. MS Excel is a program that is generally understood and used by the general population, so it can be readily accessed and implemented by a wide audience. The user does not need to understand higher level programming languages such as Visual Basic, FORTRAN, or C++. Part of the expressed goal of this model development was to incorporate the current state of the science in a readily available and easily implemented software package to serve a greater variety of users. By being in a spreadsheet format, all manipulations, parameters, and equations are readily available and transparent to the user. This allows adjustments as the user sees fit. However, the model is organized with a simple, upfront user interface so that higher level use can be performed without having to dig into the depths of the program itself. Microsoft© Excel 2003 can act as its own database, and the formula auditing toolbar allows tracking of precedent and dependent cells. Additionally, a spreadsheet is a programming environment that allows each model

module to be separated into its own worksheet. This is effectively similar to having distinct subroutines for each set of operations. The modules and their equations are described in Section 5, and the details of each worksheet within the model spreadsheet are detailed in Section 6: Model Interface Layout. Additionally, notes and equations are provided in the spreadsheets themselves so that SERAFM can act as its own user's manual.

The model itself consists of a series of modules; each solved independently using a common parameter database and linked modules for input. Thereby, the model works in a step-by-step fashion proceeding towards a solution for the desired parameters (*e.g.*, fish mercury concentrations and wildlife hazard indices) in a feed-forward fashion. The first module used in SERAFM calculates the total loading of each mercury species to the water body. This module includes direct loading to the water body via wet and dry deposition as well as indirect loading from watershed sources. Next, the solids balance module calculates the concentrations of solids in the water body. Specifically, the concentrations for abiotic, biotic, and organic solids are solved using a series of simultaneous equations. The equations are derived as coupled differential equations that are then solved assuming steady state conditions. Using the solutions for the solids balances, the mercury cycling equations for the water body are solved. The mercury equations are similarly derived as coupled differential equations that are solved simultaneously assuming steady state conditions. Using the calculated mercury species water column concentrations, bioaccumulation factors are used to predict mercury concentrations in the different types of aquatic biota. Then, assuming daily ingestion

rates of contaminated aquatic biota, hazard indices are estimated for the wildlife and human receptors.

4   OVERVIEW of SERAFM

4.1   Conceptual Model

The following lists the overall conceptual model and module structure used to simulate mercury fate and transport in this report:

• Atmospheric mercury deposition to the watershed and water body,

• Deposition processing by the watersheds followed by transport to the water body via runoff, erosion, and tributaries,

• Mercury transformation processes in the water body:

   o photolytic processes of oxidation, reduction, and degradation;

   o biochemical and abiotic oxidation; and

   o methylation and demethylation,

• Sorption and complexation processes to describe the partitioning of mercury species to silts, sands, biotic solids, and dissolved and particulate organic matter,

• Settling to, resuspension from, and burial of particulates in sediments,

• Bioavailability of mercury complexes with hydroxides, chlorine, sulfide, and dissolved organic carbon.

• Dissolved MeHg accumulation in aquatic vegetation, phytoplankton, and benthic invertebrates, and zooplankton

• Bioaccumulation of MeHg through:

   o fish predation of zooplankton and benthic invertebrates,

   o fish preying on other fish.

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4.2   Model Development

SERAFM is the Spreadsheet-based Ecological Risk Assessment for the Fate of Mercury

model. The SERAFM model ("SERAFM") implements an updated set of the IEM-2M

solids and mercury fate algorithms described in detail in the *Mercury Study Report to*

Congress (USEPA, 1997). A comparison of SERAFM predicted results to those of IEM-

2M model using the parameter values for the model ecosystem described in the Report to

Congress is presented in Table 1. This preliminary comparison of the results of the two

models suggests that updates to the IEM-2M model incorporated into the SERAFM

model result in slightly lower predicted aqueous methylmercury concentrations and fish

tissue mercury concentrations, and slightly higher predicted aqueous total mercury

concentrations. The major differences between the SERAFM model and the IEM-2M

model are as follows:

> • *Watershed Loading*: Both IEM-2M and SERAFM model soil erosion into the
>
> water body using the Revised Universal Soil Loss Equation (RUSLE).
>
> However, in SERAFM mercury loading from the watershed to the water
>
> body is modeled using run-off coefficients. SERAFM defines and uses
>
> four land-use types: impervious, upland, riparian, and wetland. The user
>
> specifies the percentage of each land-use type in the watershed. The model
>
> uses land-use specific run-off coefficients to transforms mercury loadings
>
> to the watershed from atmospheric deposition to each land-use type into
>
> loadings to the water body. SERAFM loadings to the watershed include
>
> HgII and MeHg loadings. In contrast, IEM-2M calculates the HgII
>
> concentrations in the watershed soils, accounts for reduction and

instantaneous Hg0 evasion, then simulates transport of solids via erosion
and transport of HgII via erosion and runoff to the water body.

• *Two-Layer*: SERAFM has the capability to model a layered lake system with an
epilimnion and hypolimnion, while IEM-2M uses a single, well mixed
layer to represent the water column.

• *Photo-reactions*: Recent research has demonstrated the importance of photolytic
transformations of mercury. These transformation processes have been
incorporated into SERAFM, but were not part of the original IEM-2M
model. In SERAFM, the photo-oxidation, photo-reduction, and photo-
degradation of mercury as functions of visible and UV-B light are
included, with specific light attenuation factors for each.

• *Speciation*: Speciation of mercury with hydroxides, chlorides, and sulfides is
included in the SERAFM model but not in the IEM-2M model. Currently,
this difference only affects the effective oxidation rate constant of HgII.
Future versions of SERAFM will expand its scope of modeling relative to
mercury speciation and its impact on mercury transformation rates as the
science of these processes is better understood.

• *Trophic status*: Trophic status of the lake is taken into account in the SERAFM
model, but not the IEM-2M model. Trophic status is used to calculate
visible light attenuation in the lake, the turnover rate of biomass, and the
phytoplankton and zooplankton concentrations in the SERAFM model
framework.

- *Suspended particle types in the water column*: The SERAFM model accounts

    for both zooplankton and phytoplankton as biotic materials in the system;

    the IEM-2M model accounts for one general biotic particle type.

- *Reaction rates*: The SERAFM model incorporates more recent transformation

    reaction rate coefficients and understanding of the variability of these rates

    under different conditions.

- *Partition coefficients*: The SERAFM model incorporates more recent values for

    mercury partition coefficients for each mercury species. Future versions of

    SERAFM will calculate site-specific partitioning as a function of sediment

    organic matter and the organic carbon content of suspended materials.

State variables in both the IEM-2M and SERAFM models include three mercury

species, Hg0, HgII, and MeHg. As mentioned previously, SERAFM includes four solids

types (abiotic solids, phytoplankton solids, zooplankton solids, and detrital solids) plus

dissolved organic carbon, DOC. Both IEM-2M and SERAFM simulations are driven by

external mercury loadings delivered from the atmosphere, from watershed tributaries, and

from point sources, or by internal loadings from contaminated sediments. SERAFM

calculates the time-dependent mercury species concentrations in the water column and

sediments of the specified water body. HgII and MeHg are partitioned to suspended and

benthic solids and complexed with DOC with user-specified or SERAFM default

partition coefficients for each sorbent type. Also, In SERAFM, mercury species are

subject to several transformation reactions, including photo-oxidation and dark oxidation

of Hg0 in the water column, photo-reduction and methylation of HgII in the water

column and sediment layers, and photo-degradation and demethylation of MeHg in the

water column and sediment layers. Water column oxidation, reduction and demethylation reactions are driven by sunlight, and so their input rate constants are attenuated through the water column using specified light extinction coefficients. Hg0 is subject to volatile exchange between the water column and the atmosphere governed by a transfer rate calculated from wind velocity and water depth, and by its Henry's Law constant.

4.3 SERAFM Model System and Model Structure

SERAFM is a steady state, process based model incorporating a series of modules, with each module fitting into the scheme of mercury modeling to create a complete picture of mercury exposure and risk. SERAFM is structured using Microsoft© Excel 2003 (Microsoft, Inc., 2003) to keep each sub-module separated from other sub-modules. Each sub-module is housed on a separate worksheet within the Microsoft Excel workbook that all together comprises SERAFM. This, in effect, is of similar design to having each sub-module within its own subroutine in a more formal programming language. The primary worksheet is the "Input & Output" worksheet that houses the model input and the model base rate constants for mercury transformations in the water body and sediments. SERAFM uses these input values and base rate constants, and calls on the remaining worksheets within the workbook to instantaneously calculate the output results. These output results are presented as the modeled exposure concentrations on the same worksheet as the input parameters.

4.4 SERAFM Model Scenarios

SERAFM is structured to investigate and solve three scenarios to assist with the development of a remediation strategy for aquatic ecosystems with mercury-

contaminated sediments. Scenario 1 is for the current conditions of a site that has been subject to historical loading of mercury. An example of this type of site is one associated with an industrial facility that released mercury into a nearby water body. Over time, the mercury settled into the sediments, which resulted in increased mercury concentrations in the sediment over background or reference conditions. This sediment concentration can therefore act as an additional source over time to the associated water body. Scenario 2 is the same site as if there had never been an industrial site. This is an effective background or reference condition. In this scenario, the water body and sediments have undergone mercury loading solely through atmospheric and watershed loading. There is still mercury in the system, but it is not the result of industrial loading over time. Scenario 3 is a hypothetical scenario where Scenario 1 has undergone remediation to reduce the mercury concentrations in the sediment. By using the information in Scenario 1 and 2, Scenario 3 estimates the mercury concentration in the sediment that would be necessary to protect the most sensitive ecological receptor.

5 SERAFM Modules and Equations

5.1 Solids

The steady-state concentrations of abiotic and organic solids in the water body are simulated in the solids balance module that is separate from the module containing the mercury process equations. A set of simultaneous equations were derived to calculate the concentration of the abiotic solids, *abio* and organic solids, *org*. The abiotic solids account for soil particles (sands, silts, and fines), and the organic solids account for the non-living organic solids. Because SERAFM is a steady-state model, the living biota (zooplankton and phytoplankton) turnover rate (mortality rate) is equal to the organic

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solids growth rate. These mortality rates are not solved internally within SERAFM, but are input values corresponding to the trophic level of the system (see Wetzel, 2001). The equations derived to calculate the concentrations of abiotic and organic solids in layer 1 (epilimnion) and layer 2 (hypolimnion) of the lake or pond and the sediments are presented below. All equations were first written as differential equations with respect to time, then solved assuming steady-state conditions by setting the derivative with respect to time equal to zero. The solids sources into the system include soil loading from erosion and upstream inflow. The losses from the system include downstream outflow and burial of the surface layer of sediments into deeper sediment layers. As stated previously, internal cycling includes settling, resuspension, and bulk exchange between layers (Figure 2). An internal source of organic solids is from the death of plankton, thus transforming living organic matter into non-living organic matter. An internal loss is the mineralization of non-living organic matter.

