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**BUILDING A DYNAMIC MODEL LINKING POTENTIAL MERCURY
REGULATIONS TO RISK TO SUSCEPTIBLE POPULATIONS**

By

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B.S., University of Notre Dame, 1984
M.P.H., University of Louisville, 2007**

**A Dissertation
Submitted to the Faculty of the
School of Public Health and Information Sciences
in Partial Fulfillment of the Requirements
for the Degree of**

Doctor of Philosophy

**Department of Environmental and Occupational Health Sciences
University of Louisville
Louisville, Kentucky**

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ABSTRACT

BUILDING A DYNAMIC MODEL LINKING POTENTIAL MERCURY REGULATIONS TO RISK TO SUSCEPTIBLE POPULATIONS

Caroline Biagi Chan

April 3, 2012

Human exposure to mercury has been shown to cause a number of adverse health outcomes, predominantly neurological effects. The developing fetus is most susceptible, and even low levels of exposure have been shown to produce nervous system deficits. A systems approach was used to address the problem of human exposure to mercury from the consumption of contaminated fish from local waterways. Two models were developed in order to link environmental levels of mercury with human exposure. The human exposure model characterizes the disposition of mercury in the human body and fetus. The bioaccumulation model tracks the movement of mercury from water column to fish tissue. The two models were combined in order to evaluate the outcome of potential policy scenarios.

The human disposition model projects mercury concentrations in common biomarkers of exposure in response to mercury concentrations in fish. The model predicts biomarkers for fish consumption rates representing the mean, 90th, 95th, and 99th percentiles of populations of interest.

Water quality and basin characteristics were inputs into the bioaccumulation model and fish tissue mercury the output. Mean average prediction error for calibration sites was 26% and 51% for evaluation sites. Sensitive parameters influenced the system at several points and included forested and wetlands coverage, and nutrient levels. Less sensitive parameters modified the system at only one point and included the total mercury input and the portion of the basin that is developed.

The two models were combined and the impacts of potential policies were analyzed. Evaluated policy scenarios included fish consumption advisories, emissions reductions, and watershed management strategies. Simulations indicated the characteristics of a basin combined with the unique pattern of intake rates of susceptible populations determine the risk associated with fish consumption from a given waterway. Each population had a unique pattern of biomarker response to changes in fish tissue mercury. Bioaccumulation efficiency, a result of basin characteristics, determined the responsiveness of a basin to reductions in loading. Management strategies that lowered bioaccumulation rates lessened ecosystem services to an unacceptable degree. Targeting systems with greater bioaccumulation efficiency for reductions in loading would provide the benefit of reduced contamination and greater services.

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CHAPTER 1

INTRODUCTION

Statement of the Problem

Mercury (Hg) exposure is an ongoing public health concern. Low levels of exposure can result in nervous system deficits, with developing fetuses and infants at greatest risk. The USEPA designated a reference dose of 0.1 $\mu\text{g}/\text{kg}\text{-day}$ of MeHg to protect the developing fetus from adverse effects from exposure. The reference dose was based on human epidemiologic studies with developmental and neuropsychological impairments in offspring of exposed mothers being the outcome of interest (USEPA 2010a). The 1999-2002 National Health and Nutrition Examination Study (NHANES) found that 6% of women of childbearing age had blood Hg levels indicative of exposure at or above the USEPA reference dose (CDC 2004). These results indicate that a significant portion of babies born in the US are exposed to Hg at levels that could potentially cause adverse effects. The largest source of exposure is through consumption of contaminated fish (USEPA 1997a, 2010b). As of 2010, 1.2 million miles, roughly 30%, of the nation's rivers were out of compliance with water quality standards for fish consumption because of Hg contamination (USEPA 2009, 2011a). The problem is both national and global in perspective and without a clear understanding of the relationship between the environmental and physiological disposition of Hg, effective strategies to reduce contamination have not been forthcoming.

In order to devise a strategy to reduce risk to populations from Hg exposure, an understanding of the factors that influence fetal exposure and how local emissions relate to those factors is necessary.

Sources of Hg contamination

In order to reduce human exposure to Hg, reducing MeHg levels in fish tissue is essential. Understanding the source of Hg in fish tissue, however, is complicated. MeHg in fish tissue begins with inorganic Hg (IHg) in the atmosphere. IHg is emitted by a number of processes. Natural sources of IHg include volcanic activity and erosion. This accounts for about one third of atmospheric Hg. The remaining two thirds comes from anthropogenic sources (USEPA 2010c). Approximately half of this is from reemission of previously deposited Hg, and half from new sources. Coal burning power plants are the largest source of anthropogenic emissions in the United States. Previously, medical waste and municipal waste incinerators contributed substantial amounts of Hg to the atmospheric pool, but regulatory controls have been placed on these sources and Hg emissions from incinerators have been reduced by over 90% (USEPA 2006). While some reductions in emissions from coal-fired power plants have occurred as an ancillary benefit from SO_x controls, Hg emissions from this industry remain unregulated and are the largest source of emissions in the United States.

One form of atmospheric Hg, divalent Hg, associates with particulates and settles on land and waterways through dry or wet deposition. Once it reaches waterways through direct deposition or being washed into a waterway from a rain event, it settles in the sediment. Microbes then convert the IHg into MeHg; a form that bioaccumulates and

magnifies in the food chain, and can be highest in predatory fish (USEPA 2010b). In order to reduce MeHg concentrations in fish, lower atmospheric Hg levels are required.

Regulatory Efforts

The Clean Water Act (CWA) requires states to set water quality standards in order to protect specific uses of our nation's waterways. One such use is the consumption of fish. In Kentucky and many other states, fish tissue levels of Hg are out of compliance with standards that have been set to protect children and developing fetuses from nervous system damage. Fish consumption advisories are in effect for all of Kentucky's waterways. Statewide, women of childbearing age and children under the age of six are advised to limit consumption to one meal per week. Certain waterways with higher contamination levels have more restrictive advisories, limiting consumption, depending on fish species, to one meal per month, six meals per year, or no consumption at all (Kentucky Department of Fish and Wildlife Resources, 2010).

Waters that do not meet the designated water quality standards must have Total Maximum Daily Loads (TMDL) developed for the targeted pollutants. The purpose of the TMDL is to cap point and nonpoint source pollutants at levels that will bring the waterway into compliance for the given water quality standards. The TMDL is achieved by allocating a portion of the total allowable loading to various point and nonpoint sources, the former through a permitting system (USEPA 2008a). Nonpoint source pollutants are addressed through watershed management programs. Atmospheric deposition to aquatic systems is one form of nonpoint source pollution. Because atmospheric deposition is ubiquitous, watershed management programs cannot effectively reduce Hg loading in waterways. The CWA is inadequate in addressing the

problem of Hg contamination in the nation's waters, but addressing Hg emissions through the Clean Air Act (CAA) would result in reductions in contamination of waterways.

In 1990, Congress designated Hg as a Hazardous Air Pollutant (HAP) as part of the 1990 amendments to the CAA. The amendment mandates that standards be promulgated for designated HAPs within ten years, and that compliance with those standards be achieved within three years of the standard being set. Hg compounds are one of the pollutants named as a HAP (Clean Air Act: Section 112, 1990). The outcome of this designation is that major sources of Hg emissions were required to be regulated with the maximum achievable control technology (MACT). The administrator dictates which form of technology is used to control emissions.

In 2000, under the Clinton administration, the USEPA was ready to begin regulating Hg in power plants with MACT (USEPA 2010d). It was believed that existing technology would be able to reduce Hg emissions from coal and gas burning power plants by 90%, from 48 tons to about 5 tons per year (Shore 2003). Under the Bush administration, the regulation of Hg emissions by MACT was put on hold. Industries challenged the regulation of Hg under Section 112 of the Clean Air Act. Subsequently, the USEPA, with the backing of the president and energy industry, reconsidered the December 2000 ruling that it was "appropriate and necessary" to regulate Hg emissions under Section 112. Instead, the USEPA recommended that Hg be regulated under Section 111 which regulates pollutants by establishing "standards of performance." Unlike MACT, the technology to achieve that standard is not mandated (Clean Air Act: Section 111, 1970). A standard of performance requires that emissions of a particular pollutant

not exceed a certain “standard”, or level, but it is up to the industry to determine how to comply with the given standard. In March of 2005, the USEPA issued the Clean Air Hg Rule (CAMR), a cap and trade program, to regulate Hg emissions (USEPA 2011b).

On February 8, 2008 the United States Court of Appeals for the District of Columbia vacated the rule that delisted coal-fired electric utilities from Section 112 of the CAA. The delisting was found unlawful because, under Section 112(c)(9), specific findings must be given in order to delist a source. The USEPA delisted coal-fired electric utilities without presenting any specific findings (Federal District Court of Appeals for the District of Columbia, 2008). Because the removal from Section 112 was unlawful, regulation under Section 111 was prohibited, effectively invalidating the cap and trade regulatory approach of the CAMR.

With the approach of another election in 2008, developing regulations to address Hg emissions from electric utilities was put on hold, resulting in 20 years of no progress on the issue at the federal level. This stalemate led several states to consider implementing their own regulations to reduce Hg emissions (USEPA 2012). Because Hg emissions into the atmosphere can travel great distances, industries have contended that regulations to limit Hg emissions need to also occur at the international level to benefit local waterways. Research, however, has demonstrated that local hotspots do occur near emission sources (Volz et al., 2007). Subsistence fishers and their families who live near these emission sources may be disproportionately affected. Individuals with low socioeconomic status may rely on fishing as an affordable source of protein and consequently bear a greater burden of exposure from this food source than less disadvantaged populations. Regulations at the state level would play a role in mitigating

these hotspots, but because government entities cannot regulate outside their own borders, this piecemeal approach would still allow hotspots to occur from emissions from neighboring states.

As some states have taken action in regulating Hg emissions, the USEPA has again issued a rule regulating Hg emissions. The Hg and Air Toxics Standards (MATS) were promulgated in December of 2011, with utilities having until 2016 to comply. MATS set emission standards for Hg, particulate matter as a surrogate for other toxics, and HCl as a surrogate for acid gases (USEPA 2011c). The standard applies to existing and new sources of coal and gas fired electric utilities. While the cost of implementing these standards is estimated to be \$9.6 billion per year, health benefits are estimated at between \$37 billion and \$90 billion per year and will result in a 90% reduction in Hg emissions from electric utilities.

Regulation of Hg emissions from electric utilities at the national level is an important step in addressing the problem of human exposure to Hg. Electric utilities account for 50% of US Hg emissions (USEPA 2011c) and will certainly reduce the problem of Hg hotspots. However, Seigneur et al. (2004) estimated that only 25% to 32% of total Hg (THg) deposition in the United States was from North American sources. Selin and Jacob (2008) reported that 20% of THg deposition in the United States was from North American sources, but also reported considerable regional variability with 60% of Hg wet deposition in the northeast from regional sources. While reducing Hg emissions from the United States' largest source will help, it will not solve the problem.

This project focuses on the problem from the perspective of a state agency seeking to address the problem of mercury exposure. The project was initially developed

in cooperation with the Kentucky Department of Environmental Protection. The Environmental Quality Commission for the state formed a Mercury Task Force to address the problem of Hg contamination in fish (EPPC et al. 2006). The recommendations put forth by the Task Force included strengthened testing and analysis for Hg and working to correlate sampling in air, precipitation, and fish tissue. The availability of data in the various media and cooperation and interest from Kentucky Department of Environmental Protection employees made Kentucky an ideal state to focus on for model development.

Purpose

The problem to be addressed by this research was human exposure to Hg through the consumption of fish from local waterways. The purpose was to gain understanding in the system that moves Hg from emission sources, through environmental compartments, to exposure to susceptible populations. This understanding could be used to assist decision makers in the process of assessing possible policy choices in order to minimize risk to vulnerable populations. The goal of this project was to model the reduction in human risk that could be obtained by the implementation of various policy choices.

A dynamic model was constructed that evaluated the behavior of the complex system of Hg dynamics in the environment as well as its relationship to human exposure. Complex systems are non-linear and characterized by feedback loops (Meadows and Robinson, 1985). Because of this complexity, attempts to address these problems often lead to unexpected results. System dynamics require breaking the system down into its component parts and carefully analyzing the relationships between those parts and the factors that influence those relationships (CIESD 2006). The goal of this process is to provide new insights into the behavior of the system. In addition, dynamic models can

identify parameters that have the greatest influence on the behavior of the system. “What if?” scenarios can be postulated to translate management decisions into human health impacts. STELLA (isee systems, Inc., Lebanon, NH) was the system dynamics modeling software tool used for this project. STELLA simulates complex systems, tracks changes within the system and subsystems, and simulates the effects of interventions.

Dynamic modeling was used to predict changes in Hg concentration in environmental compartments and biomarkers of exposure in response to reductions in loading and manipulation of environmental variables. A systems approach allowed the assessment of “what if?” scenarios including reductions in Hg loads, changes in basin characteristics, and climate change scenarios. The model allows users to evaluate potential policy options and pose better questions to decision makers seeking to protect susceptible populations.

Scope of the Study

The complete problem of Hg exposure encompasses following Hg from emission source, through atmospheric, terrestrial, and aquatic compartments, its conversion to MeHg and incorporation in the aquatic food web where it bioaccumulates. Finally, human exposure occurs with the consumption of contaminated fish. This study examines the system from the point of Hg in the water column through population exposure. The dynamics of Hg in aquatic systems varies based on watershed characteristics. Simulations are defined by stream basin and population. Model output is given as fish tissue concentration of Hg and the distribution of biomarkers for the defined population.

The project was broken into three steps:

1. Predict the reduction in risk to susceptible populations by relating fish consumption to Hg levels in maternal and fetal blood based on a dynamic

- whole-body physiologically based pharmacokinetic model of hypothetical individuals with intake rates representing the 50th, 90th, 95th and 99th percentiles of the population of interest.
2. Develop a model to predict fish tissue Hg levels based on site-specific parameters that influence bioaccumulation.
 3. Join the two models and use the complete model to investigate the impact of potential regulatory policies on the reduction in risk to identified populations.

The complex problem of human exposure to Hg through fish consumption was examined through a systems approach. Two parts of the problem, population exposure and bioaccumulation in fish, were examined separately. As described in step 1, the dynamics of population exposure was simulated with a dynamic model that projected biomarkers of exposure for the distribution of intake rates of specified populations given a fish tissue Hg concentration. The second dynamic model, as delineated by step 2, projected fish tissue Hg levels for defined stream basins given water quality and watershed variables from available regulatory data. To examine the complete problem of Hg in the environment, a third model would be necessary to simulate the movement of Hg through atmospheric and terrestrial compartments and its subsequent movement to the stream. This third model was not developed due to the lack of emissions and wet deposition data, particularly at the basin level. As a tool for regulators, model usage is dependent on the availability of input data. Regulatory agencies monitor Hg in water more frequently than wet deposition or ambient air data, making the water column a good starting point for modeling the system.

Step three specifies the models be combined and the impact of potential regulatory strategies be investigated. The two models were combined and output analyzed from the perspective of a regulatory decision maker charged with protecting

populations from the adverse impacts of Hg exposure. Potential policy scenarios were projected with the combined model in order to examine what could be learned from a systems approach to the problem of Hg exposure as well as to determine what better questions should be asked in the search for solutions to this problem.

Three types of policy scenarios were considered in this evaluation: emission reduction regulations, watershed management strategies, and fish consumption advisories. Emission reduction regulations result in lower contamination levels in the environment and subsequently lowered exposure for populations that consume those fish. However, the timeframe from the implementation of the regulation to a sufficient reduction in fish tissue levels of Hg to protect populations may take decades (Knights et al. 2009). The long timeframe for remediation of contamination requires that regulators look at other options to protect populations. Watershed characteristics can influence the efficiency of bioaccumulation in a basin. While regulating land cover or land use would not be a likely policy strategy for mitigating Hg exposure, forecasting the outcome of proposed changes in a basin may be a factor in approving or disapproving land use activities. Because mitigation of Hg contamination has been difficult to achieve, the combination of fish consumption advisories and educational outreach is the current policy used to protect the public from possible adverse effects from Hg exposure.

CHAPTER II

REVIEW OF THE LITERATURE

Human Exposure

In order to predict the reduction in risk to susceptible populations, the disposition of MeHg in the human from fish consumption was modeled. Early human studies measured the disposition of Hg in various compartments of the body. Additionally, some studies measured the half-life of Hg in the blood and tissue. These studies provided the basis for the development of the physiologically based pharmacokinetic model.

A study by Miettinen, Rahola, Hattula, Rissanen, and Tillander (1971), measured the elimination of MeHg after volunteers consumed fish that had been fed ^{203}Hg labeled MeHg. Radioactivity was measured in feces, urine, and blood, as well as the whole body through scans to determine the disposition of MeHg. Results indicated that about 6% of the Hg was eliminated in the feces during the three to four days following the meal, representing about 1.9% per day, but this rate decreased thereafter. Elimination in urine was 0.01% per day. When examining whole blood, 90% of MeHg was found in the red blood cell component. The half life in red blood cells was 50 ± 7 days. The half life for the whole body was found to be 76 ± 3 days. This study provided important information about the absorption of Hg into the bloodstream and eliminated in feces.

Khershaw, Clarkson, and Dhahir (1980) built on the work of Miettinen et al. by measuring the elimination of MeHg from blood after volunteers ate a meal of fish with a known concentration of MeHg. The dose of MeHg the volunteers received was calculated

known concentration of MeHg. The dose of MeHg the volunteers received was calculated not to exceed 20 µg/kg body weight, a dose expected below the maximum safety level set by the Swedish Expert Group. Frequent blood sampling occurred for the first 12 to 15 hours after the meal, with less frequent sampling as time after the meal progressed. Hair samples were taken at the start of the study and several months later. The ratio of red blood cell to plasma MeHg was found to be 20-22. Peak concentrations were found at about 14 hours after the meal. During the initial 20 to 30 hours after the meal, MeHg concentrations in blood rose rapidly, and then declined. A slower decline ensued over the next 5 months of follow-up for what was characterized as a biphasic decline. The half-time in whole blood was 52 ± 4 days. The study found that 5.9% of the dose remained in the blood after the initial rise and decline. For hair samples a growth rate of 1.1 cm/month was assumed. Because $\frac{1}{2}$ cm lengths were analyzed at a time, blood levels for each 2 week period were averaged. A limitation of this approach is that the initial high blood concentrations cannot be reflected in measuring a segment of hair. The average hair-to-blood ratio was 292. This study adds information about excretion of Hg into hair, a commonly used biomarker of Hg exposure.

To understand the effects of MeHg exposure to populations, a calculation of steady-state Hg levels in blood is necessary. The studies of Miettinen et al. (1971) and Khershaw et al. (1980) determined the half-lives of MeHg in blood and the whole body at roughly 50 days for blood and 76 days for the whole body. These values can be used to calculate a proportionality constant, k , which relates daily intake with blood concentration at steady state by the formula: $C_{\infty} = kI$, where C_{∞} is blood concentration at steady state in units of µg/kg, I is daily intake in µg/kg, and k is in day/kg (Sherlock,

Hislop, Newton, Topping, and Whittle, 1984). These single intake studies resulted in a proportionality constant of 0.9 day/kg (Kershaw et al., 1980) and 1.0 day/kg (Miettinen et al., 1971). However, several chronic exposure studies found values of k that were close to 0.2 day/kg (Sherlock et al., 1984). A study was designed to determine the proportionality constant based on consumption of fish with known levels of MeHg over a three month period, with blood monitoring for a further three months. Subjects were assigned to one of four groups that had varying intake rates of the fish meals, and therefore varying exposures to Hg. Exposure levels were expected to create significant increases in the blood levels of the subjects over background. Because of the 50 day half-life of Hg in blood, the three month exposure period was expected to bring blood Hg concentrations to 70% of steady state for the assigned intake rates. Hg levels in blood were measured before the start of exposure and at regular intervals during exposure. After adjustment for body weight, the values obtained for k were found to be 0.8 days/kg for all four exposure groups (Sherlock et al., 1984). These findings agree well with the single intake findings, giving confidence to the values found for clearance of MeHg from the blood and body, which becomes important when examining exposure to the developing fetus.

The developing fetus is most at risk for adverse effects from Hg exposure, with the brain being the organ of interest. Measurement of fetal exposure has most frequently been through Hg concentrations in cord blood. Maternal blood concentrations and measurement of Hg in maternal hair have also been used as surrogates (Cernichiari et al., 2007). Maternal blood and hair concentrations of Hg have both been shown to be highly correlated to fetal cord blood concentrations. How this relates to fetal brain exposure is unknown, especially since brain size and growth rate during fetal development changes

with time. However, autopsies of the brains of infants who died shortly after birth have found that MeHg levels in maternal blood, maternal hair, infant blood, and infant brain do correlate. The authors contend that any of these biological measures give an accurate estimate of exposure to the fetal brain, and that maternal hair has the advantage that it can be used to determine past exposure levels. Because all of these biomarkers correlate with the exposure of interest, Hg exposure to the fetal brain, all of the markers were included in the model.

Several studies examined the ratio between maternal and cord blood and provided information for developing the model to predict fetal blood Hg levels. A longitudinal study examining MeHg in cord blood and the blood of pregnant and lactating women found cord blood correlated well with maternal blood at an average of 1.8 times maternal blood concentrations, with the 5th and 95th percentiles being 0.88 and 3.1 times maternal Hg concentration (Vahter et al., 2000). Maternal blood concentrations were lower at gestational week 36 and three months postpartum compared to gestational week 11. At 15 months postpartum, blood concentrations were higher than gestational week 11. Questionnaires indicated that most women indicated a decrease in fish consumption with the pregnancy. The authors suggest that because the half-life of MeHg in blood is roughly two months, fetal exposures can occur from exposures prior to pregnancy. The higher cord blood Hg concentrations were explained partly by the comparatively higher levels of fetal hemoglobin than maternal hemoglobin resulting in the one-way transport of MeHg to the fetus.

Cord blood levels of Hg were the basis for the calculation of the USEPA reference dose, with the response of interest being neuropsychological effects in children. The dose

was calculated by relating maternal blood Hg levels to intake rates of Hg contaminated fish, with the assumption of a 1:1 ratio between cord blood and maternal blood levels. Studies have consistently shown that cord blood levels of Hg are close to two times the maternal blood concentration (Bjornberg et al., 2005a; Vahter et al., 2000), so small changes in maternal blood levels may have larger effects on fetal exposure. Instead of addressing the variability between maternal and cord blood in the dose conversion, the USEPA chose to address this difference in the application of uncertainty factors (USEPA 2010a). Stern and Smith (2003) examined the cord blood: maternal blood ratio in order to determine if uncertainty from this factor can be reduced when addressing risk assessment. A meta-analysis of published studies was used to generate a central tendency estimate for this ratio as well as a coefficient of variation. Monte Carlo analysis was used to generate a distribution. Ten studies were included in the analysis with widely varying population characteristics. Weighted, based on sample size, and un-weighted Monte Carlo analyses were compared. The best fit was found for the weighted log-normal distribution for the ratio, with a mean of 1.7 and standard deviation of 0.9 (Stern and Smith, 2003).

Stern (2005) went further to do a reassessment of the USEPA's dose reconstruction by using the central tendency estimate and variability from the earlier study for the cord blood: maternal blood concentrations of Hg. Stern was able to reduce the need to use an uncertainty factor to account for pharmacokinetic variability between maternal and cord blood, but found that his analysis resulted in a maternal ingested dose half the USEPA's value. Stern's analysis reduced the uncertainty in the conversion of cord blood Hg level to maternal ingested dose. The reduction in ingested dose combined with the elimination

of one uncertainty factor suggests a reference dose that is more certain, but is essentially unchanged.

The literature provided ample information relating ingestion of contaminated fish to disposition throughout the body and to the fetus. The absorption fraction, half life in blood and tissue, and the ratio of the concentration in maternal blood to fetal blood were essential elements in developing the model. These factors were critical in predicting exposure across the distribution of intake rates.

Bioaccumulation

The exposure of interest for this study was MeHg from consumption of locally caught fish. In order to relate this exposure to policy choices regulating emissions, the simulation of Hg movement through the environment was necessary. A first step in understanding this process was to examine the movement of Hg through the food web to the point of human exposure. An examination of parameters that influence bioaccumulation of a food web model was undertaken to better understand the relevant issues that impact the degree of contamination in fish for a given watershed.

Hope (2003) constructed a food web model in order to relate predatory fish tissue Hg levels to water column Hg levels. The author noted that the USEPA provides a national default value for biomagnification, but local conditions influence this process, and therefore local data should be used to predict accumulation in a given food web. The Willamette River was the system of concern, and the model was constructed by detailing the species in this system and their feeding preferences. Intake for each species was calculated by noting the components of the diet, and calculating intake based on the fraction of the diet for each component. This was repeated for each trophic level. Intake

rates, assimilation efficiency, and elimination rates were used to determine Hg concentrations for each organism. Hg concentrations for each species in the food web were calculated, with predatory fish tissue concentrations being the outcome of interest (Hope, 2003). The model predicted water column values that would result in the fish tissue criterion set by the USEPA being surpassed by a given percentage of predatory fish (5%, 50% or 95% levels). These modeled water column values were lower than the national default value which is provided by the USEPA, confirming the value of using local data to predict biomagnification.

As primary producers at the base of food webs, the accumulation of MeHg in algae is a key step in the biomagnification of MeHg in the food web. Research into the uptake mechanism of MeHg into algae has produced conflicting evidence as to whether the mechanism is active or passive facilitated transport (Moye et al. 2002). A study was designed to characterize the transport of MeHg into algal cells. Four species of algae were chosen representing both prokaryotic and eukaryotic cells, with each species having differing cell membrane characteristics. To distinguish between active and passive transport, tests were undertaken that varied temperature, altered light regimes, introduced metabolic inhibitors, and exposed cells to radiation. Radiation treatment was used to kill cells, and has been found to affect cell membrane permeability. Decreasing exposure to light reduces photophosphorylation and would be expected to decrease active transport. Phosphorylation uncouplers decrease the production of ATP needed for active transport, and temperature changes affect enzyme activity.

Results suggested that both active transport and passive diffusion play a role in MeHg accumulation in algae. Uptake showed a bimodal character, exhibiting two distinct

slopes depending on MeHg concentration. The authors suggest that the higher slope at lower MeHg concentrations represented a form of active transport. Results from the inhibitor tests showed that MeHg uptake is sensitive to inhibition of photophosphorylation. Differences in cells with varying surface area to volume ratios did show that passive diffusion was not a major mechanism of MeHg uptake. The radiation test showed reduced uptake after exposure, suggesting an active transport mechanism. The temperature sensitivity test resulted in a linear uptake relationship, suggesting passive uptake. Another finding was that the prokaryotic species, *Schizothrix*, showed significantly lower MeHg accumulation. A eukaryotic species, *Thalassiosira*, also exhibited lower MeHg accumulation than the remaining two eukaryotic species. The lower accumulation rates found with these two species may involve the nature of their chloroplasts. *Schizothrix* does not contain chloroplasts and the chloroplasts in *Thalassiosira* are surrounded by two additional membranes. The authors suggest that chloroplast membranes may be the site of active transport. Taking into consideration the results of all tests, both active and passive transport may be involved in MeHg uptake by algae and further research is needed to elucidate transport mechanisms. However, the results suggest that the composition of the algal community may be a factor in determining the degree of biomagnification in a particular waterway.

Bloom dilution has been studied as a mechanism for lowered fish tissue MeHg levels in eutrophic systems. Bloom dilution is the concept that in eutrophic systems, a fixed amount of MeHg molecules is divided between greater numbers of cells than in oligotrophic or mesotrophic system. Consequently, a lower concentration per algal cell is found in eutrophic systems than in nutrient dilute systems. Pickhardt et al. (2002)

designed a study to test this hypothesis using stable isotopes of MeHg and divalent Hg. Algae were incubated in tanks with varying concentrations of nutrients. After two weeks, the stable isotopes were added. *Daphnia* were added 48 hours later.

As expected, algal biomass responded positively to increasing nutrient supplies. At the time of *Daphnia* introduction to the tanks, samples were taken and divalent and MeHg levels were measured in the algae. Decreasing concentrations of both forms of Hg were found with increasing phosphorus levels. The result of higher algal biomass and lower Hg per gram of algae validates the bloom dilution hypothesis.

Zooplankton Hg levels were measured at two and three weeks after introduction into the tanks. As expected, MeHg accumulation in zooplankton from the high nutrient tanks was significantly lower than in the low nutrient tanks. Divalent Hg, however did not show a linear trend, and was found at lower concentrations than the MeHg. The authors explain that MeHg is found within the algal cell cytoplasm and is readily assimilated. The divalent Hg is most frequently surface-bound and is not likely to be assimilated with feeding. These results strongly support the hypothesis that eutrophic status leads to lower levels of Hg in fish tissue through bloom dilution.

The concept of somatic growth dilution (SGD) was examined by Karimi et al. (2007). The trophic transfer of MeHg from algae to *Daphnia pulex* was examined in relation to the nutritive quality of the algae, *Ankistrodesmus falcatus*. The study hypothesized that the consumption of high quality algae would induce disproportionate growth in biomass relative to MeHg accumulation. Past work has shown that zooplankton grow more efficiently at higher concentrations of phosphorus relative to nitrogen or carbon. *Daphnia* were fed with either high quality (low C:P) or low quality (high C:P)

algae containing radiolabeled MeHg. Results indicated that growth of *Daphnia* on the high quality diet was approximately 3.5 times greater than those fed the low quality algae. Conversely, the rate of ingestion was lower for those fed the high quality algae. This greater growth was a result of more mass gained per unit uptake along with a decrease in the amount of food consumed. Measurements of the MeHg in both groups of *Daphnia* found that those fed the lower quality algae had MeHg levels that were 1.3 times higher than the high quality group. The effect of SGD may be an important function of MeHg accumulation in food webs. The author's postulate that this difference in accumulation based on waters with higher phosphorus content may be one factor in the variation found in fish tissue levels.

In stream systems, periphyton predominate over free-floating algae. A study by Cleckner et al. (1999) showed high rates of methylation of IHg in periphyton mats. The study reported evidence that periphyton mats have active communities of sulfate reducing bacteria. Periphyton mats have redox microstructures that can enhance microbial sulfate reduction. Methylation within the periphyton mat is important because these mats form the lowest trophic level for these aquatic communities. Uptake of MeHg by the periphyton or bacteria within the biofilm serves as a direct path into the food web.

The literature shows that THg in waterways does not predict predatory fish tissue levels (Ward et al. 2010a). A number of parameters influence the degree of bioaccumulation. These include food web complexity and (Riva-Murray et al. 2011), nutrient levels (Karimi et al. 2007, Pickhardt et al. 2002, Ward et al. 2010b), and the presence of humic substances (Miskimmin et al. 1992, Ward et al. 2010a). These factors were included in the development of the food web sector of the model.

Hg readily moves between compartments, and is present as three chemical species in the environment: elemental Hg, divalent Hg and MeHg. Each species behaves differently. Toxicity and fate are determined by environmental conditions and the species present. A number of physical, chemical, and biological factors influence the fate and transport of Hg in a given system. Ultimately, the dynamics of divalent Hg control the amount of Hg entering and concentrating in the food web (Orihel et al. 2007, Selin and Jacob 2008). An understanding of these factors was necessary in order to develop the physical environmental compartments of the model.

Hg Chemistry

Characteristics of two streams in Minnesota were compared to determine water chemistry parameters associated with MeHg discharge. Weekly samples were taken from April through October of 2003. A heavy rain in June resulted in a discrete episode of increased MeHg discharge. Dissolved oxygen (DO), temperature, pH, total suspended solids (TSS), dissolved organic carbon (DOC), sulfate, nitrate, iron, manganese, orthophosphate, and potassium levels were measured (Balogh et al. 2004). Discharge was inversely related to alkalinity and alkalinity was used as a surrogate for discharge. A heavy rainfall event (12 cm) resulted in elevated concentrations of both total and MeHg. It was postulated that higher temperatures and moist conditions prior to the rain event contributed to MeHg production. These peaks indicated that runoff contributed to Hg loading by transporting MeHg from areas of production, possibly wetlands, in the watershed. Minor runoff events in August and September did not result in increases in Hg loading.

Other chemical parameters changed during the major runoff event in conjunction with increases of total and MeHg. Corresponding to the peak in MeHg, DO was found to be at a minimum and orthophosphate and manganese concentrations reached a maximum. Concentrations of DOC and pH also peaked, while nitrate and sulfate concentrations were at a minimum. Iron concentrations peaked a few days later. These chemical conditions indicate that MeHg peaked when stream water exhibited reducing conditions. The MeHg was found almost entirely in the filtered portion, indicating that it was associated with DOC. Wetlands are a major source of DOC. This suggests that the rain event washed MeHg into the streams from wetlands. These wetlands have been characterized as having high peat content which has been shown to result in elevated MeHg in porewater.

Balogh et al. (2003) monitored Hg levels in three rivers in Minnesota by weekly sampling over a year. THg levels were measured for all weeks. MeHg was recorded sporadically for the first portion of the study and then weekly. Additional measurements were taken of total suspended solids (TSS), volatile suspended solids, chlorophyll *a* and total Kjeldahl (organic) nitrogen. THg levels were associated with TSS, and both increased after a rain event. The suspended sediments in these rivers were associated with erosion from the watershed. MeHg showed a statistically significant relationship with TSS although with more variability than was found with THg. MeHg levels varied over time. One episode of elevated MeHg corresponded with leaf fall and may have been related to this allochthonous input. When comparing levels between the three rivers, MeHg levels were lower in the river with less organic matter.

Studies have consistently shown that dissolved organic matter (DOM) plays a role in lowering the bioavailability of Hg(II) in food webs (Ravichandran 2004). However, the composition of DOM varies from ecosystem to ecosystem making it difficult to ascertain the stoichiometric relationship between Hg(II) and DOM. A study by Haitzer, et al. (2003) examined the composition and binding of DOM from several environments and the effect of pH on Hg-DOM binding, and presented a model of bidentate binding to describe the findings. The authors hypothesized that Hg(II) would bind to reactive thiol sites with the second functional binding group varying. They further hypothesized that a decrease in pH would decrease DOM binding.

DOM was isolated and characterized from seven sites. The conditional binding constant of the DOM, K_{DOM} , was determined for each isolate and for a range of pHs (from 4-7). The binding of Hg(II) to DOM was then modeled using simulated distribution ratios (the distribution between inside and outside the bag). The results found that the distribution coefficients varied for the sites by approximately one order of magnitude. The influence of pH showed a clear trend of decreased binding with decreasing pH. Based on structural information from X-ray absorption fine structure spectroscopy, the authors hypothesized that Hg binds to a thiol and a second functional group that may be nitrogen, oxygen, or sulfur. The model predicted pKa values in the range of 8-12 for the thiol group, and less than 10 for the second site. The expected pKa value for fully deprotonated binding sites was 25-35. The model had a good fit with the experimental data. The slope of the line for the model was close to two, indicating bidentate binding.

The authors conclude that the strength of binding of Hg(II) to DOM is consistent for different isolates, that one binding site is a thiol, and that a bidentate model fits the

data. Interaction of Hg(II) with DOM is dependent on pH, with greater binding at higher pH.

Aquatic Systems

Two lakes with similar morphometric characteristics, Sargent and Richie, were studied in order to determine factors that contributed to higher levels of MeHg in northern pike in Sargent Lake (Gorski et al. 2003). Samples of water, zooplankton, benthic invertebrates from the littoral zone, and fish (yellow perch and pike) were collected. Water was analyzed for total and MeHg, DOC, pigments, and suspended particulate matter. Pigments were used to calculate abundance of algal groups. Biotic samples were analyzed for total and MeHg. In addition, trophic level was determined by measuring $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ for the various organisms. The lighter isotopes are preferentially excreted resulting in a 0.34% enrichment of $\delta^{15}\text{N}$ per trophic level and 0.1 – 0.2% increase for $\delta^{13}\text{C}$. Bioaccumulation (BAF) and biomagnification factors (BMF) were calculated for the two lakes. The BAF was calculated as the concentration of MeHg in biota divided by the concentration in water. The BMF was the concentration in predator divided by the concentration in prey.

Sargent Lake was found to have lower levels of total and MeHg, DOC, suspended particulate matter and chlorophyll *a*. Algal abundance was not determined, but pigment analysis indicated that Sargent Lake had a greater percentage of green algae and less blue-green algae than Richie Lake. While MeHg levels were less in Sargent Lake, partitioning to particulate matter was almost twice that of Richie Lake. In addition, bioaccumulation factors for zooplankton, insects, and age-1 and adult perch were also

about twice that of Richie Lake. Biomagnification factors were also higher for Sargent Lake for each trophic level, although the difference in BMFs was small.

The trophic structure and levels were similar in both lakes. Zooplankton in Sargent Lake accumulated higher levels of MeHg than Richie Lake. The authors suggested that better food quality (fewer blue-green algae) may have enhanced accumulation. The authors also suggested that higher levels of DOC in Richie Lake may have reduced bioavailability in that lake. Levels of MeHg in insects were also higher in Sargent Lake, although the differences were not significant. Differences in perch populations were only found with larger adults. Perch in Sargent Lake accumulated 66% more Hg after 40 mm of growth. This increased accumulation may account for the greater Hg concentration in pike for that lake. The carbon isotope has been used to determine if food sources are benthic or pelagic in nature. Both perch and pike in Richie Lake exhibited a $\delta^{13}\text{C}$ signature that suggested a diet with benthic origins. The $\delta^{13}\text{C}$ profile suggested that fish in Sargent Lake fed primarily on pelagic food sources. This difference in food webs may have contributed to the difference in Hg levels in predatory fish. The authors conclude that the factors that contributed to higher Hg concentrations in pike were higher bioavailability and bioaccumulation due to lower levels of DOC, higher rates of bioaccumulation and magnification in zooplankton, and higher biomagnification in perch. Differences in food origin (benthic or pelagic) may have also contributed to differences in accumulation. The authors acknowledge that more research is needed to validate their conclusions.

A similar study comparing Hg bioaccumulation and trophic dynamics in geographically diverse stream systems was undertaken by Chasar et al. (2009). The

objective was to determine if bioaccumulation in predatory fish in stream systems behaved similarly to lake systems. Eight streams, both urban and non-urban, were sampled. Aquatic biota and stream water were sampled over three years. Biota were placed in three categories: invertebrates, forage fish, and predatory fish. A strong correlation was found between water column total and MeHg, DOC and tissue concentrations in all categories of biota. The correlation was strongest for predatory fish, with MeHg concentration in water being the strongest predictor of predatory fish tissue levels. In comparing the Hg contamination in predatory fish across the range of environmental conditions, the supply of MeHg at the base of the food web was a stronger determinant of contamination levels than trophic position or trophic transfer efficiency. This finding is affirmed with the positive correlation found for percent wetland in the watershed, a factor that has been identified by other studies as being associated with higher levels of MeHg contamination.

Terrestrial systems

Several studies have examined the dynamics of Hg fluxes between the atmosphere and soil. An observational study by Fleck et al. (1999) examined Hg concentrations from three separate sites in surface mineral soil, forest floor, woody tissue, and 1994 and 1995 needles. The objective of the study was to determine if foliar and woody Hg represented internal cycling of Hg from soil or if it originated from atmospheric sources, signifying an additional input into the watershed. Measurements indicated that woody tissue levels differed by area, but did not differ by soil Hg levels. For needles, the 1994 needles had twice the concentration of the 1995 needles. Needle concentrations were not related to soil or forest floor concentrations. The authors

concluded that Hg in foliage and trees comes from atmospheric sources, and should be considered inputs into the system.

Litterfall is thought to contribute to the flux of Hg to soils. Other sources of inputs to soil include precipitation and throughfall. Rea et al. (2002) collected foliage, soil, ambient air, and litterfall samples at two mixed hardwoods watersheds over a growing season. They found a ten-fold increase in foliar Hg over the growing season for all species. Soil concentrations were 5-18 times higher at one watershed; however foliar concentrations did not reflect this difference supporting the concept that foliar Hg is atmospheric in source. Steady accumulation in Hg over the growing season also suggested that leaves continuously accumulated gaseous elemental Hg. A model of the dry depositional flux based on meteorological data and canopy characteristics found that dry depositional flux was greater than the estimated accumulation rate of Hg. Differences in Hg concentrations were found between species in litterfall, possibly reflecting differing biochemical processes during nutrient reabsorption prior to leaf drop. Based on measurements, the authors conclude that litterfall accounts for about 40% of the THg flux in the watersheds studied, and that this flux represented an input of Hg into the system.

In addition to litterfall and precipitation, throughfall can be a source of Hg into terrestrial systems. Throughfall occurs when precipitation falls through a canopy and washes off dry deposited material. Rea et al. (2001) designed a study to examine the significance of dry deposition and foliar leaching of Hg in throughfall of hardwood forests. Measurement of net throughfall Hg (total throughfall Hg minus the concentration in precipitation) varied with the antecedent dry period. Foliar leaching of Hg was not supported because leaching increases with increased precipitation amount, which was not

found in this study. The results suggest that throughfall Hg represented wash off of dry deposited Hg on leaf surfaces.

A study to quantify and determine the relative importance of litterfall to Hg flux, as well as to determine the influence of plant community composition on litter was undertaken by Sheehan et al. (2006). Two watersheds in Acadia National Park were examined, and vegetation communities were categorized as hardwood, softwood, mixed, or scrub. Hg in litterfall, throughfall, and precipitation were measured and THg flux was calculated for the vegetation types. The concentration of Hg in hardwood litterfall was lower than all other vegetation categories. Softwood litterfall had the highest mean Hg concentration. However, in calculating Hg flux, the larger mass of hardwood litterfall in the fall balanced the lower concentration resulting in similar annual estimates of Hg deposition in litter. The authors note that hardwood forests deposit litterfall at the end of the growing season, whereas softwood forests deposit litterfall at lower rates throughout the year. In comparing sources of Hg deposition, the authors found a ratio of 1: 1.5: 1.5 for Hg flux, comparing precipitation to throughfall to litterfall. They note that studies that report Hg deposition only by measures of precipitation may be inadequate because total flux may be much greater.

Movement of Hg from terrestrial compartments to aquatic compartments depends on the dynamics of Hg in soil. Demers et al. (2007) studied the dynamics of Hg in decomposing litterfall and soil in deciduous and coniferous forests. Litterfall in two forest plots, one deciduous and one coniferous, was collected, and leaves were partially dried, weighed, and placed in mesh bags and subsequently redeployed, with 10 replicate bags per plot. Individual bags were removed over time, and mass, nitrogen, and Hg content

were measured. Decomposition rates were determined, and net Hg and nitrogen flux into the decaying litter was calculated for each interval between bag collections. Throughfall was measured for a portion of the experimental period, and throughfall amount estimates were then used for the entire period, related to total precipitation. Hg in precipitation was estimated from a nearby MDN site. A soil core was taken and Hg measured in the organic horizons. Soil leachate flux was estimated from measurements of water flux. After two years of decomposition, litter mass decreased while both concentration and mass of Hg in the litterfall increased for both types of leaf litter, with 141% increase in deciduous litter and 128% increase in coniferous litter. However, these concentrations were still less than that of the uppermost organic horizon. The highest concentrations of Hg in soil were found in the horizon with intermediate decomposition of organic matter. Throughfall inputs could not account for the increase of Hg in the deciduous litter, although this could account for the increase in the coniferous stand. A biotic mechanism was suggested for the increasing Hg because of the similarity in the pattern of flux of nitrogen in the litter. A significant correlation between nitrogen and Hg was found for the deciduous stand, and near significance was reached for the coniferous stand. The authors suggest that fungal translocation from the organic horizons of soil may explain this increase because sequestration of metals has been attributed to fungal translocation by other studies. The soil profile showed that the Hg pool in the deciduous forest floor was more than twice that of the coniferous soil pool. Factors that may explain this difference are slower decomposition rates, less litterfall mass, less capture of throughfall inputs by litter, and possibly greater volatilization of throughfall inputs. The authors conclude that incorporation of Hg into decaying leaf litter will increase its residence time on the forest

floor rather than allowing the movement of it through the soil profile. Retention in the top layers may slow the response of aquatic systems to decreases in atmospheric inputs by making it continually available for washout to waterways.

Atmospheric dynamics

Hg emissions from coal-fired power plants are the largest source of emissions in the United States (USEPA 2010e). The stack emissions from these facilities contain elemental Hg, reactive gaseous Hg, and particulate-bound divalent Hg. The species composition is largely controlled by the type of coal, the operating conditions of the plant, and the presence of particulate control devices (Kellie et al., 2004). Galbreath and Zygarlicke (1996) reported that greater than 50% of Hg emissions in coal combustion are in the form of divalent Hg. While this form of Hg is soluble and can more easily be removed by scrubbers than elemental Hg, when emitted, it is more likely to be deposited locally or regionally.

In the atmosphere, the largest portion of Hg is present as elemental Hg. This form is stable and tends to be transported great distances, as its atmospheric residence time is estimated to be $\frac{1}{2}$ to 2 years (USEPA 1997b). Oxidation of elemental Hg to divalent Hg has been shown to slowly occur in cloud water droplets. Divalent Hg tends to quickly associate with particulates and is hydrophilic. Divalent Hg deposits to land in precipitation, or may settle directly to earth through dry deposition. The atmospheric residence time for divalent Hg is comparatively short, hours to months, depending on the size of particle to which the divalent Hg is bound (USEPA 1997b). Lindberg and Stratton (1998) found that concentrations of reactive gaseous Hg had seasonal and daily trends, correlating with temperature and solar radiation.

Whole systems

An inherent difficulty in designing a study that examines how Hg moves from the atmosphere through a catchment and eventually into a waterbody where it concentrates in the food web is the nature of how the Hg moves and is stored in different compartments. A whole-ecosystem study was conducted in the Experimental Lakes Area of northwestern Ontario. Two experimental approaches were undertaken in order to better understand the movement of Hg through different compartments and the relative importance of newly deposited Hg in the bioaccumulation process. An entire catchment was manipulated by the application of Hg. The applied Hg consisted of different isotopes for three compartments that were expected to differ in the fate and transport of Hg. These isotopes allowed the researchers to monitor the movement of newly deposited Hg and to ascertain its importance relative to ambient concentrations of Hg in the process of methylation and bioaccumulation in fish (Harris et al., 2007). Separate isotopes were added annually to three components of the watershed: the lake, wetland, and upland. The paper reported the results after three years of applications.

The upland and wetland spikes were applied by airplane to vegetation while the lake spike was applied by boat to the surface water. After three years of applications, the results showed that the Hg was still moving from the points of application to the soil or sediment where large amounts of Hg are stored. None of the wetland Hg was detected in the lake, and only a small amount of upland spike was exported to the lake, although the amount increased each year (0.1%, 0.3%, and 0.6%). Methylated lake Hg spike was found within days in the anoxic sediment. Over the three year period, increasing amounts of methylated lake spike was found in the water, sediment, and biota—including young

of the year yellow perch. The upland spike was not found in the biota until the third year, and wetland spike was not detected during the study. The slow movement of Hg spike from the terrestrial zones of the catchment reflects the soil acting as a sink for Hg. The wetland exported fairly large amounts of ambient MeHg to the lake, but after three years, the spike was still largely tied up in the vegetation above the water table. Wetlands with higher water tables may see more rapid movement of Hg from wetland to lake. The authors conclude that changes in atmospheric loading may lead to an initial rapid decline in Hg levels in fish from reductions in Hg directly deposited to the lake surface. This would be followed by a long, slow decline, perhaps over centuries, as upland and wetland soils slowly reach steady state with the atmosphere while releasing small amounts of Hg to waterways. This suggests that for stream systems with little direct atmospheric loading to the water surface, the time frame for declines in Hg levels in fish tissue from atmospheric loading will be long.

A closer look at the dynamics of newly deposited Hg versus older ambient Hg in aquatic systems was undertaken with the use of mesocosms set up in the littoral zone of a lake. Hg was applied for two years in the mesocosms, with each year using a different isotope. Monitoring of the water column, sediment, periphyton, and various biota allowed the comparison of the newly deposited Hg versus older Hg in the system. The objective was to examine how the distribution, methylation, and bioaccumulation of Hg changed over time (Orihel et al., 2008). The results showed the spikes moving from the water column to the sediment over time in agreement with other studies that indicate the sediments act as a sink for Hg. Methylation of the first year Hg increased over time, and remained at higher concentrations in the second year than the methylation of the second

year spike. Concentrations of Hg in the biota showed mixed results. In the second year, some organisms showed higher concentrations of the first year spike, some showed higher concentrations of the second year spike, and some had roughly equal concentrations. The authors grouped the organisms according to these results, and found that organisms associated with the water column with short life spans had higher concentrations of newer Hg. Biota associated with the benthic food chain and with longer life spans had higher concentrations of the older Hg spike. The organisms that had roughly equal amounts of the two spikes were found to be omnivores that fed both in the water column and on benthic organisms. The authors conclude that continuing methylation of older Hg in the sediments will result in a slow recovery after reduction in atmospheric loading, but that Hg concentrations in organisms associated with short-lived pelagic organisms in the food web will decline more quickly than concentrations in organisms supported by benthic food webs. The results suggest that the rate of reduction in fish tissue concentrations of Hg after reductions in atmospheric loading may depend on the particular feeding preferences of the species of interest.

A number of models addressing the fate and transport of Hg in the environment have been described in the literature. The task of representing the movement of Hg in the environment is complicated by the number of environmental compartments in which Hg is found, and the three species of Hg with differing chemical characteristics. Macleod et al. (2005) addressed this complexity by constructing a mass balance model that addressed the movement of each species through the defined compartments of air, water, soil, sediment and vegetation. The model did not include a food web compartment. The model depicted transformation processes from one species and compartment into another

species in the same compartment, as well as movement of the same species from one environmental compartment to another. The model was a regional model of the San Francisco Bay Area and included the San Francisco Bay Estuary and the Central Valley catchment. Input and concentration data were obtained from regulatory sources to estimate Hg species concentrations in each compartment. Confidence factors were 95% confidence intervals around a median. For parameters with a single measure, a confidence factor was estimated depending on the degree of uncertainty. Fluxes were determined by partitioning between species and compartments.

The study determined that the dynamics of Hg cycling in that region were controlled by divalent Hg. This species was the most prevalent in all compartments except the atmosphere. In addition, it was found that sediment dynamics controlled Hg concentrations in the aquatic system. Hg concentrations in sediment were controlled by sediment layer mixing, depth, and sediment burial rate relative to resuspension and advection to the ocean. In this particular system, historic gold mining, a point source, resulted in substantial erosion of contaminated sediments from upstream sources. Systems with only atmospheric loading may have different drivers controlling the dynamics of mercury cycling. The mass balance approach allowed the identification of the components of the system that controlled the movement of Hg through the system.

A study examining the response time of fish tissue Hg to changes in atmospheric deposition was undertaken using ecosystem-scale fate and bioaccumulation models available from the USEPA (Knightes et al., 2009). Five separate water bodies with differing watershed and flow characteristics were modeled using appropriate available models, including Watershed Characterization System Hg Loading Model (WCS-MLM),

Spreadsheet-based Ecological Risk Assessment for the Fate of Hg (SERAFM), Water Quality Analysis Simulation Program (WASP), and Bioaccumulation and Aquatic System Simulator (BASS). For atmospheric deposition, baseline wet and dry deposition rates were estimated using the Community Multi-scale Air Quality Model (CMAQ). To investigate temporal changes in fish tissue concentrations, a 50% reduction in atmospheric loading was input into the simulations. Results indicated that larger watersheds and longer food chains lead to a slower decline in fish tissue Hg levels. The results were in agreement with the study by Harris et al. (2007) that found an initial rapid decline followed by a longer slow reduction that may take from decades to centuries to reach steady state with the new loading scenario.

The literature describes many factors that influence the movement and transformation processes of Hg through environmental compartments. These factors were included in the model to more accurately simulate the processes that occur at the chosen sites. In addition, whole system studies and descriptions of modeled systems give information about the expected behavior of the ecosystem when an emission reduction scenario is postulated. This understanding was used during the calibration and evaluation of the model.

Approach

STELLA models are often used to simulate the interaction of various types of systems, such as interactions between population growth, economic systems, and other outcomes (e.g. health). Because STELLA allows the interactions of these different systems, it is often chosen as a tool to assess possible policy choices (Sierman, 1991).

A model to demonstrate the effectiveness of a dynamic model in simulating the interaction of physical, chemical, and biological systems was developed by Wood and Shelley (1999). Constructed wetlands are an efficient and cost-effective treatment option for municipal wastewater. A concern is the accumulation of toxic metals in the sediments of these systems. A dynamic model was constructed to better understand the factors that control the bioavailability of metals in constructed wetlands. The model was constructed with STELLA software. The model was effective in integrating the physical, biological, and chemical processes that influence the bioavailability of metals in constructed wetlands, and identifying which factors had the greatest influence on pore water concentrations. In addition, analysis of individual metals predicted which metals would exhibit toxicity first. The model output also suggested that when constructing the wetlands, addition of sulfide may be a strategy for reducing initial toxicity and seeding with organic soils may reduce toxicity later. The study demonstrated the utility of dynamic models in understanding the factors that influence the processes of complex ecosystems.

Often, management or policy decisions about complex problems need to be made with the involvement of stakeholders with varying levels of understanding. STELLA, as a system dynamics tool, has been shown to be helpful in involving stakeholders in the process of exploring various policy options and aiding in the understanding of sometimes unexpected results. Water managers in Las Vegas, NV were faced with the complex problem of a decreasing water supply and an increasing population (Stave, 2003). Only two basic strategies, or a combination of the two, could be applied to address the problem: decrease consumption (conserve) or increase supply (find more). Because

finding new sources of water was not a likely solution, the involvement of the community and its support of a chosen strategy was seen as essential to the success of implementing any management plan.

A STELLA model was built that simulated the movement of water from Lake Mead through distribution and consumption in Las Vegas, through the wastewater treatment system, and back into Lake Mead. Losses to the system were through outdoor use and evapotranspiration. Parameters that influenced the system were population size, hotel use, per capita demand, and total water supply. Because treated wastewater is returned to Lake Mead upstream from the water intake, this flow represents a credit to the system. For community involvement, resource managers conducted workshops with stakeholders using the constructed model. The model was explained and the pathway from Lake Mead through distribution and use to treatment and back to Lake Mead was shown. Participants were told the goal was to increase the time before demand became greater than supply. Workshop attendees suggested various parameters to represent policy decisions. Suggested plans included increasing supply, making hotels conserve more, reducing indoor residential water use, reducing outdoor residential water use, slowing population growth, and combining strategies. The strategy that stimulated the most discussion was that increasing indoor water use increased supply because it returned water to the system. Participants found that despite the lavishness of some of the hotel water features, conservation by hotels had a minimal effect on supply, but reduction of residential outdoor water use was an effective conservation strategy. The study demonstrated the effectiveness of dynamic modeling as a tool for communication and stakeholder involvement when devising strategies to address complex problems.

Literature examples show the effectiveness of using dynamic models to simulate the interaction between various types of systems. In addition, STELLA models have been shown to be effective in determining policy choices. As a software modeling tool, STELLA has shown the ability to facilitate communication between the decision makers and stakeholders. The purpose of this study was to test the ability of the model to effectively simulate the complex problem that links Hg in stream systems to risk to susceptible populations in order to assess possible policy choices.

The literature contains many examples of addressing the individual parts of Hg movement from emissions to human exposure. Models of the disposition of Hg in humans, biomagnification through food webs, fate and transport through environmental compartments, and atmospheric transport from emissions to deposition are well represented. However, models that connect human exposure to global, regional, and local sources of emissions or translate the impact of policy decisions to changes in health outcomes to human populations are lacking. In addition, models in the literature are predominantly mass balance, steady state models. While these models may be able to predict final concentrations of Hg in a given environmental compartment, they cannot predict the time frame for reaching steady state. Dynamic models can quantify changes that occur and give the time frame for those changes.

A model is constructed to simulate the behavior of real systems as a means to better understand or predict possible outcomes of various scenarios. Because real systems are complex and contain a multitude of variations, each model is a simplification and can never be completely accurate. George E. P. Box expressed this judgment succinctly by

stating, “Essentially, all models are wrong, but some are useful” (Box and Draper, 1987). In order to determine the usefulness of a model, a careful examination of its purpose and its ability to adequately meet that purpose are necessary. In determining if a model is adequate, it is necessary to examine the uncertainty associated with the model and make a judgment about whether the uncertainty associated with the model renders the information the model provides unreliable for the purpose for which the model is employed.

Sterman (1991) discussed the importance of a clear purpose in model construction. A useful model addresses a specific problem. The purpose of the model provides the criterion to simplify and set boundaries for the exercise. If an entire system is modeled without any simplification, it would not provide any more clarity than the real system itself. While not the only type of model, simulation models, like the model in this project, attempt to mimic real systems. If the structure of the system is adequately represented, conditions can be imposed upon the system and the resulting behavior in the system can be used for foresight and policy decisions. Sterman pointed out that foresight differs from point predictions in that foresight anticipates the behavior of the system. For the purpose of making policy decisions, point predictions have no advantage over broad, qualitative knowledge, making the effort expended to make precise predictions wasted.

Both uncertainty and variability affect the range of the confidence interval around model output (McColl et al. 2000). Variability refers to the natural randomness that is inherent in a system. For example, in environmental systems, temperature varies throughout each day, throughout the year, and from year to year. Variability cannot be substantially reduced with more or better data. The ability to accurately represent

temperature in a model is limited by the random variability of the parameter. Uncertainty, however, refers to inaccuracies due to a lack of knowledge. Uncertainty can be reduced by collection of more or better data, but frequently at substantial cost. It can be further characterized as model uncertainty or parameter uncertainty. Model uncertainty is the lack of knowledge within the structure and representations in a model. This could be reflected in an oversimplification of model structure or the use of an inaccurate equation to represent a relationship between two parts of the model. Parameter uncertainty is lack of knowledge about the numerical values that represent variables in the model. Some variables are difficult to measure, while some may be measured with bias.

The purpose of a model establishes the boundaries or precision needed. Precise simulation of complex environmental problems would require an enormous effort in data collection that would still result in a wide range of possible outcomes because of natural variability. However, regulatory decisions to address these problems can reasonably be made with a comprehensive understanding of how the system in question behaves in response to imposed changes. The purpose of this project was to gain understanding in the system that moves Hg from emission sources, through environmental compartments, to exposure to susceptible populations. This understanding can be used to assist decision makers in the process of evaluating possible policy choices in order to minimize risk to the most vulnerable. The usefulness of this project is not in how precisely it can predict fish tissue Hg levels or the decrease in risk to susceptible populations at some time in the future; its usefulness comes from the foresight gained by better understanding how the system responds to various regulatory scenarios.

The finished model can make the connection between policy choices and human health outcomes related to global, regional, and local sources of Hg emissions. The dynamic model quantifies changes that occur and gives the time frame for those changes. By using a systems thinking approach and constructing a dynamic model, the project can assist regulatory decision makers in the process of assessing possible policy choices in order to minimize risk to the most vulnerable, giving decision makers the foresight needed to make informed policy choices.

CHAPTER III

METHODS

Model Development

The Hg model was completed in three steps. The first step, shown in Figure 1, was the development of a model to simulate the disposition of Hg in the human body to project common biomarkers of exposure. The distribution of intake rates for defined populations was simulated in order to forecast the pattern of biomarkers for that population. The second step, shown in Figure 2, was the development of model to depict the movement of Hg from the water column to bioaccumulation in fish for a user-defined stream system. For the third step, the two models were joined and the impact of locally caught fish on susceptible populations was simulated. A discussion of the data that would be needed to develop the third portion of the system—from atmosphere through terrestrial compartments to the stream--is found at the end of this chapter.

The model was developed using STELLA version 9.0.3 (isee systems, Lebanon, NH). STELLA is an icon-based modeling program that graphically represents components of systems and how they interact (isee systems 2010). In the model, stocks, shown as rectangles, represent compartments in which Hg accumulates, and flows, the arrows, show the movement of Hg from one compartment to another or into or out of the system. Each flow is controlled by an equation that can be impacted by multiple variables. Equations can be found in Appendix A. These variables are represented by

circles in the model and are called converters. The model uses a monthly time scale with a 100-year run and a time step of 0.25. Euler's method was used for integration.

Calibration involves refinement of model parameters to effectively simulate actual measured environments. Evaluation of the model occurs when the calibrated model effectively predicts measurements from another data set (Cowan et al. 1995). According to Forrester and Senge (1980), evaluation is the process of building confidence in the usefulness of the model. They also assert that models that respond to extreme conditions in an expected manner typically have improved outcomes when using more typical values. Calibration and evaluation data sets for the human disposition model were taken from literature sources. For the environmental compartments, seven calibration and seven evaluation sites with available regulatory data were chosen. The model was developed and calibrated using stream basins from the state of Kentucky. To evaluate the model and to test its general utility for other regions, stream basins from outside of Kentucky but within the greater Ohio River Valley were used. Seven evaluation sites from the surrounding region were chosen based on availability of data.

The structure of the modeled system controls the dynamics of storage and movement through the human system. Initial values for all stocks, equations for the flows, and values or equations for converters are given in Appendix A.

The final step was projection, or testing the impact of mitigation policies. Options to perturb certain parameters were added in order to project the effects of possible regulatory or watershed management strategies. Sensitivity analysis of the bioaccumulation model found the most sensitive input parameters were nutrient loads and the fraction of the watershed that were forested or in wetlands. These three variables were

modified within their plausible range to examine potential watershed management strategies. Total Hg input was perturbed for potential regulatory strategies. In order to modify a variable, the user selects the “perturb variable” input and then adjusts the corresponding slider to the desired value. For the variables that are input into the model as monthly means (THg input and nutrients), the value that is set on the slider is input for each month, eliminating any seasonal variations that may naturally occur. This final step asks what impact a change in policy will have on human exposure. Relevant questions to be answered were: what reduction in loading is necessary to reduce fish tissue concentrations to levels that reduce the risk to susceptible populations? How do watershed characteristics impact bioaccumulation efficiency? How responsive will a defined basin be to reductions in Hg loading?

Population Biomarkers of Exposure model

The user chooses the population to be modeled on the interface page of the model (Figure 3). The distribution of intake rates is represented as an array in the model, so that biomarker values are calculated for the mean, 90th, 95th, and 99th percentiles for the chosen population. These percentiles were chosen to give decision makers some flexibility in choosing a level of protection for populations. Intake rates and population descriptions are given in Table 1. During a model run, graphical output is produced on the interface page for the three biomarkers: blood MeHg, hair THg, and fetal blood MeHg.

Intake rates for populations of interest were taken from the literature. The *Exposure Factors Handbook* provided the intake rates for all but two of the populations modeled, and gave ingestion of freshwater fish in g/day (USEPA and NCEA 1997). The

two exceptions were the Anglers 2 population and the Subsistence Fishers 1 population. The Anglers 2 intake rates were taken from Connelly et al. (1996) and describe the consumption patterns of Lake Ontario sports fishers. The Subsistence Fishers 1 intake rates were calculated from summary statistics given in Burger et al. (1999) and represent a rural southern subsistence population. While several populations were described in the paper, the distribution of intake rates used in this study was calculated for the population with income under \$20,000. The standard error was used as the variance parameter instead of the standard deviation in the calculation of the lognormal distribution to give a more accurate estimate of fish ingestion.

Figure 2. The bioaccumulation model directly links to the human disposition model through the intake concentration converter.