$$V_1 \frac{dS_{abio}^{w,1}}{dt} = +L_C \cdot A_C \cdot 10^3 [g/kg] + Q_{in} S_{abio,in} + \left(-Q_{out} - Q_{ex} - v_{s,abio} \cdot A\right) \cdot S_{abio}^{w,1} + Q_{ex} \cdot S_{abio}^{w,2} = 0$$

$$V_2 \frac{dS_{abio}^{w,2}}{dt} = +\left(v_{s,abio} \cdot A + Q_{ex}\right) \cdot S_{abio}^{w,1} + \left(-Q_{ex} - v_{s,abio} \cdot A\right) \cdot S_{abio}^{w,2} + v_r \cdot A \cdot S_{abio}^{sed} = 0$$

$$V_1 \frac{dS_{org}^{w,1}}{dt} = +k_{mort} \cdot S_{phyto}^{w,1} \cdot V_1 + \left(-Q_{out} - Q_{ex} - v_{s,org} \cdot A\right) \cdot S_{org}^{w,1} + Q_{ex} \cdot S_{org}^{w,1} = 0$$

$$V_2 \frac{dS_{org}^{w,2}}{dt} = \left(v_{s,org} \cdot A + Q_{ex}\right) \cdot S_{org}^{w,1} + \left(-Q_{ex} - v_{s,org} \cdot A\right) \cdot S_{org}^{w,2} + v_r \cdot A \cdot S_{org}^{sed} = 0$$

$$V_{sed} \frac{dS_{abio}^{sed}}{dt} = v_{s,abio} \cdot A \cdot S_{abio}^{w,2} - v_r \cdot A \cdot S_{abio}^{sed} - v_b \cdot A \cdot S_{abio}^{sed} = 0$$

$$V_{sed} \frac{dS_{org}^{sed}}{dt} = v_{s,org} \cdot A \cdot S_{org}^{w,2} - v_r \cdot A \cdot S_{org}^{sed} - k_{min} \cdot V_{sed} \cdot S_{org}^{sed} - v_b \cdot A \cdot S_{org}^{sed} = 0$$

Where:

V_j: volume of the lake layer j [m^3], where j can be *1*, *2*, or *sed*, representing lake layer 1 (epilimnion), layer 2 (hypolimnion), or the sediment layer

$S_k^{l,j}$: solids/particulate concentration [g/m^3], where k is the solid type, k can be *abio* for the abiotic particles, *zoo* for zooplankton, and *phyto* for phytoplankton, and *org* for organic solids (non-living); l is the phase of interest, where l can be *w* for the water column or *sed* for the sediment layer. and j is *1* or *2* to distinguish between lake layers 1 and 2

$S_{abio,in}$: solids concentration in the inflow [g/ m^3]

L_C: load of abiotic solids (soil) from the catchment to the water body [kg/m^2/yr]

A_C: area of the catchment (watershed) [m^2]

A: surface area of the water body (same for all layers: 1, 2, and sediment) [m^2]

10^3 g/kg: conversion factor for kg to g

Q_l: volumetric flow rate [m^3/yr], where l is where the flow is with respect to the water body, *in* is for inflow, *out* is for outflow

Q_{ex}: volumetric exchange rate [m^3/yr] between the two lake layers

$v_{m,k}$: velocity [m/yr] of solids, m is the velocity type, where *s* is settling, *r* is resuspension, and *b* is burial; and k is solids type, where *abio* stands for abiotic solids (e.g., sands, silts, fines), and *org* stands for organic solids (non-living biotic material)

k_{mort}: mortality rate of phytoplankton [yr^{-1}]

k_{min}: mineralization rate of organic solids [yr^{-1}]

$$Q_{ex} = \frac{E_{12}A}{0.5 \cdot (z_2 + z_1)}$$

z_j: thickness of layer j [m], where j is layer 1 or 2.

E_{12}: Exchange between layers [m^2/yr], values for E are dependent on the system. For example, in lake systems,

E_{12} [m2/yr] = 365*0.0142*(0.5(z₁+z₂))$^{1.49}$

(Schnoor, 1996, and references therein)

5.2 Equilibrium Partitioning

Mercury partitions strongly between solid and aqueous phases. To account for this partitioning, the model calculates the fraction of mercury present as purely dissolved, partitioned to abiotic solids, partitioned to biotic solids (both non-living and living), and complexed with dissolved organic carbon (DOC). The partitioning of the various mercury species between the different phases (solids, aqueous, DOC-complex) is modeled using instantaneous, linear relationships (Figure 3), *i.e.*, partition coefficients defined as:

$$K_{sorbant,i} = \frac{C_{sorbed,i}}{C_{dissolved,i}}$$

Where:

      i: mercury species [Hg0, HgII, MeHg]

      $K_{sorbant,i}$:   partition coefficient [(g i / g sorbant) / (g i / L water)]

      $C_{sorbed,i}$:   concentration of i sorbed on sorbant phase [g i / g sorbant]

      $C_{dissolved,i}$:   concentration dissolved in water [g i / L water]

Using these partition coefficients, the fraction of each species of Hg present in each phase can be calculated. The equations for these calculations are:

$$f_{aq,i}^{w,j} = \frac{1}{1+10^{-6}\left(K_{abio,i}^{w} \cdot S_{abio}^{w,j} + K_{zoo,i}^{w} \cdot S_{zoo}^{w,j} + K_{phyto,i}^{w} \cdot S_{phyto}^{w,j} + K_{org,i}^{w} \cdot S_{org}^{w,j} + K_{DOC,i}^{w} \cdot S_{DOC}^{w,j}\right)}$$

$$f_{abio,i}^{w,j} = K_{abio,i}^{w} \cdot S_{abio}^{w,j} \cdot 10^{-6} \cdot f_{aq,i}^{w,j}$$

$$f_{DOC,i}^{w,j} = K_{DOC,i}^{w} \cdot S_{DOC}^{w,j} \cdot 10^{-6} \cdot f_{aq,i}^{w,j}$$

$$f_{zoo,i}^{w,j} = K_{zoo,i}^{w} \cdot S_{zoo}^{w,j} \cdot 10^{-6} \cdot f_{aq,i}^{w,j}$$

$$f_{phyto,i}^{w,j} = K_{phyto,i}^{w} \cdot S_{phyto}^{w,j} \cdot 10^{-6} \cdot f_{aq,i}^{w,j}$$

$$f_{org,i}^{w,j} = K_{org,i}^{w} \cdot S_{org}^{w,j} \cdot 10^{-6} \cdot f_{aq,i}^{w,j}$$

$$f_{aq,i}^{sed} = \frac{\theta_{sed}}{\theta_{sed} + K_{abio,i}^{sed} \cdot S_{abio,i}^{sed} \cdot 10^{-6} + K_{org,i}^{sed} \cdot S_{org,i}^{sed} \cdot 10^{-6}}$$

$$f_{sed,i}^{sed} = 1 - f_{aq,i}^{sed}$$

Where:

      θ_{sed}:   sediment porosity [unitless]

      $f_{k,i}^{l,j}$:   fraction associated with mercury species i, where i is Hg0, MeHg, or HgII; k is the associated fraction of interest, k can be aq for the aqueous fraction of species i, $abio$ for fraction of species i associated with the abiotic particles, DOC for fraction of species i complexed in DOC, zoo for the fraction of species i associated with zooplankton, $phyto$ for fraction of species i associated with phytoplankton, and org for the fraction of species i associated with organic solids (non-living); l is the phase of concern, where l can be w for the water column or sed for the sediment layer; and j is the water body layer, 1 or 2.

      $K_{k,i}^{l}$:   partition coefficient for mercury species i, where i is Hg0, MeHg, or HgII; k is the particle of concern, where k can be $abio$ for the abiotic particles, DOC for complexation with DOC, zoo for zooplankton, $phyto$ for phytoplankton, and org for organic solids (non-living); and l is the phase of concern, where l can be w for the water column or sed for the sediment layer.

5.3   Mercury Loading Equations

Mercury loading to a water body can occur through direct mercury deposition to the water body and through transport of deposited mercury on the watershed into the water body. The total loading of mercury to the water body is therefore modeled as the sum of direct loadings from wet and dry deposition plus that in runoff and erosion from impervious, wetland, upland, and riparian zones of the catchment watershed. Mercury load in the runoff and erosion from each land-use type is calculated by multiplying the net flux of the wet plus dry mercury by the area of the specific land-use type times the run-off coefficient associated with that land-use type. All of these loadings are summed then to determine the total mercury load of each mercury species to the water body (Figure 4).

5.4   Mercury Process Equations

In the water body, mercury is subjected to several transformation and transport processes. Describing these results in a series of coupled equations to calculate mercury concentrations for the different species (Hg0, HgII, MeHg) in the different media (water and sediments). The transformation processes (oxidation, reduction, methylation, demethylation, and photo-lytic degradation/demethylation) are modeled using first-order rate kinetics. Transport processes are modeled with respect to the associated process. Dissolved mercury is carried along with the corresponding flow (inflow, outflow, exchange, dispersion, diffusion); direct loading is modeled as a mass flux input; sorbed mercury is carried along with its specific sorbent particulate (settling, burial, resuspension); and Hg0 volatilization is modeled as a first order evasion rate. These processes are illustrated in Figure 5.

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$$V_1 \frac{dC_{Hg0}^{w,1}}{dt} = L_{T,Hg0} + Q_{in}C_{Hg0,in} + \left[k_{red}^{w,1} \cdot V_1\right] \cdot C_{HgII,1}^{w} + \left[k_{mer}^{w,1} \cdot V_1 + k_{photodemeth}^{w,1} \cdot V_1\right] \cdot C_{MeHg}^{w,1}$$

$$+ \left[-Q_{out} - Q_{ex} - k_{vol,Hg0} \cdot V_1 - k_{oxid}^{w,1} \cdot V_1 - v_{s,abio} \cdot f_{abio,Hg0}^{w,1} \cdot A - v_{s,org} \cdot f_{org,Hg0}^{w,1} \cdot A\right] \cdot C_{Hg0}^{w,1} + Q_{ex} \cdot C_{Hg0}^{w,2} = 0$$

$$V_1 \frac{dC_{HgII}^{w,1}}{dt} = L_{T,HgII} + Q_{in}C_{HgII,in} + \left[k_{oxid}^{w,1} \cdot V_1\right] \cdot C_{Hg0}^{w,1} + \left[k_{demeth}^{w,1} \cdot V_1\right] \cdot C_{MeHg}^{w,1}$$

$$+ \left[-Q_{out} - Q_{ex} - k_{vol,HgII} \cdot V_1 - k_{red}^{w,1} \cdot V_1 - k_{meth}^{w,1} \cdot V_1 - v_{s,abio} \cdot f_{abio,HgII}^{w,1} \cdot A - v_{s,org} \cdot f_{org,HgII}^{w,1} \cdot A\right] \cdot C_{HgII}^{w,1} + Q_{ex} \cdot C_{HgII}^{w,2}$$

$$V_1 \frac{dC_{MeHg}^{w,1}}{dt} = L_{T,MeHg} + Q_{in}C_{MeHg,in} + \left[k_{meth}^{w,1} \cdot V_1\right] \cdot C_{HgII}^{w,1}$$

$$+ \left[-Q_{out} - Q_{ex} - kw_{vol,MeHg} \cdot V_w - k_{demeth}^{w,1} \cdot V_1 - k_{mer}^{w,1} \cdot V_1 - k_{photodemeth}^{w,1} \cdot V_1 - v_{s,abio} \cdot f_{abio,MeHg}^{w,1} \cdot A - v_{s,org} \cdot f_{org,MeHg}^{w,1} \cdot A\right] \cdot C_{MeHg}^{w,1}$$

$$+ Q_{ex} \cdot C_{MeHg}^{w,2}$$

$$V_2 \frac{dC_{Hg0}^{w,2}}{dt} = + \left[k_{red}^{w,2} \cdot V_2\right] \cdot C_{HgII}^{w,2} + \left[k_{mer}^{w,2} \cdot V_2 + k_{photodemeth}^{w,2} \cdot V_2\right] \cdot C_{MeHg}^{w,2}$$