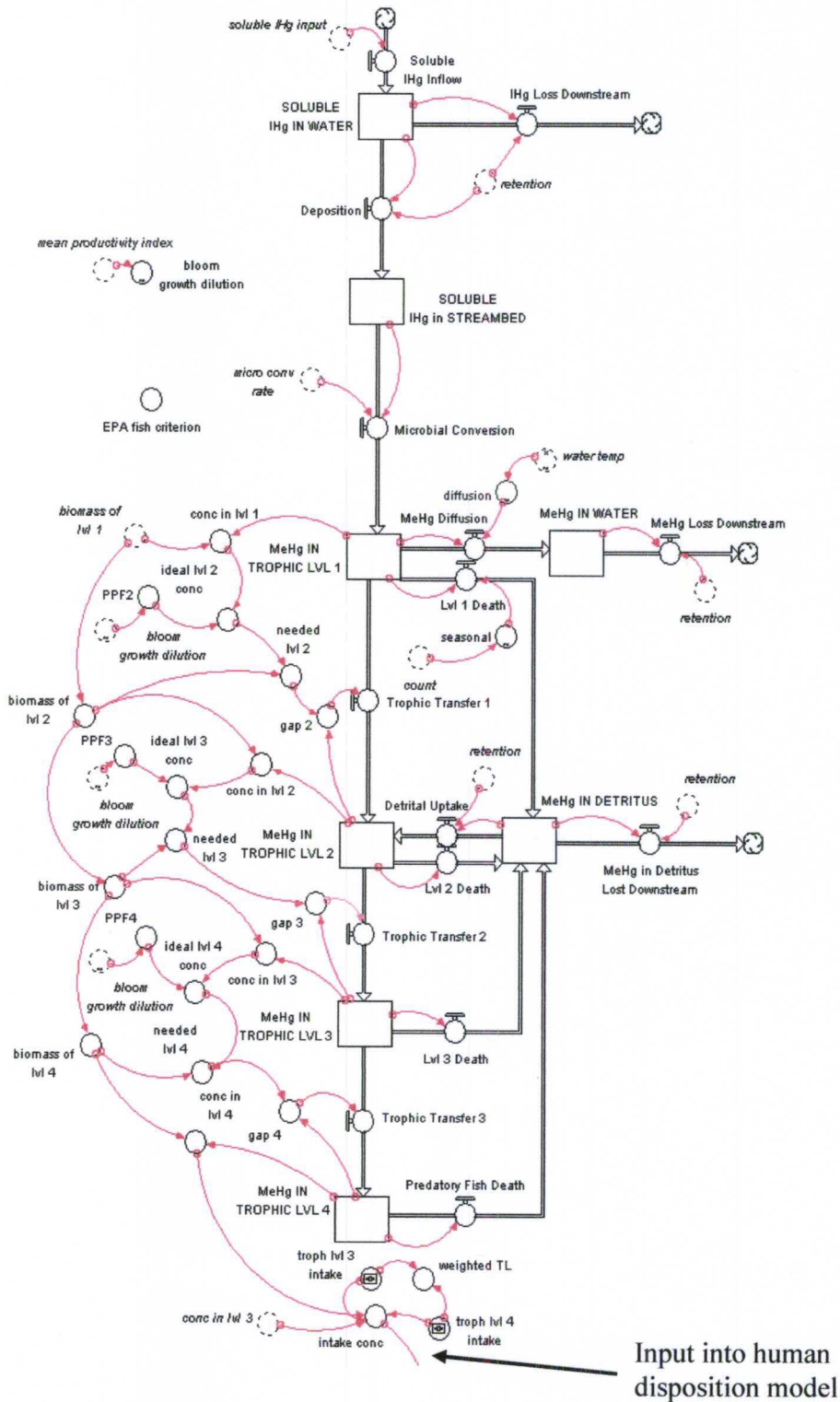


Figure 3. User input and model output are given on the interface page. User inputs include population choice, the mean trophic level the population consumes, and the option to perturb basin characteristics. Output includes fish tissue Hg level for the chosen trophic level and the distribution of biomarkers of exposure for the chosen population.

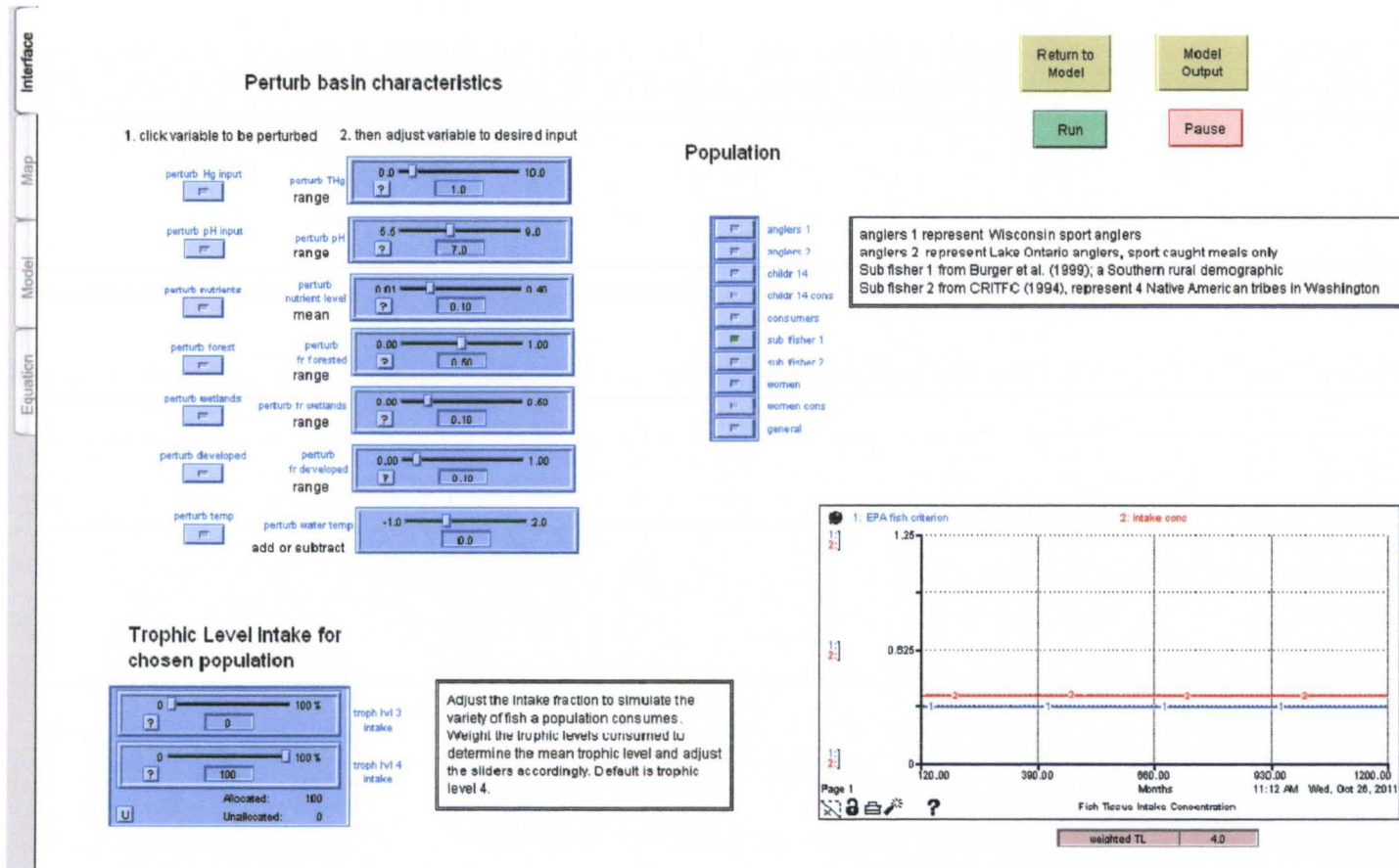


Figure 3, continued.

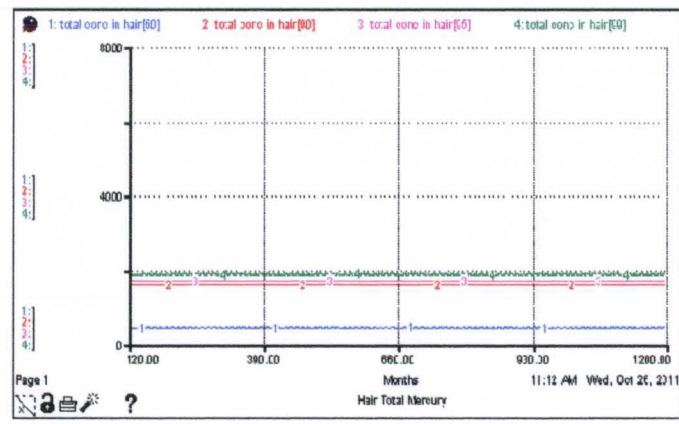
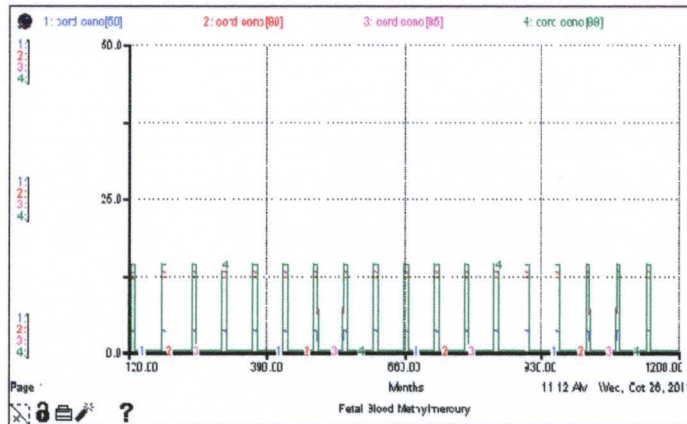
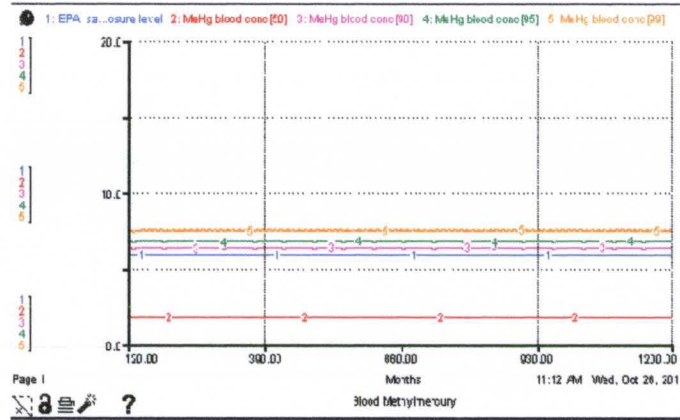


Table 1. Distribution of intake rates of freshwater fish for populations in g/day.

Population	Percentile				Source*	Description
	Mean	90	95	99		
General	4.7	12.6	32.2	82.5	1	US population
Consumers only	68	170.8	224.8	374.7	1	US population that consumes fish
Women (15-44)	5.3	10.9	28.8	70.9	1	All women of childbearing age
Women (15-44) Consumers	61.4	148.8	185.4	363.6	1	Women of childbearing age who consume fish
Children (0- 14)	1.9	1.3	13.9	40.8	1	Children ages 0 to 14
Children (0-14) Consumers	45.7	108.4	136.2	214.6	1	Children ages 0 to 14 who consume fish
Anglers 1	7.4	20.6	24.6	41.1	1	Wisconsin sport anglers
Anglers 2	17.9	13.2	17.9	39.8	2	Lake Ontario sport fishers
Subsistence Fishers 1	55.5	150	200	338	3	Subsistence fishers on Savannah River
Subsistence Fishers 2	58.7	110	170	389	1	4 Native American tribes in Washington State

*Source

1. NCEA (1997) Exposure Factors Handbook
2. Connelly et al. (1996)
3. Burger et al. (1998)

MeHg ingestion is calculated from the fish tissue concentration and the distribution of intake rates of the population selected by the user. Miettinen et al. (1971) reported that about 95% of ingested MeHg is absorbed into the bloodstream. The model flow “MeHg Absorption” calculates the amount of MeHg that is absorbed into the bloodstream. “BLOOD MeHg” is both a clearinghouse for the disposition of MeHg throughout the body, and the stock from which the biomarker, MeHg blood concentration, is calculated. Pathways leading from “BLOOD MeHg” include removal by defecation, transfer to tissue, excretion in hair, and the fetal pathway.

The MeHg defecation pathway includes the “MeHg defecated” flow which is calculated as a fraction of “BLOOD MeHg”. Defecation is thought to account for about 80-90% of Hg loss (Smith et al. 1994). However, it is unclear what portion is lost through demethylation by gut fauna (Clarkson et al. 2007) or through transformation to IHg in the tissues and subsequent transport to gut for defecation (Farris et al. 1993). Since no consensus was found in the literature, both processes are simulated. The relative portion that is converted to IHg in the tissue versus converted in the gut does not impact the purpose of the model: to accurately forecast biomarkers based on intake rates. Therefore, the rate of conversion to IHg in the tissue was adjusted on the basis of accurately predicting biomarkers and matching literature values for reaching steady state and half-life of ingested MeHg.

The MeHg in hair pathway includes the “Excretion in Hair” and “Outgrowth” flows, and the “MeHg in 1 CM HAIR” stock. THg in hair is a commonly used biomarker of exposure. The converters “hair to blood ratio”, “mass of 1 cm hair”, and “MeHg blood conc” are used to calculate the mass of MeHg that moves through the “Excretion in Hair”

flow. The “monthly hair MeHg” converter calculates the amount of Hg in 1 cm of hair (from the entire scalp) based on the ratio of hair concentration to blood concentration. This is multiplied by 0.8 because only a portion of hair Hg is organic. The inorganic portion is excreted separately through the inorganic pathway (Bakir et al. 1973, Phelps et al. 1980).

The stock “MeHg IN 1 CM HAIR” is used to calculate MeHg concentration in hair, the organic fraction of the biomarker of interest. The “Outgrowth” flow moves the MeHg out of the stock at a monthly rate, simulating the constant growth of hair, and with it, the MeHg that is excreted in hair. Total hair Hg is calculated by adding the organic and inorganic fractions in hair.

The fetal pathway includes the stock “FETAL MeHg” and the flows “Placental Transfer” and “Birth”. This pathway simulates fetal exposure, and the biomarker of interest is cord blood concentration. For this model a pregnancy is generated at 5 year intervals. When a population of children is selected, the fetal pathway is switched off. The mass of Hg needed in the fetus is calculated from the maternal MeHg blood concentration (“MeHg blood conc”) and the ideal fetal blood concentration (“ideal fetal conc”). The ideal fetal blood concentration is determined by the literature-derived ratio and the maternal MeHg blood concentration. This concentration is then converted to mass by the “fetal bl vol” converter. The Hg is transferred to the fetus over a 9 month interval. Literature values are not available for cord blood throughout the course of pregnancy; so as a biomarker, cord blood concentration represents exposure for the full-term neonate. Fetal bodyweight (“fetal bw”) is set at 3.25 kg, and is divided by 9 for linear growth to the full term neonate. Fetal blood volume is also divided by 9 for linear

growth to full term. The “Birth” flow empties the “FETAL BLOOD MeHg” stock after 9 months. A limitation of this flow is that emptying occurs over a one month time period when it is instantaneous *in vivo*. Over the time scale modeled, this slowing of Hg loss through this pathway does not affect the accuracy of the modeled biomarkers.

The primary pathway MeHg follows out of “BLOOD MeHg” is to “TISSUE MeHg” (“Bl to Tissue MeHg Transfer” flow). A set of converters is used to calculate the amount of MeHg that needs to move from “BLOOD MeHg” to “TISSUE MeHg”, or vice versa, in order to maintain or attain the expected steady state ratio between blood and tissue published in the literature. The literature reports that the ratio between tissue and blood ranges from 5:1 to 10:1 (Cernichiari et al. 2007), so an expected ratio of 7.5:1 was applied. Ingested MeHg moves from absorption into blood and then to tissue in less than a month. The monthly time scale of the model requires that each movement from one stock to another take a minimum of one month. In order to circumvent this limitation and more closely model the rapid movement of MeHg from ingestion into tissue, a fraction of the “MeHg Absorption” flow is added to the fraction taken from the “BLOOD MeHg” stock in the calculation for the flow “Bl to Tissue MeHg Transfer”. The fraction was determined by adjusting to reach the literature reported ratio between blood and tissue in the shortest time. This streamlining of movement enabled attainment of steady state ratios in a more realistic time frame.

Two converters, “MeHg blood conc” and “MeHg tissue conc”, are tools for the user. Stocks give the mass of MeHg, but the literature primarily reports concentrations in various compartments. “MeHg blood conc” reports the biomarker maternal blood concentration. It is the mass of MeHg in the “BLOOD MeHg” compartment divided by

the volume of blood. The “MeHg tissue conc” is not a biomarker. However, calculating this value facilitated the calibration process by determining whether the model was giving the expected ratio in the disposition of MeHg between tissue and blood.

Conversion to IHg occurs through the “Converted to IHg” flow. This process moves Hg from the “TISSUE MeHg” stock into the “TISSUE IHg” stock. The “TISSUE IHg” stock represents IHg in all compartments of the body. It should be noted that some tissues, such as kidney, concentrate IHg whereas other tissues may have lower concentrations. The converter, “rate constant convert to IHg”, determines the fraction of tissue MeHg that is converted to IHg. This conversion rate was not determined by literature values, but by adjusting the rate so that the half-time in the body and the ratio between blood MeHg and tissue MeHg came closest to matching literature values. Three pathways flow out of “TISSUE IHg” and represent losses to the system. These are the flows “fecal loss of IHg”, “IHg loss in urine”, and “IHg in hair”.

The biomarkers of interest do not specifically look at IHg. However, the hair Hg biomarker typically measures THg which is approximately 80% MeHg and 20% IHg (Phelps et al. 1980). Therefore, the IHg in hair pathway is simulated and used in the calculation of THg concentration in hair. Similar to the MeHg excretion in hair pathway, this pathway consists of the flows “Inorganic Hair Exc” and “Outgrowth of IHg in Hair”, and the stock “IHg in 1 CM HAIR”. Monthly hair IHg is calibrated to be a fraction of “TISSUE IHg”. This fraction, 0.0296 in the “IHg hair fraction” converter, was determined by back calculating the portion of “TISSUE IHg” that would be required to make the 20% of IHg in hair necessary to attain the desired ratio of hair THg to blood MeHg. The remainder of this pathway replicates the MeHg in hair pathway. Total

concentration in hair (“total conc in hair”) is calculated by adding “IHg conc in hair” and “MeHg conc in hair”.

The flow “IHg Defecation” simulates the loss of IHg through the feces. It helps balance the loss of MeHg through defecation to achieve the percent of THg lost through this pathway found in the literature. “IHg defecation rate” sets the fraction of “TISSUE IHg” that is lost due to defecation.

The loss of IHg in the urine pathway is simulated by the flow “Urine IHg loss”. The kidneys tend to accumulate IHg and slowly release the Hg into the urine (Passos et al. 2007, Young et al. 2001). Because the rate of mercury excretion through urine is not well documented in the literature, the loss through this pathway balances the loss through the hair and fetal pathways along with the 80-90% loss through the feces (Clarkson and Magos 2006).

Bioaccumulation

The bioaccumulation model examines the movement of Hg in stream systems from water column to fish tissue. The purpose of this model was to assist regulatory decision makers in the process of determining where and how resources can be used to protect populations from adverse Hg exposures. Because the intended users are regulators, existing data from readily available regulatory sources were used as inputs. The objective was to gain insight into how the unique characteristics of basins in this region interact to impact the bioaccumulation process. This insight can then be used to determine which basins are likely to have elevated fish tissue levels or shed light on the impact of proposed changes in land cover or other watershed characteristics, or the responsiveness of a basin to reductions in Hg loading.

Land cover and water chemistry data were inputs into the model and were assumed to be at steady state. Output was fish tissue MeHg levels. The user sets the trophic level of the fish to simulate the mean intake of a population of interest. The user chosen fish tissue Hg concentration is used as an input into the human disposition model. Model output was compared to actual fish tissue data to determine model accuracy.

Basins used to calibrate and evaluate the model were primarily from the Ohio River Valley, a region that has not been well represented in the literature examining Hg bioaccumulation. These sites exhibit considerable variation in land use and land cover and span several physiographic regions, from mountainous, heavily forested basins in the Appalachian Highlands to basins in the Interior Plains that are highly cultivated. While increased bioaccumulation has been associated with wetlands coverage and has been a focus of research, wetlands coverage is minimal in the Ohio River Valley (Emery and Spaeth 2011, White et al. 2005). This region offers the unique opportunity to examine the relationships between other drivers of Hg bioaccumulation.

Basic Structure

The basic structure of the bioaccumulation model is shown in Figure 2. Hg enters the system through the flow “IHg Inflow”. IHg moves into the INORGANIC Hg IN WATER stock. From this stock, the Hg can move out of the system by flowing downstream, or be deposited through sedimentation to the streambed, represented by the IHg IN STREAMBED stock. This stock also represents any IHg that may be moved to the floodplain or retained by woody debris or held within the system by any other means. Basins with extensive wetlands have been associated with high MeHg concentrations.

However, for basins with little or no wetlands, the location of microbial conversion of IHg to MeHg is less certain. The literature suggests that this conversion occurs in the biofilm associated with algal communities (Bell and Scudder 2007, Desrosiers et al. 2006, Tsui et al. 2009, Tsui et al. 2010). Because of this association, the model depicts the movement of the IHg in the streambed, after microbial conversion to MeHg, as moving directly into the TROPHIC LVL 1 stock. The TROPHIC LVL 1 stock represents the MeHg contained within the periphyton as defined in the broad sense as including the community of algae, bacteria, fungi, and exudates. The MeHg can follow one of three pathways out of the TROPHIC LVL 1 stock. It can diffuse into the water column and be lost downstream; it can be contained within the declining periphyton and subsequently enter the detrital pathway; or it can be consumed by trophic level 2 organisms. Living organisms with their associated MeHg are assumed to remain within the stream system. Loss of Hg to the system is through movement to detritus and then loss downstream.

The bioaccumulation process is represented by movement of MeHg from one trophic level to the next, with an alternate “Death” flow removing a portion of the MeHg at each trophic level. All MeHg in trophic level 4 eventually moves into the “Death” flow for that level. The “Death” flows move MeHg to the MeHg IN DETRITUS stock. From there, the MeHg can exit the system by being lost downstream or be recycled into the bioaccumulation process by consumption from trophic level 2 organisms.

The bioaccumulation of MeHg through the food web is represented by a series of stocks labeled as trophic levels. The mass of MeHg needed in each is calculated by determining the biomass of each trophic level and determining the concentration of MeHg based on the previous trophic level. The determination of the biomass of trophic

level 1 is discussed below. The concentration of MeHg in each trophic level is then a function of the mass of MeHg in that trophic level and the corresponding biomass.

To determine the mass of MeHg that flows to subsequent trophic levels (TL), predator prey factors (PPFs) are used. The PPF is the ratio of MeHg concentrations of TL_n to TL_{n-1} . A suggested mean value from several studies is given in the *Mercury Study Report to Congress* Volume III, Appendix D (USEPA 1997b). For a given amount of MeHg, the eutrophic system, with a larger crop of algae, will distribute the MeHg through a larger number of algal cells resulting in a dilution effect at the base of the food web (Chen and Folt, 2005). This effect, called bloom dilution, affects all subsequent levels of the food chain. In addition, the algae in high-nutrient systems produce more biomass per unit ingested by consumers than in nutrient-poor systems, an effect called somatic growth dilution (Karimi et al., 2007). Bloom dilution and somatic growth dilution lead to eutrophic systems having lower predator prey factors than oligotrophic systems. These effects were combined in a function called “bloom growth dilution” and used to adjust the PPFs. The output of the graphical function is dependent on the mean productivity index, described below. The adjusted PPF is used to determine a target MeHg concentration and the corresponding mass of MeHg needed to achieve that concentration. The mass already resident in the stock is then subtracted from the amount needed to achieve the ideal concentration and that mass of MeHg is moved to the next trophic level.

The death flows for each trophic level move MeHg into the MeHg IN DETRITUS stock. For primary producers, the death flow is controlled by the seasonal pattern of periphyton loss, with highest loss in fall. When moving to subsequent trophic levels,

lifespan tends to increase. For TL2, the assumption is made that organisms live for one year. The flow is controlled by removing 1/12 of the mass each month. For TL3, the mortality rate for bluegill, 0.56/year, was used to determine loss of MeHg through death. Trophic level 4 used the mean mortality rate for predatory fish found in Kentucky, 0.36/year (Froese and Pauly 2011).

MeHg IN DETRITUS represents the MeHg found in non-living organic matter in the system. Some of this matter is lost downstream based on retention while the remainder is taken up by detritivores, accounted for in trophic level 2 for this model.

Subroutines

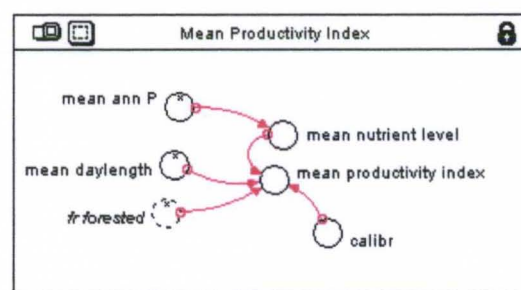
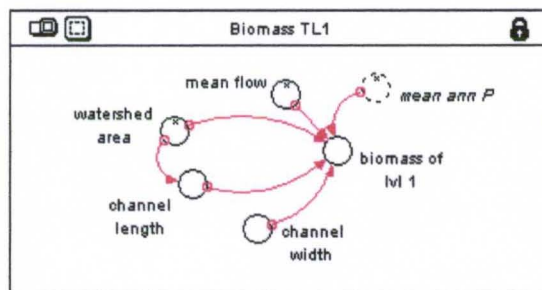
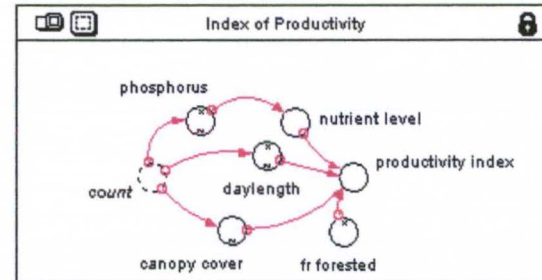
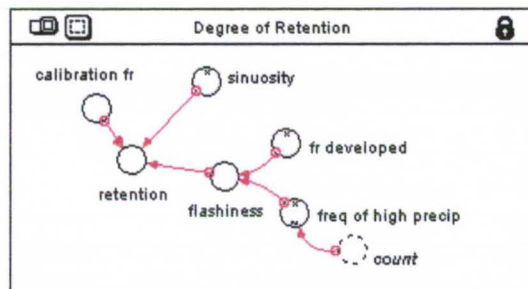
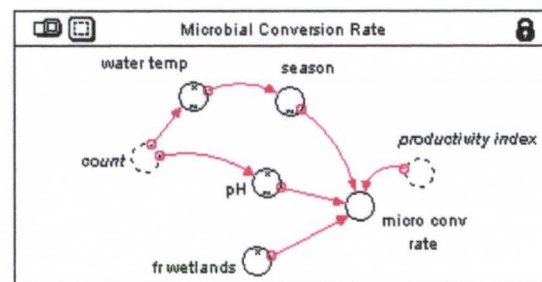
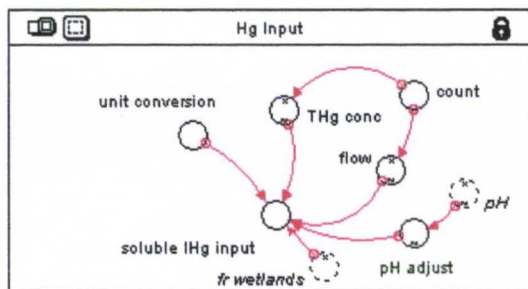
The bioaccumulation model subroutines are shown in Figure 4.

IHg Input. The Hg Input sector determines the amount of Hg that enters the system. Typically, more than 90% of THg entering a stream is IHg (USEPA 1997b). For the Hg input, the mass of THg is calculated by multiplying the mean monthly THg concentration by the mean monthly flow. Particulate-bound Hg is not available for conversion to MeHg, and, in the short term, is not available for bioaccumulation. Balogh et al. (1997) found that the concentration of dissolved Hg remained relatively constant while THg varied widely in association with suspended solids. In this model, only the dissolved Hg enters the modeled stream system, and the particulate-bound Hg is ignored. In the study by Balogh et al. (1997), the range of dissolved Hg was 0.2-0.7 ng/l. Several additional sites on the upper Mississippi River showed little variation and had a maximum of approximately 1 ng/l. Additional studies found ranges of dissolved IHg that were as high as 2-3 ng/L (Balogh et al. 2008, Dittman et al. 2009, Shanley et al. 2008, Tsui and Finlay 2011). These higher values were associated with higher concentrations of dissolved

organic carbon (DOC), frequently associated with more wetlands or forested coverage (Tsui and Finlay 2011). DOC data were not available for the Kentucky sites. The model reflects the stable dissolved IHg concentration by using the minimum function in STELLA. This function returns the minimum of either the mean THg concentration or 1 ng/l as the Hg input into the model. Because a lower pH is associated with an increased availability of IHg for methylation, an adjustment is made to the minimum value with a graphical function, “pH adjust”. An increasing portion of the THg is designated as dissolved as the pH becomes more acidic, with the graphical function adding up to 3 ng/l to the dissolved IHg for a pH as low as 5.5.

Retention. IHg input into the model is determined by the measured mean concentration and monthly discharge, which is the assumed throughput of water in the system for the monthly time period. From the IHg IN WATER stock, the Hg can be deposited to the stream bed or lost downstream. When contemplating the mass of Hg in a stream system, the majority of the mass is carried downstream and lost to the system. The amount that remains in the system does so by sedimentation, which may be minimal for many low to mid-order stream systems, or by deposition on banks during flood events (Allan and Castillo 2007). In this model, the amount of Hg that remains is characterized by the variable “retention” which is calculated in the “Degree of Retention” sector. The factors that are used to determine retention include sinuosity and flashiness. Higher sinuosity reflects a greater meander and slower movement through the system resulting in

Figure 4. Subroutines for the bioaccumulation model.



increased sedimentation. The calculation of sinuosity is discussed below. Flashiness reflects a decrease in the infiltration of precipitation in soils resulting in more rapid rise and fall of discharge. In the model, flashiness is determined by the fraction of developed land in the basin and the frequency of high precipitation. A calibration factor was applied to maximize model fit. For each iteration of the model, the mass of Hg that will be retained is determined and then the remaining Hg is lost downstream.

Microbial Conversion. The conversion of IHg to MeHg is complex and likely occurs by several processes. The model assumes that the conversion occurs in association with periphyton and is consistent with evidence that this conversion occurs within the biofilm (Bell and Scudder 2007, Cleckner et al. 1999, Tsui et al. 2009, Tsui et al. 2010). While microbial conversion may occur in other locations, it is likely that across the region for which the model was developed, the processes and locations of conversion are likely to be similar. The assumption is made that all MeHg is initially associated with periphyton and is represented with the MeHg IN TROPHIC LVL 1 stock. The MeHg can then move up the food chain from ingestion by consumers, or diffuse into the water column and subsequently be lost downstream. MeHg Diffusion is controlled by the converter “season”, with warmer temperatures resulting in greater diffusion rates. MeHg Lost Downstream is controlled by the retention subroutine.

Variables used to calculate the microbial conversion rate were water temperature, pH, fraction wetlands, fraction forested, productivity index, and day length.

Determination of this rate occurs in the “Microbial Conversion Rate” sector. Each of these variables was scaled to a 0 to 1 range and then weighted so that the full weights of the variables added to 1. This value is then multiplied by 0.36, the range of microbial

conversion rates found in Warner et al. (2005) giving an estimate of the microbial conversion rate found in stream systems. The mean monthly water temperature is converted to a graphical function called “season” that reflects the increase in primary producer growth during warmer weather.

Productivity Index. An index was developed for the effect of productivity on the microbial conversion rate. Periphyton mats are thought to contribute to increased methylation rates. As mats grow and become denser, small anoxic microzones within the mat may develop. The large surface area within the mat favors microbial growth. The bacterial community, along with the oxic/anoxic borders, promotes conversion of IHg to MeHg (Mauro et al. 2002, Tsui et al. 2010, Ward et al. 2010a). This effect is accounted for in the “Index of Productivity” sector. Phosphorus was assumed to be the limiting nutrient for all sites, and was used as a surrogate for potential productivity. In stream systems, light often limits productivity. Light limitation was introduced to the index of productivity by including the fraction forested, canopy cover, and monthly length of daylight hours. “Canopy cover” is a graphical function that relates the effects of season to the fraction of the watershed that is forested. Stream productivity is often greatest in forested basins before spring leaf out. The graphical function limits the effect of shading to months with canopy coverage.

Biomass TL1. While the biomass of primary producers varies with the seasons, this pattern diminishes for subsequent trophic levels. The biomass of trophic level 1 is used to estimate the biomass of all subsequent trophic levels. In order to minimize this seasonal pattern in higher trophic levels, the mean annual biomass of trophic level 1 is estimated in the “Biomass TL1” sector. This variable is calculated by using the multiple

regression equation determined by Lamberti and Steinman (1997). They found that watershed area, dissolved reactive phosphorus, and mean annual flow explained 70% of the variation in biomass of stream systems. The equation predicts areal gross primary production. To calculate total biomass, channel length and width are multiplied by the areal gross primary production. Channel length is calculated according to Leopold (1994, p 222). A mean channel width of 5 m was estimated to be the productive area of the stream. After trophic level 1, the biomass of subsequent trophic levels is estimated to be 10% of the prior trophic level based on transfer efficiencies in the literature (Pauly and Christensen 1995).

While mean annual biomass is constant for each trophic level, monthly means were used to determine the movement of Hg through the system. This resulted in a slight sinusoidal wobble for projected fish tissue levels that is not likely to be reflected in a real system.

Mean Productivity Index. This index is determined in the “Mean Productivity Index” sector, and its determination is similar to the “productivity index” variable. The differences between the two are that mean annual phosphorus is used instead of the mean monthly value, canopy cover is not accounted for, and a calibration factor is applied.

Data Sources

The purpose of the model is to be a tool for regulators, therefore the model used existing data from regulatory sources for calibration and evaluation. Sources of data for all sites can be found in Table 2 with references for the sources in Appendix B.

Water Quality. Sites were chosen based on the availability and co-location of both fish tissue and water quality data. For calibration sites, water quality variables were

obtained for the years 1999 through 2007 and included THg, phosphate-phosphorus as P, pH, and water temperature. In general, the sampling strategy for each site was measurements taken bimonthly with monthly sampling every five years. This resulted in 2 to 9 samples for each month. Means were calculated, and for months with $n < 4$, the means of the prior and subsequent months were included to diminish the effect of low sample numbers. THg measurements were used as inputs for the model. Prior to 2002, the limit of quantification (LOQ) was 50 ng/L. Methods changed in 2002 and the subsequent LOQ was 0.5 ng/L (R. Payne, KDOW, personal communication, 10/26/2010). Because almost all samples tested before 2002 were below the higher quantification limit, only data collected after the change in methods were used to calculate monthly means for THg. While each site varied slightly in the total number of samples, the samples collected before 2002 represented approximately one third of all Hg samples for each site.

Water quality data for evaluation sites were limited. Often, co-located fish tissue and water quality data were not available and the closest monitoring station to the fish sampling site was used. When water quality data were sparse, data from one or more of the nearest monitoring sites were merged to determine a mean. Several evaluation sites had no THg data available. The default for these sites was set at 1 ng/l.

Fish tissue. Fish tissue data were limited for calibration sites, with four sites having only one sample. The Mud River site had the largest sample size with 14 samples. Most samples were composites of the same species and similar size. Species, length, weight, and Hg concentration were available. Skin-on fillets were used to determine Hg concentrations in scaled fish, while skin-off fillets were used for scale-less fish (E. Eisiminger, KDOW, personal communication, 2/3/2011). Data availability varied

between the evaluation sites. Georgia had the most fish tissue samples, 9 and 16 samples for Spring Creek and Talking Rock Creek, respectively. The remaining sites had three or more samples. Details of the available samples, including species, size, and Hg tissue concentrations, can be found in Appendix B.

Species sampled varied considerably. In order to strengthen the evaluation of the model, fish were grouped into trophic levels, with panfish assigned to TL3, piscivorous fish to TL4, and all other fish defined as TL3.5. Because fish tissue concentrations increase with size, a standard size fish was selected for model projection. Willis et al (1993) delineated length categories for the most commonly caught and consumed fish species. As an estimate of the most commonly consumed size fish, “quality” length was chosen. Samples that were between 0.75 and 1.25 times the quality length were included in the analyses. Tygarts Creek had only one fish tissue sample and it was outside the bounds stipulated for length. Consequently, this site was not included in error analysis, but was instructional in evaluating the effects of land cover on bioaccumulation. Several samples were of species without length categories. A boxplot of error rates by trophic level was used to identify any outliers from the samples without length categories. One outlier was identified and was excluded from further analyses. In addition, 2 striped bass from Talking Rock Creek in Georgia were excluded. These TL4 samples had a mean tissue concentration that was one third of the TL3.5 samples from the same site. Possible reasons for lower than expected Hg concentrations were small sample size or that the fish were thermally stressed and had migrated into the creek from the downstream

Table 2. Data sources. References for sources can be found in Appendix B.

Variable	State	Source	
Fish Tissue	Georgia	USEPA Region 4 TMDL reports	
	Indiana	Indiana Department of Environmental Management (IDEM)*	
	Kentucky	Kentucky Division of Water (KDOW)*	
	Tennessee	Tennessee Department of Environment and Conservation*	
	West Virginia	West Virginia Department of Health and Human Services	
Water Quality	Georgia	STORET/Georgia Dept of Natural Resources	
	Indiana	STORET/IDEM	
	Kentucky	STORET/KDOW	
	Tennessee	STORET/Tennessee Department of Environment and Conservation	
	West Virginia	STORET/WV Division of Environmental Protection (WVDEP)	
Discharge		US Geological Survey	
Precipitation		National Climatic Data Center	
Day length		ptaff	
GIS	Land cover	National Land Cover 2001 Dataset	
	Streams/ Basins	Georgia	Georgia GIS Data Clearinghouse
		Indiana	Indiana Spatial Data Portal
		Kentucky	Kentucky Geological Survey: Geospatial Data Library
		Tennessee	Tennessee Spatial Data Server
		West Virginia	West Virginia GIS Technical Center

*Data obtained directly from agency. All other data were obtained from internet sources, referenced in Appendix B.

reservoir (J. Hakala, GA DNR, personal communication, 8/17/2011). Final sample sizes for trophic levels 3, 3.5, and 4 were 7, 12, and 3 respectively for calibration sites and 16, 27, and 2 for evaluation sites.

Geophysical Parameters. Using GIS methods, the contributing watershed for each site was delineated and the water monitoring and fish tissue sampling station marked. If the water monitoring station did not fall neatly at the downstream end of a sub-basin, the watershed boundary was redrawn to more accurately represent the contributing watershed. The smaller basins were dissolved to form the contributing watershed for the sample site, and the watershed area was calculated.

Land use was determined through the National Land Cover 2001 Dataset (Homer et al. 2004). The land use data were clipped by the contributing watershed. The three forested, two wetlands, and four developed categories were condensed into single categories and the fractions of the basin that were forested, wetlands, and developed were determined.

Sinuosity was calculated using the following equation (Allan and Castillo 2007):

$$\text{Sinuosity} = \frac{\text{Channel distance}}{\text{Straightline downvalley distance}}$$

For each watershed, GIS methods were used to measure channel distance and straight-line distance for two headwater reaches, two mid-stream reaches and two reaches near the sample site. Sinuosity was calculated and the mean of the six calculations was used.

U.S. Geological Survey (USGS) data were used for mean monthly flow values. For sites that had a USGS station at the water monitoring station, the mean flow was

taken from the USGS website. For other sites, the ratio approach described in Rashleigh et al. (2004) was employed. Frequency of high precipitation was determined from daily precipitation data for the NOAA station closest to each sample site (NCDC 2010). More than 50 years of data were available for all stations. Frequency of high precipitation was defined as the mean of the number of days with precipitation over half an inch for each month.

Variables are input into the model using a linked Excel file. For monthly means, these variables are frequency of high precipitation (freq of high precip), THg concentration (THg conc), water temperature (water temp), pH, phosphorus, day length, and flow. Variable constants are mean annual phosphorus (mean ann P), mean day length, mean flow, watershed area, sinuosity, fraction forested (fr forested), fraction wetlands (fr wetlands), and fraction developed (fr developed).

Output and Options

User options and model output are on the interface page of STELLA, shown in Figure 3. The user selects one of 10 populations to be simulated. Because different populations may consume substantially different types of fish, the interface contains sliders that the user sets to simulate the mean intake trophic level of the population of interest. A numeric display shows this mean trophic level after the program is run. For example, sports fishers may primarily be interested in piscivorous fish. For that population, the intake concentration desired would most likely be TL4. The sliders would be weighted 100% for TL4. A subsistence fisher population may rely primarily on panfish and catfish. No slider represents TL3.5, so if 60% of the intake were catfish,

weighting would be 30% TL4 and 30% TL3, for catfish. The remaining 40% of consumption was panfish represented by TL3. Adding this 40%, the final breakdown would be 70% TL3 and 30% TL4. The mean trophic level consumed would be displayed as 3.3.

In order to assess policy choices and drivers of the system, the user can modify several variables. The variables are THg input, pH, nutrients, the fraction of the basin that is forested, developed, or in wetlands, and water temperature. The user selects the variable to be perturbed and then adjusts the corresponding slider to the desired value.

Output is given in graphical form. The fish tissue concentration for the user-specified trophic level is shown in one graph. Population outcomes are also shown. Graphs for blood MeHg, total hair Hg, and fetal blood Hg show the distribution of that projected biomarker for the population simulated. Because of the complexity of the system, a number of months are required for the model to adjust to a steady state condition based on individual site factors. In order to minimize confusion from this equilibration process, the graphical display begins after a steady state is achieved at 120 months and continues to 1200 months for the 100 year run.

Policy and Climate Change Analyses

Fish Consumption Advisories and Population Choice

Changing behavior by choosing a lower trophic level fish for consumption can modify exposure. This strategy examined how consumption guidelines might alter exposure by examining the response in population biomarkers to fish from the same basin but different trophic levels. While fish consumption advisories are typically set based on

general criterion, in order to protect public health, decision makers must answer two questions: 1) which population has the greatest exposure? And 2) what portion of the population will be protected? An analysis was undertaken to demonstrate the response of the distribution of the blood MeHg biomarker of susceptible populations to changes in Hg concentration in fish tissue, and whether biomarkers for the examined populations fell below the USEPA fish tissue criterion. Fetal blood MeHg and total hair Hg biomarkers were also examined. The patterns of change in biomarkers for populations were compared.

Emissions Reductions

Because the model does not include an atmospheric component, Hg emission reduction scenarios cannot be directly simulated. Two strategies were used to project the consequences of possible reduction scenarios. The first strategy was to modify the THg input into the model; a method that simulates the implementation of a TMDL. This strategy allows the user to project the concentration of THg in the stream that would bring fish tissue into compliance. The second strategy projected the impacts of a percentage reduction in Hg. This method looked at reducing Hg loads by set percentiles (10%, 25%, 50%, 75%, and 90%), and therefore is more reflective of possible regulations that reduce emissions from local sources. With this analysis, both THg input and dissolved IHg input reduction scenarios were examined. The emissions reductions scenarios were analyzed by projecting outcomes in three streams and trophic level 4 fish.

Watershed Management Strategies

Previously, the most sensitive input parameters were found to be nutrient loads and the fraction of the watershed that was forested or in wetlands. The effects of

perturbing these three variables on susceptible populations were examined. The impact on the 95th percentile intake rate of 6 populations was projected by modifying these basin variables from their measured values to plausible low and high values. Nutrient loads were tested at 0.0100 mg/l and 0.3500 mg/l phosphorus. The fraction of the basin that was forested was modified to 0.05 and 0.95. The fraction wetlands coverage was set to 0.01 and 0.35. Trophic level 4 fish were chosen for the intake concentration for all analyses.

Climate Change

Climate change is expected have varying impacts depending on location. In Kentucky, the impacts are expected to be an increasing temperature and more frequent and intense precipitation events (Partnership for a Green City 2011). In order to gain understanding of the possible impacts that climate change may have on the problem of Hg contamination, three climate change scenarios were analyzed. The first scenario looked at the changes that increased monthly temperature means might have on the problem of Hg. The second scenario looked at the impact of more frequent high-precipitation events. The third scenario analyzed the impact of the combination of increased monthly temperatures and more frequent high-precipitation events.

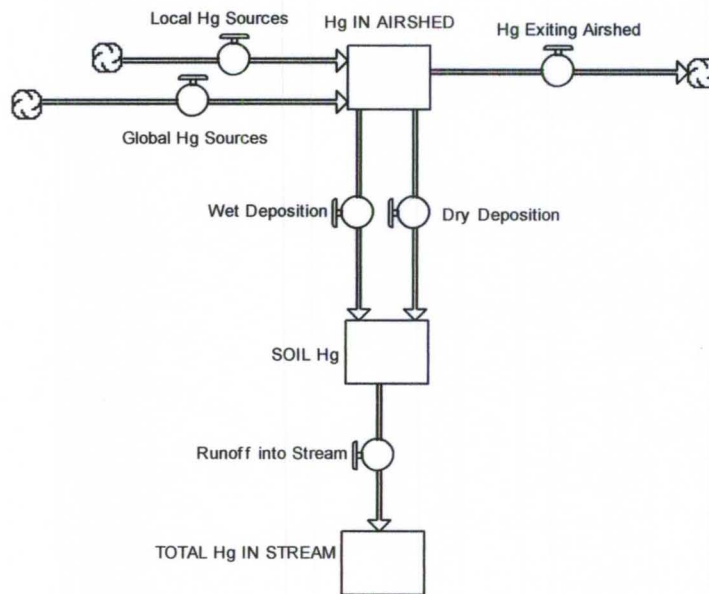
Data requirements needed for atmospheric model

To model the entire system, a third step, a model that tracks Hg from emission source, to atmosphere, wet and dry deposition to the basin, and subsequent movement into the water column of the modeled stream system would be needed. This step was not completed. The two challenges that resulted in deferring the completion of this step were

the paucity of monitoring data needed for this step and the degree of uncertainty already present within the two completed models (steps 1 and 2).

In order to calibrate and evaluate each section of the model, real data are needed for inputs and output in order to determine model accuracy. The third model was to simulate the movement of Hg from emission or atmospheric source to the water column of a specific stream system. Figure 5 shows a simplified structure of the system for the movement of Hg from atmospheric loading to water column, and as such provides a visual guideline for data needs.

Figure 5. STELLA representation of Hg movement from atmospheric loading to stream.



In order to determine the Hg load and loading into the airshed of a basin, data from local emissions is necessary as well as data on background levels of atmospheric Hg concentration in the region. Hg emission estimates are available from the USEPA on the TRI Explorer website. The Toxics Release Inventory (TRI) supplies industry-provided

estimates of Hg stack emissions on an annual basis (USEPA 2011d). However, these are estimates and not measurements but can give a general idea of the quantity of local Hg emissions and show trends over time. The estimates are annual values, while the model is built with a monthly time step in order to simulate seasonal patterns. The majority of Hg stack emissions are from coal-fired electric utilities that may display seasonal patterns of coal use. Measurements of monthly stack emissions would reduce uncertainty to the greatest degree, and beyond that, monthly means of speciated measurements of Hg emissions would reduce uncertainty to the greatest extent. Hg emissions are comprised of gaseous elemental Hg, reactive gaseous Hg, and particulate-bound Hg. The impact of local and regional sources on a watershed varies with the composition of species emitted, with reactive gaseous Hg and particulate-bound Hg with shorter half-lives and a greater tendency to deposit locally or regionally. The composition of species emitted varies with the type of coal and the air pollution control equipment installed at the facility (Strivastava 2010).

In addition to local sources of atmospheric Hg, an idea of global sources is also necessary. Global sources could be determined by subtracting local sources from measurements of ambient air Hg. The Kentucky Division for Air Quality has monitored ambient air Hg at 2 sites in Kentucky (A. Keatley, KDAQ, personal communication, 1/2007). One site was downwind from a coal-fired utility, while the second was designated a control site, and was located away from emission sources. By comparing the two sites, an assumption could be made that the control site represents global sources to the region. With TRI and readily available wind direction data, an estimate of Hg loading

into a defined watershed could be made. However, the uncertainty associated with this estimate would be great.

To simulate deposition of Hg from atmosphere to land, wet and dry deposition rates are needed. Data on wet deposition are available from the Mercury Deposition Network (MDN) (NADP 2011). This national network measures Hg in rain. A limitation of this source is that monitors are sited to be regionally representative of wet deposition, and consequently do not represent sites downwind from emission sources. Because divalent Hg can be a significant portion of emissions and is readily deposited through precipitation, an accurate measure of wet deposition is necessary to understand loading to a basin. A number of factors determine the portion of Hg emissions that is divalent and the fraction can vary widely depending on the utility in question. Without accurate measures of the speciation of stack emissions, basin-level wet deposition monitoring would be needed to reduce uncertainty to a reasonable level. KDAQ had undertaken wet deposition monitoring at several sites, but due to budget constraints has discontinued processing samples at most sites (A. Keatley, personal communication, KDAQ, 6/2008).

Dry deposition stems from the elemental gaseous Hg component of atmospheric Hg and loading in a basin is largely dependent on land cover. Dry deposition data is not generally available. It could, however, be estimated by its relationship with land cover. Forested coverage increases dry deposition due to its increased surface area and the impact of litterfall (Rea et al. 2001, Sheehan et al. 2006). The relationship between forested coverage and deposition could be used to estimate dry deposition rates.

Soil type also influences the movement of Hg from land to waterway. Divalent Hg tends to bind to organic matter, so soils with larger amounts of organic matter would

slow the movement of Hg from land to waterway (Demers et al. 2007). Soil data are available from the Natural Resources Conservation Service (NRCS no date). In addition to soil type, land cover would also have to be factored into the movement of Hg to a waterway. Land cover determines the speed at which overland runoff occurs. Typically, urban areas have greater overland runoff than forested areas as a result of impervious and compacted surfaces. This information, combined with precipitation data, would be the key factor in determining the timeframe for the movement of Hg from soil to waterway. Soil is typically a sink for divalent Hg, so for emission reduction scenarios, this compartment would be a major control point in determining the time it takes from implementation of the new loading scenario to reaching steady state in fish tissue.

Hg in the water column is the input for the bioaccumulation model and therefore is the output for this model, and as such is necessary for calibrating and evaluating this model. Each state or tribe has a different sampling regimen. While THg in the water column data are readily available for the simulated Kentucky basins, water column Hg data for many of the basins in the surrounding region are scarce.

Much of the data necessary to complete this portion of the model have substantial natural variability. Wind speed and direction data are necessary to determine the portion of local emissions that enter the basin airshed. Precipitation data are needed to calculate wet deposition and runoff. The natural variability in weather increases uncertainty in model output. While weather data are available for many years which decreases confidence intervals around monthly means, climate change is modifying weather patterns, reducing confidence that monthly means reflect current patterns. While climate change scenarios are one use of the overall model, the data used to calibrate the model

may not reflect more recent trends than the long term monthly means obtained from weather data.

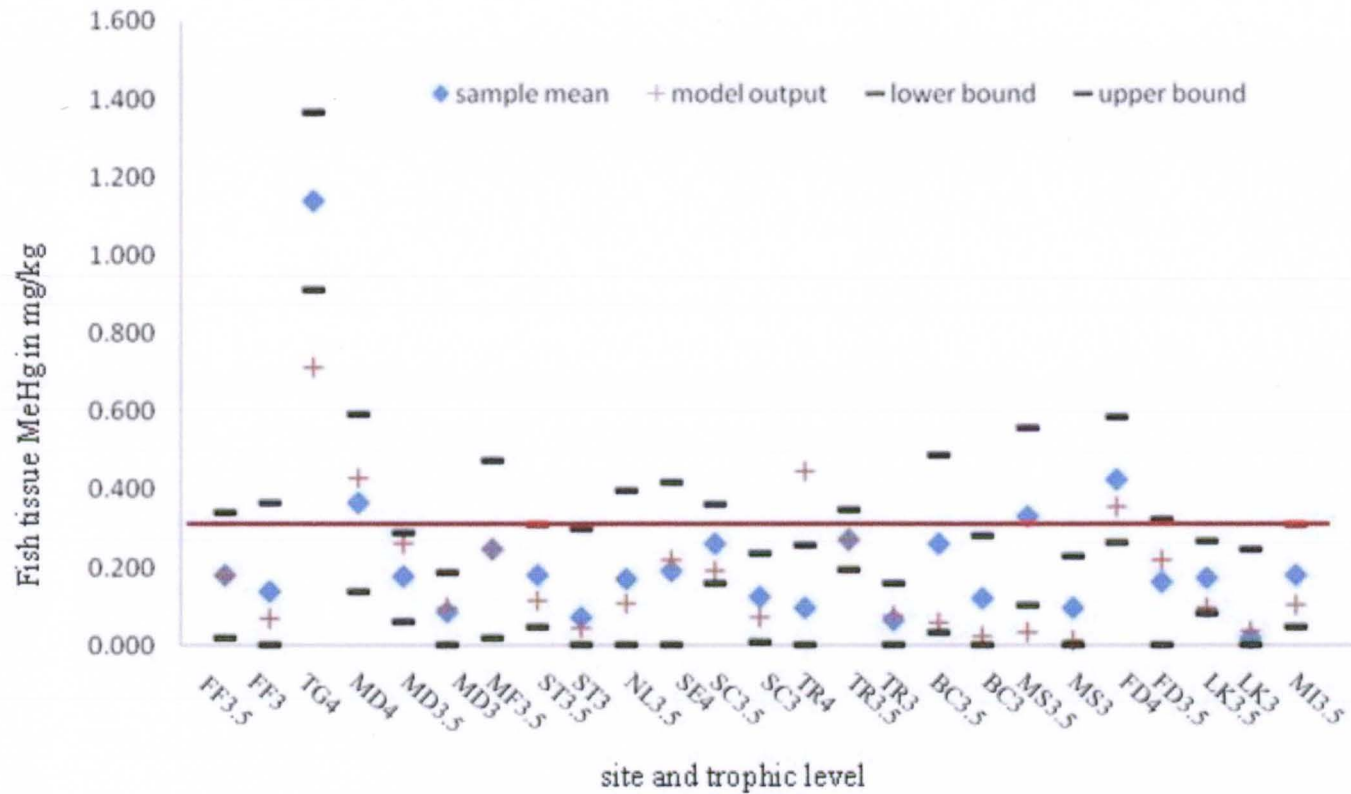
The greatest source of uncertainty for this portion of the model stems from the lack of sufficient emissions and deposition data. The literature supports the concept that nearby sources can contribute to local loading creating Hg hotspots (Hatcher and Filippelli 2011, Volz et al. 2007, White et al. 2009). Without sufficient measurement of loading and deposition, identification of hotspots will be uncertain. An example is the Indiana sites used to evaluate the bioaccumulation model. Fish tissue Hg concentrations were much higher than the model projected. These basins were located downwind from several emission sources. Wet deposition data indicated that Hg in precipitation was much higher in that area of the state than other areas. Studies have linked Hg in wet deposition to bioaccumulation in fish (Gorski et al. 2008, Hammerschmidt and Fitzgerald 2006, Orihel et al. 2007). To accurately project loading from atmosphere into waterways, wet deposition data is essential at the basin level.

If the atmospheric model were developed, the uncertainty in the output of this model would amplify the uncertainty already associated with the bioaccumulation and human disposition models. The uncertainty associated with these portions of the Hg problem is already significant. Figure 6 shows the 95% confidence interval around the sample mean. This confidence interval represents the natural variability found in fish tissue samples from the National Fish Tissue database (USGS et al. 2006). The graph shows that the uncertainty associated with fish tissue samples is often larger than the USEPA fish tissue criterion. Adding the considerable uncertainty associated with the

atmospheric model would push the level of uncertainty to the point that model output would be meaningless.

While certain portions of the system could be adequately represented, the lack of data for Hg emissions and wet deposition combined with the natural variability inherent in environmental systems makes completing the system by adding the atmospheric and terrestrial compartments untenable. The output of this step would be the loading of IHg into the water column, which is the input to the bioaccumulation model. The uncertainty found in the bioaccumulation and population biomarker models would be amplified to an unacceptable degree if this component was added to the system.

Figure 6. Uncertainty around the sample mean of fish tissue Hg for site and trophic level combinations. The 95% confidence interval is based on an analysis of the National Fish Database. For site abbreviations, see Table 6.



CHAPTER IV

RESULTS

Calibration and Evaluation

Population Biomarkers

The model was calibrated to literature sources to maximize biomarker accuracy. The relationship between ingestion of MeHg and blood MeHg level was calibrated according to Sherlock et al. (1984). Instead of estimating dose, this study measured fish intake with known MeHg levels over a period of time to relate ingestion to blood MeHg levels at steady state. The results found a steady state blood MeHg concentration of 0.8 $\mu\text{g/L}$ for every 1 $\mu\text{g/day}$ ingested. Because children weigh less than adults, this figure is unlikely to hold true for the modeled populations of children. No literature source was found that related ingestion to steady state MeHg concentrations in children, so the assumption was made that disposition between blood, hair, and tissue in children was the same as in adults, and the ratio was derived from model output. The ratio for children was found to be 1.3 $\mu\text{g/L}$ for every 1 $\mu\text{g/day}$ ingested.

The ratio between hair Hg and blood MeHg shows a greater degree of variation between individuals than other biomarkers (Budtz-Jorgensen et al. 2004, Cernichiari et al. 2007, Phelps et al. 1980). A ratio of 250 ug/kg total hair Hg to 1 ug/L blood MeHg, which is the most commonly used ratio in epidemiology studies (Clarkson et al. 2007), was selected for use in this model.

Stern and Smith (2003) did a meta-analysis of studies measuring the relationship between maternal and cord blood. Their analysis reported ratios from studies that looked at MeHg only, THg only, and combined both MeHg and THg studies. They reported that studies measuring MeHg only produced a higher ratio (mean ratio of 1.9) than the meta-analysis that combined both MeHg and THg (mean ratio of 1.7). They recommended the ratio from all studies combined be used because of uncertainty in the source of IHg and the small difference it produced in ratios. This model was calibrated with the ratio from the MeHg only analyses (1.9). The model structure shows movement of MeHg from maternal blood to the fetal blood compartment, with no inflow of IHg. While IHg does cross the placenta, it does not concentrate in fetal blood like MeHg. Vahter et al. (2000) reported a mean ratio of 0.9 for the relationship of cord blood to maternal blood IHg. Because maternal blood volume is greater than fetal blood volume, the inclusion of IHg in the measurements to determine the ratio between fetal and maternal blood levels lowers this ratio. MeHg is thought to be more toxic to the fetus and crosses the placental barrier with greater ease than IHg. Use of the higher ratio for decision making is more protective of the fetus.

Consistency of model output was examined across the distribution of intake rates for all biomarkers. Chi-squared analyses were conducted using PASW Statistics 18, comparing the expected values from literature sources to the observed model output. In addition, scatterplots were generated for a visual assessment of the comparisons.

Table 3 shows the outcomes from the distribution of ingestion rates from various populations. Model output is similar for all biomarkers to values predicted from literature sources. Table 4 shows the p-values from chi-squared analyses. There were no significant

differences between model output and the literature values (all p-values > 0.05).

Scatterplots of predicted versus observed values demonstrate that, while not significantly different, the model appears to slightly overestimate biomarker concentrations at the highest ingestion rates (Figure 7A-C).

For evaluation, the model's projections were compared to additional literature sources to further strengthen confidence in the output. Table 5 lists the literature sources that were used to evaluate the relationships between ingestion and blood MeHg, blood MeHg and total hair Hg, and maternal and fetal blood MeHg concentrations. Scatterplots were generated to visually assess if model output differed from these sources. In addition, the mean and 95% confidence interval of the slopes of the literature sources for each biomarker were compared to the slope of model output (Figure 8A-C).

For the literature values that measure the relationship between intake and steady state blood concentrations of MeHg, values were generated from the equations taken from the seven literature sources listed in Table 3 from the WHO (1976) and Kershaw et al. (1980). A range of intake rates were selected (25, 50, 75, and 100 ug/d) and entered into the regression equation from each literature source to generate steady state blood concentrations. For comparison to ingestion rates from the model, the daily intake rates were converted to monthly rates and new regression equations were determined.

Table 3. Model outcome compared to predicted outcome for the distribution of ingestion rates for various populations.

Population		Blood concentration ug/L				Hair concentration ug/kg				Fetal blood concentration ug/L			
		mean	90	95	99	mean	90	95	99	mean	90	95	99
General	predicted	1.3	3	7.7	19.8	325	750	1925	4950	2.5	5.7	14.6	37.6
	model output	1.2	3.2	8.2	21	300	804	2053	5262	2.3	6.1	15.5	39.8
Consumers	predicted	16.3	41	53.9	90	4075	10250	13475	22500	31	77.9	102.4	171
	model output	17.3	43.6	57.3	95.6	4337	10895	14339	23901	32.5	82.5	108.5	180.9
Women (15-44)	predicted	1	2.6	6.9	17	250	650	1725	4250	1.9	4.9	13.1	32.3
	model output	1.1	2.8	7.3	18.1	274	695	1836	4520	2.1	5.3	13.9	34.2
Women (15-44) consumers	predicted	14.7	35.7	44.6	87.3	3675	8925	11150	21825	27.9	67.8	84.7	165.9
	model output	15.7	38	47.4	92.8	3916	9490	11857	23191	29.6	71.8	89.6	175.3
Children (0-14)*	predicted	0.7	0.5	5	14.7	175	125	1250	3675				
	model output	0.7	0.5	5.4	15.7	170	116	1241	3644				
Children (0-14) consumers*	predicted	16.4	39	49	77.2	4100	9750	12250	19300				
	model output	17.6	41.8	52.5	82.8	4082	9683	12166	19169				
Anglers 1	predicted	1.8	4.9	5.9	19.7	450	1225	1475	4925	3.4	9.3	11.2	37.4
	model output	1.9	5.3	6.3	21	472	1313	1569	5242	3.6	9.9	11.9	39.6
Anglers 2	predicted	1.2	3.2	4.3	9.5	300	800	1075	2375	2.3	6.1	8.2	18.1
	model output	1.2	3.4	4.6	10.2	312	842	1141	2537	2.4	6.4	8.6	19.2
Subsistence Fishers 1	predicted	12.8	48.7	52	57.6	3200	12175	13000	14400	24.3	92.5	98.8	109.4
	model output	13.6	51.8	55.3	61.2	3399	12949	13823	15309	25.7	98	104.6	115.8
Subsistence Fishers 2	predicted	14.1	26.4	40.8	93.4	3525	6600	10200	23350	26.8	50.2	77.5	177.5
	model output	15	28.1	43.4	99.2	3744	7016	10842	24811	28.2	53	82	187.6

Fish tissue concentration for all samples was 0.3 mg/kg. Predicted values for blood concentration are based on Sherlock et al. (1984).

Predicted hair concentrations were calculated based on Clarkson (2007). Predicted fetal blood concentrations were based on Stern and Smith (2003).

*Blood concentrations for the populations of children was not taken from Sherlock because his work was based on an adult body weight. The predicted values were back-calculated from the model, with the assumption that disposition in children is the same as disposition in adults.