$$+ \left[-Q_{ex} - k_{oxid}^{w,2} \cdot V_2 - v_{s,abio} \cdot f_{abio,Hg0}^{w,2} \cdot A - v_{s,bio} \cdot f_{bio,Hg0}^{w,2} \cdot A - R_{sw} \cdot f_{aq,Hg0}^{w,2}\right] \cdot C_{Hg0}^{w,2} + Q_{ex} \cdot C_{Hg0}^{w,1}$$

$$+ \left[R_{sw} \cdot \frac{f_{aq,Hg0}^{sed}}{\theta_{sed}} + (v_{rs} + v_b) \cdot f_{sed,Hg0}^{sed} \cdot A\right] \cdot C_{Hg0}^{sed}$$

$$V_2 \frac{dC_{HgII}^{w,2}}{dt} = + \left[k_{oxid}^{w,2} \cdot V_2\right] \cdot C_{Hg0}^{w,2} + \left[k_{demeth}^{w,2} \cdot V_2\right] \cdot C_{MeHg}^{w,2}$$

$$+ \left[-Q_{ex} - k_{red}^{w,2} \cdot V_2 - k_{meth}^{w,2} \cdot V_2 - v_{s,abio} \cdot f_{abio,HgII}^{w,2} \cdot A - v_{s,bio} \cdot f_{bio,HgII}^{w,2} \cdot A - R_{sw} \cdot f_{aq,HgII}^{w,2}\right] \cdot C_{HgII}^{w,2}$$

$$+ Q_{ex} \cdot C_{HgII}^{w,1} + \left[R_{sw} \cdot \frac{f_{aq,HgII}^{sed}}{\theta_{sed}} + (v_{rs} + v_b) \cdot f_{sed,HgII}^{sed} \cdot A_w\right] \cdot C_{aq,HgII}^{sed}$$

$$V_2 \frac{dC_{MeHg}^{w,2}}{dt} = + \left[k_{meth}^{w,2} \cdot V_2\right] \cdot C_{HgII}^{w,2}$$

$$+ \left[-Q_{ex} - k_{demeth}^{w,2} \cdot V_2 - k_{mer}^{w,2} w_{mer} \cdot V_2 - k_{photodemeth}^{w,2} \cdot V_2 - v_{s,abio} \cdot f_{abio,MeHg}^{w,2} \cdot A\right.$$

$$\left. - v_{s,bio} \cdot f_{bio,MeHg}^{w,2} \cdot A - R_{sw} \cdot f_{aq,MeHg}^{w,2}\right] \cdot C_{MeHg}^{w,2}$$

$$V_{sed} \frac{dC_{Hg0}^{sed}}{dt} = \left[R_{sw} f_{aq,Hg0}^{w,2} + \left(v_{s,abio} \cdot f_{abio,Hg0}^{w,2} + v_{s,bio} \cdot f_{bio,Hg0}^{w,2}\right) \cdot A\right] \cdot C_{Hg0}^{w,2}$$

$$+ \left[-R_{sw} \cdot \left(\frac{f_{aq,Hg0}^{sed}}{\theta_{sed}}\right) - (v_{rs} + v_b) \cdot f_{sed,Hg0}^{sed} \cdot A - k_{oxid}^{sed} \cdot V_{sed}\right] C_{Hg0}^{sed} + \left[k_{red}^{sed} \cdot V_{sed}\right] \cdot C_{HgII}^{sed}$$

$$+ \left[k_{mer}^{sed} \cdot V_{sed}\right] \cdot C_{MeHg}^{sed}$$

$$V_{sed} \frac{dC_{HgII}^{sed}}{dt} = \left[R_{sw} f_{aq,HgII}^{w,2} + \left(v_{s,abio} \cdot f_{abio,HgII}^{w,2} + v_{s,bio} \cdot f_{bio,HgII}^{w,2}\right) \cdot A\right] \cdot C_{HgII}^{w,2} + \left[k_{oxid}^{sed} \cdot V_{sed}\right] \cdot C_{Hg0}^{sed}$$

$$+ \left[-R_{sw} \cdot \left(\frac{f_{aq,HgII}^{sed}}{\theta_{sed}}\right) - \left(v_{rs} + v_b\right) \cdot f_{sed,HgII}^{sed} \cdot A_w - \left(k_{red}^{sed} + k_{meth}^{sed}\right) \cdot V_{sed}\right] C_{HgII}^{sed} + \left[kb_{demeth} \cdot V_{sed}\right] \cdot C_{MeHg}^{sed}$$

$$V_{sed} \frac{dC_{MeHg}^{sed}}{dt} = \left[R_{sw} f_{aq,MeHg}^{w,2} + \left(v_{s,abio} \cdot f_{abio,MeHg}^{w,2} + v_{s,bio} \cdot f_{bio,MeHg}^{w,2}\right) \cdot A\right] \cdot C_{MeHg}^{w,2} + \left[k_{meth}^{sed} \cdot V_{sed}\right] \cdot C_{HgII}^{sed}$$

$$+ \left[-R_{sw} \cdot \left(\frac{f_{aq,MeHg}^{sed}}{\theta_{sed}}\right) - \left(v_{rs} + v_b\right) \cdot f_{sed,MeHg}^{sed} \cdot A - \left(k_{demeth}^{sed} + k_{mer}^{sed}\right) \cdot V_{sed}\right] C_{MeHg}^{sed}$$

Where:

$C_i^{l,j}$:   concentration of mercury species i [g/m^3], where I is Hg0, MeHg, or HgII; l is the phase of interest, where l can be w for the water column or sed for the sediment layer. and j is 1 or 2 to distinguish between lake layers 1 and 2

$C_{i,in}$:   concentration of mercury species i [g/m^3] in the inflow

$k_{rxn}^{l,j}$:   reaction rate constant [yr^{-1}] where l is the phase of interest, where l can be w for the water column or sed for the sediment layer. and j is 1 or 2 To distinguish between lake layers 1 and 2, and rxn is the reaction of interest where

> *red* is the reduction of Hg0 to HgII
> *oxid* is the oxidation of HgII to Hg0
> *meth* is the methylation of HgII to MeHg
> *demeth* is the demethylation of MeHg to HgII
> *photodemeth* is the photoreduction of MeHg to Hg0
> *mer* is demethylation of MeHg to Hg0 via *mer* cleavage

the implementation of these rate constants into these equations is described in greater detail in the kinetic rate constants section below.

$k_{vol,i}$:   volatilization rate [per year] of mercury species i

$L_{T,i}$:   total loading of mercury species i [g/yr]

R_{sw}:   pore water diffusive volume [m^3/yr], defined as

$$R_{sw} = \frac{E_{sw} \cdot A_w \cdot \theta_{sed}}{z_{sed}} \cdot 3.1536x10^7 \text{ [sec/yr]}$$

where

$E_{sw,i}$:   pore water diffusion coefficient [m^2/s] for species i where i is Hg0, HgII, or MeHg.

A_w: interfacial area of sediment layer [m^2]

θ_{sed}:   sediment porosity [unitless]

z_{sed}:   sediment depth [m]

$3.1536x10^7$: conversion factor for seconds to year

These equations are used for all three scenarios except for the sediment layer. There are three scenarios that SERAFM calculates mercury concentrations.

The first scenario is one where the total mercury concentration, HgT, is known in the sediment. These concentrations are the result of years of historical release to the water body or via direct loading to the sediment. For scenario 1, the sediment mercury concentration includes direct loading, atmospheric loading, and watershed loading. In this scenario total mercury in the sediment, C_{HgT}^{sed}, is known. This information is incorporated into the system of equations by replacing the equation for C_{HgII}^{sed} with the following

$$C_{HgII}^{sed} + C_{HgII}^{sed} + C_{HgII}^{sed} = C_{HgT}^{sed}$$

Scenario 2 represents the background/reference scenario; this is the hypothetical case where the system had not undergone industrial loading or release. This scenario accounts for what the current conditions would be solely under the influence of watershed loading and direct atmospheric deposition. The system of equations for scenario 2 is as presented.

Scenario 3 represents a proposed clean-up level in the sediments. The sediment concentration is determined and the rest of the system is determined with this information. Therefore, the system of equations is the same as in Scenario 1, but with a proposed C_{HgT}^{sed}.

For Scenarios 1 and 3, there are still nine unknowns in the system of equations (Hg0, HgII, and MeHg in the three media of epilimnion, hypolimnion, and sediments), except now HgT is known. Because HgII is generally the predominant form

of mercury in the sediments (Hg0 is typically <1% HgT and MeHg is <5% HgT), this
methodology was found to work most effectively.

5.5   *Mercury Transformation Rate Constants*

The three species of mercury are coupled via transformation reactions.
These reactions include:

- Reduction of HgII to Hg0,

- Oxidation of Hg0 to HgII,

- Methylation of HgII to MeHg,

- Demethylation of MeHg to HgII,

- Photodegradation (photodemethylation) of MeHg to Hg0, and

- *Mer* operon cleavage of MeHg to Hg0.

These reactions are modeled using first order rate kinetics. However, these
reactions may only act on mercury depending on the speciation of mercury and the
partitioning of mercury. To account for this, the base rate of reaction was modified by
the fraction of mercury dissolved in the aqueous phase, sorbed to abiotic particles, sorbed
to biotic particles, and complexed with DOC. Additionally, the fraction of HgII present
as $Hg(OH)_2$ may be a factor. The methodology for calculating rate constants is described
below for each reaction modeled.

5.5.1   Water Column Abiotic Methylation: HgII → MeHg

$$k_{meth} = k_{meth,base} * f_{HgII}^{aq} \qquad\qquad \text{[for oxic water]}$$

$$k_{meth} = k_{meth,base} * \left(f_{HgII}^{aq} + f_{HgII}^{DOC} \right) \qquad \text{[for anoxic water]}$$

In an oxic water column, the abiotic methylation base rate constant is multiplied by the fraction of aqueous HgII, because abiotic methylation is believed to only affect dissolved, non-complexed aqueous mercury. In an anoxic water column, the abiotic methylation base rate constant is multiplied by the sum of the fractions of dissolved and DOC-complexed HgII (Matilainen and Verta, 1995).

5.5.2 Sediment Biotic Methylation: HgII → MeHg

Sediment biotic methylation is modeled such that all fractions of HgII in the sediment are available to methylated.

$$k_{meth} = k_{meth,base}$$

5.5.3 Water Column Demethylation: MeHg → HgII

Demethylation of MeHg in the water column has been suggested to be suppressed by color and particulates, and the presence of DOC was found to increase the rate of biotic demethylation. Therefore, demethylation acts on the total dissolved MeHg (including DOC-complexed) (Matilainen and Verta, 1995)

$$k_{demeth} = k_{demeth,base} * \left(f_{HgII}^{aq} + f_{HgII}^{DOC} \right)$$

5.5.4 Sediment Biotic Demethylation: MeHg → HgII

Sediment biotic demethylation is modeled such that all fractions of HgII in the sediment are available to methylated.

$$k_{meth} = k_{meth,base}$$

5.5.5 Biotic Reduction of HgII: HgII → Hg0

Reduction of HgII is believed to only occur on HgII in the form of $Hg(OH)_2$. For this reaction, the phase of HgII is not the factor, but rather the ligands associated with HgII. Therefore, the fraction of HgII as $Hg(OH)_2$ is multiplied by the base rate constant (Mason et al., 1995).