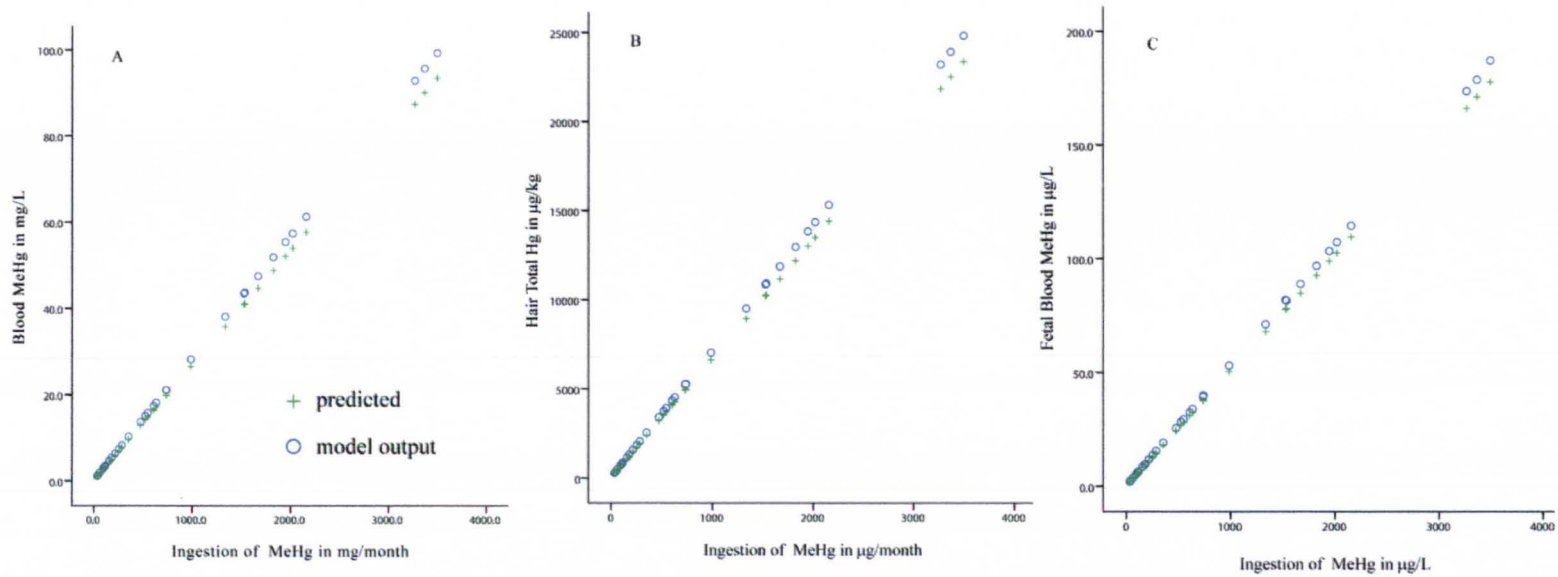


Figure 7. Comparison of model output to predicted values based on calibration sources for each biomarker of interest. Predicted values were generated from defined intake rates for each population and based on a MeHg fish tissue concentration of $300 \mu\text{g}/\text{kg}$. The comparison show the relationship between ingestion and (A) blood MeHg, (B) total hair Hg, and (C) fetal blood MeHg.

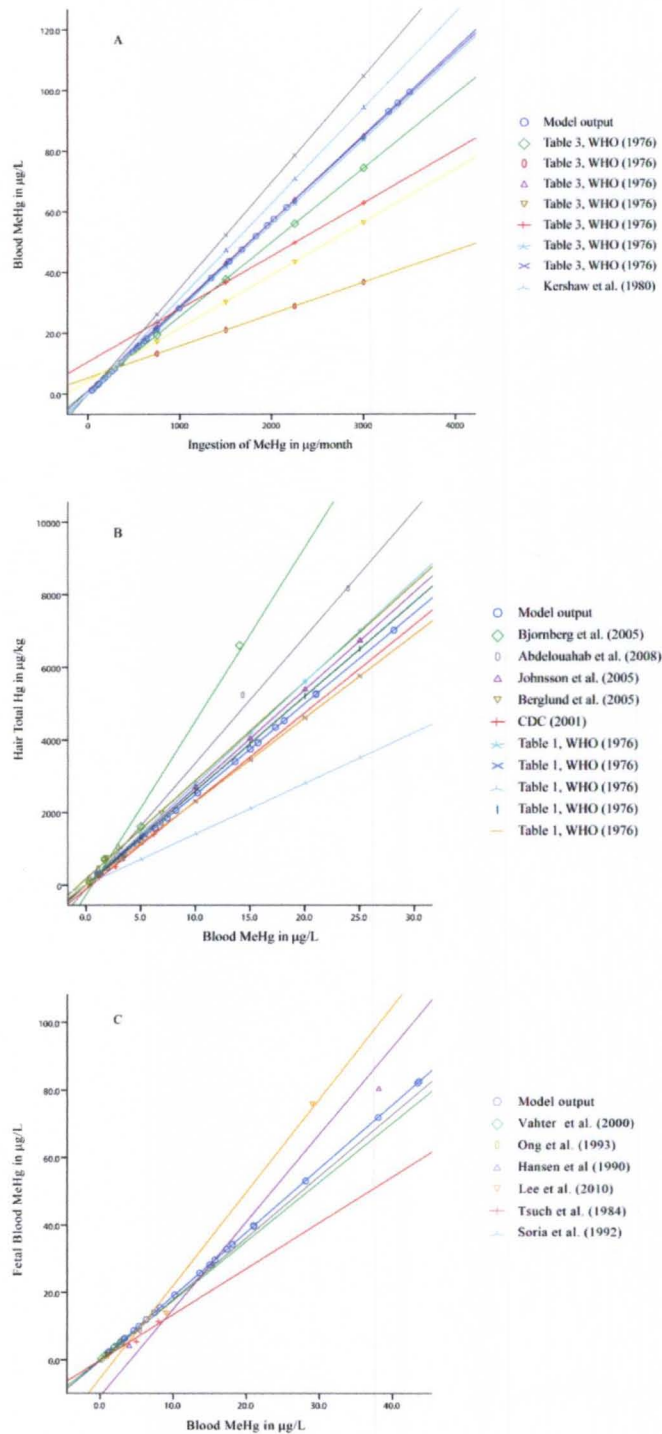


Figure 8. The model was evaluated by comparing output to literature sources for each biomarker for a range of exposures. The relationships shown are between (A) ingestion and blood MeHg, (B) blood MeHg and total hair Hg, and (C) blood MeHg and fetal blood MeHg.

Table 4. Chi-squared analysis p-values of predicted versus observed model output.

Ingestion rate	Blood	Hair	Fetal Blood
mean	0.500	0.456	0.450
90	0.524	0.395	0.450
95	0.395	0.395	0.382
99	0.395	0.395	0.382

Table 5. Literature sources for evaluation.

Literature Source	Ingestion/ Blood MeHg	Blood MeHg/ Hair THg	Blood MeHg/ Fetal Blood MeHg
as cited in Table 3 of WHO (1976)	X		
Kershaw et al. (1980)	X		
Abdelhouahab,et al. (2008)		X	
Bjornberg et al. (2005b)		X	
as cited in Table 1 of WHO (1976)		X	
Vahter et al. (2000)			X
Tsuchiya et al. (1984)			X
Ong et al. (1993)			X
Hansen et al. (1990)			X

For evaluation of the relationship between maternal and fetal blood, the summary statistics reported from five literature sources were used as data points to generate regression equations. These summary statistics included the mean for all studies and the range or the 95% confidence interval. In addition, some studies also reported the median or a range of percentiles. The slope of the regression for each literature source was then determined.

The relationship between blood MeHg and hair THg was evaluated by comparing the slope of model output to the slopes of nine literature sources that studied 11 populations. Summary statistics were used to generate a regression equation for five

literature sources. For the remaining six sources, regression equations were reported and a range of blood MeHg concentrations were input into the equations to generate hair concentrations for the scatterplot. The regression equations for five of these sources were reported in Table 1 from the WHO (1976).

Figure 8A compares the model output to eight literature sources for the relationship between ingestion and blood Hg levels. The mean and 95% confidence interval of the slope for the literature values was 0.024 (0.008-0.040). The slope for model output was 0.028. The slope of model output was not different from literature values.

The relationship between blood MeHg and total hair Hg concentrations for model output and the results of 9 literature sources that reported on 11 populations is shown in Figure 8B. Model output falls within the range of measurements found in the literature. The mean of the slopes for the literature values was 283 with a 95% confidence interval of 235 to 331. The slope of model output, 250, falls within that range, reflecting no difference between model output and literature sources.

The relationship between maternal and fetal blood MeHg for five literature sources and model output is shown in Figure 8C. The slopes of literature sources had a mean and 95% confidence interval of 2.06 (1.49-2.62). The slope of model output was 1.89 and falls within the range of literature sources.

Bioaccumulation

Seven watersheds in Kentucky were chosen to calibrate the model. Seven basins from outside of Kentucky were chosen to evaluate the model and to determine the limits

of model application. All basins were selected based on the availability of fish tissue and water quality data. Evaluation basins were further limited to sites with similarities to calibration sites in basin area and wetlands coverage. Locations of calibration and evaluation watersheds are shown in Figure 9, with general site characteristics given in Table 6. More detailed maps showing land cover for calibration and evaluation basins can be found in Appendix C. The Floyds Fork basin, at 70 km², was substantially smaller than the other calibration watersheds, which had areas between 399 and 930 km². Evaluation basins similarly had one smaller basin, Spring Creek in Georgia with an area of 98 km². The range of the remaining basins was 220 to 1440 km².

Natural variability in environmental systems is considerable. Examination of fish tissue data showed considerable variability with samples of the same species from the same site. In order to compare model output to trophic level means for a particular site, an understanding of the natural variability inherent within stream systems was necessary. The National Fish Database contains over 100,000 records of Hg in fish tissue from various sources compiled by the USGS (USGS and NIEHS 2006). This database was analyzed to quantify the natural variability found between fish of the same species of similar size from the same site and collection year. Many of these samples were composites of similarly sized fish of the same species. The dataset was analyzed by selecting for the most commonly sampled species that fit within the range of 0.75 and 1.25 times the quality length for that species. Selections were further grouped and limited to samples that had six or more of the same species from the same site and collected the same year. This resulted in 1010 groups. The standard deviation was determined for each of these

Table 6. Site characteristics.

Site	Site Abbr	Area sq km	Mean annual Q m ³ /s	Mean pH	Mean P mg/l	fraction forested	fraction developed	fraction wetlands	Sinuosity
Calibration Sites ^a									
Floyds Fork	FF	70	1.0	7.79	0.1920	0.359	0.375	0.006	1.81
Mayfield Creek	MF	759	12.2	6.96	0.1972	0.234	0.064	0.042	1.00
Mud River	MD	689	11.1	7.37	0.0607	0.497	0.059	0.007	2.00
Nolin	NL	930	14.1	7.46	0.2139	0.246	0.093	0.000	1.59
Salt River	ST	451	7.2	8.03	0.2889	0.244	0.088	0.000	2.13
Slate Creek	SE	399	5.7	7.85	0.1005	0.343	0.027	0.000	1.44
Tygarts Creek	TG	720	8.8	7.63	0.0193	0.688	0.078	0.000	1.60
Evaluation Sites									
∞ Big Creek, IN	BC	220	2.1	8.06	0.0704	0.099	0.092	0.000	1.48
Little Kanawha River, WV	LK	1448	17.0	7.32	0.2085	0.857	0.051	0.000	1.40
Middle Island Creek, WV	MI	1282	16.1	7.36	0.2085	0.877	0.046	0.000	1.25
Muscatatuck River, IN	MS	733	8.0	8.05	0.1506	0.471	0.050	0.000	1.19
N. Fork Forked Deer River, TN	FD	448	5.2	6.85	0.2141	0.162	0.077	0.095	1.06
Spring Creek, GA	SC	98	1.4	8.07	0.0796	0.477	0.072	0.005	1.21
Talking Rock Creek, GA	TR	738	8.1	7.83	0.0441	0.796	0.064	0.003	1.25

Abbr = abbreviations, Q = discharge, P = Phosphorus

^aAll calibration sites are in Kentucky

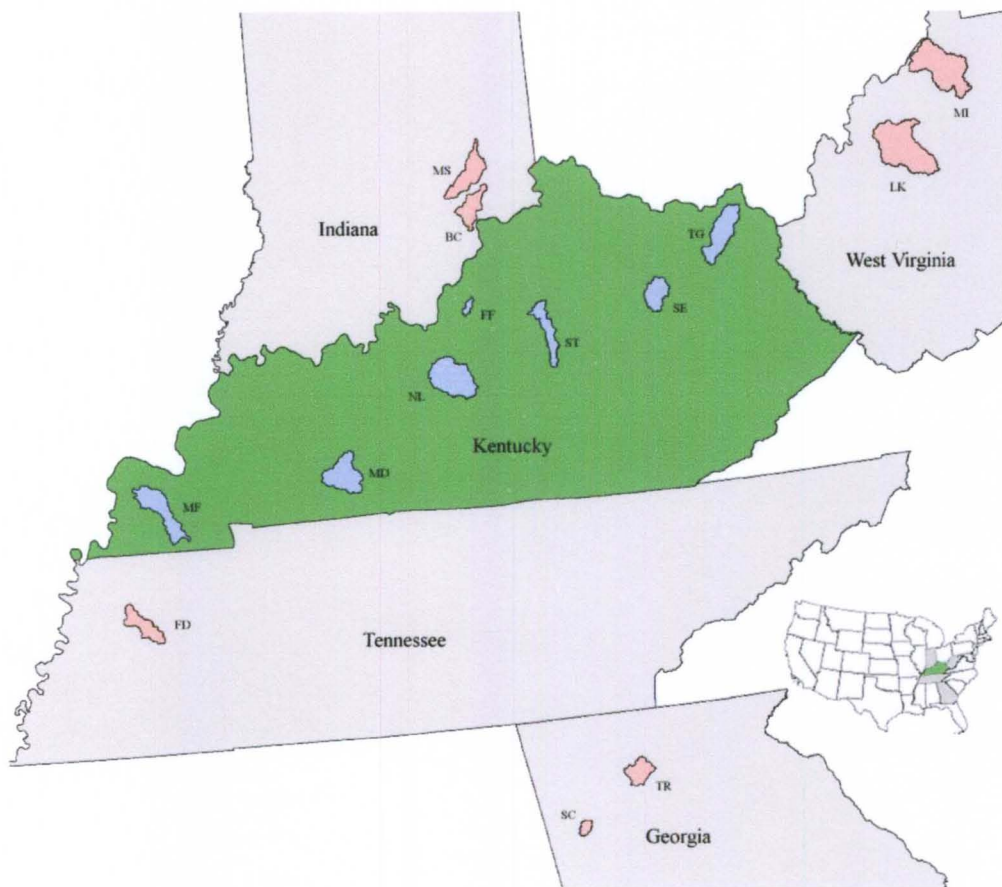


Figure 9. Map of calibration and evaluation basins. Sites in the green state are calibration basins, while sites in the gray states are evaluation basins. See Table 6 for abbreviations of site names.

groups, and the mean of these standard deviations was found to be 0.116. This mean was used to calculate a 95% confidence interval (CI) around the fish tissue means for calibration and evaluation sites. If the calculated lower bound of the confidence interval was negative, this lower bound was set to 0.

Fit was evaluated by two methods; by calculating prediction error and comparing model output to the 95% CI. Sample means, the bounds of the 95% CI, and prediction error are shown in Table 7. Mean error for calibration sites was 26% and 51% for

evaluation sites. The model projection fell within the 95% CI for all but one of the 23 trophic level-site combinations. The site that was outside of these bounds was the Muscatatuck River in Indiana. The model projection was much lower than the sample mean. Error for the two Indiana sites and TL3 of the Little Kanawha River in West Virginia was more than twice that of other evaluation sites. The model projection was much lower than the actual samples for all four trophic level-site combinations in Indiana, but higher for TL3 of the Little Kanawha River. Without these three sites, the mean error for the remaining evaluation sites was 26%. Mean error was lowest for TL4 and highest for TL3 (Table 8).

Land cover varied between basins. Forested coverage varied widely while wetlands coverage was minimal to non-existent for all but two basins. With one exception, most basins were in rural areas with little development. Regression analyses of land cover fractions compared to error were undertaken to evaluate if the model performed more accurately based on land cover attributes. No difference was found for model accuracy based on land cover (data not shown).

To test the robustness of the model a sensitivity analysis was performed. For sensitivity to Hg loading, both total and dissolved Hg were manipulated for three systems with a range of land cover uses. Figure 10 shows the response of fish tissue to percent reductions in both total and dissolved Hg for Tygarts Creek, the Mud River, and Mayfield Creek. Reductions in THg showed a threshold effect in fish tissue levels, while reductions in dissolved Hg were linear.

Table 7. Fish tissue Hg (mg/kg) of sample mean with 95% confidence interval compared to model output and calculated prediction error.

Site	TL	sample	Error calculation		model	error
			lower	upper		
95% CI						
Calibration sites						
FF	3.5	0.179	0.018	0.340	0.177	0.01
FF	3	0.138	0.000	0.365	0.068	0.51
MD	4	0.366	0.139	0.593	0.430	0.17
MD	3.5	0.176	0.062	0.290	0.260	0.48
MD	3	0.085	0.000	0.186	0.096	0.13
MF	3.5	0.247	0.020	0.474	0.248	0.00
ST	3.5	0.179	0.048	0.310	0.114	0.36
ST	3	0.073	0.000	0.300	0.045	0.38
NL	3.5	0.170	0.000	0.397	0.106	0.38
SE	4	0.190	0.000	0.417	0.217	0.14
MEAN						0.26
Evaluation sites						
SC	3.5	0.262	0.160	0.364	0.191	0.27
SC	3	0.123	0.009	0.237	0.071	0.42
TR	3.5	0.271	0.195	0.347	0.268	0.01
TR	3	0.065	0.000	0.158	0.076	0.17
BC	3.5	0.260	0.033	0.487	0.057	0.78
BC	3	0.120	0.000	0.281	0.022	0.82
MS	3.5	0.330	0.103	0.557	0.033	0.90
MS	3	0.097	0.000	0.228	0.012	0.88
FD	4	0.426	0.265	0.587	0.355	0.17
FD	3.5	0.162	0.001	0.323	0.217	0.34
LK	3.5	0.174	0.081	0.267	0.096	0.45
LK	3	0.018	0.000	0.245	0.035	0.94
MI	3.5	0.179	0.048	0.310	0.103	0.42
MEAN						0.51

Table 8. Prediction error by trophic level.

	Trophic Level		
	3	3.5	4
Calibration sites	0.34	0.25	0.16
Evaluation sites	0.65	0.38	0.17

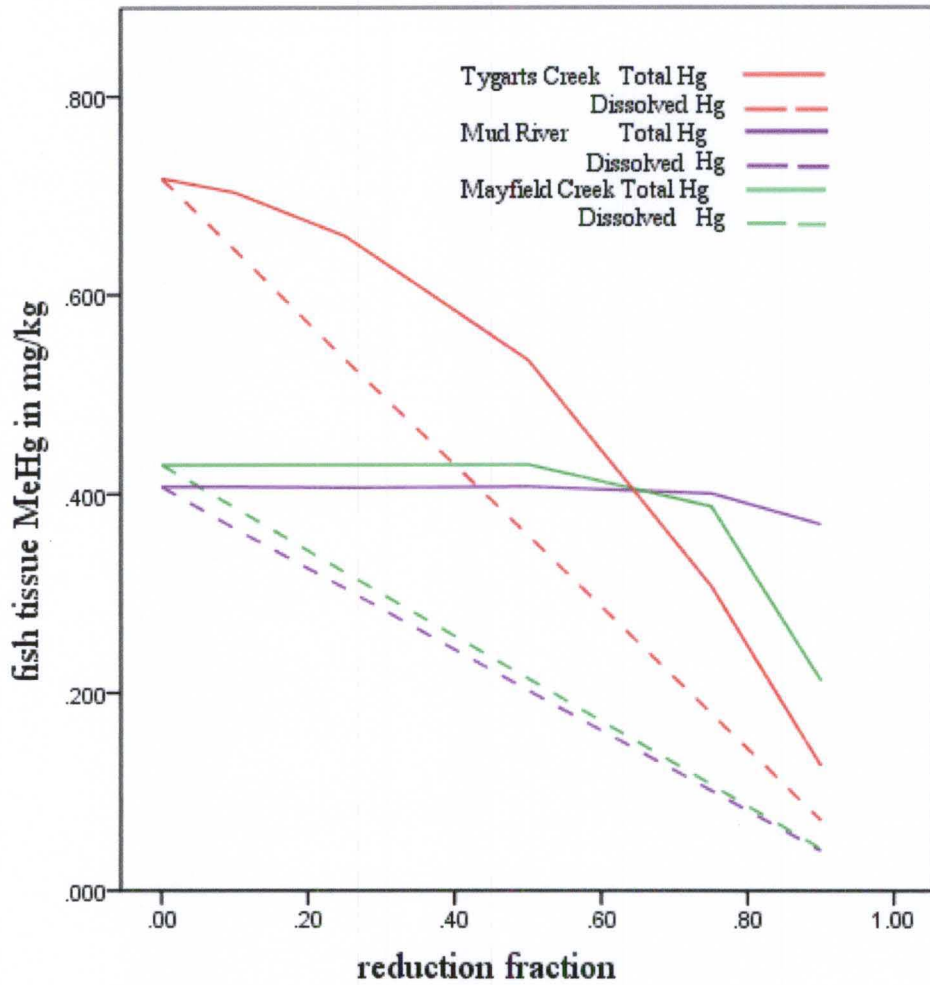


Figure 10. Sensitivity of model output to reductions in total and dissolved Hg for three basins representing a range of land cover characteristics.

The sensitivity of the model to other input variables was tested by assessing the impact of manipulating these variables one at a time within a plausible natural range for one of the modeled systems. The Mud River site was chosen for the sensitivity analysis because of ample water quality and fish tissue data and land cover and water quality parameters that were average compared to the other systems. Parameters that were manipulated included the nutrient level, pH, sinuosity, water temperature, and the fractions of land cover that were forested, wetlands, or developed. Model output in

response to these changes is shown in the Table 9. When phosphorus levels were increased by 300%, model output decreased by 10%, but when levels were halved, model output increased by more than 50%. Similarly, when the fraction of land cover that was forested was halved, a 5% change in output was realized, but when it was doubled, the model projected fish tissue levels more than 100% greater. An increase of wetlands coverage to 35% resulted in a fish tissue increase of more than 300%. Alternatively, manipulating the water temperature, pH, and the fraction of the watershed that was developed resulted in changes in output of less than 10%. Modifying sinuosity resulted in an output change of less than 15%.

Table 9. Sensitivity analysis. Manipulation of variables for the Mud River system. Output is fish tissue Hg in mg/kg.

TL	Initial	nutrient level		fraction forested		fraction wetlands		pH		sinuosity	water temperature	
		X 3	X 0.5	X 0.5	X 2	X 3	Δ to 0.35	-2.0	+1.0	Δ to 1.0	+ 1 ^o C	+ 3 ^o C
4	0.446	0.399	0.797	0.424	0.910	0.449	1.880	0.451	0.438	0.386	0.438	0.426
3.5	0.246	0.223	0.436	0.235	0.500	0.248	1.040	0.249	0.243	0.214	0.243	0.236
3	0.051	0.047	0.080	0.049	0.088	0.051	0.215	0.051	0.050	0.044	0.050	0.048

TL – trophic level

“Initial” indicates model output before variable manipulation.

Policy and Climate Change Analyses

Fish Consumption Advisories and Population Choices

Figure 11 illustrates the blood MeHg biomarker for the intake rates of the mean, 90th, 95th, and 99th percentile of each population in response to a range of fish tissue Hg levels. Comparing the biomarker across populations, it is apparent that the angler populations had the lowest exposure levels, and the children and women consumers had the highest exposures, illustrating the importance of the population chosen to determine if populations are adequately protected. In addition to the general level of exposure, each population had a unique pattern of blood MeHg concentrations. For the anglers 1 and 2 and children consumers populations, the pattern shows the 99th percentile intake rate had a much higher blood MeHg concentration than the mean, 90th and 95th percentiles. Conversely, for the women consumers and subsistence fishers 2 populations, the blood MeHg levels were fairly evenly spaced between each distribution rate. For the subsistence fishers 1 population, the 90th, 95th, and 99th percentile intake rates had very similar blood MeHg levels, well above the mean. While the response pattern of each population was unique in the distribution of blood MeHg biomarker, for a given population, this pattern was the same for total hair Hg and fetal blood Hg biomarkers (data not shown).

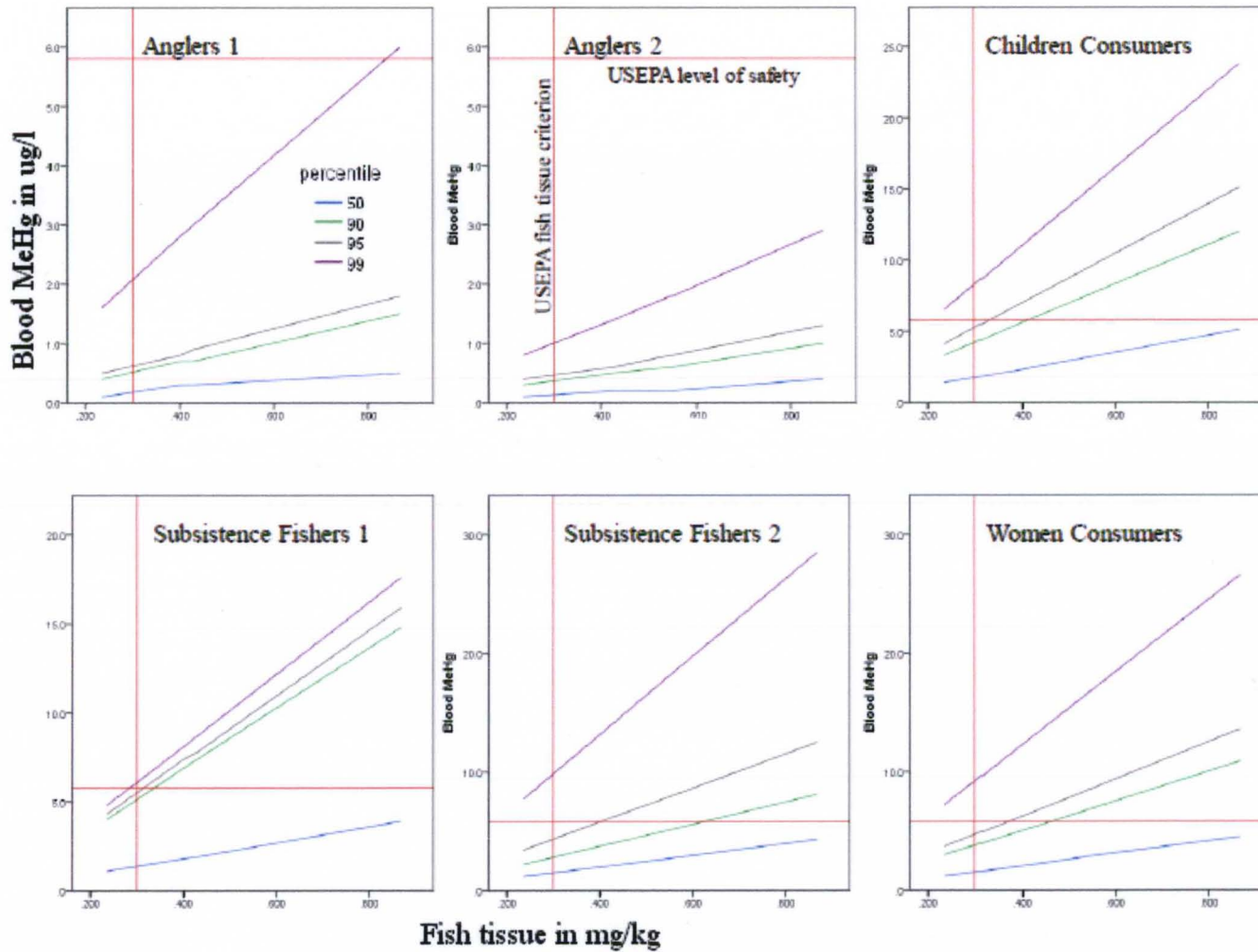


Figure 11. Response of the blood MeHg biomarker to changes in fish tissue concentration for susceptible populations.

In addition to identifying the population most at risk from a particular water body, agencies must also choose a level of action. Commonly, the central tendency, 90th or 95th percentile of intake rates is selected (Shilling et al. 2010). Figure 11 includes both the USEPA level of safety for MeHg in blood (5.8 ug/l) (USEPA 2010a) and the USEPA criterion for MeHg in fish tissue (0.300 mg/kg) (USEPA 2011e). The figures illustrate that 95% of all the simulated populations are protected when fish tissue concentrations of MeHg are below the USEPA criterion of 0.300 mg/kg. However, as evidenced by the number of fish consumption advisories, many stream systems exceed this level. In this model simulation, the 95th percentile of the subsistence and consumer populations exceeded the USEPA level of safety for MeHg in blood at levels just above the USEPA fish tissue criterion. Thus, while the criterion is protective for these populations, the margin of error is small. For the Subsistence Fishers 1 population, the 90th, 95th, and 99th percentile intake rates are very similar. While only the 99th percentile exceeds the level of safety for blood MeHg at intake concentrations at the USEPA criterion, the 90th and 95th percentile exceed the level of safety at fish tissue concentrations just above the criterion. Compared to the Women Consumers population, a fish tissue concentration of 0.360 mg/kg is required for the 95th percentile to exceed the level of safety, while a concentration of 0.460 is required for the 90th percentile to exceed the safety level. Clearly, the choice of population and the portion of the population to be protected are both critical decisions in determining the action level for setting fish consumption advisories.

Emissions Reductions

Figure 12 shows the response of the Subsistence Fishers 1 population to reductions in THg for three stream systems. For all three stream systems, the portion of the population that consumes fish at or below the mean intake rate for that population remains below the level established as protective of the developing fetus by the USEPA. However, as the concentration of Hg is decreased, the portion of the population that is protected is dependent on the stream system being simulated. Ninety-nine percent of the population is protected with a Hg concentration in water of 0.5 ng/l for the Mud River, but that level of reduction only affords protection for 90% of the population fishing from Mayfield Creek, and does less than that for Tygarts Creek. For Mayfield and Tygarts Creeks, a Hg concentration of 0.3 ng/L would be needed to protect 99% of the Subsistence Fisher 1 population. Even though these 2 systems offer the same degree of protection at this level, the reduction in blood MeHg is much greater in Tygarts Creek than Mayfield Creek for a reduction from 1 ng/l to 0.3 ng/l of THg in the water column.

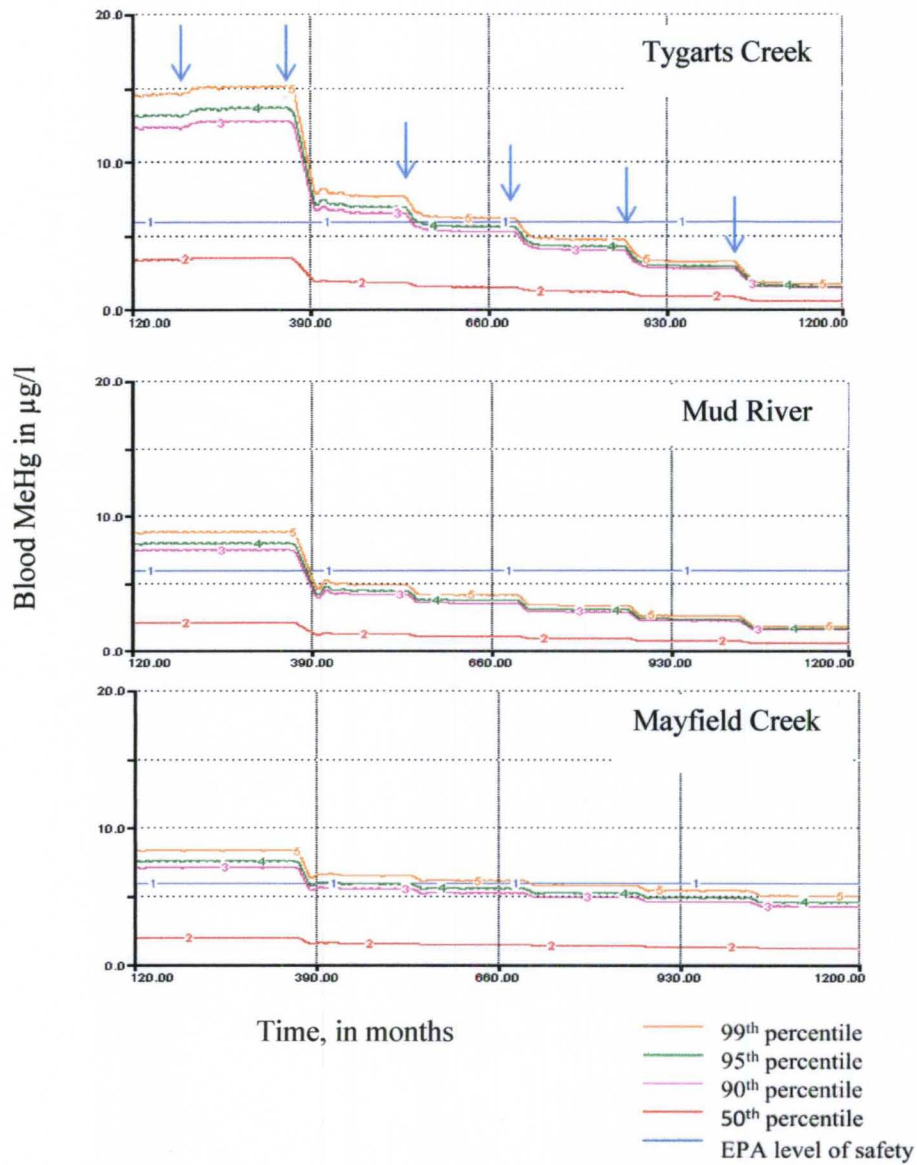


Figure 12. Impact of reduction in THg on blood MeHg biomarker for the Subsistence Fisher 1 population. Arrows reflect changes in THg in water concentration from measured mean monthly THg, to 1.0, 0.5, 0.4, 0.3, 0.2, 0.1 ng/l.

Watershed Management Strategies

Figure 13 shows the response in population biomarkers to modification of sensitive watershed parameters. The degree of change in fish tissue Hg and subsequent population exposure resulting from changes in watershed variables depend on the modeled basin and the variable being modified. Whether this change in a watershed parameter has substantial impacts on population biomarkers also depends on the population being simulated.

The previous analysis of the bioaccumulation model found that the system was sensitive to perturbations in three watershed variables: nutrient loads and the fraction of the watershed that was forested or in wetlands. When nutrient levels were set at a minimal level (Figure 13A), population Hg biomarkers increased substantially for 4 of the 6 populations in the Mayfield Creek and Mud River basins while all blood MeHg levels remained relatively unchanged for Tygarts Creek. Nutrient levels were highest in Mayfield Creek (mean annual P of 0.1972 mg/l), average in the Mud River (mean annual P of 0.0607 mg/l), and low in Tygarts Creek (mean annual P of 0.0193 mg/l). As expected, the deviation in nutrient levels imposed by the user for Tygarts Creek caused no change because this system already had low nutrient levels. Surprisingly, the magnitude of response for both Mayfield Creek and the Mud River were similar even though the default levels of phosphorus differed by a factor of 3. Setting a high level of phosphorus reduced population biomarkers for 4 of the 6 populations in Tygarts Creek, but elicited little change in any populations in Mayfield Creek or the Mud River over the default level. These responses suggest a threshold range of phosphorus over which higher

levels will not decrease fish tissue further and lower levels of the nutrient will not result in further increases in fish tissue. Within this range, nutrient levels impact the efficiency of bioaccumulation. When assessing a stream system, regulators can use this information to determine if changes in fertilizer use in the basin will modify bioaccumulation efficiency.

No response in population biomarkers was found for Mayfield Creek when the fraction of the basin that was forested was set to a low fraction (Figure 13B). This reflects the existing low forested coverage in the basin. When the fraction that was forested was increased, 4 populations had a greater than 200% increase in blood MeHg. The Anglers 1 and 2 populations increased to a lesser degree than the other populations. The Mud River showed a minimal response to a reduction in forested coverage for 4 populations, but a substantial increase in blood MeHg for those same populations when the fraction of forested coverage was high. Tygarts Creek showed a greater response to a low forested coverage level for 4 populations, while no response was found for a higher fraction of forested coverage. Forested coverage increases bioaccumulation efficiency, substantially increasing exposure for populations with high consumption rates.

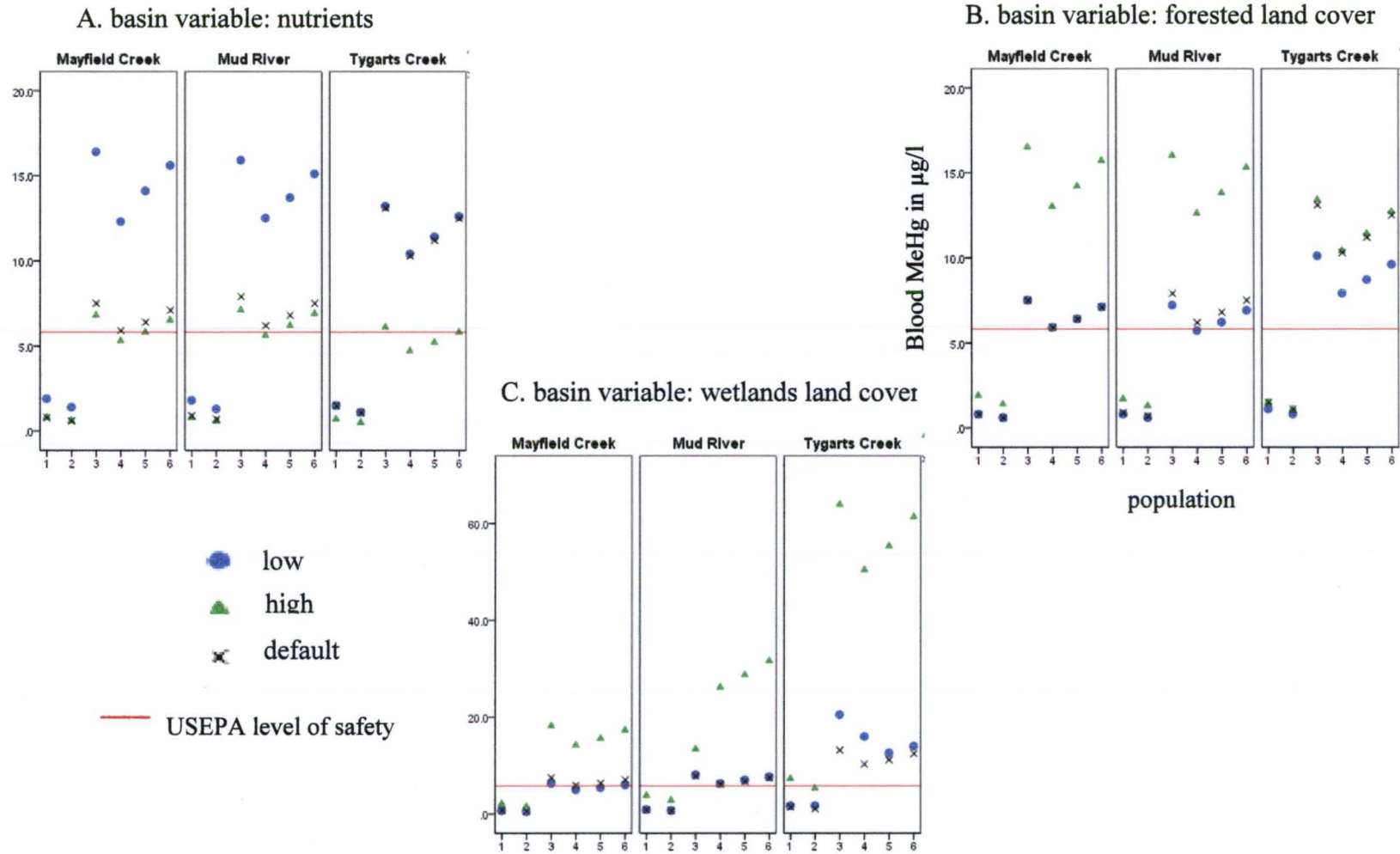


Figure 13. Impact of changes in sensitive basin parameters on populations. X-axis: population: 1=anglers 1, 2=anglers 2, 3=subsistence fishers 1, 4=subsistence fishers 2, 5=children consumers, 5=women consumers

Manipulating wetlands coverage from low to high values showed a similar pattern (Figure 13C). Mayfield Creek, which had the highest wetlands coverage of the three streams at 4%, showed little change in blood MeHg when lowering coverage to 1%, but a strong response of increased blood MeHg when wetlands coverage was raised to 35% for 4 of the populations. Population blood MeHg responded similarly for the Mud River, although a slightly larger response was seen in the Anglers 1 and 2 populations for high wetlands coverage. Biomarker response was greatest for Tygarts Creek which has no wetlands coverage. Setting wetlands coverage to the low level resulted in a slight increase in blood MeHg for 4 populations, and the high wetlands coverage setting showed substantial increases in all population biomarker levels. The presence of wetlands in a basin increases exposure to susceptible populations.

Climate Change Scenarios

Table 10 shows the outcome of climate change on TL4 fish tissue. Water temperature had little effect on bioaccumulation efficiency in these streams. Increasing the frequency of high precipitation events, as defined by the number of events greater than 0.5 inches, resulted in substantial reductions in fish tissue Hg for the three simulated stream systems. The combination of increased water temperature and high precipitation also resulted in reductions in fish tissue Hg, reflecting the stronger effects of intense precipitation events.

Table 10. Climate change scenarios. TL4 fish tissue in mg/kg.

Parameter	Parameter change	Mayfield Creek	Mud River	Tygarts Creek
	none	0.406	0.427	0.717
water temperature (°C)	+1	0.407	0.428	0.715
	+2	0.407	0.431	0.717
	+3	0.407	0.432	0.720
frequency of high precip	+0.5	0.379	0.405	0.675
	+1	0.354	0.380	0.632
	+1.5	0.328	0.357	0.591
combined analysis water temp (°C)/high precip	+1/+0.5	0.380	0.406	0.671
	+2/+1	0.355	0.383	0.634
	+3/+1.5	0.329	0.364	0.594

CHAPTER V

DISCUSSION

The purpose of the project was to design a model to evaluate the problem of human exposure to Hg from consumption of fish from local waterways. This model could assist decision-makers in the process of determining regulations or management strategies to protect populations of interest from excess Hg exposure. The model has two components. The human disposition model projects exposures to various populations based on fish tissue concentrations that are input by the user. The bioaccumulation model projects fish tissue Hg levels in defined basins. While models are available that focus on different aspects of this problem, combining the bioaccumulation and human disposition components facilitates the decision making process by directly connecting environmental contamination to the exposure of susceptible populations.

In the development of any model, a balance is sought between generating an accurate forecast with the simplest representation of the system, while being transparent. Transparency refers to a clear understanding of the model by both peer reviewers and the actual users of the model. Simplicity calls for breaking a system down to its most basic components so that it is easier to understand. Enough details of the system must be included for the model to be accurate for a variety of scenarios. The balance between simplicity and enough details can be difficult to judge. The ideal balance for these three competing goals depends on the purpose of the model (NRC 2007). Because the purpose

of this model is to be a tool for regulatory decision-makers who may need to explain policy or management recommendations to lawmakers or stakeholders with limited scientific background, the goal is to accurately forecast population outcomes with the greatest simplicity in a format that could be understood by the educated layperson. The stock and flow diagrams will further enable these stakeholders to understand the parts of the system that may aid or hinder the reaching of ecosystem and human health goals, and the need for regulatory or management strategies that may not be intuitive.

The use of STELLA as a modeling tool has been successful in helping lay stakeholders understand complex systems in the process of developing policies that require stakeholder support for implementation. Stave (2003) developed a STELLA model to simulate the dynamics of water supply and use in Las Vegas. The model was used to analyze the impact of various policy options in order to maximize water supply over time. An important component of the policy analysis was to garner public support for the final policy recommendation. The STELLA model was successful in creating an understanding of the system without overwhelming the stakeholders with complicated technical equations. This understanding of the system was instrumental in implementing a water conservation policy that required stakeholder cooperation.

Human disposition model

It is important to distinguish between projected biomarkers of exposure and risk of an adverse effect (ECETOC 2005). The USEPA set the reference dose for MeHg at 5.8 $\mu\text{g}/\text{L}$ in cord blood for protection of the developing fetus and includes a safety factor of 10 (USEPA 2010a). The reference dose is often applied to maternal blood, but was established with the assumption that the ratio between fetal and maternal blood MeHg

was unity. Fetal blood concentrations of MeHg are approximately 90% higher than in maternal blood, so a corresponding maternal blood level would be expected to be lower than the reference dose (Stern and Smith 2003). Decisions made from interpreting biomarkers of exposure must consider the uncertainty surrounding the relationship between biomarker levels and adverse effects as well as the natural variability in individuals and populations of the pharmacokinetics of MeHg (ECETOC 2005). With the long-term objective of linking proposed Hg regulations or management strategies to the protection of human populations, it is important to remember that this model does not simulate changes in an individual over a lifetime, but progressive changes in Hg levels in a population over 100 years. In analyzing population biomarkers, Hg disposition in individuals representing the distribution of intake rates for a given population are simulated. While the most accurate method of forecasting effects would be to model the movement of Hg through these individuals, the literature provides conflicting information on exactly how Hg is transported and transformed within the human body. A simplification of the dynamics of Hg disposition in the body was used to simulate common biomarkers and loss to the human system. Because of this simplification, this model should not be used to predict Hg concentrations in individuals or specific tissues. The model only forecasts the central tendency of certain biomarkers for a distribution of intake rates of defined populations.

The human disposition model forecasts blood MeHg, fetal blood MeHg, and total hair Hg concentrations in response to the intake rates of freshwater fish for various populations. The distribution of intake rates gives the user the opportunity to project what portion of the population would fall below the USEPA reference dose if fish tissue

concentrations of Hg are reduced by a given amount. By limiting the intake to freshwater fish, the model more accurately simulates exposure from local sources. However, many populations consume larger amounts of marine or store-bought freshwater fish from non-local waters and exposure for those populations are likely to be inaccurate with this model. Subsistence fishers and anglers are likely to have the greatest portion of their fish intake from local sources, and therefore this model is expected to characterize Hg exposure in these higher risk populations more accurately than populations that ingest fish from other sources.

Ten population choices, described in Table 1, are available for users. Regulatory decision-makers should choose the population whose fish intake most closely resembles the population of concern. With a basic understanding of STELLA modeling, a user could alter the model to include the intake rates for any population of interest. While it seems counterintuitive that angler populations have lower intake rates at the highest percentiles than the general population, sampling methods and the frequency of fish meals impact the intake rates. With the exception of the angler and subsistence fisher populations, intake rates were derived from a national survey that asked subjects about fish meals over the past three days (USEPA and NCEA 1997). Consumers were those that reported any fish consumption during those three days. Because fish meals may be infrequent, a 3-day diary may have overestimated daily intake when extrapolated to a monthly rate. Both angler populations and the Subsistence Fishers 2 population used a 1-year assessment of fish consumption (CRITFC 1994, Connelly et al. 1996, USEPA and NCEA 1997). The Subsistence Fishers 1 population was assessed over an eight-month period (Burger et al. 1999). Many anglers fish more frequently during certain seasons,

and therefore fish intake may be much higher at certain times of the year. A longer assessment period for those who consume fish seasonally would result in a lower daily intake rate than if the assessment was taken during the highest consumption period. These methods may have resulted in a bias toward higher daily intake rates for the more general populations and lower daily intake rates for the angler and subsistence fisher populations.

The user sets a mean trophic level for consumption for the chosen population. While the trophic level can be adjusted during the model run, it cannot be adjusted to simulate the variability of trophic levels consumed by individuals. Anglers often prefer to fish for the predatory fish, such as largemouth bass and walleye, that tend to have the highest levels of Hg contamination. Subsistence fishers and children may consume more panfish because they are easier to catch. Panfish are typically lower on the food chain and subsequently have lower Hg concentrations. Because local consumers typically do not limit themselves to one species, the user may conservatively choose to enter the highest trophic level consumed, or, less conservatively, adjust the trophic level by weighting to reflect the intake of various species by a particular population from a particular waterway.

Perhaps the greatest challenge to the development of this model originates from varying time scales. Hg movement through environmental compartments occurs on a slower time scale than Hg movement through the human body. While changes in steady state levels in environmental compartments may take years or decades, changes within the human body can occur relatively quickly. In STELLA, a single time scale must be chosen for the entire model. The time scale of months was chosen to allow for simulation of seasonal changes in environmental compartments and to allow a 100 year model run

without encountering memory problems. However, for human disposition, this time scale introduced complications. Movement from one stock to another takes at least 1 month, whereas *in vivo*, this movement may occur in hours or days. In order to minimize this limitation, the human sector of the model was streamlined. This streamlining was achieved by consolidating certain pathways. One consolidated pathway was the entero-hepatic shunt. The model structure shows only the loss of MeHg through defecation instead of representing the entire pathway. The entire pathway includes MeHg removal from blood by the liver and subsequent secretion into the gut where most is reabsorbed into the blood and the remainder is lost through defecation. Streamlining pathways assisted the model in achieving steady state more quickly.

Because of the monthly time scale, time to reach steady state and the half-life of Hg in the human system is slower than what is found in the literature. The literature suggests that steady state for a new intake rate of Hg is reached in approximately a year (Sherlock et al. 1984). For this model, steady state within the human takes almost three years to be attained. Similarly, the half-life of Hg in the body is approximately 2 ½ months (Miettinen et al. 1971). The half-life of Hg in the model is about 12 months. When projecting changes over the short term, these differences are unacceptable. However, when examining change in populations over decades along with the uncertainty associated with Hg movement through environmental compartments, the imprecision of reaching steady state in three years instead of one year is likely to have a negligible effect on regulatory decision making.

The notion of steady state Hg levels in blood and other human compartments is somewhat misleading. Exposure to Hg occurs through periodic meals of contaminated

fish and is therefore intermittent. After a meal, blood Hg levels peak after several hours and then have a biphasic decline. An initial rapid drop in Hg levels is followed by a much slower decline with a half-life of about 2 ½ months (Kershaw et al. 1980, Miettinen et al. 1971). For individuals that only occasionally eat fish, use of a steady state ratio to predict a biomarker of exposure could be misleading because the actual concentration in any sample would be highly dependent on the amount of time that had passed since the last meal. For individuals and populations that consume fish on an almost daily basis, the assumption that a steady state concentration has been attained is more reasonable. Hg concentration in blood would still be close to peak levels when the next exposure occurred. The question of biological relevance for projected biomarkers that have been derived by assuming a steady state ratio for individuals with intermittent exposures depends on whether acute or chronic exposure to Hg is responsible for adverse effects in the developing fetus. That question has not yet been answered, but these values based on steady state intake give some approximation for the amount of exposure. The steady state assumption is more accurate for populations that eat frequent fish meals. These populations are more likely to have the highest exposures to Hg, and subsequently are at greater risk for adverse effects.

To investigate whether the values obtained from the model developed in this study are similar to the expected values based on previous literature, traditional Chi-squared techniques were employed. These techniques test for differences between observed and expected values. Model output values were not significantly different than the calibration sources over a wide range of exposure levels. That is, the values obtained from the model were expected based on previous research. It should be noted however,

that the model slightly overestimates biomarkers at the highest ingestion rates. At these levels, though, the variation in sampled populations is also at its greatest. The slight overestimation of biomarkers was shown to be negligible and insignificant when compared to population variability as shown by evaluation of the model and does not threaten the validity of the model.

Evaluation of the model consisted of comparing the model's parameter estimates (e.g. regression coefficients) with parameter estimates observed in the relevant literature. The relationship between ingestion and blood MeHg was validated using parameter estimates observed in eight studies (Table 5). The parameter estimates from these studies varied somewhat, perhaps reflecting variability in the populations sampled or bias from sampling methods. The current model's parameter estimates were similar to the mean of parameter estimates from the eight studies and fell within the range of parameter estimates from these studies. This comparison established that the model produces valid and reliable estimates for blood MeHg levels based on a given consumption rate of contaminated fish.

Similarly, parameter estimates for the model for fetal blood MeHg relative to maternal blood MeHg also fell within the range of literature sources. Unfortunately, only summary statistics from the literature were available for comparison. The use of summary statistics, instead of actual measurements or the regression equation derived from actual data, may introduce a limitation for this comparison. There is a theoretical potential that the variation is greater for one of the comparison groups (maternal or fetal blood). Therefore, when the mean, range, or other markers of the sample are compared, this may bias the ratio between the two datasets. However, because these are summary

statistics and several data points were used, the effect of possible outliers is likely minimized, but may need to be studied in future more sophisticated studies.

The relationship between blood MeHg and hair THg was compared to nine literature sources describing 11 populations. No difference was found between model output and these sources. Hair is frequently preferred as a biomarker for Hg exposure because it is easy to collect, is highly correlated with blood MeHg, and shows the history of exposure over time (Cernichiari et al. 2007). However, hair Hg levels are more variable than blood MeHg levels for a given exposure. This model was designed to give the central tendency after a given exposure, so users need to be cognizant that hair Hg concentrations in individuals from a given population will vary widely with an identical exposure.

The results suggest the developed human disposition model accurately projects the central tendency of biomarkers of exposure based on ingestion rates and fish tissue concentrations for populations of interest. It is a first step in linking environmental Hg levels to effects on nearby populations. With knowledge of the Hg concentration in fish from local waters, decision-makers can use the model to assess the portion of a population that is at risk and subsequently determine the decrease in fish tissue concentration needed to protect susceptible populations. The human disposition model depicts the disposition of Hg after ingestion in a simplified, yet understandable format, balancing accuracy, simplicity, and transparency.

Bioaccumulation model

The bioaccumulation model simulates the fate of Hg from water column into fish tissue in several steps. The first step controls the process of conversion of IHg into MeHg or its movement downstream. This process is treated as a single mixed-box reactor; that is, the individual processes that determine the reaction rate are not simulated. Land use determines the physical and chemical factors that determine the portion of IHg that is retained in the stream system, converted into MeHg, or is lost downstream. From this point forward, the model is a simple, multi-compartment bioaccumulation model, with minimal impact from land cover factors.

Others have developed models that simulate the fate and bioaccumulation of Hg in aquatic systems. The Hg Cycling Model (MCM) simulates the fate and bioaccumulation of Hg in lake systems, (Hudson et al. 1994). The Spreadsheet-based Ecological Risk Assessment for the Fate of Hg (SERAFM) model looks at Hg in aquatic systems with a focus on contaminated sites (Knightes and Ambrose 2006). The Hg module in the Water Quality Analysis Simulation Program (WASP) simulates the fate of Hg in both lentic and lotic water bodies; however, it does not simulate bioaccumulation in the food web (USEPA 2011f). The MERGANSER model is a Hg model that looks at predictors of fish tissue and piscivorous bird blood Hg levels. This model is specific to the northeast US and limited to lakes and reservoirs (Simcox et al. 2011). Each of these Hg models has its own strengths and weaknesses and focuses on a specific area of Hg dynamics. The STELLA model described here is unique in that it focuses on how watershed characteristics of stream systems affect bioaccumulation. With the exception of the SERAFM model that looks at contaminated sites, the other Hg models simulate Hg

dynamics in lake systems. This effort expands Hg models into stream systems which differ from lakes in terms of drivers of microbial conversion and movement of Hg out of the system. With more than 1.2 million river miles under a fish consumption advisory for Hg, a more complete understanding of the drivers of bioaccumulation in stream systems is needed (USEPA 2011a).

Phosphorus is assumed to be the limiting nutrient and is used as a surrogate for potential productivity and to estimate the biomass of trophic level 1. In a review of studies of nutrient limitation in North America, Borchardt (1996) found that nutrient limitation varied by region. The analysis found the northern half of the US was predominantly phosphorus limited, the Southwest and Ozarks nitrogen limited, and the Pacific Northwest was co-limited. The study sites were located in the region that Borchardt identified as to be most likely phosphorus limited. While the nutrient that limits potential productivity within a region may vary, it is likely that the limiting nutrient was phosphorus. If not, then co-limitation was the next most likely condition. In forested basins, productivity is more frequently limited by light, not nutrients. Limitation by light was also simulated in the model structure.

DOC is a heterogeneous group of organic molecules consisting primarily of humic substances. Although IHg is thought to bind to thiol groups on DOC, the relationship between DOC and Hg is complex (Haitzer et al. 2003). Dissolved THg and DOC in stream systems are highly correlated (Brigham et al. 2009, Dittman et al. 2009, Tsui and Finlay 2011). Increasing levels of DOC have been found to be associated with both increased and lowered bioavailability in aquatic systems (Tsui and Finlay 2011). DOC is thought to increase Hg in stream systems by transporting Hg into stream systems

(Balogh et al. 2004). Wetlands have been shown to export increased amounts of DOC and dissolved MeHg during rain events, while forested systems show increased THg inputs into streams during rain events (Balogh et al. 2004, Brigham et al. 2009). For systems with wetlands or soils with high humic content, Hg levels have been found to be correlated with DOC. In contrast, DOC has been shown to lower methylation rates by making IHg unavailable through complexation (Gorski et al. 2008, Miskimmin et al. 1992, Ravichandran 2004). However, this relationship breaks down for systems that primarily have Hg loading directly from the atmosphere (Ravichandran 2004). The Kentucky study sites have little, if any, wetland coverage. While DOC data were not available, data were available for total organic carbon (TOC). A test to determine if adjusting the dissolved IHg input into the model based on TOC as a surrogate for DOC found no improvement in fit. As a result, TOC was not included as an input into the model. Because Hg loading in Kentucky is primarily from atmospheric sources, the relationship between DOC and Hg may not be strong. Systems with a strong relationship between DOC and Hg, such as systems with significant wetlands coverage, may have improved fit with adjustment of the dissolved IHg fraction by adding DOC as a variable.

Wetlands have been shown to contribute significant loads of MeHg to stream systems during hydrologic events and connectivity to wetlands is associated with higher fish tissue MeHg while a lower pH has been shown to increase methylation and bioaccumulation (Balogh et al. 1997, Balogh et al. 2008, Haitzer et al. 2003, Miskimmin et al. 1992, Scudder et al. 2009). The pH of a system influences the relationship between DOC and Hg methylation. While DOC transports increased amounts of Hg into stream systems, the availability of that Hg is dependent on pH. In more acidic systems, the

competition for binding sites from hydrogen ion increases and results in more availability of Hg for methylation. The dissolved IHg input was adjusted by taking into account the pH of the system, although this adjustment did not improve overall mean prediction error. Calibration sites went from 28% to 26% and evaluation sites from 50% to 51%.

However, improvement was substantial for higher trophic levels at those few sites with higher wetlands coverage and lower pHs. Error for Mayfield Creek decreased from 36% to 0% for TL3.5. For N. Fork Forked Deer River, prediction error for TL4 dropped from 46% to 17%. Error increased, however, for TL3.5 from 13% to 34% at that Tennessee site. Because improvement for the systems with lower pH and higher wetlands coverage was substantial, this adjustment was included in the model. These systems were not well represented in this study but are likely to be closely looked at by regulators.

The minimal variation in wetlands coverage and the small range of pHs between the modeled basins are certainly limitations in the evaluation of the model. Only 2 sites had wetlands coverage greater than 1% and a mean pH below 7.0. While the two systems with higher wetlands coverage and lower pH had minimal error, more testing is needed to build confidence that the model adequately represents the impact of wetlands coverage and pH on bioaccumulation.

Unlike lentic systems, nutrient levels may not be the limiting factor in primary productivity in stream systems. Light is often limiting for smaller streams. Canopy cover in conjunction with stream width may limit productivity in the stream and consequently be a primary driver for bioaccumulation within the biota (Lamberti and Steinman 1997, Vannote et al. 1980). In lower order streams, the canopy may shade the entire stream, and productivity may be minimal after leaf out. As stream order increases, the width of the

stream increases and the canopy opens up resulting in higher levels of productivity for intermediate sized streams. Larger rivers are deeper and tend to carry more suspended solids, both of which reduce light penetration to periphyton-bearing substrates, lowering productivity. Watersheds that are largely forested have reduced productivity compared to stream systems with abundant light. A reduction in the biomass of primary producers leads to a higher concentration of MeHg at the base of the food web. This effect magnifies through the food web, leading to higher fish tissue concentrations in more pristine settings. The modeled basins were small to intermediate in size. Tygarts Creek in particular is a smaller, heavily forested basin. The model predicted this basin to have the highest fish tissue concentrations, which was confirmed by the collected sample. Although the sample was beyond the upper bound of the length range and therefore not included in the error analysis, the model projected this sample, a sauger, to have the highest fish tissue concentration at 0.708 mg/kg. The actual sample was 1.140 mg/kg. Quality length for sauger is 300 mm, and this sample was 432 mm. The model does not adjust for length, but the model projection supported the expectation that this system would have elevated bioaccumulation.

In the sensitivity analysis, the response to changes in Hg loading differed for total and dissolved Hg. Changes in THg input had little effect on reductions in fish tissue for Mayfield Creek and the Mud River until the amount was reduced to levels below the 1 ng/l dissolved Hg default. Tygarts Creek, however, showed greater responsiveness to THg reductions. Compared to the other 2 systems, Tygarts Creek is more forested, has substantially less agricultural coverage, and has the lowest mean THg concentrations. Despite having lower THg loading, fish tissue levels are highest in this system. In all

three systems, dissolved Hg showed a linear relationship with fish tissue Hg. Balogh et al. (1997) found that in areas with high suspended solids, THg does not correlate to Hg that is available for microbial conversion. The responses to reductions in loading of both THg and dissolved Hg for these three systems support the concept that measures of THg do not correlate with Hg available for methylation and that dissolved Hg is a better predictor of methylation potential. While Hg must be available for bioaccumulation to occur, basin characteristics drive the availability and efficiency with which Hg enters the food web and bioaccumulates. The sensitivity analysis of Hg loading shows the model accurately simulates the differences that basin characteristics impose on Hg availability and bioaccumulation efficiency.

The sensitivity analysis also showed that manipulation of pH, and the fraction of land cover that was developed resulted in minimal changes in output. Changes in the nutrient level or the forested or wetlands coverage, however, had a non-trivial impact on fish tissue concentrations. While a lower pH does make IHg more bioavailable, this is only one factor in determining the mass of Hg that enters the food web. Development in a basin increases the speed of transport of Hg through the system, but does not increase or decrease methylation rates. While each of these variables had some influence on bioaccumulation, the combination of nutrient levels, and forested and wetlands coverage of the basin appear to be the strongest drivers within the modeled systems. The structure of the stream system, as illustrated by the STELLA model, reveals the basis for the greater impact of the most critical variables. These variables impact the structure of the system at multiple points.

Nutrient levels and forested coverage are both related to primary productivity. The relationship between bioaccumulation and productivity is complex. Productivity impacts the model at several points in the system including the calculation of the microbial conversion rate, the estimate of biomass in the system, and the trophic transfer factors. Increased productivity in the form of extensive periphyton mats increases the methylation of Hg, thereby increasing the mass of MeHg in the biota. Countering this, increased productivity decreases bioaccumulation through both bloom dilution and somatic growth dilution. Hill and Larsen (2005) found that light limitation increased the concentration of MeHg in biofilm in artificial streams. Hg uptake was constant under different light regimes, but growth of microalgae was dependent on light. Ward et al. (2010) studied somatic growth dilution in Atlantic salmon. Fry raised under the same conditions were stocked in various streams and sampled approximately 4 months later. Individual growth rate accounted for 38% of the variation in Hg concentration in fish tissue, building support for somatic growth dilution as being an important factor in bioaccumulation in stream systems.

The largest impact on bioaccumulation came from land cover factors that influence the amount of IHg in the stream that is converted into MeHg. Chasar et al. (2009) found that, across wide environmental conditions, the supply of MeHg at the base of the food web was the largest factor to influence bioaccumulation, and that trophic structure and transfer efficiencies were only important predictors when comparing streams with similar land cover and Hg loading. Riva-Murray et al. (2011) similarly found that MeHg at the base of the food web was more important than trophic structure across larger environmental scales. At a smaller scale, when examining biota from

different reaches of the same stream system, they found significant spatial heterogeneity in Hg in biota within basins that had heterogeneous in-stream habitat. This heterogeneity may be reflecting the different mix of functional feeding groups. Of the functional feeding groups at the base of the food web, scrapers would feed directly on periphyton, shredders on coarse particulate organic matter (CPOM)—of which the biofilm is an important nutritive component, and omnivores that feed from both categories. While the algal-based periphyton would be expected to be the food source with the highest MeHg concentrations, the biofilm associated with CPOM may also be a source. Without having a thorough survey of the feeding groups in each stream, the proportions for each stream will be unknown. The assumption is made that the variation in the composition of functional feeding groups at the base of the food web is relatively small across the region depicted. Bradley et al. (2011) also observed spatial variation in filtered MeHg concentrations in stream reaches corresponding to connectivity to wetlands or floodplains or shallow, open-water areas. Smaller reaches may have atypical land cover and habitat characteristics compared to the characteristics of the larger basin containing that reach. Therefore, when using the model, the size of the basin should be considered. The model was developed and calibrated primarily for mid-sized streams. Use for smaller or larger basins has not been tested and is likely beyond the scope of the current model's performance.