5.5.6 Photolytic Reactions

In a water body, deposited HgII is reduced to Hg0 by ultraviolet and visible wavelengths of sunlight as well as microbially mediated reduction pathways (Amyot et al., 2000; Mason et al., 1995). In turn, Hg0 is oxidized back to HgII, driven by sunlight as well as by "dark" chemical or biochemical processes (Lalonde et al., 2001; Zhang and Lindberg, 2001). Therefore, the average light intensity across the lake/pond is an important parameter, and is modeled as a function of depth for the layer using the Beer-Lambert Law (see, *e.g.*, Schwarzenbach et al., 1993). The photolytic dependent rate of photo-degradation (photo-demethylation) is a function of the intensity of the visible radiation; photo-reduction is a function of both the intensities of visible and ultraviolet radiation; and photo-oxidation is a function of the intensity of the ultraviolet radiation. Ultraviolet and visible radiation have different attenuation coefficients. Visible light attenuation coefficients are determined based on Wetzel (2001) corresponding to lake trophic status. Ultraviolet attenuation coefficients are calculated as a function of dissolved organic carbon concentration (Scully and Lean, 1994 as cited by LaLonde et al., 2001) by:

$$\eta_{UV-B} = 0.4415 * (DOC)^{1.86}$$

The layer average rate constants for these processes are determined and incorporated into the overall mercury transport and transformation process mass balance equations as denoted in the above equations

5.6   Aquatic Biota Mercury Concentrations

Mercury concentrations in phytoplankton, zooplankton, benthic invertebrates, and fish (trophic levels 3 and 4) are calculated using a simple bioaccumulation factor, BAF, approach. Default BAFs are provided within SERAFM. An average BAF for trophic level 3 and 4 fish are provided along with 5th, 25th, 75th, and 95th percentile values. These values are meant to provide default, defensible input values if no site-specific values are available, however, it is preferable that site-specific BAFs are used and incorporated into the model formulation using the "Input&Output" worksheet.

$$BAF = \frac{ug \ Hg}{kg \ fish \ tissue} \bigg/ \frac{ug \ Hg}{L \ water}$$

5.7   Wildlife and Human Exposure Risk

Wildlife exposure risks, via hazard indices, are calculated using a standard technique outlined in the Wildlife Exposure Factors Handbook (USEPA, 1993). The calculated hazard quotient, HQ, is calculated for each wildlife species of interest using the calculated total dose of mercury per day given the calculated concentration in the diet, the ingestion rate, and the body weight for that species. Each species can be exposed to mercury from all four lower trophic levels, including phytoplankton, zooplankton, benthic invertebrates, predator fish, and prey fish, as well as via drinking the surface water itself.

$$Potential \ Dose = \frac{Conc \bullet IngestionRate}{BodyWeight}$$

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$$Total\ Dose = \sum \%Diet_{trophiclevel_i} \bullet Potential\ Dose_i + \left(drinking\ rate \bullet [Hg]_{water}\right)$$

The Hazard Quotient (HQ) is then calculated as:

$$HQ = \frac{Total\ Dose}{TRV\ or\ RfD}$$

Where TRV is the toxicity reference value and the RfD is the reference dose. The

TRV for avian species are 13 ug/kg/d and for mammalian species it is 16 ug/kg/d. The

RfD is 0.3 ug/kg/d for a man, an adult, and a Native American, and 0.1 ug/kg/d for a

woman and a child. Parameterization for these calculations comes from the Wildlife

Exposure Handbook and the work outlined by Nichols et al. (1999). SERAFM calculates

HQs for mink, otter, kingfisher, loon, osprey, eagle, tree swallow, hooded merganser and

wood duck. The first six species were studied specifically by Nichols et al. (1999), while

the last three were included because of the specific site for which SERAFM was created.

Additionally, human exposure risks are calculated for men, women, average adult

(including men and women), children, and Native Americans.

5.8   SERAFM Steady-State Solution Technique

As mentioned previously, SERAFM is solved using a steady-state assumption. In order

to solve the resulting system of coupled linear algebraic equations, a solution software

function was written using Visual Basic for Applications (VBA) in Microsoft Excel.

This specific function, called LINEAR_SOLVE, uses LU Decomposition to solve the

dreived linear algebra equation: $\mathbf{A}*\mathbf{x}=\mathbf{b}$, where $\mathbf{A}$ is an m x n matrix, $\mathbf{x}$ is an n x 1 matrix,

and $\mathbf{b}$ is an m x 1 matrix. By using this VBA function, the SERAFM predictions are

updated instantaneously whenever any parameter is changed.

6 MODEL INTERFACE LAYOUT

The layout of the SERAFM model consists of a set of distinct worksheets within the workbook. Each worksheet is separated so that each module and component is kept separate. This is, in effect, similar to having separate subroutines in a computer program. Necessary parameters and equations are linked and referenced to one master cell or group of cells so that changes can be made in one place and will be carried throughout the workbook. Microsoft© Excel 2003 lets the user follow how cells are linked by using the trace precedents and trace dependents function keys on the formula editing toolbar. SERAFM also lets the user interact with the model on different levels. There is one master worksheet where the user can work with the primary information required for the model. This worksheet is the primary interface where the user interacts with the program, since it also presents to the user the model results. The user can also delve deeper into the model by working in worksheets more specific to the different modules or different aspects of the model. The details of each worksheet are described within the worksheet itself. In this way, the SERAFM model user is not overburdened with this manual, but can find the details here as needed. In this section, the details of the user interface, *i.e.*, the "Input & Output" worksheet are described. Then, a brief discussion on each of the remaining worksheets is given. Equations and references specific to the calculations in each worksheet are provided on the specific worksheet. The units for each parameter in each cell are given to the right of the cell; notes are provided according to the reference numbers in the column right of that.

6.1   *Input & Output Worksheet*

The Input & Output spreadsheet is effectively the master spreadsheet. This worksheet is broken down into the input parameters: "watershed characteristics" and "rate constants;" and the predicted output: "exposure concentrations" and "human and wildlife exposure risk results." Cells for input parameters on this worksheet are shaded in the cool colors of blues and greens, and the output cells are shaded in the warm colors of oranges and yellows. The input parameters on this worksheet represent the basic or primary parameters that are required to run the model, other parameters are provided on their corresponding worksheet.

6.1.1   Watershed Characteristics

The "Watershed Characteristics" section of this worksheet includes the primary level of parameter inputs required to run the model. These parameters are set at default values when the model is initially opened, but this is done simply to act as placeholders. All values that are in cells B5 to B44 should be updated with actual data that describe the water body being investigated. Most of the parameters in this worksheet are self-explanatory, but to reduce confusion, some details of the parameters and the specification of their values are given here.

The first set of parameters involves the structure of the catchment watershed associated with the water body. First, the user uses the drop down menu to choose the "Watershed Location," as either "East" or "West," to tell the model whether the watershed is located east or west of the Mississippi River. This is used to assign Default precipitation rates and soil erosion coefficients for the Revised Universal Soil Loss Equation. The watershed area is entered in units of square meters. Next, the model

carves the watershed into four different land-use types: impervious, wetland, riparian and upland. The model does not consider the spatial resolution of these land-use types, only the total percent of the watershed that each covers. "Percent Impervious" is assumed to runoff directly into the water body, and is associated with the urban landscape. "Percent Wetland" is that percentage of the watershed that is an wetland or associated with wetland. "Percent Riparian" is the percent of the watershed associated with the rivers and streams leading to the water body. The "Percent Upland" is the remaining part of the watershed; SERAFM calculates this percentage by difference given the percentages assigned to the other land-use types in the watershed. Additionally, a "% with Known Contaminated Soil," is included for the case where the user knows the mercury concentration in a certain percentage of the watershed soils. If the user knows the concentration in soils for the entire watershed, then this would be 100%; if some other percent of the watershed has known soil concentrations, then that value can be entered here. If this feature is used, then the values must be entered in the "Known Mercury in Contaminated Soils" cells (B40-42).

The next set of parameters to be specified involves the physical structure and hydrology of the water body. Lake/pond area is entered in units of square meters. The epilimnion and hypolimnion thickness are then entered next in units of meters. If the water body is well-mixed or if the water body of interest is a river, then a hypolimnion thickness of 0.1 m or less is recommended; this thickness value will approximate a boundary layer at the sediment/water interface. The model approximates the water body as a rectangular shape. Therefore, the values used for layer thickness should be a mean length associated with the depth from the surface of the water body to the thermocline for

the epilimnion thickness, and a mean length associated with the depth from the thermocline to the sediment floor for the hypolimnion thickness. The layer thicknesses could also be specified such that they produce the actual volume of water in the layer to which it is assigned. Because the model approximates the lake as a rectangular box, the surface area of the epilimnion and hypolimnion are identical to the lake or pond surface area and the volume of each layer is calculated by the model by multiplying the thickness by the lake or pond surface area. The choice for the thickness of each layer is not necessarily a trivial one, so the user is left the option of deciding the best option depending on the construct or contour of the system. Next, the user must enter "YES" or "NO" from the drop down menu for whether there is anoxia in the hypolimnion or not. If the hypolimnion is anoxic, then the methylation rate in the hypolimnion is defaulted to 0.01 per day versus 0.001 per day. The hydraulic residence time of the system is entered in units of years. Hydraulic residence time is the inverse of flushing rate. Using the volume of the lake (lake area multiplied by depth), SERAFM calculates the volumetric flow rate into and out of the lake by dividing the volume by the hydraulic residence time. This calculated value for inflow and outflow is set as the default. The values for inflow and outflow can be specified by the model user, if necessary.

The next set of parameters to be specified involves lake/pond water quality characteristics. The pH of the lake is entered, as is the epilimnion and hypolimnion temperature (in degrees Celsius). Because the model assumes steady state conditions, the user must decide whether to use annual average or summer average values. The choice depends on the user's needs and what is deemed to be most applicable for the assessment being performed. The air temperature needs to be similarly defined. The annual

precipitation rate is set at a default value of 21 cm/yr (western lakes) and 102 cm/yr (eastern lakes). This is an important parameter because it is used along with the concentration of mercury in rainfall to calculate the default loading rate of mercury from wet deposition. No water balance is performed on the water body since as lake volume is assumed to be constant (dV/dt = 0), as is consistent with a steady state assumption.

The trophic status of the water body is determined by the model based on the DOC value specified for the epilimnion. Specifically, the trophic status in the model is determined as being oligotrophic if DOC < 3 mg/L, mesotrophic if 3 mg/L ≤ DOC < 5 mg/L, eutrophic if DOC ≥ 5 mg/L, and dystrophic if DOC>10mg/L and color >50 PtCo (taken from Wetzel, 2001).

The model defaults to have no inflow mercury concentrations. If the inflowing water has known, appreciable mercury concentrations, these values can be entered in cells B33 - B35. Also, if, for example, the model were to be used for several water bodies in series, then the calculated output mercury water concentration of one water body whose outflow is the inflow for the next water body could be entered here.

Lastly, the current measured total mercury concentration in the bulk sediment is entered in units of milligrams per kilogram (micrograms per gram) dry weight in cell B37. For the current conditions scenario that is run first, the model does not solve for this parameter; this parameter is fixed, but the remaining concentrations are calculated. The model will still solve for the distribution of the mercury species in the sediment (concentration and percent Hg0, HgII, and MeHg), but will hold the specified total mercury concentration in sediment to the input value specified.

6.1.2 Rate Constants

The default mercury transformation and fate process rate constants are listed here in units of per day. Methylation and demethylation have base default rates set for each layer in the system: epilimnion, hypolimnion, and sediment. Biotic reduction in the water column has one rate throughout the water column, and reduction is assumed negligible in the sediments. Oxidation and reduction rate constants are given for both photolytic reactions (in units of per day per Einstein per square meter per day) and dark reactions (per day). These rate constants are an area of appreciable research, so the default values presented here are to be taken as initial starting points. Calibration of these rate constants will be necessary for any given water body. A literature review of reported rate constants for these processes and supporting the default values used in the model are presented in Appendix A. Bioaccumulation factors are also defaulted to the values presented in the spreadsheet.

6.1.3 Exposure Concentrations

The next part of this worksheet is the model output. The model calculates the exposure concentrations for the contaminated sediment case, the background condition, and the proposed target-level conditions. The species of mercury concentrations presented are Hg0, HgII and MeHg, as well as the sum of these concentrations as HgT. These concentrations are presented as both filtered and unfiltered values in both the water column and sediment. A column is also set up on the worksheet for the measured concentrations to be entered. The error of the predicted model results versus the entered measured (*e.g.*, observed) concentrations is then calculated as absolute error and relative error, where:

$$\text{Absolute Error} = \text{Observed - Predicted} \qquad\qquad \text{EQN 1}$$

$$\text{Relative Error} = \frac{\text{Observed - Predicted}}{\text{Observed}} \bullet 100\% \qquad\qquad \text{EQN 2}$$

These error calculation columns are provided to assist the user with the calibration

process.

6.2   Human and Wildlife Exposure Risk Results

Last on this worksheet are the "Human and Wildlife Exposure Risk Results." On

this table is a select group of wildlife with their calculated hazard indices. Details on the

calculations are presented in Section 5.7: Wildlife and Human Exposure Risk and Section

6.2 Wildlife.

6.3   Wildlife Worksheet

The "Wildlife" worksheet is where the calculations for the hazard indices for

wildlife and humans are calculated. The parameters used for these calculations are

presented for each wildlife type. The animals chosen consist of birds and mammals.

Specifically, they are: mink, otter, kingfisher, loon, osprey, eagle, tree swallow, hooded

merganser, and wood duck. Humans are also included, and are broken down into five

subgroups: man, woman, adult (regardless of sex), child, and Native American. The

mercury bioaccumulation factors for the trophic levels are also listed on this sheet.

6.4   Parameters Worksheet

The "Parameters" worksheet is where a master list of the bulk of system

parameters used in the model are maintained. Parameters consist of those describing

water body hydrology, watershed characteristics, and water body characteristics. Parameters listed in the "Input & Output" worksheet are linked to this spreadsheet so that those and other parameters are housed in the same worksheet. These parameters serve as the source of links used in other spreadsheets where calculations are done. If parameters are to be overridden, this worksheet is where that is accomplished.

6.5 Mercury Params Worksheet

The "Mercury Params" worksheet holds physical-chemical parameters that are specific for the different species of mercury (Hg0, HgII, and MeHg). These parameters include molecular weight, Henry's law constant, partition coefficients and diffusivities. Other worksheets in the model are linked to this location of parameters.

6.6 Water Body Hg Worksheet

The "Water Body Hg" worksheet is where the calculations for the mercury concentrations in the water body are performed for the cases where the sediment mercury is an unknown (*i.e.,* the site has not received direct historical loading of mercury and where the water body sediment is a sink for mercury, second scenario). The rate constants used in the calculations are linked to their source as are the necessary parameters used in the equations. The coupled differential equations describing the transformation and transport processes for each mercury species in each medium are presented. The matrix for solving these equations is also presented along with the solution vector. The predicted concentrations are then linked in a table format to clearly present their values as calculated in the model [g/m^3], which are then converted to more familiar units [ng/L].

6.7   Water Body C sed Hg Worksheet

The "Water Body C sed Hg" worksheet is where the calculations for the mercury concentrations in the water body are performed for the case where the sediment mercury acts as a source (*i.e.*, the site has received historical contamination of mercury, causing the sediment to act as a possible source of mercury to the water body, first scenario). The rate constants used in these calculations are linked to their source as are all the necessary parameters used in the equations. The coupled differential equations describing the transformation and transport processes for each mercury species in each medium are presented. The matrix for solving these equations is presented along with the solution vector. The predicted concentrations are then linked in a table format to clearly present their values.

6.8   Target C sed Hg Worksheet

The "Target C sed Hg" worksheet uses the calculations from the "Water Body Hg" and "Water Body C sed Hg" worksheets, which are used to approximate the concentration needed in the sediment to ensure protection of the most sensitive species, as calculated through the wildlife spreadsheet. This series of calculations also provides the mercury species concentrations in the various media that would result given this target level of sediment clean-up would be possible.

6.9   Hg Loading Worksheet

The "Hg Loading" worksheet calculates the total loading of mercury into the water body. Total loading is calculated as the sum of the individual loadings. The loadings modeled are: wet deposition, dry deposition, watershed runoff, soil erosion load, and gaseous diffusion from the atmosphere to the water body.

6.10 Gas Diff Loading Worksheet

The "Gas Diff Loading" worksheet calculates the loading (mass transfer) of mercury from the atmosphere by gaseous diffusion. The gaseous diffusion loading is modeled using two-film theory, accounting for liquid and gas transfer. The diffusion between the air and the water body is separated into the two component fluxes: flux from the air to the water body and the reverse flux from the water to the air. This separation permits calculation of dispersion as a gaseous diffusion loading in this spreadsheet, and the flux out as a loss term in the water body equations for the uppermost layer.

6.11 Equilibrium Partitioning Worksheet

The "Equilibrium Partitioning" worksheet uses the results from the solids balance equations (see Section 6.11 Solids Balance and Section 5.1) and the partition coefficients from the "Mercury Params" worksheet (see Section 6.4 Mercury Params and Section 5.2) to calculate the fraction of mercury associated with abiotic and biotic particulates for each mercury species in the water body layers and the sediment layer. The equations used to calculate each fraction are presented. These are then linked to the mercury calculation spreadsheets (see Section 6.5 Water Body Hg, Section 6.6 Water Body C Sed Hg, and Section 6.7 Target C sed Hg).

6.12 Solids Balance Worksheet

The "Solids Balance" worksheet calculates the abiotic and dead biotic solids concentration for each medium in the model (*i.e.*, epilimnion, hypolimnion, and sediment). The coupled differential equations describing the processes for solids transport in each medium are presented. The matrix for solving these equations is

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presented along with the solution vector. The predicted solids concentrations are then linked in a table format to clearly present the concentration values.

6.13 Rate Constants Worksheet

The "Rate Constants" worksheet links the rate constants defaulted in the "Input & Output" worksheet and converts them into the yearly units of the model. Rate constants that are dependent on other parameters are also calculated within this worksheet. The rate constants considered in this sheet include: methylation (abiotic and biotic, water column and sediment), demethylation (water column and sediment), reduction, photo-demethylation, photo-oxidation and photo-reduction. Equations and parameters specific to each rate constant calculation are provided in the worksheet.

7   MODEL IMPLEMENTATION

7.1 Primary User Interface

Upon opening SERAFM, a user will first need to go to the "Input&Output" worksheet. Here the user will enter the primary input parameters. Placeholder values currently reside in Cells B5 - B44. These should be replaced with site-specific and region-specific values. Upon entering these values, the Output Values will be updated automatically. In the Exposure Concentrations section, a column for the model predicted results for Scenario 1: Historically Contaminated Sediment presents the mercury concentrations for unfiltered and filtered species and the sediment concentrations (H5 – H36) are calculated. The Measured Concentrations for the site can be entered in the specific cells in column J. Then the absolute errors and relative errors are calculated for all species of mercury, filtered and unfiltered, in all media, as well as fish tissue

concentrations. These errors can be used to assist in any calibration of the model by adjusting the values of the model parameters to minimize the errors. Specifically, the generally important and sensitive parameters are the rate constants and partition coefficients.

Next to the columns for the Scenario 1: Contaminated Sediment column are the Scenario 2: Background Conditions and Scenario 3: Conditions at Proposed Target-Levels. The Scenario 2 column corresponds to the concentrations that would result given only the background loadings from watershed and the atmosphere. This is effectively the best that one could expect if the sediments were not additionally contaminated. Scenario 3, column Q, refers to the predicted concentrations that would be required for the most sensitive species to be protected (HI =1). The way the model is currently set up, the Required Cleanup Levels column is approximate, using a rough linear approximation. To find an exact result, the "Goal Seeking" tool can be used.

7.2   *Model Notes*

The modules written on each worksheet are summarized in this report. Details specific to given manipulations and parameters are described as Notes within each spreadsheet. It has been our experience that this is the most useful technique for new user's implementing a new model. Equations used within each module are presented as text windows, and the equations themselves are presented in the corresponding cells. Parameters are described within the worksheet in which they are used.

8 REFERENCES

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TABLES

Table 1. Proposed Tiers for Data Measurements for the ERASC Request No. 10: Remediation Goals for Sediment Mercury

	Mercury Measurements			Ancillary Measurements		Number of Measurements/ Sampling Dates	Number of Replications for Non-Biotic Mercury and Ancillary Measurements[1]	Biota: Fish[2]	Food Web
First Tier	Water	MeHg	Filtered	Water	TSS	3 - e.g., early, mid, and late summer	3+3	One Piscivore and One Mixed Feeder Fish Species: 5 samples of each species	
			Unfiltered		TOC				
		HgT	Filtered		DOC				
			Unfiltered						
	Sediment	MeHg	Filtered	Sediment	Bulk density				
			Unfiltered		TOC				
		HgT	Filtered		DOC				
			Unfiltered						
	Fish Tissue								
Second Tier				Water	Particle size Distribution	5 - late spring; early, mid and late summer, early fall	5+3	2-3 Species of Piscivorous and 2-3 Species of Mixed Feeder Fish(5 samples of each species)	Mercury concentration in macro-benthos
					Temperature				
				Sediment	Particle size Distribution				
Third Tier				Water	Temp	7 - early and late spring; early, mid and late summer, early and late fall	7+3	3-5 Species of Piscivorous and 3-5 Species of Mixed Feeder Fish (5 samples of each species)	Food Web Dynamics; Biomass Growth Rates
					pH				
					DO				

Notes: [1] Replication of samples will need to occur spatially and for duplication. The two numbers given represent: first, minimum number of samples taken in different locations, and second, minimum number of repeated samples in one location. For example, for "5+3," five total samples will be taken in 5 different locations (to cover spatial variability), and 2 more samples at any one location will be taken (to allow for estimation of sampling error).

[2] Fish concentrations will need to be standardized for weight, length, or age; or compared to model results as a function of weight, length, or age.