Ecological variation within natural settings is large. Stream flow, sunshine and rain, temperature, nutrient levels, growth rates, and other variables fluctuate daily and from year to year. Fish of the same species and size sampled from the same location will vary in tissue Hg concentration. Variable inputs into the model are monthly or annual

means from several years of monitoring. While flow and meteorological data represent many years, water quality data were typically means from eight or nine years for calibration sites and fewer for evaluation sites. The assumption in these simulations is that these means represent a steady state system. It is not known whether the means from these years are typical for these basins over the long term, whether the samples encompass data that are outliers, or whether there have been recent changes in water quality, weather, or flow. If the assumption of steady state is incorrect, then model output may be biased.

A limitation of this model is that input parameters inherently have a high degree of variability and the use of regulatory data further compounds the issue. Fish tissue and water quality monitoring may be undertaken by different regulatory programs and therefore may not be coordinated in time and place. Budget concerns may also limit sampling. Frequent and coordinated sampling of variables would minimize uncertainty.

The natural variation between fish tissue samples from the same species and site limits confidence in the ability to accurately project the concentration of Hg in any particular sample. A mean standard deviation of 0.116 was found when examining groups of 6 or more samples from the National Fish Database. When monitoring for regulatory purposes, the number of samples are often limited due to the cost of analyzing the samples. The combination of considerable variability and low sample size, even when these are pooled samples, generally results in a wide 95% confidence interval. Because confidence intervals are wide, the accuracy of model output is more difficult to assess. The ultimate purpose of the overall model is to gain insight into the complex problem of Hg in the environment and to understand the factors that control bioaccumulation and its

impact on local susceptible populations. Regulatory agencies sample fish tissue to determine which waterways present a risk to populations from fish consumption. At times, agencies have based consumption advisories on as few as one sample (E. Eisiminger, KDOW, personal communication, 10/2010). More frequent and intensive sampling efforts would ensure that an elevated sample was truly representative of the Hg concentrations in that system.

This model seeks to project the fish tissue MeHg concentration in a generic fish species based on trophic level and basin characteristics. Accuracy will vary based on the species and size of fish to which the model output is compared. When examining prediction error by trophic level at each site, the mean error for projecting fish tissue Hg levels was 26% for sites in Kentucky and 51% for sites in nearby states. This is comparable to other models that project fish tissue concentrations. The National Descriptive Model for Hg in Fish Tissue developed by the USGS reported a prediction error of 38% (Wente 2004). The model developed by Trudel and Rasmussen (2006) was within 25% of actual value for 70% of predictions.

One difficulty in developing this model was defining Hg loading to the stream system. Hg was simulated from water column to fish tissue. The model was developed to be helpful to the regulatory community, and as such, uses only available regulatory data. The model was developed and calibrated using data from the Kentucky Division of Water, and monthly means of THg in the water column were used for the input into the system. Dissolved Hg is considered a more accurate measure of IHg that is available for conversion to MeHg, but dissolved Hg data were not available. Dissolved Hg levels are not always correlated to THg levels, especially in systems with high suspended solids

(Balogh et al. 1997). Measures of DOC, which are more closely related to dissolved Hg levels in stream systems, were not available (Brigham et al. 2009). Actual loading is dependent on a number of variables including the amount of precipitation and the concentration of Hg in that precipitation, the pH of the soil in the watershed, land use, and more. Using the monthly mean for Hg loading introduces uncertainty. Spikes of Hg loading, both particulate and dissolved, may occur during precipitation events that may not be reflected in monthly sampling, particularly in basins that may be downwind of emission sources. Simulating the processes that influence loading into the stream would increase model accuracy. This step would require the development of the third model for which data are not available.

The bioaccumulation model was evaluated by comparing model output to fish tissue data for seven basins in the region surrounding Kentucky. The model was not as consistent in projecting fish tissue concentrations for evaluation sites. Surprisingly, sites proximal to the state of Kentucky had higher prediction errors than other evaluation sites. In particular, the 2 sites in Indiana had prediction errors ranging from 78% to 90% for the 4 trophic level-site combinations. These sites are in the southeast portion of the state downwind from a number of coal-fired power plants. A report by the USGS on Hg in precipitation in Indiana found that portion of the state to consistently have the highest Hg wet deposition, suggesting that these 2 watersheds may be located in a Hg hotspot (Risch and Fowler 2008). Hammerschmidt and Fitzgerald (2006) found a positive correlation between wet deposition of Hg and MeHg concentrations in largemouth bass filets. Gorski et al. (2008) found that Hg in precipitation was more bioavailable than Hg in surface waters. The higher loading of dissolved Hg in precipitation may account for the

elevated Hg in fish samples at the Indiana sites compared to model output. Without the Indiana sites, mean prediction error for the evaluation sites was 35%. Adding wet deposition of Hg to the model might improve model performance. However, wet deposition data at a spatial scale that is relevant to modeling basins in the Ohio River Valley are lacking.

In addition to the elevated error at the Indiana sites, TL3 of the Little Kanawha River in West Virginia had the highest error, 94%. This elevated error is misleading. For the lower trophic levels, the magnitude of projected and actual values were lower, so differences between those values resulted in higher error even though the differences were not biologically relevant. For the Little Kanawha River, the sample mean was 0.018 mg/kg and the projected value was 0.035 mg/kg resulting in an error of 94%. If we look at TL3.5 of Spring Creek, the sample mean was 0.262 mg/kg and the projected outcome was 0.191 mg/kg for an error of 27%. The difference of 0.017 mg/kg found at Little Kanawha is biologically less significant than the difference of 0.071 mg/kg found at Spring Creek. The error calculations do not convey the biological significance or magnitude of the error. This scaling of error values at least partially explains the decreasing error with increasing trophic level found in Table 8. Mean prediction error for evaluation sites without the Indiana and Little Kanawha sites was 26%, the same error found for calibration sites.

The basins used to both calibrate and evaluate the model represent a wide variety of geomorphic land types and land uses. In general, the more forested basins were located in more mountainous areas. While there was considerable variability in prediction error between sites, land cover was not associated with error. This diversity of land types and

uses build confidence in the ability of the model to be generalized to other basins in humid temperate regions with similar basin size and wetlands coverage.

As the understanding of the factors that influence bioaccumulation increases, regulators can begin to predict which stream systems are most likely to have fish with elevated Hg levels. This knowledge can inform regulatory agencies as to which stream systems should be given priority for sampling and interventions. This becomes more important as state budgets become leaner and cost-effectiveness is demanded in all programs. An understanding of watershed factors can also begin to suggest possible management strategies to reduce bioaccumulation in streams that are out of compliance.

The dynamic bioaccumulation model effectively predicts fish tissue MeHg levels based on watershed characteristics and THg concentrations in the water column. The model was calibrated and evaluated using 14 diverse basins in or near the Ohio River Valley, a region of North America that is not well-represented in the Hg bioaccumulation literature. The physiographic diversity and wide span of land uses convey confidence that the model will project with reasonable accuracy fish tissue Hg levels in other similar basins in the temperate humid domain. Because natural variability in many of the variables examined in the stream systems is great, more consistent and intensive sampling of water quality and fish tissue would improve confidence in model output. If wet deposition data were available on the scale of the individual basin, adding this factor might further improve model accuracy. Additional evaluation of the model is needed before simulating bioaccumulation in basins with significant wetlands coverage.

Projecting policy and climate change scenarios

Combining the human disposition and bioaccumulation models provided a means to examine the interaction between the environment and susceptible populations. The central problem examined in this project was human exposure to Hg through the consumption of locally caught fish. Understanding the entire system, including both the environmental fate of Hg and the dynamics of population exposure, are necessary to devise a strategy to protect populations.

Fish Consumption Advisories

The current strategy for protecting populations from the adverse impacts of Hg exposure from fish consumption is to limit exposure by issuing fish consumption advisories and educating the public about these advisories. However, fish consumption also provides substantial health benefits. It reduces coronary heart disease mortality and stroke and increases cognitive development in the developing fetus (Cohen et al. 2005, Driscoll et al. 2011). The message these advisories attempt to convey is that women of child-bearing age and young children should reduce consumption of fish with high levels of Hg contamination and substitute fish with lower concentrations, thus preserving health benefits while reducing risks. Cohen et al. (2005) found the gains from reduced neurodevelopmental effects were offset by decreased cognitive development in children and increased coronary heart disease mortality and stroke. Consequently, improvements in public health were less than expected or even negative, particularly when non-targeted portions of the population reduced total consumption along with the targeted women of child-bearing age. Effectively communicating the benefits and risks of fish consumption

to susceptible populations becomes more difficult as the message becomes more complex.

Certain populations may have substantially higher exposures from consumption of locally caught fish than the general population. Some Native American tribes, Inuit, and certain Asian populations have been found to have higher fish consumption rates than the general US population (Hightower et al. 2006, Shilling et al. 2010). Because of cultural differences and practices, risk communication messages must be tailored to each unique population to be effective. Even when tailored to a specific population, fish consumption advisories are not always successful in producing the desired behavior changes. Driscoll et al. (2011) found that, after being presented with culturally specific fish consumption information, one targeted population intended to cease all fish consumption while another indicated no intention to modify consumption behavior at all.

Understanding the degree to which these populations are exposed and directing risk communication to those most affected is essential to protecting those most at risk (Burger et al. 1999, Shilling et al. 2010). This study used populations described in the literature that were not specific to the basins being simulated, although it is assumed that some of the fishers in the modeled basins would have characteristics similar to the literature derived populations. For decision makers, it is important to consider the unique populations that consume fish from the waterway being examined. While the USEPA criterion for fish protected the 95th percentile for all of the populations examined in this study, there may be other subsistence populations that have higher intake rates. These populations may not be protected. For some of the simulated populations, the 99th percentile intake rate had substantially greater exposures, showing biomarkers well above

the USEPA level of safety. For these populations, educational campaigns targeted to the population of concern would be essential to protect those at the upper end of the intake distribution.

The unique distributions of intake rates for each population demonstrate that both the population examined and the percentile chosen for action contribute to the impact of a chosen policy. For decision makers, these population profiles evoke the better questions: what population is most at risk? What portion of the population is protected by the USEPA fish tissue criterion? And what percentile of intake rate adequately protects that population? An important use of this model is that decision makers can project the unique profile of biomarkers of exposure for a population of concern.

Emissions Reductions

The CWA mandates that states set TMDLs for pollutants that are out of compliance for the designated use for a given waterway. As required by law, many states have established TMDLs for Hg in waterways as a result of non-compliance of fish tissue levels for Hg. The TMDL approach, however, is limited by the reality that setting a maximum loading rate for a non-point source pollutant does not actually mean that controls exist to limit loading. The CWA specifies watershed management strategies to reduce non-point source loading into waterways. These strategies are not relevant to atmospherically deposited pollutants like Hg. In order to reduce loading from the atmosphere, atmospheric sources must be reduced. Emission reduction regulations are the obvious means to reducing Hg contamination in fish, but these regulations have been difficult to promulgate, and the relationship between emissions and loading into waterways is complex and needs further study.

When a waterway exceeds an established criterion, the regulating agency determines the daily amount of contaminant the waterway can receive to come back into compliance. Because each stream system is unique, the TMDL will vary depending on the unique characteristics of the basin. While regulating agencies set TMDLs to bring fish tissue Hg into compliance, the impact on a susceptible population will depend on several variables. We can view the reduction in THg inputs (Figure 12) as scenarios of possible TMDLs put forth by a regulating agency. Because of its greater forested coverage and lower nutrient levels, Tygarts Creek exhibited greater efficiency in bioaccumulation of MeHg than Mayfield Creek; therefore changes in Hg loading had a greater response in fish tissue and a greater subsequent impact on populations.

The relationship between emissions reductions and loading to streams is complicated and not simulated by this model. Atmospheric deposition occurs through precipitation and dry deposition, and subsequent loading is dependent on many variables including soil type, land cover, and rain events. Because of the importance of global sources, reductions in local or regional emissions will result in a smaller reduction to loading in streams. While this model does not project the decrease in loading to streams from a particular emissions reduction scenario, it can look at percent reductions from established monthly means. Balogh et al. (1997) found that THg in streams varied with suspended solids while dissolved Hg remained stable. Particulate-bound Hg is not likely to be immediately available for conversion to MeHg, which would account for the threshold effect found in Figure 10. For systems with heavy loads of particulate-bound Hg, large reductions in inputs may be necessary before a response is seen in fish tissue levels. The linear relationship between percent reduction in dissolved Hg input and fish

tissue Hg further support the concept that dissolved Hg, as opposed to THg, is a driver of bioaccumulation in stream systems. The slope of the relationship between the percent reduction of dissolved Hg and fish tissue is steeper for systems with more efficient bioaccumulation. In terms of policy implications, systems that have low suspended solids and efficient bioaccumulation can be expected to respond more quickly to reductions in Hg loading. Targeting these systems for reduced loading would result in a greater impact in lowering fish tissue Hg than systems that have more anthropogenic influences.

Watershed Management Strategies

While the extent of the response in population biomarkers was different depending on the basin variable that was perturbed, a similar pattern of response was seen for the 6 populations examined. The magnitude of biomarker change for the Anglers 1 and 2 populations was less than the subsistence and consumer populations. This pattern was independent of the stream that was simulated or the variable that was perturbed and points to the importance of population choice for decision makers when setting guidelines for setting a level of safety. Having a clear understanding of how population intake rates were assessed is also necessary when evaluating a system. Intake rates for the angler populations and Subsistence Fishers 2 population were assessed over a year (CRITFC 1994, Connelly et al. 1996). The Subsistence Fishers 1 population was assessed over 8 months (Burger et al. 1998). Many anglers fish seasonally, and deriving a monthly rate from annual intake may underestimate intake for certain seasons. Conversely, the consumer population intake rates were extrapolated from a 3-day diary. Anyone who had consumed fish in this time was considered a consumer, and the monthly rate was then determined. This may have overestimated the monthly intake for these populations

(USEPA and NCEA 1997). While many populations may have little exposure from local waterways, certain populations may have heavy exposures. Knowledge of the populations that consume fish from a stream system under consideration and their consumption patterns is essential to the decision making process.

While changes in basin variables can change bioaccumulation rates and subsequent population exposures, the environmental changes that decrease fish contamination would be viewed by many as detrimental because these same variables provide essential ecosystem services. An inverse relationship exists between nutrient loads and bioaccumulation efficiency. High nutrient loads, however, lead to eutrophication. Eutrophic stream systems provide a lower level of ecosystem services, with algal blooms, murky water, and, at high enough levels of nutrients, the loss of the ability to support aquatic life. Bioaccumulation is lower in basins with less forested coverage. Ecosystem services provided by forests include recreational opportunities, production of oxygen, carbon sequestration, soil production and retention, promotion of the recharging of groundwater, and regulation of flow regimes (UNEP 2009). Wetlands coverage is also correlated with bioaccumulation efficiency. Wetlands ecosystem services include flood control, groundwater recharge, sediment and nutrient removal and storage, and water purification (Ramsar 2011). For all three basin variables examined, changes that reduced contamination in fish also reduced the ecosystem services provided by that system. Because systems with greater bioaccumulation efficiency also have a greater response to changes in loading, targeting these systems for reductions in loading would provide the benefit of reduced contamination and greater services.

Climate Change

Increases in mean temperature and the frequency of high precipitation events were projected to simulate the expected effects of climate change in three basins in Kentucky. An increase in mean temperature resulted in a negligible increase in fish tissue Hg. Increases in the frequency of high precipitation events; however, resulted in marked decreases in fish tissue Hg. The combination of these two factors similarly resulted in decreases in fish tissue Hg, with little mitigating effect from increased temperatures. These decreases were the result of increased flashiness in streams leading to a decrease in retention of Hg in the stream system. That is, Hg moved out of the basin faster and therefore was not available for conversion and bioaccumulation.

Climate change is expected to bring more extremes in weather, including more frequent flooding in some areas while other areas are expected to experience more frequent droughts. In considering changes in precipitation, the second and third climate change scenarios only simulated the expected impacts resulting from more frequent high precipitation events as it relates to retention in the basin. It did not consider the increased loading that may occur from wet deposition if total precipitation were to increase. Hg wet deposition has been associated with total precipitation and the pattern of precipitation. Several studies have found the highest Hg concentrations in precipitation events that were high intensity or short duration (Risch and Fowler 2008, Keeler et al. 2005, Keeler et al. 2006, Mason et al. 1997). As discussed previously, Hg in wet deposition has been found to be more available for conversion to MeHg and subsequently leads to more efficient bioaccumulation in a system (Hammerschmidt and Fitzgerald 2006, Gorski et al. 2008). Therefore, changes in precipitation patterns will likely lead to changes in Hg loading in a

basin. While the expected result of increased flashiness is reduced retention, an increase in precipitation could counteract the rapid movement of Hg out of the system through increased loading. Because the model was not developed to specify loading sources and patterns, the effects of increased wet deposition into the system could not be simulated.

Limitations

The purpose of the proposed model is two-fold: to be a tool for regulatory decision makers in determining if proposed policy scenarios reduce risk to susceptible populations; and to gain a better understanding of the interactions that control Hg dynamics and human exposure. The scope of this model is large in terms of both time frame and the size and complexity of the simulated system. Considerable parameter uncertainty results from the lack of sufficient data for many parameters. In addition, uncertainty about climate change decreases confidence in meteorological parameters for which a great deal of data were available. Model uncertainty is also present in that certain relationships in the structure of the model are ill-defined. Examples include retention rate of Hg in the stream, methylation rates, and oversimplification of the food web in calculating bioaccumulation in predatory fish. Estimations were made with expert judgment by consulting literature sources and professionals with experience in the field.

Despite the uncertainties, a system dynamics approach, with its emphasis on relationships and feedback loops between the many parts of the system, can reasonably describe the behavior of this complex problem. The information available to describe these relationships included clearly defined boundaries, a wealth of research in the literature describing the relationships of most parts of the system, and adequate

regulatory data for the specific sites to be modeled. The usefulness of this project is not how precisely it predicts fish tissue Hg levels or the decrease in risk to susceptible populations at some time in the future; its usefulness comes from the foresight gained by better understanding how the system responds to various regulatory scenarios.

Conclusion

The dynamic model simulated the problem of Hg exposure by examining the system from the point of Hg in the water column to its concentration in population biomarkers. Combining the environmental and population exposure components permitted the assessment of the interplay of watershed and population characteristics on human exposure. Possible policy scenarios were evaluated while viewing the problem as one system, suggesting important questions to be considered when assessing a contaminated system. These questions include:

- What population has the greatest exposure from this stream?
- What does the pattern of intake of fish for this population look like?
- What portion of this population is protected by the USEPA level of safety?
- How efficient is bioaccumulation in this stream system?

Ultimately, the CWA requires the reduction of Hg levels in fish tissue to meet water quality criterion. One approach would be to alter the efficiency of bioaccumulation. However, efficiency is related to watershed characteristics and changes in sensitive variables that reduce efficiency also reduce valued ecosystem services to an unacceptable extent. Meeting water quality criterion will require regulations that reduce the loading of Hg into waterways and this can only be achieved by regulating Hg emissions. Bringing

these waterways into compliance through Hg emissions regulations is expected to take decades to centuries, and therefore shorter term policies are required to protect populations from adverse exposures (Selin 2011). For the short term, fish consumption advisories must be used to protect populations from adverse exposures. Ultimately, the unique characteristics of a basin combined with the unique pattern of intake rates of susceptible populations determine the risk associated with fish consumption of a given waterway, and this combination should be the determinant for setting advisories and determining a risk communication strategy.

The combined bioaccumulation and population biomarker model can be an effective tool for regulators when assessing a stream system for Hg contamination. The model simulates both the pattern of uptake of a designated population and the unique basin characteristics as one system. By projecting reductions in THg, an appropriate TMDL can be determined and a general idea of the responsiveness of the system can be evaluated. In addition, by focusing on the populations that fish from the system, knowledge of the degree of risk for those populations can be assessed and risk communication messages can be designed to target those most at risk.

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APPENDIX A

MODEL EQUATIONS

Biomass TL1

- biomass_of_lv1_1 = $10^{(.717+.689*\text{LOG10}(\text{watershed_area}/10000)-.494*\text{LOG10}(\text{mean_flow}*.000386)+.387*\text{LOG10}(\text{mean_ann_P}*.000))/12/1000*\text{channel_width}*\text{channel_length}}$
 UNITS: kg
 DOCUMENT: Uses Lambert and Steinman's regression equation to generate GPP (1997). The equation uses watershed area, discharge and SRP to generate GPP. These 3 factors explain 70% of variation in GPP.

conversion factors:

watershed area: convert from m2 to hectares
 flow: from m3/mo to L/s
 from /yr to /mo
 from g to kg

Units assigned: kg

- channel_width = 5
 DOCUMENT: A mean channel width of 5 meters is chosen. In larger systems, the middle sections of the stream are deep and fast and won't support periphyton growth.
- channel_length = $((\text{watershed_area}*.000001*.3881)^{0.94})^{2.6}*1609.344$
 DOCUMENT: Calculates total channel length based on the area of the watershed. Equation is from "A view of the river" by Leopold 1994, p 222.


 Equation requires square miles, so conversion of area to square miles, and then conversion from miles (in length) to meters.
- mean_flow = 22875459.7943632
 DOCUMENT: mean annual flow
- watershed_area = 717600000
 UNITS: m²
 DOCUMENT: Watershed area in m2. Input from linked Excel file.

Degree of Retention


- calibration_fr = .015
- flashiness = $(1+(IF\ \text{perturb_developed}=1\ \text{THEN}\ \text{perturb_fr_developed}\ \text{ELSE}\ \text{fr_developed})*.5)*\text{freq_of_high_precip}$
 DOCUMENT: Development increases overland runoff and quicker movement of water to the stream channel and out of the system. In order to account for this increase in flashiness, half the fraction developed of the watershed is added to one.
- fr_developed = 0.078
 DOCUMENT: Portion of watershed that is developed. Input from linked Excel file.
- perturb_developed = 0
- perturb_fr_developed = .1
 DOCUMENT: Allows manipulation of the portion of the watershed that is developed. The fraction developed is multiplied by the value set by the user.


- retention = (((1+(sinuosity/4*.5)-flashiness/5*.5))*calibration_fr))
 UNITS: Unitless
 DOCUMENT: Reflects degree of retention of energy, debris, Hg, etc. in the watershed. Large portion of anthropogenic management (flood control, channelization) lead to faster movement out of the system (lower retention number) while large amounts of debris in the system slow removal (increase retention). High precip is a factor that influences lateral connectivity--matter is deposited on/above banks. Each factor contributes an equal amount to retention.


 Includes calibration factor.
- sinuosity = 1.6
 UNITS: Unitless
 DOCUMENT: Sinuosity is a standard measure of meander in a stream. A straighter stream (sinuosity closer to 1) the more like an open pipe the stream is, and the lower the retention in the stream.

 Input from linked Excel file..
- ☑ freq_of_high_precip = GRAPH(count)
 (1.00, 2.30), (2.00, 2.00), (3.00, 2.50), (4.00, 5.10), (5.00, 2.80), (6.00, 2.90), (7.00, 3.20), (8.00, 2.50), (9.00, 1.80), (10.0, 1.60), (11.0, 1.90), (12.0, 2.20)
 UNITS: Unitless
 DOCUMENT: This is the mean of the number of days for each month with precipitation over 0.5 inches. Input from linked Excel file.

Hg Input

- count = INT(Counter(1,13))
 DOCUMENT: cycles through the months of the year for monthly inputs
- perturb_Hg_input = 0
- perturb_THg = 1
 UNITS: Unitless
 DOCUMENT: This is connected to the slider on the interface page. It allows the user to decrease mercury entering the system at points in time.
- soluble_IHg_input = (MIN((IF perturb_Hg_input=1 THEN perturb_THg ELSE THg_conc),1)+((IF perturb_wetlands = 1 THEN perturb_fr_wetlands ELSE fr_wetlands)*10+pH_adjust))*flow*unit_conversion
 UNITS: mg/m³
 DOCUMENT: This calculates the mass of soluble mercury entering the system. According to Balogh, Meyer, and Johnson (1997), Environ Sci Technol, the amount of total mercury varies widely in the system depending on suspended solids (ie, variation comes from particulate bound Hg). However, the amount of soluble mercury remains stable, with a maximum of about 1 ng/l.. Only soluble Hg is available for microbial conversion, so that portion is included in this system.
- unit_conversion = .001
 DOCUMENT: conversion factor for converting ng/L to mg/m³
- ☑ flow = GRAPH(count)
 (1.00, 3.5e+007), (2.00, 4.4e+007), (3.00, 5e+007), (4.00, 3.8e+007), (5.00, 2.9e+007), (6.00, 1.4e+007), (7.00, 8.2e+006), (8.00, 6e+006), (9.00, 6.2e+006), (10.0, 4.8e+006), (11.0, 1.2e+007), (12.0, 2.7e+007)
 UNITS: m³
 DOCUMENT: Mean monthly flow in m³/month. Input from the linked Excel file.

pH_adjust = GRAPH(pH)
 (5.50, 3.00), (5.85, 2.56), (6.20, 2.22), (6.55, 1.44), (6.90, 1.00), (7.25, 0.05), (7.60, 0.005), (7.95, 0.00), (8.30, 0.00), (8.65, 0.00), (9.00, 0.00)

THg_conc = GRAPH(count)
 (1.00, 3.13), (2.00, 2.33), (3.00, 1.53), (4.00, 1.06), (5.00, 1.16), (6.00, 1.65), (7.00, 1.09), (8.00, 0.66), (9.00, 0.94), (10.0, 1.53), (11.0, 1.29), (12.0, 0.77)

UNITS: g-10⁻⁹/l

DOCUMENT: Mean monthly total mercury input from linked Excel file.

Index of Productivity

fr_forested = 0.688

DOCUMENT: Fraction of the watershed that is forested. Input from the linked Excel file.

nutrient_level = ((IF perturb_nutrients=1 THEN perturb_nutrient_level ELSE phosphorus)*1000)

UNITS: mg/m³

DOCUMENT: Presumes P is limiting, as found in Lamberti and Steinman (1997).

Units of mg/m³. Input units are mg/L for nutrients.

perturb_forest = 0

perturb_fr_forested = .5

DOCUMENT: Allows manipulation of the portion of the watershed that is forested. The fraction forested is multiplied by the value set by the user.

perturb_nutrients = 0

perturb_nutrient_level = .1


DOCUMENT: Allows manipulation of the nutrient (phosphorus) level in the watershed. The monthly mean is multiplied by the value set by the user.

productivity_index = (((1-(16-daylength)/7)*(1-(IF perturb_forest=1 THEN perturb_fr_forested ELSE fr_forested))*(canopy_cover)*perturb_fr_forested))*nutrient_level/3

UNITS: mg/m³


DOCUMENT: generates an index of productivity based on nutrient level and light limitation.

canopy_cover = GRAPH(count)

 (1.00, 0.00), (2.00, 0.00), (3.00, 0.00), (4.00, 0.075), (5.00, 0.845), (6.00, 0.89), (7.00, 0.905), (8.00, 0.905), (9.00, 0.905), (10.0, 0.835), (11.0, 0.00), (12.0, 0.00)

DOCUMENT: This graphical function impacts light limitation. For basins with high forested coverage, light limitation is only applied after leaf out in spring/summer.


daylength = GRAPH(count)

 (1.00, 9.80), (2.00, 10.9), (3.00, 12.1), (4.00, 13.4), (5.00, 14.3), (6.00, 14.9), (7.00, 14.5), (8.00, 13.5), (9.00, 12.4), (10.0, 11.1), (11.0, 10.0), (12.0, 9.50)

DOCUMENT: Graphical function giving number of daylight hours. Source: ptaff (2005)

http://ptaff.ca/soleil/?lang=en_CA

phosphorus = GRAPH(count)

 (1.00, 0.0309), (2.00, 0.0234), (3.00, 0.0159), (4.00, 0.0232), (5.00, 0.0205), (6.00, 0.0185), (7.00, 0.0193), (8.00, 0.0178), (9.00, 0.0155), (10.0, 0.0177), (11.0, 0.0118), (12.0, 0.0174)

UNITS: mg/l

DOCUMENT: Mean monthly Phosphate phosphorus as P input into the model through linked Excel file.

Mean Productivity Index

- $\text{calibr} = 3.06$
DOCUMENT: calibration factor
- $\text{mean_ann_P} = 0.019325$
DOCUMENT: Mean annual phosphorus. Input from linked Excel file.
- $\text{mean_daylength} = 12.2$
DOCUMENT: annual mean of daylight hours. Input from linked Excel file.
- $\text{mean_nutrient_level} = ((\text{IF perturb_nutrients}=1 \text{ THEN perturb_nutrient_level ELSE mean_ann_P}) * 1000)$
DOCUMENT: Presumes phosphorus is limiting. Mean of monthly phosphorus means. Conversion from mg/L to mg/m³ (multiply by 1000).
- $\text{mean_productivity_index} = ((1 - (16 - \text{mean_daylength}) / 7) * (1 - (\text{IF perturb_forest}=1 \text{ THEN perturb_fr_forested ELSE fr_forested}))) * \text{mean_nutrient_level} * \text{calibr}$
UNITS: mg/m³
DOCUMENT: Productivity index generated by nutrient level and light limitation. Calibration factor applied.

Microbial Conversion Rate

- $\text{fr_wetlands} = 0$
DOCUMENT: Fraction of the watershed that is wetlands. Input from the linked Excel file.
- $\text{micro_conv_rate} = (\text{MIN}(\text{MIN}(\text{MIN}(\text{IF perturb_wetlands} = 1 \text{ THEN perturb_fr_wetlands ELSE fr_wetlands}) * 20 * .25) + (\text{season} * .25) + ((9 - (\text{IF perturb_pH_input}=1 \text{ THEN perturb_pH ELSE pH})) / 3 * .25) + (\text{productivity_index} / 40 * .25)), 1) * .36)$
DOCUMENT: Microbial conversion rate is based on the range of ratios found in Warner et al. (2005). The ratio of MeHg to THg typically falls between .03 and .39.

The factors influencing this ratio have been assigned weights according to how much they influence microbial conversion (this is part of the calibration process). Weighted variables add up to 1. This fraction is then multiplied by 0.36, the range of values found from Warner (0.39 - 0.03).

Weights:

pH .25
fraction wetlands .25
season .25
productivity .25

- $\text{perturb_fr_wetlands} = .1$
DOCUMENT: Allows manipulation of the portion of the watershed that is wetlands. The fraction wetlands is multiplied by the value set by the user.
- $\text{perturb_pH} = 7$
DOCUMENT: Allows manipulation of the pH in the stream. The value of the slider is added to the pH.
- $\text{perturb_pH_input} = 0$
- $\text{perturb_temp} = 0$
- $\text{perturb_water_temp} = 0$
- $\text{perturb_wetlands} = 0$
- $\text{pH} = \text{GRAPH}(\text{count})$

1	2	3	4	5	6	7	8	9	10	11	12
---	---	---	---	---	---	---	---	---	----	----	----

 (1.00, 7.83), (2.00, 7.78), (3.00, 7.73), (4.00, 7.68), (5.00, 7.73), (6.00, 7.40), (7.00, 7.49), (8.00, 7.39), (9.00, 7.58), (10.0, 7.48), (11.0, 7.65), (12.0, 7.82)
 DOCUMENT: reads mean pH from excel file for each month.

season = GRAPH(IF perturb_temp = 0 THEN water_temp ELSE (water_temp+perturb_water_temp))
 (0.00, 0.00), (2.60, 0.00), (5.20, 0.00), (7.80, 0.005), (10.4, 0.08), (13.0, 0.23), (15.6, 0.865), (18.2, 0.94), (20.8, 0.985), (23.4, 0.99), (26.0, 1.00)

DOCUMENT: Relates the impact of water temperature on microbial activity.

water_temp = GRAPH(count)
 (1.00, 4.00), (2.00, 6.40), (3.00, 8.70), (4.00, 11.4), (5.00, 17.8), (6.00, 21.8), (7.00, 23.9), (8.00, 22.8), (9.00, 19.0), (10.0, 14.6), (11.0, 9.60), (12.0, 5.20)

DOCUMENT: Input of mean monthly water temperature from linked Excel file.