Table 2. Comparison of SERAFM and IEM-2M mercury concentrations using parameter values for model ecosystem described in the Mercury Study Report to Congress

Parameter	IEM-2M	SERAFM
Unfiltered Aqueous MeHg	0.8 ng/L	0.31 ng/L
Unfiltered Aqueous HgT	1.16 ng/L	2.50 ng/L
Trophic Level 4 Fish	0.44 ug/g	0.21 ug/g

FIGURES

Figure 1. Mercury in the Environment

Mercury
in the
Environment

Dry
Deposition
$Hg^{2+}(p,v)$

Wet
Deposition
Hg^{2+}

Dry
Deposition

Litterfall and
Throughfall

Runoff and
Erosion

Watershed
Processes

Evasion
(Hg^0)

Hg^0

Transformation

MeHg

Hg^{2+}

Resuspension

Settling

Diffusion

Hg^{2+} MeHg

Burial
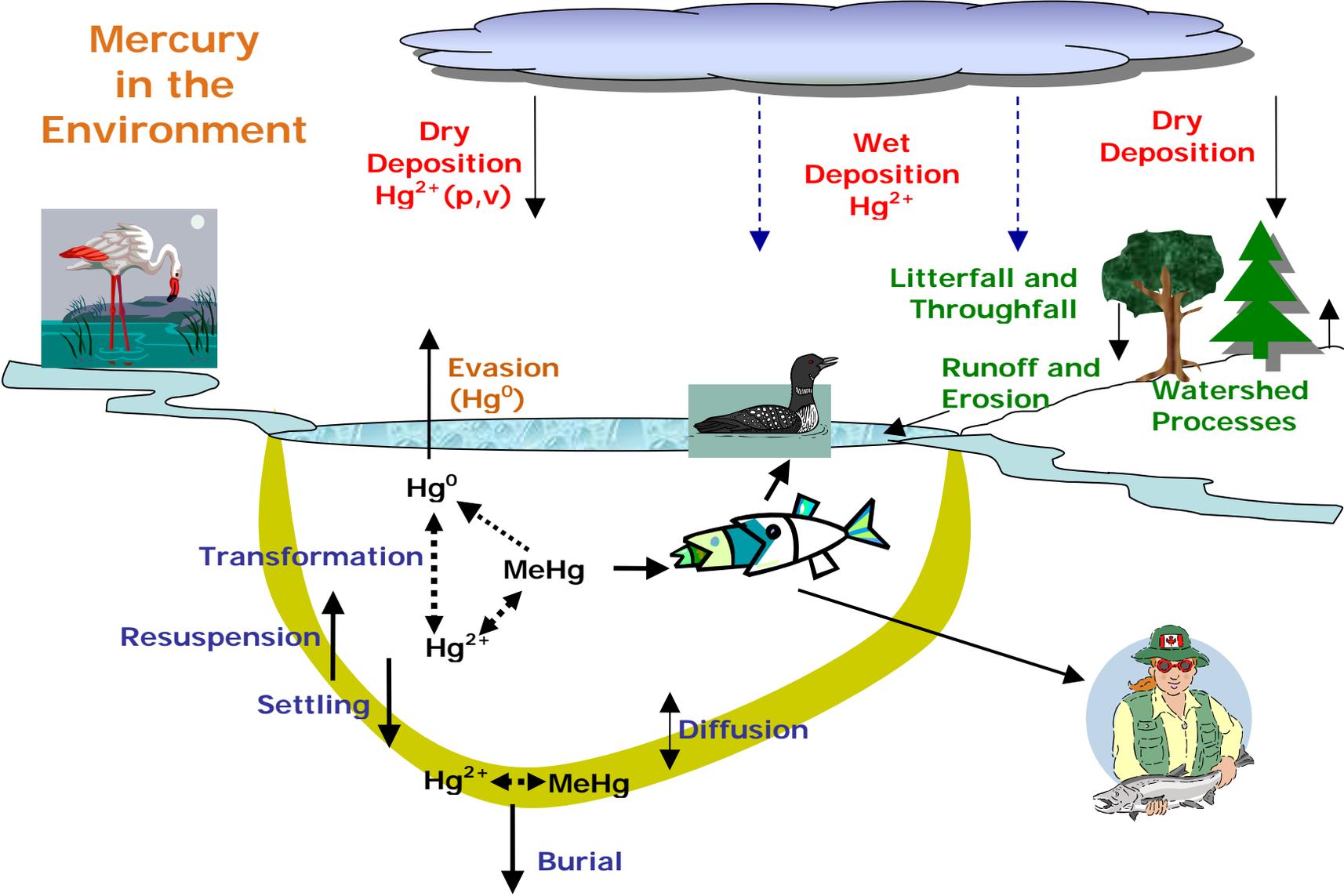
Figure 2. Solids Cycle in the Water Body

F-2
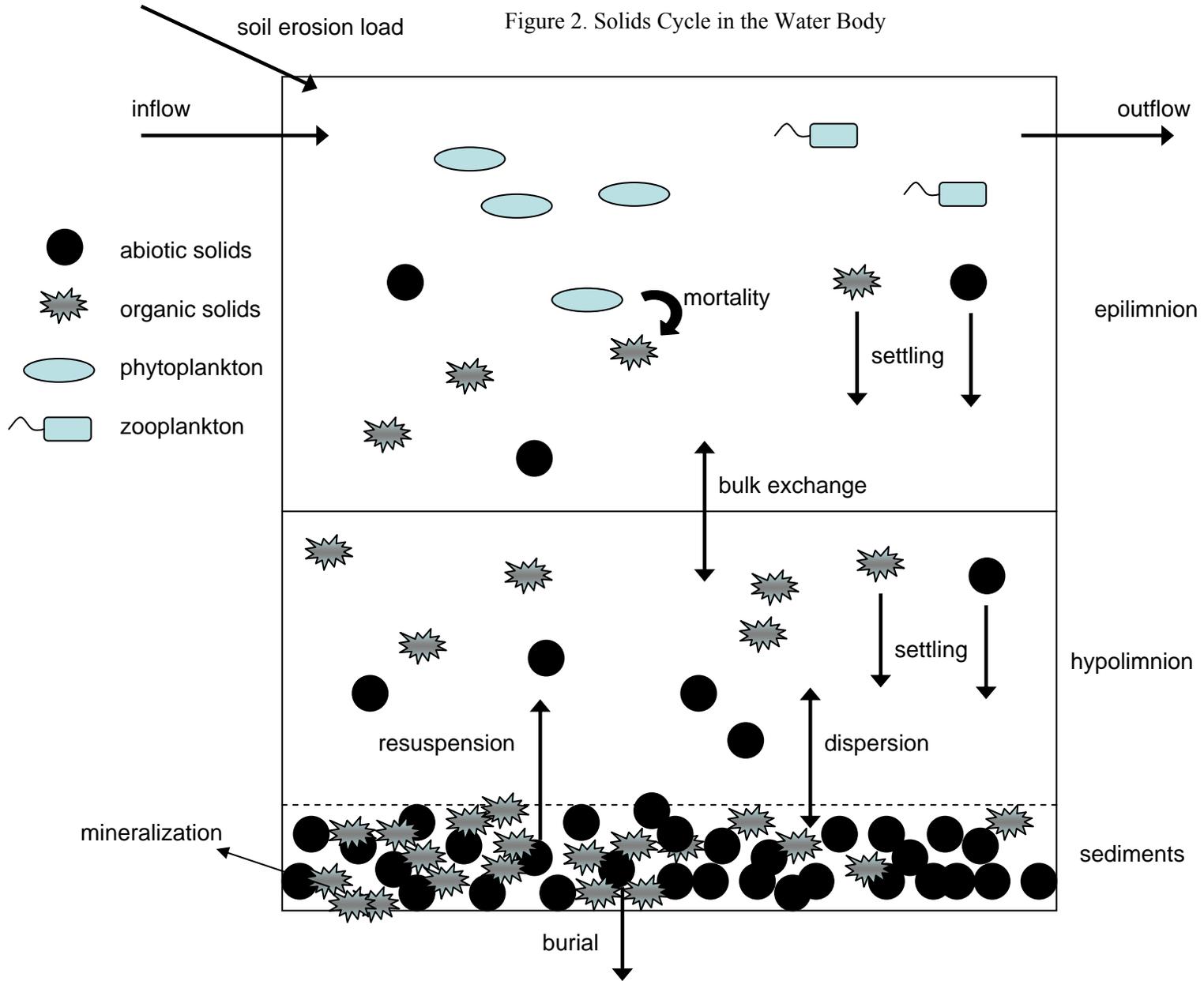
Figure 3. Equilibrium Partitioning of Mercury to Solids and DOC

●	abiotic	⬭ phytoplankto
✳	organic	⌒▭ zooplankton

DOC dissolved organic carbon
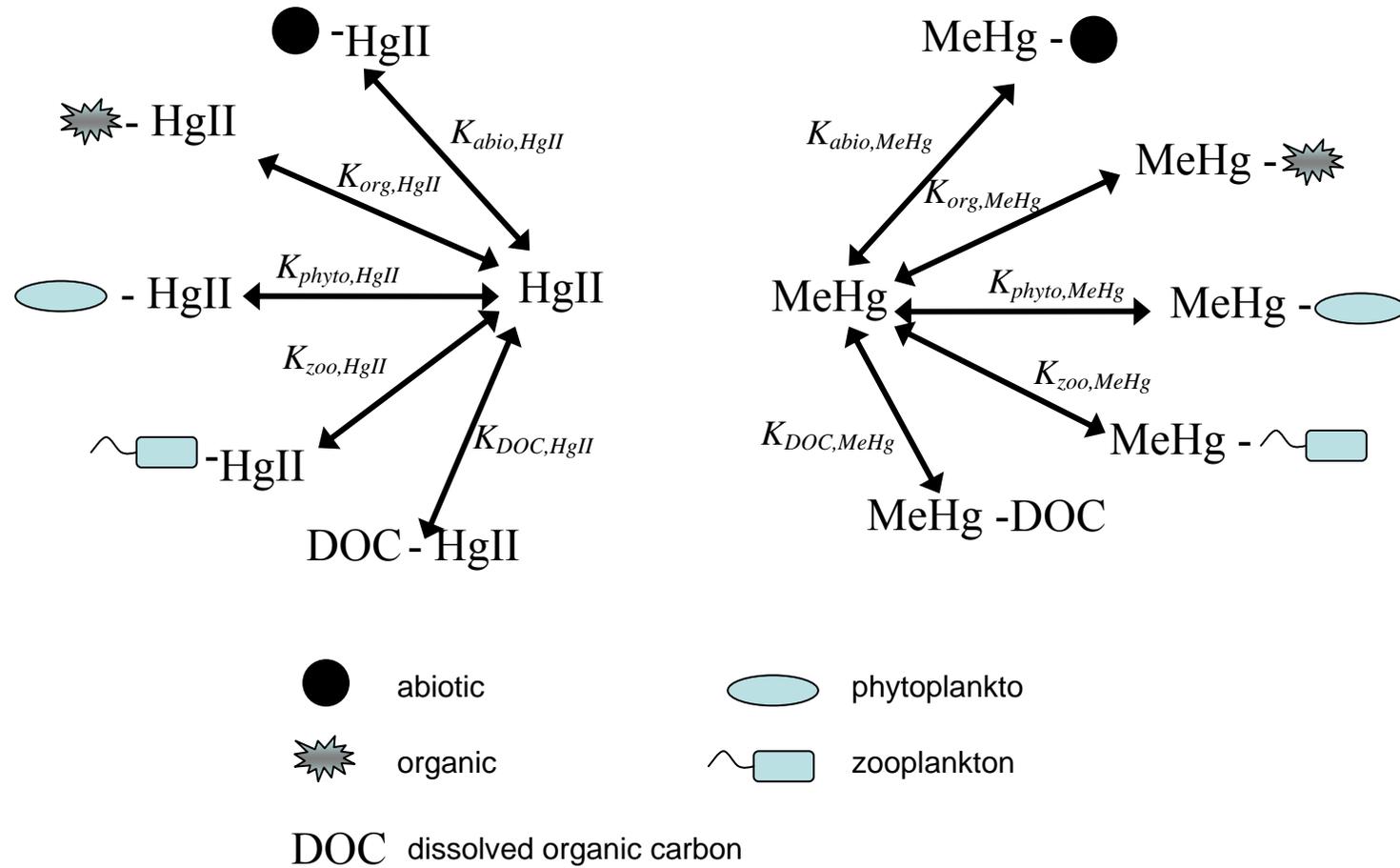
Figure 4. Mercury Loading to the Water Body (Atmospheric and Watershed)

```
┌─────────────────────────────────────────────────────────────────┐
│   Wet Deposition = Precipitation x Hg Conc. in Precipitation      │
└─────────────────────────────────────────────────────────────────┘
                                    │
                                    ▼
┌─────────────────────────────────────────────────────────────────┐
│      Atmospheric Loading = Dry Deposition + Wet Deposition        │
└─────────────────────────────────────────────────────────────────┘

┌──────────┐   ┌──────────────┐   ┌────────────┐   ┌────────────┐
│ Gaseous  │   │   % Known    │   │ % Riparian │   │ % Wetlands │
│ Diffusion│   │ Contaminated │   └────────────┘   └────────────┘
│          │   │    Soils     │   ┌────────────┐   ┌──────────────┐
└──────────┘   └──────────────┘   │  % Upland  │   │ % Impervious │
                                  └────────────┘   └──────────────┘

┌─────────────────────────────────────────────────────────────────┐
│                        Water Body                                 │
└─────────────────────────────────────────────────────────────────┘
```
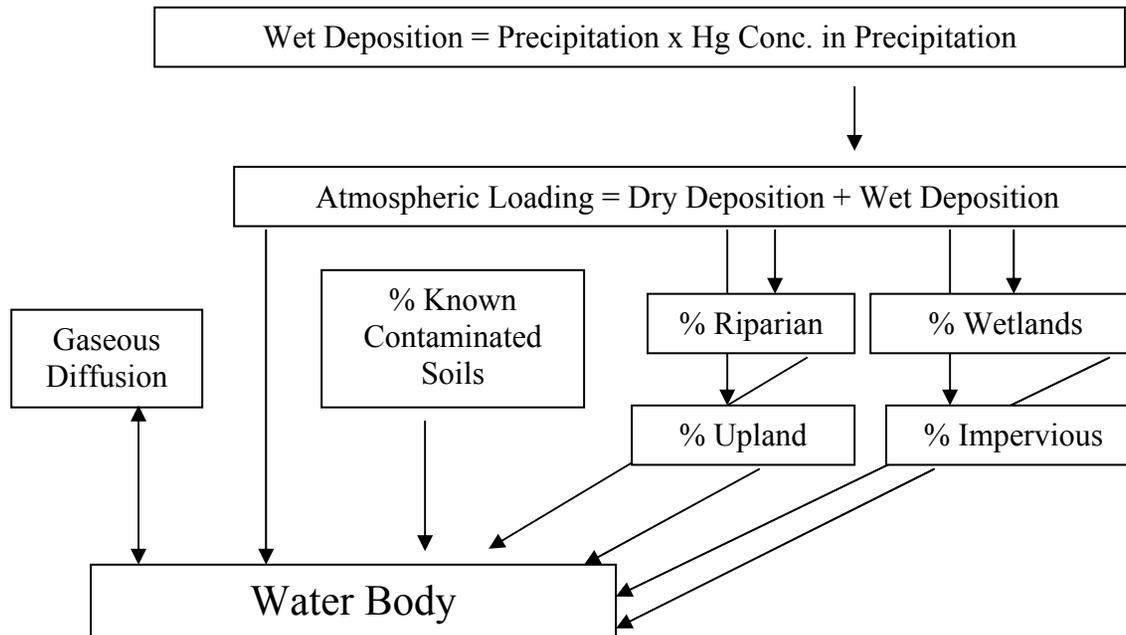
Figure 5. Mercury Fate Process Formulation in the Water Body
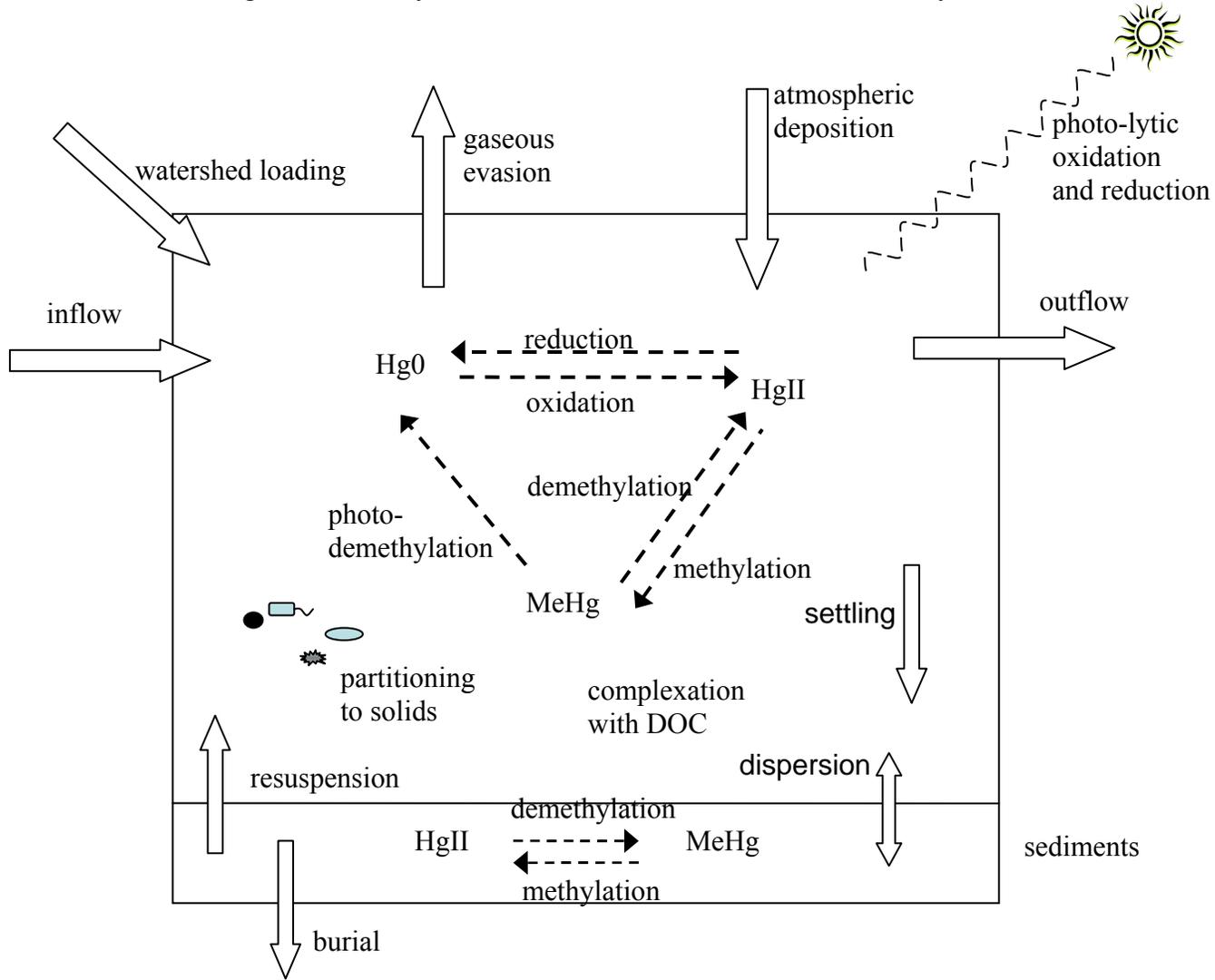
APPENDIX

Literature Mercury Process Rate Constants

Default Rate Constants of Mercury Transformation Processes

Process	Media	Value	Units
Methylation	Epilimnion	0.001	per day
	Hypolimnion	0.001	per day
	Sediment	0.001	per day
Demethylation	Epilimnion	0.0001	per day
	Hypolimnion	0.001	per day
	Sediment	0.002	per day
Biotic Reduction	Water Column	0.03	per day
Photo-Degradation (MeHg --> Hg0)	Water Column	0.002	per day per E/m2-day
Photo-Reduction (HgII --> Hg0) Visible Light	Water Column	0.03	per day per E/m2-day
Photo-Reduction (HgII --> Hg0) UV-B	Water Column	28.25	per day per E/m2-day
Photo-Oxidation (Hg0 --> HgII) UV-B	Water Column	58.85	per day per E/m2-day
Dark Oxidation	Water Column	1.44	per day
Trophic Level 1 BAF: Phytoplankton	Phyto	4.94E+05	(ug/kg)/(ug/L)
Trophic Level 2 BAF: Zooplankton	Zoo	1.61E+06	(ug/kg)/(ug/L)
Trophic Level 2 BAF: Benthos	Benthos	2.48E+06	(ug/kg)/(ug/L)
Trophic Level 3 BAF: Fish	Fish	1.60E+06	(ug/kg)/(ug/L)
Trophic Level 4 BAF: Fish	Fish	6.80E+06	(ug/kg)/(ug/L)

Mercury Process Rate Constants

From Mercury Report to Congress [3]

Rate Constants, day^{-1}	Watershed Soil, day^{-1}	Water Column, day^{-1}	Benthic Sediments, day^{-1}
Volatilization of Hg^0	0.082	0.10	0
Oxidation	0	0	0
Reduction	0.000025	0.0075	0.000001
Methylation	0.00005	0.001	0.0001
Demethylation of HgII	0.0025	0.015	0.002
Mer demethylation to Hg^0	0	0	0

Methylation in Water Column: HgII → MeHg

Process	Rates	Notes	References
Abiotic Methylation	0.000024 - 0.00124 d^{-1}, peak in summer, yearly average ~ .00033 d^{-1} *	Methylation in aerobic waters was abiotic; was suppressed by color and particulates; increase with T, pH, decrease with color	Matilainen and Verta, 1995. [1]
Epilimnetic Methylation	0.000005 L/mg DOC/day	Default Rate in R-MCM, for Epilimnion	R-MCM. [2]
Methylation	0.001 d^{-1}	Mercury Report to Congress	Mercury Report to Congress. [3]
Potential Methylation	0.0001 – 0.003 d^{-1}	Maximum potential methylation rate, as summarized in Mercury Report to Congress	Gilmour and Henry, 1991. [4]
Methylation	0.0001 – 0.0014 d^{-1} or 0.67 – 9.38 ng/L/d	pH 6.0 – 8.3, ELA Lakes, ON, oligo to eutrotrophic lakes	Xun, et al, 1987. [5]
Methylation	0.0003 – 0.0031 d^{-1} or 2.01 – 20.77 ng/L/d	pH 5.3 – 5.9 ELA Lakes, ON, oligo to eutrophic lakes	Xun, et al, 1987.
Methylation	< 0.0005 d^{-1} or < 33 ng/L/d	pH 6.5, small oligotrophic lake, Lake Clara, WI	Korthals & Winfrey, 1987. [6]
Methylation	0	Impounded lake, Southern Indian Lake, MB	Ramlal et al. 1987 [7]
Methylation	0.003 ng/L/d (3m, 4.4 mg/L DO), 0.03 ng/L/d (9m, 0.9 mg/L DO)), 0.11 ng/L/d (15m)	Net MeHg production rates increased with depth/decreasing DO; alkaline, hypereutrophic lake (Onondaga Lake, NY). Low transparency, pH 7.5.	Henry et al, 1995. [8]
Methylation	0.0001 – 0.003 per day	Lab Spiked Experiments	Xun et al., 1987; Korthals and Winfrey, 1987; Gilmour and Henry, 1990, as cited in Fitzgerald, et al., 1994. [9]

* yearly average calculated as ¼ of summer average. This average comes from assuming a relatively sinusoidal annual pattern of a max in the summer going to almost zero in the winter, and around half in the spring and fall.

Photodegradation of MeHg in water column: MeHg $\rightarrow$ Hg0

Process	Medium	Chemistry	Rates	Notes	References
Photodegradation of MeHg	Water Column	MeHg $\rightarrow$ HgII/Hg0	$0.002*PAR$ d^{-1}, PAR = $E/m^2/d$	Two figures, k = 0.0022*PAR and k = 0.0019*PAR.	Sellers et al. 1996. [10]
Photo-Reduction	Water Column	HgII $\rightarrow$ Hg0	DGM Production [fM/h]= 0.289 +0.2(PAR) – 5.02e-5(PAR)^2	For six dates: 3 in Aug, 1 in Sept, 2 in Nov. PAR in $kJ/m^2/h$	Amyot et al. 1994. [11]
Photo-Reduction	Water Column	HgII $\rightarrow$ Hg0	--	Photo-reduction under UV light in tropical waters showed that filtration had no effect on photoreduction, particulates favor the reaction under anaerobic conditions, O_2 and N_2 had no effect on reaction.	Beucher et al., 2002. [12]
Reduction	Water Column	HgII $\rightarrow$ Hg0	$0.005 – 0.1$ d^{-1}	Reduction rates in equatorial Pacific and Wisconsin lakes	Mason, et al. 1994 [13]
Reduction	Water Column	HgII $\rightarrow$ Hg0	0.1 d^{-1} (summer, 3 m); 0.05 d^{-1} (summer, 9 m); 0.22 d^{-1} (May, 6m)	Reduction Rates at Palette Lake	Vandal et al. 1995. [14]

Photo-Oxidation in Water Column: Hg0 → HgII

Process	Medium	Chemistry	Rates	Notes	References
Photo-Oxidation	Water Column	Hg0 → HgII	0.25 ± 0.02 hr^{-1} per 5.5 uE/m^2/s, DOC 3.5 – 4.3 mg C/L, Cl$^-$4.7 – 5.3 e-4 M.	Lab showed oxidation of Hg0 requires, Cl$^-$, a photoreactive compound (e.g., quinine), light. In Natural waters, Cl^0 was not needed.	LaLonde, et al., 2001. [15]
Dark Oxidation	Water Column	Hg0 → HgII	0.06 hr^{-1}, pseudo-first order	Oxidation of Hg0 in saline water in dark	LaLonde, et al, 2000.
Redox	Water Column	Hg0 → HgII vs HgII → Hgo		Amyot compares his reduction rates to oxidation rates and believes they are of similar value because the oxidation rates were done at 1/10 the intensity of incident UV radiation	LaLonde, et al., 2000

Demethylation in Water Column: MeHg → HgII

Process	Medium	Chemistry	Rates	Notes	References
Biotic Demethylation	Water Column	MeHg → HgII	<0.001 to 0.132 d^{-1}, peak in summer, summer avg 0.0835 d^{-1}, ~0.021 yearly avg*	Experiments in dark, sterilized &/or filtered showed no demethylation: biotic; rates increased with T and organic matter	Matilainen and Verta, 1995.
Demethylation	Water Column	MeHg → HgII	0.0020 – 0.00254 d^{-1}	pH 6.0 – 8.3, ELA Lakes, ON, oligo to eutrotrophic lakes	Xun, et al, 1987.
Demethylation	Water Column	MeHg → HgII	0.0021-0.0238 d^{-1}	pH 5.3 – 5.9 ELA Lakes, ON, oligo to eutrophic lakes	Xun, et al, 1987.
Demethylation	Water Column	MeHg → HgII	0.001-0.005 d^{-1}	pH 6.5	Korthals & Winfrey, 1987,
Demethylation	Water Column	MeHg → HgII	0.015 d^{-1}	Mercury Report to Congress	Mercury Report to Congress.
Potential Demethylation	Water Column	MeHg → HgII	0.001 – 0.025 d^{-1}	Maximum potential demethylation rate, as summarized in Mercury Report to Congress	Gilmour and Henry, 1991.

Reduction in Water Column: HgII → Hg0

Process	Medium	Chemistry	Rates	Notes	References
Abiotic Reduction	Water Column	HgII → Hg0	0.011 per day	Abiotic formation rates for dH_2O, dH_2O with trace metals, and microwaved mystic lakewater	Mason et al., 1995.[16]
Reduction	Water Column	HgII → Hg0	$0.0028 - 0.07$ d^{-1} (max depth 10.3 m; 9.8 ha; pH 4.7; ALK -7 ueq/L; 2.6 mg DOC/L); $0.012 - 0.28$ d^{-1} (max depth 18.2 m; 70 ha; pH 7.25; ALK 128 ueq/L; 5.06 mg DOC/L)	Using observed evasion rates, these Hg0 formation rates were estimated for two years (1989 and 1990) for two lakes with given characteristics	Fitzgerald et al., 1994.
Abiotic reduction	Water Column	HgII → Hg0	0.22 d^{-1}	Laboratory presented abiotic production rate of Hg0 in the presence of humid acids	Alberts et al., 1974 as cited by Fitzgerald et al., 1994.
Ice Over Hg0				In Wisconsin lakes, no significant increase in [Hg0] during winter ice over	Personal communication with G.M. Vandal as cited by Fitzgerald et al., 1994.
Hg0 Formation/Reduction	Water Column	HgII → Hg0		Strong positive correlation between pH and Hg0 formation, with supersaturation of Hg0 between up to 12 times that of saturation concentration	Vandal, et al., 1991.[17]
Hg0 Formation/Reduction	Water Column	HgII → Hg0	Conversion rates of $0.02 - 0.04$ d^{-1}	required to balance estimated evasional fluxes of 200-400 pml/m2/d	Mason et al., 1995.

Reduction	Water Column	HgII → Hg0	<0.005 to 0.079 d^{-1}	Range of rates from Apr to Nov '93 for Upper Mystic Lake, Boston. Rates highest in April, July, and Oct., low in June and Nov	Mason et al., 1995.
Reduction	Water Column	HgII → Hg0		Correlation between chl a and Hg0 formation rate,	Mason et al., 1995.
Biotic Reduction	Water Column	HgII → Hg0		Argue that reduction in natural waters primarily by small organisms (<3um diam).	Mason et al., 1995.
Reduction	Water Column	HgII → Hg0	0.038 d^{-1} (1m), 031 d^{-1}, (5m), .02 d^{-1} (7m), .011 d^{-1} (9m), <0.005 d^{-1} (19m)	Hg0 production decreased with Depth	Mason et al., 1995.
Reduction	Water Column	HgII → Hg0	0.05 – 0.3 d^{-1}; low DOC (1.1 – 2.3 mg/L): 0.2 – 0.4 d^{-1}, high DOC (5.0 – 8.7 mg/L): 0.02-0.2 d^{-1}	Volatile mercury percent formation in arctic lakes, UV penetrates deeper in low DOC lakes suggesting higher rates correlated with light penetration.	Amyot, et al. 1997.[18]

Methyl Mercury in Sediments

Process	Medium	Chemistry	Rates	Notes	References
MethylMercury	Sediments	MeHg	Typical %MeHg 1 – 1.5%		Ulrich et al., 2001[19]
Methylation	Sediments	HgII → MeHg	0.006, 7e-5, 2.5e-5 d^{-1}; 2.25 – 8.75 ug/m3/d (avg: 5.92)	Gross methylation rates	Gilmour and Riedel, 1995.[20]
Methylation	Sediments	HgII → MeHg	0.0001 d^{-1}	Mercury Report to Congress	Mercury Report to Congress
Methylation	Sediments	HgII → MeHg	0.8 – 96 ng/g/d or 0.0004 – 0.048 d^{-1} for pH 6-7 (epi) in slurries; or for pH 4-5: 0 -38 ng/g/d or 0.002 – 0.0019 d^{-1}		Ramlal et al., 1985 cited by Gilmour and Henry, 1991.
Methylation	Sediments	HgII → MeHg	0.03 -1.9 ng/g/d; 0.0005 – 0.028 d^{-1}		Korthals & Winfrey, 1987, as cited by Gilmour and Henry, 1991
Methylation	Sediments	HgII → MeHg	0.3 – 2.3 ng/g/d; 0.45 – 0.0017 d^{-1}		Steffan et al. 1988. as cited by Gilmour and Henry, 1991.
Methylation	Sediments	HgII → MeHg	0.5 ng/g/d or <0.001 d^{-1} (LOI<1%), 1.5 ng/g/d or 0.015 d^{-1} (LOI 60%);		Kudo et al. 1977. as cited by Gilmour and Henry, 1991.
Methylation	Sediments	HgII → MeHg	6 ng/g/d or 0.0005 d^{-1}		Spangler et al. 1973 as cited by Gilmour and Henry, 1991.
Methylation	Sediments	HgII → MeHg	0 – 62.4 ng/g/d or 0 – 0.0312 d^{-1}; 0 – 148 ng/g/d or 0 – 0.0744 d^{-1}		Ramlal et al, 1987 as cited by Gilmour and Henry, 1991.

Methylation	Sediments	HgII $\rightarrow$ MeHg	1-9 ng/g/d; 0.0009 – 0.01 d^{-1}	Jensen and Jernelov, 1969 as cited by Gilmour and Henry, 1991.
Methylation	Sediments	HgII $\rightarrow$ MeHg	0.05 – 3.0 ng/g/d or 0.00001 – 0.0003 d^{-1}; 0.19 – 3.85 ng/g/d or 0.00038 – 0.0077 d^{-1}	Gilmour and Mitchell 1988(a,b), Gilmour et al, ?? as cited by Gilmour and Henry, 1991.
Methylation	Sediments	HgII $\rightarrow$ MeHg	0.8 - 6.8 ng/g/d or 0.02 – 0.17 d^{-1}; and 2.8 – 4 ng/g/d or 0.07 – 0.1 d^{-1}	Jackson. 1989. as cited by Gilmour and Henry, 1991.
Methylation	Sediments	HgII $\rightarrow$ MeHg	0.001 – 0.016 d^{-1}	Hintelmann et al. 2000[21] and references therein
Methylation	Sediments	HgII $\rightarrow$ MeHg	0.0006 – 0.18 d^{-1}	Stordal and Gill, 1995.[22]

Demethylation in Sediments: MeHg → HgII

Rates	Notes	References
0.002 – 0.0254 d^{-1}; 0.0021 – 0.0238 d^{-1}		Xun et al. 1987, as cited by Gilmour and Henry, 1991.
0.001 – 0.005d^{-1} ; 0.003 – 0.062 d^{-1}		Korthals and Winfrey, 1987, as cited by Gilmour and Henry, 1991.
0.015 d^{-1}		Steffan et al. 1988, as cited by Gilmour and Henry, 1991.
0.037 – 0.137 d^{-1}; 0.01 d^{-1}		Kudo et al. 1977, as cited by Gilmour and Henry, 1991.
0.038 – 0.074 d^{-1}; 0.0048 – 0.065 d^{-1}		Ramlal et al. 1987, as cited by Gilmour and Henry, 1991.
0.001 d^{-1}		Jensen and Jernelov, 1969, as cited by Gilmour and Henry, 1991.
0.0005 – 0.0043 d^{-1}; 0.0002 – 0.00025 d^{-1}		Jackson. 1989, as cited by Gilmour and Henry, 1991.
0.390 – 0.528 d^{-1}		Hintelmann et al., 2000.

Reduction in Sediments: HgII → Hg0

Notes	References
At conc. of 65 pg/L Hg0, or 10% HgT as Hg0	Vandal, et al. 1995.

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