Not in a sector

BLOOD_MeHg[Population_Intake](t) = BLOOD_MeHg[Population_Intake](t - dt) +
 (MeHg_Absorption[Population_Intake] - Bl_to_Tissue_MeHg_Transfer[Population_Intake] -
 Excretion_in_Hair[Population_Intake] - Placental_Transfer[Population_Intake] -
 MeHg_Defecated[Population_Intake]) * dt
 INIT BLOOD_MeHg[Population_Intake] = 0
 {ug MeHg}

DOCUMENT: This stock acts as a clearinghouse for MeHg in the body. Inputs are primarily from ingestion, but can also be from tissue if the steady state between blood and tissue is disrupted. MeHg in blood moves to hair, tissue, the fetus, or is defecated.

INFLOWS:

MeHg_Absorption[Population_Intake] = IF (TIME < 1200) THEN
 (MeHg_ingestion[Population_Intake]*MeHg_absorption_fraction) ELSE (0)
 {ug MeHg per month}

DOCUMENT: Absorption represents the intake of mercury through fish consumption minus the MeHg that is not absorbed through the gut. The ingested MeHg is multiplied by the absorption fraction to determine the amount that is absorbed into the blood stream.

The use of the IF THEN ELSE statement was used in the development of the model to look at half-time in blood. At TIME < 1200, the absorption flow remains on for the full run. The absorption of Hg can be turned off (to 0) during a model run by changing the 1200 to a lower number, and the response of the system to n input can be observed.

OUTFLOWS:

Bl_to_Tissue_MeHg_Transfer[Population_Intake] = (MeHg_tissue_gap[Population_Intake] +
 ((1-expected_ratio)*MeHg_Absorption[Population_Intake]))+0*MeHg_Defecated[Population_Intake]
 {ug per month}

DOCUMENT: This flow is designed to calculate the mass of Hg that must move from BLOOD MeHg to TISSUE MeHg (or vice versa) in order to maintain (or attain) the steady state ratio (expected ratio) that has been found in studies. In addition, the amount flowing into the BLOOD MeHg stock is considered, with the proper portion of that flow also being moved to the TISSUE MeHg stock. This addition was necessary because of the time scales involved. The time scale from which blood mercury moves into tissue is faster than the monthly time scale of the model.

The connector from MeHg Defecation flow (and multiplication by 0 in equation) is to force the priority of the Hg Defecation flow to be higher than this flow.

- > Excretion_in_Hair[Population_Intake] = monthly_hair_MeHg[Population_Intake]
{ug MeHg per month}
DOCUMENT: Moves the amount of mercury into the HAIR stock based on the blood concentration and the literature-based ratio.
- > Placental_Transfer[Population_Intake] = IF (bw=31.5) THEN (0) ELSE (IF ((MOD(TIME,60))<9) THEN (needed[Population_Intake]/9) ELSE (0))
{ug MeHg per month}
DOCUMENT: This project shows the potential exposure of a fetus based on population intake rates. Therefore, the approach is to show exposure in snapshots. Pregnancies are generated at 5 year intervals. The fetal blood mercury amounts are derived by the ideal ratio as determined by Stern and Smith (2003). The growth of a fetus over 9 months and subsequent time course of exposure is beyond the scope of this project. The amount of mercury needed to obtain the ideal cord blood: maternal blood ratio is calculated for the full term fetus. That quantity is transferred to the fetus over a 9 month interval (needed/9). Birth occurs after 9 months.

If a population of children is being modeled, this pathway is turned off. The mechanics is by noting if the body weight is that of the standard child (31.5), then the flow is set to 0, otherwise the above logic applies.

- > MeHg_Defecated[Population_Intake] = BLOOD_MeHg[Population_Intake]*MeHg_def_fraction
{ug MeHg per month}
DOCUMENT: This represents the flow of MeHg that enters the gut and is defecated through the entero-hepatic shunt. It is calibrated on the basis of trying to achieve literature-based half-times of Hg in the body (in combination with IHg Defecation).

- FETAL_BLOOD_MeHg[Population_Intake](t) = FETAL_BLOOD_MeHg[Population_Intake](t - dt) + (Placental_Transfer[Population_Intake] - Birth[Population_Intake]) * dt
INIT FETAL_BLOOD_MeHg[Population_Intake] = 0
{ug MeHg}

DOCUMENT: The stock is emptied after 9 months through the Birth flow.

INFLOWS:

- > Placental_Transfer[Population_Intake] = IF (bw=31.5) THEN (0) ELSE (IF ((MOD(TIME,60))<9) THEN (needed[Population_Intake]/9) ELSE (0))
{ug MeHg per month}
DOCUMENT: This project shows the potential exposure of a fetus based on population intake rates. Therefore, the approach is to show exposure in snapshots. Pregnancies are generated at 5 year intervals. The fetal blood mercury amounts are derived by the ideal ratio as determined by Stern and Smith (2003). The growth of a fetus over 9 months and subsequent time course of exposure is beyond the scope of this project. The amount of mercury needed to obtain the ideal cord blood: maternal blood ratio is calculated for the full term fetus. That quantity is transferred to the fetus over a 9 month interval (needed/9). Birth occurs after 9 months.

If a population of children is being modeled, this pathway is turned off. The mechanics is by noting if the body weight is that of the standard child (31.5), then the flow is set to 0, otherwise the above logic applies.

OUTFLOWS:

↪ Birth[Population_Intake] = IF ((MOD(TIME,60))>9) THEN (FETAL__BLOOD_MeHg[Population_Intake])
 ELSE (0)
 {ug MeHg per month}
 DOCUMENT: Birth occurs after 9 months of gestation. While birth is rather abrupt in real life, this stock is emptied over a month period.

IHg_in_1CM_HAIR[Population_Intake](t) = IHg_in_1CM_HAIR[Population_Intake](t - dt) +
 (IHg_Hair_Exc[Population_Intake] - Outgrowth_of_IHg_in_Hair[Population_Intake]) * dt
 INIT IHg_in_1CM_HAIR[Population_Intake] = 0
 {ug IHg}
 DOCUMENT: Represents the mass of inorganic mercury in 1 cm hair. This is used to calculate total hair mercury concentration, one of the biomarkers of exposure.

INFLOWS:

↪ IHg_Hair_Exc[Population_Intake] = TISSUE_IHg[Population_Intake]*IHg_hair_fraction
 DOCUMENT: Moves IHg from tissue to hair, calibrated to move the correct amount of inorganic mercury in hair to achieve the ideal ratio between total mercury in hair and blood methylmercury.

OUTFLOWS:

↪ Outgrowth_of_IHg_in_Hair[Population_Intake] = IHg_in_1CM_HAIR[Population_Intake]
 {ug IHg per month}
 DOCUMENT: Moves the IHg out after one month to simulate a growth rate of 1 cm/month. This mimics the history of exposure over time as described by Cernichiari et al. (2007).

MeHg_IN_1_CM_HAIR[Population_Intake](t) = MeHg_IN_1_CM_HAIR[Population_Intake](t - dt) +
 (Excretion_in_Hair[Population_Intake] - Outgrowth[Population_Intake]) * dt
 INIT MeHg_IN_1_CM_HAIR[Population_Intake] = 0
 {ug MeHg}
 DOCUMENT: Hair mercury is a commonly used biomarker for Hg exposure. The usual process is to measure hair in 1 cm segments, with each segment representing a month of exposure. A stock of 1 cm of hair MeHg represents one month's exposure. A record then can be obtained for exposure over time.

The Outgrowth flow then empties the stock so that the next month's measurement is accurate.

INFLOWS:

↪ Excretion_in_Hair[Population_Intake] = monthly_hair_MeHg[Population_Intake]
 {ug MeHg per month}
 DOCUMENT: Moves the amount of mercury into the HAIR stock based on the blood concentration and the literature-based ratio.

OUTFLOWS:

↪ Outgrowth[Population_Intake] = MeHg_IN_1_CM_HAIR[Population_Intake]
 {ug MeHg per month}
 DOCUMENT: Moves the MeHg out after one month to simulate a growth rate of 1 cm/month. This mimics the history of exposure over time as described by Cernichiari et al. (2007).

MeHg_IN_DETritus(t) = MeHg_IN_DETritus(t - dt) + (Predatory_Fish_Death + Lvl_2_Death + Lvl_3_Death +
 Lvl_1_Death - MeHg_in_Detritus_Lost_Downstream - Detrital_Uptake) * dt
 INIT MeHg_IN_DETritus = 0
 UNITS: mg
 DOCUMENT: This stock represents the methylmercury within dead biota in the system. The methylmercury can be eaten by detritivores or washed downstream and lost to the system. Detritivores are represented in trophic level 2.

INFLOWS:

☞ Predatory_Fish_Death = MeHg_IN_TROPHIC_LVL_4*.36/12

UNITS: mg/mo

DOCUMENT: Removes MeHg from the stock that occurs from death of the fish.

Current value of .36 is mean of natural mortality for the predatory fish found in Kentucky streams that were used to calibrate the model.

☞ Lvl_2_Death = MeHg_IN_TROPHIC_LVL_2/12

UNITS: mg/mo

DOCUMENT: Assumption that primary consumers have a 1 year life span.

Represents methylmercury within trophic level 2 that leaves trophic level 2 through death, not consumption.

☞ Lvl_3_Death = MeHg_IN_TROPHIC_LVL_3*.56/12

UNITS: mg/mo

DOCUMENT: This is the natural mortality rate for bluegill, which is a representative forage fish. (TL3)

☞ Lvl_1_Death = MeHg_IN_TROPHIC_LVL_1*seasonal

UNITS: mg/mo

DOCUMENT: Graphical input of common pattern of death for primary producers in streams (periphyton). Mats grow rapidly in spring, and begin to die in mid-summer due to lack of oxygen (low flow and sunlight). This flow represents the movement of methylmercury from live primary producers to dead primary producers that stay within the modeled system. Mercury in periphyton mats that get lost downstream are represented in the MeHg Loss Downstream flow.

Loss of periphyton mats tends to occur seasonally, with mats dying as they get thicker and older. This dynamic is represented by the graphical function "seasonal".

OUTFLOWS:

☞ MeHg_in_Detritus_Lost_Downstream = MeHg_IN_DETRITUS*(1-retention)

UNITS: mg/mo

DOCUMENT: Downstream loss of MeHg in detritus based on retention in the stream.

☞ Detrital_Uptake = SMTH1(MeHg_IN_DETRITUS*retention,24)

UNITS: mg/mo

DOCUMENT: Represents the movement of methylmercury within the system from within dead biota back into trophic level 2.

The smooth function is used to dampen the wobble caused by the seasonal nature of methylmercury production.

☐ MeHg_IN_TROPHIC_LVL_1(t) = MeHg_IN_TROPHIC_LVL_1(t - dt) + (Microbial_Conversion - Trophic_Transfer_1 - Lvl_1_Death - MeHg_Diffusion) * dt

INIT MeHg_IN_TROPHIC_LVL_1 = 4

UNITS: mg

DOCUMENT: The assumption is made that methylation occurs in association with periphyton or biofilm, and so is associated with the lowest trophic level.

INFLOWS:

↳ Microbial_Conversion = SOLUBLE_IHg_in_STREAMBED*micro_conv_rate
 UNITS: mg/mo
 DOCUMENT: microbial conversion of inorganic mercury to methylmercury is assumed to occur in association with periphyton. Sunlight degrades MeHg, and accounted for in this flow also.

OUTFLOWS:

↳ Trophic_Transfer_1 = SMTH1(gap_2,24)
 UNITS: mg/mo
 DOCUMENT: This flow represents the movement of methylmercury from primary producers (in this case, periphyton and biofilm) to primary consumers through consumption.

The amount of MeHg that moves through the flow is calculated based on the Predator Prey Factor 2 (PPF2). This is the ratio of the concentration of MeHg in trophic level 2 to trophic level 1. A general PPF2 is taken from the Mercury Study Report to Congress (1997). The amount is adjusted based on the nutrient status of the stream to reflect the effect of growth dilution on bioaccumulation.

The smooth function is used to dampen the wobble caused by the seasonal nature of methylmercury production.

↳ Lvl_1_Death = MeHg_IN_TROPHIC_LVL_1*seasonal
 UNITS: mg/mo
 DOCUMENT: Graphical input of common pattern of death for primary producers in streams (periphyton). Mats grow rapidly in spring, and begin to die in mid-summer due to lack of oxygen (low flow and sunlight). This flow represents the movement of methylmercury from live primary producers to dead primary producers that stay within the modeled system. Mercury in periphyton mats that get lost downstream are represented in the MeHg Loss Downstream flow.

Loss of periphyton mats tends to occur seasonally, with mats dying as they get thicker and older. This dynamic is represented by the graphical function "seasonal".

↳ MeHg_Diffusion = MeHg_IN_TROPHIC_LVL_1*diffusion
 UNITS: mg/mo
 DOCUMENT: Very small amounts of methylmercury can be found in the water column. The assumption is that it has diffused from the biofilm or periphyton into the water column.

MeHg_IN_TROPHIC_LVL_2(t) = MeHg_IN_TROPHIC_LVL_2(t - dt) + (Trophic_Transfer_1 + Detrital_Uptake - Trophic_Transfer_2 - Lvl_2_Death) * dt
 INIT MeHg_IN_TROPHIC_LVL_2 = 3
 UNITS: mg
 DOCUMENT: Methylmercury in primary consumers and detritivores.
 INFLOWS:

-> Trophic_Transfer_1 = SMTH1(gap_2,24)

UNITS: mg/mo

DOCUMENT: This flow represents the movement of methylmercury from primary producers (in this case, periphyton and biofilm) to primary consumers through consumption.

The amount of MeHg that moves through the flow is calculated based on the Predator Prey Factor 2 (PPF2). This is the ratio of the concentration of MeHg in trophic level 2 to trophic level 1. A general PPF2 is taken from the Mercury Study Report to Congress (1997). The amount is adjusted based on the nutrient status of the stream to reflect the effect of growth dilution on bioaccumulation.

The smooth function is used to dampen the wobble caused by the seasonal nature of methylmercury production.

-> Detrital_Uptake = SMTH1(MeHg_IN_DETRITUS*retention,24)

UNITS: mg/mo

DOCUMENT: Represents the movement of methylmercury within the system from within dead biota back into trophic level 2.

The smooth function is used to dampen the wobble caused by the seasonal nature of methylmercury production.

OUTFLOWS:

-> Trophic_Transfer_2 = SMTH1(gap_3,24)

UNITS: mg/mo

DOCUMENT: This flow represents the movement of methylmercury from primary consumers (in this case, macroinvertebrates) to secondary consumers through consumption.

The amount of MeHg that moves through the flow is calculated based on the Predator Prey Factor 3 (PPF3). This is the ratio of the concentration of MeHg in trophic level 3 to trophic level 2. A general PPF3 is taken from the Mercury Study Report to Congress (1997). The amount is adjusted based on the nutrient status of the stream to reflect the effect of growth dilution on bioaccumulation.

The smooth function is used to dampen the wobble caused by the seasonal nature of methylmercury production.

-> Lvl_2_Death = MeHg_IN_TROPHIC_LVL_2/12

UNITS: mg/mo

DOCUMENT: Assumption that primary consumers have a 1 year life span.

Represents methylmercury within trophic level 2 that leaves trophic level 2 through death, not consumption.

$MeHg_IN_TROPHIC_LVL_3(t) = MeHg_IN_TROPHIC_LVL_3(t - dt) + (Trophic_Transfer_2 -$

$Trophic_Transfer_3 - Lvl_3_Death) * dt$

INIT $MeHg_IN_TROPHIC_LVL_3 = 2$

UNITS: mg

DOCUMENT: Methylmercury in forage fish.

INFLOWS:

-> Trophic_Transfer_2 = SMTH1(gap_3,24)

UNITS: mg/mo

DOCUMENT: This flow represents the movement of methylmercury from primary consumers (in this case, macroinvertebrates) to secondary consumers through consumption.

The amount of MeHg that moves through the flow is calculated based on the Predator Prey Factor 3 (PPF3). This is the ratio of the concentration of MeHg in trophic level 3 to trophic level 2. A general PPF3 is taken from the Mercury Study Report to Congress (1997). The amount is adjusted based on the nutrient status of the stream to reflect the effect of growth dilution on bioaccumulation.

The smooth function is used to dampen the wobble caused by the seasonal nature of methylmercury production.

OUTFLOWS:

-> Trophic_Transfer_3 = SMTH1(gap_4,24)

UNITS: mg/mo

DOCUMENT: This flow represents the movement of methylmercury from forage fish to piscivorous fish through consumption.

The amount of MeHg that moves through the flow is calculated based on the Predator Prey Factor 4 (PPF4). This is the ratio of the concentration of MeHg in trophic level 4 to trophic level 3. A general PPF4 is taken from the Mercury Study Report to Congress (1997). The amount is adjusted based on the nutrient status of the stream to reflect the effect of growth dilution on bioaccumulation.

The smooth function is used to dampen the wobble caused by the seasonal nature of methylmercury production.

-> Lvl_3_Death = MeHg_IN_TROPHIC_LVL_3*.56/12

UNITS: mg/mo

DOCUMENT: This is the natural mortality rate for bluegill, which is a representative forage fish. (TL3)

MeHg_IN_TROPHIC_LVL_4(t) = MeHg_IN_TROPHIC_LVL_4(t - dt) + (Trophic_Transfer_3 - Predatory_Fish_Death) * dt

INIT MeHg_IN_TROPHIC_LVL_4 = 1

UNITS: mg

DOCUMENT: Methylmercury in piscivorous fish.

INFLOWS:

-> Trophic_Transfer_3 = SMTH1(gap_4,24)

UNITS: mg/mo

DOCUMENT: This flow represents the movement of methylmercury from forage fish to piscivorous fish through consumption.

The amount of MeHg that moves through the flow is calculated based on the Predator Prey Factor 4 (PPF4). This is the ratio of the concentration of MeHg in trophic level 4 to trophic level 3. A general PPF4 is taken from the Mercury Study Report to Congress (1997). The amount is adjusted based on the nutrient status of the stream to reflect the effect of growth dilution on bioaccumulation.

The smooth function is used to dampen the wobble caused by the seasonal nature of methylmercury production.

OUTFLOWS:

-> Predatory_Fish_Death = MeHg_IN_TROPHIC_LVL_4*.36/12

UNITS: mg/mo

DOCUMENT: Removes MeHg from the stock that occurs from death of the fish.

Current value of .36 is mean of natural mortality for the predatory fish found in Kentucky streams that were used to calibrate the model.

MeHg_IN_WATER(t) = MeHg_IN_WATER(t - dt) + (MeHg_Diffusion - MeHg_Loss_Downstream) * dt

INIT MeHg_IN_WATER = 1

UNITS: mg

DOCUMENT: This stock represents the methylmercury found in the water column.

INFLOWS:

-> MeHg_Diffusion = MeHg_IN_TROPHIC_LVL_1*diffusion

UNITS: mg/mo

DOCUMENT: Very small amounts of methylmercury can be found in the water column. The assumption is that it has diffused from the biofilm or periphyton into the water column.

OUTFLOWS:

-> MeHg_Loss_Downstream = MeHg_IN_WATER*(1-retention)

UNITS: mg/mo

DOCUMENT: The methylmercury is frequently produced in periphyton mats and other areas associated with productivity, and therefore is subject to high uptakes rates into the food web. However, high flow events can wash MeHg and even whole periphyton mats, with the associated MeHg downstream out of the system.

SOLUBLE_IHg_in_STREAMBED(t) = SOLUBLE_IHg_in_STREAMBED(t - dt) + (Deposition - Microbial_Conversion) * dt

INIT SOLUBLE_IHg_in_STREAMBED = 2

UNITS: mg

DOCUMENT: This stock represents the soluble inorganic mercury that is retained in the system. It may be particulate-bound inorganic mercury that deposits in a pool and subsequently enters solution, or it may be soluble IHg that, as it moves through a periphyton mat, is sorbed by biofilm.

INFLOWS:

-> Deposition = SOLUBLE_IHg_IN_WATER*retention

UNITS: mg/mo

DOCUMENT: Represents the amount of inorganic mercury that remains in the system each month. It may be particulate-bound IHg that is deposited to the streambed in a slow-moving pool and subsequently dissolves, or it might be soluble IHg that is taken up by biofilm.

The majority of IHg in the system moves out of the system by being carried downstream. Only the amount retained is available for conversion to methylmercury.

OUTFLOWS:

-> Microbial_Conversion = SOLUBLE_IHg_in_STREAMBED*micro_conv_rate

UNITS: mg/mo

DOCUMENT: microbial conversion of inorganic mercury to methylmercury is assumed to occur in association with periphyton. Sunlight degrades MeHg, and accounted for in this flow also.

□ $SOLUBLE_IHg_IN_WATER(t) = SOLUBLE_IHg_IN_WATER(t - dt) + (Soluble_IHg_Inflow - IHg_Loss_Downstream - Deposition) * dt$
 INIT SOLUBLE_IHg_IN_WATER = 50
 UNITS: mg

INFLOWS:

↔ Soluble_IHg_Inflow = soluble_IHg_input
 UNITS: mg/mo
 DOCUMENT: The amount of soluble Hg entering the system as determined by the Hg Input sector.

OUTFLOWS:

↔ IHg_Loss_Downstream = SOLUBLE_IHg_IN_WATER*(1-retention)
 UNITS: mg/mo
 DOCUMENT: The vast majority of inorganic mercury in the system is associated with suspended particulate matter and is lost downstream. The IHg is not available for conversion to methylmercury.

↔ Deposition = SOLUBLE_IHg_IN_WATER*retention
 UNITS: mg/mo
 DOCUMENT: Represents the amount of inorganic mercury that remains in the system each month. It may be particulate-bound IHg that is deposited to the streambed in a slow-moving pool and subsequently dissolves, or it might be soluble IHg that is taken up by biofilm.

The majority of IHg in the system moves out of the system by being carried downstream. Only the amount retained is available for conversion to methylmercury.

□ $TISSUE_IHg[Population_Intake](t) = TISSUE_IHg[Population_Intake](t - dt) + (Converted_to_IHg[Population_Intake] - IHg_Hair_Exc[Population_Intake] - IHg_Defecation[Population_Intake] - Urine_IHg_Loss[Population_Intake]) * dt$
 INIT TISSUE_IHg[Population_Intake] = 0
 {ug IHg}

DOCUMENT: MeHg can be converted to IHg in the tissue. This stock represents IHg in tissue. Different organs may have varying concentrations of IHg, but this stock represents all in the body.

INFLOWS:

↔ Converted_to_IHg[Population_Intake] =
 TISSUE_MeHg[Population_Intake]*rate_constant_convert_to_IHg
 {ug IHg per month}
 DOCUMENT: This flow represents the rate of conversion of MeHg to IHg within the tissue, and was calibrated to optimize the MeHg blood concentration: tissue MeHg ratio and time to steady state. The addition of Disposition*0 is to give the flow the correct outflow priority.

OUTFLOWS:

↔ IHg_Hair_Exc[Population_Intake] = TISSUE_IHg[Population_Intake]*IHg_hair_fraction
 DOCUMENT: Moves IHg from tissue to hair, calibrated to move the correct amount of inorganic mercury in hair to achieve the ideal ratio between total mercury in hair and blood methylmercury.

↔ IHg_Defecation[Population_Intake] = TISSUE_IHg[Population_Intake]*IHg_def_rate
 {ug per month}
 DOCUMENT: It is believed that some Hg loss to the system occurs through removal of IHg from the blood by the liver and excretion into the gut by bile, or direct excretion across the luminal tract (Clarkson et al. 2007). It is calibrated on the basis of trying to achieve literature-based half-times of Hg in the body (in combination with MeHg Defecation).

↔ Urine_IHg_Loss[Population_Intake] = TISSUE_IHg[Population_Intake]*tissue_to_urine_transfer_rate
 {ug per month}
 DOCUMENT: Calibrated to balance defecation loss and half-times in body.

□ TISSUE_MeHg[Population_Intake](t) = TISSUE_MeHg[Population_Intake](t - dt) +
 (Bl_to_Tissue_MeHg_Transfer[Population_Intake] - Converted_to_IHg[Population_Intake]) * dt
 INIT TISSUE_MeHg[Population_Intake] = 100
 {ug MeHg}
 DOCUMENT: At steady state, tissue MeHg and blood MeHg have a desired ratio of 7.5:1. Movement from tissue can occur back to blood or can be to IHg in tissue (representing demethylation in tissue).

INFLOWS:

↔ Bl_to_Tissue_MeHg_Transfer[Population_Intake] = (MeHg_tissue_gap[Population_Intake] +
 ((1-expected_ratio)*MeHg_Absorption[Population_Intake]))+0*MeHg_Defecated[Population_Intake]
 {ug per month}
 DOCUMENT: This flow is designed to calculate the mass of Hg that must move from BLOOD MeHg to TISSUE MeHg (or vice versa) in order to maintain (or attain) the steady state ratio (expected ratio) that has been found in studies. In addition, the amount flowing into the BLOOD MeHg stock is considered, with the proper portion of that flow also being moved to the TISSUE MeHg stock. This addition was necessary because of the time scales involved. The time scale from which blood mercury moves into tissue is faster than the monthly time scale of the model.

The connector from MeHg Defecation flow (and multiplication by 0 in equation) is to force the priority of the Hg Defecation flow to be higher than this flow.

OUTFLOWS:

↔ Converted_to_IHg[Population_Intake] =
 TISSUE_MeHg[Population_Intake]*rate_constant_convert_to_IHg
 {ug IHg per month}
 DOCUMENT: This flow represents the rate of conversion of MeHg to IHg within the tissue, and was calibrated to optimize the MeHg blood concentration: tissue MeHg ratio and time to steady state. The addition of Disposition*0 is to give the flow the correct outflow priority.

- anglers_1 = 1
 DOCUMENT: This converter is a switch. When this population is chosen, it takes on a value of "1". When not chosen, it has a value of "0".
- anglers_2 = 0
 DOCUMENT: This converter is a switch. When this population is chosen, it takes on a value of "1". When not chosen, it has a value of "0".
- biomass_of_lv_2 = biomass_of_lv_1*.1
 UNITS: kg
 DOCUMENT: Biomass of each level is set to 10% of biomass of the level below
- biomass_of_lv_3 = biomass_of_lv_2*.1
 UNITS: kg
 DOCUMENT: biomass of each level is set to 10% of level below
- biomass_of_lv_4 = biomass_of_lv_3*.1
 UNITS: kg
 DOCUMENT: biomass of each level is set to 10% of level below

- $\text{blood_vol} = \text{IF} (\text{bw}=31.5) \text{ THEN } (2.4) \text{ ELSE } (5)$
{L blood}
DOCUMENT: Blood volume is 5 L for adults (IRIS). For children, it was found to average 75.4 ml/kg (so 31.5 kg multiplied by .0754 gives 2.4 L). Source for formula for children: Graham, G.(1963); Blood volume in children. Annals R Coll Surg Engl. 33(3): 149-158.
- $\text{body_burden_IHg}[\text{Population_Intake}] = \text{TISSUE_IHg}[\text{Population_Intake}]$
{ug IHg}
DOCUMENT: used in calculating total body burden Hg
- $\text{body_burden_MeHg}[\text{Population_Intake}] = \text{BLOOD_MeHg}[\text{Population_Intake}] + \text{TISSUE_MeHg}[\text{Population_Intake}]$
{ug MeHg}
DOCUMENT: used in calculating total body burden Hg
- $\text{bw} = \text{IF} (\text{childr_14} + \text{childr_14_cons} > 0) \text{ THEN } (31.5) \text{ ELSE } (67)$
{kg}
DOCUMENT: Body weight is that used by the EPA for the pregnant woman. Found in the IRIS documentation on MeHg exposure pg 6. If the population being modeled is of a child, then the body weight is 31.5, which is the mean body weight for 9 year old boys and girls given in Table 3 of Chapter 7 of the Exposure Factors Handbook. This population represents children from age 0 to 14 and so it has a highly varied body weight. The weight of a 9-year-old was arbitrarily chosen to represent the group.
- $\text{childr_14} = 1$
DOCUMENT: This converter is a switch. When this population is chosen, it takes on a value of "1". When not chosen, it has a value of "0".
- $\text{childr_14_cons} = 1$
DOCUMENT: This converter is a switch. When this population is chosen, it takes on a value of "1". When not chosen, it has a value of "0".
- $\text{conc_in_M}_1 = \text{MeHg_IN_TROPIC_LVL}_1 / \text{biomass_of_M}_1$
UNITS: mg/kg
DOCUMENT: The mass of MeHg in TL1 divided by the biomass in TL1. This value is used to determine the amount of MeHg that needs to move to TL2.
- $\text{conc_in_M}_2 = \text{MeHg_IN_TROPIC_LVL}_2 / \text{biomass_of_M}_2$
UNITS: mg/kg
DOCUMENT: Mass of MeHg in TL2 divided by the biomass in TL2. This is used to determine the mass of MeHg that needs to move to TL3.
- $\text{conc_in_M}_3 = \text{MeHg_IN_TROPIC_LVL}_3 / \text{biomass_of_M}_3$
UNITS: mg/kg
DOCUMENT: Mass of MeHg in TL3 divided by the biomass of TL3. This is used to determine the mass of MeHg that needs to move to TL4. It is also the output for fish tissue concentration for TL3 (panfish).
- $\text{conc_in_M}_4 = \text{MeHg_IN_TROPIC_LVL}_4 / \text{biomass_of_M}_4$
UNITS: mg/kg
DOCUMENT: MeHg in TL4 divided by the biomass of TL4. This is the model output for fish tissue concentration for TL4 (piscivorous fish).
- $\text{consumers} = 1$
DOCUMENT: This converter is a switch. When this population is chosen, it takes on a value of "1". When not chosen, it has a value of "0".
- $\text{convert_units} = 100$
DOCUMENT: convert mg/kg to ng/kg

- `cord_conc[Population_Intake] = IF ((MOD(TIME,60) >0) AND (MOD(TIME,60) <9)) THEN (FETAL__BLOOD_MeHg[Population_Intake]/(fetal_bl_vol*(MOD(TIME,60)/9))) ELSE (0)`
{ug MeHg per L blood}
DOCUMENT: As with the flow of MeHg through the placenta, the total blood volume for a full term infant is evenly divided over a 9 month period. The dynamics of fetal growth is beyond the scope of this project. By spreading the volume over the entire 9 months of gestation, it gives a more accurate portrayal of what fetal blood concentrations are, again, allowing some adjustments in maternal compensation.

The MOD statement keeps track of when a pregnancy is occurring (every 5 years), and returns the month of the pregnancy. By multiplying the fetal blood volume by the month and dividing by the total months of pregnancy, the blood volume is a fraction of the pregnancy. (So if it is month 2, the total fetal blood volume is multiplied by 2/9). The MOD>0 statement is necessary to prevent a divide by 0 error.
- `EPA_fish_criterion = .3`
DOCUMENT: Fish tissue concentration set by EPA as water quality criterion for methylmercury in fish.
- `EPA_safe_exposure_level = 5.8`
{ug MeHg per L blood}
DOCUMENT: Maternal blood concentration which EPA has determined to be protective of the developing fetus.

EPA 2009a. Mercury: Human exposure. (03/17/2010 2010; <http://www.epa.gov/mercury/exposure.htm>)
- `expected_ratio = 1/7.5`
{no units}
DOCUMENT: According to Cernichiari et al. (2007) The biological monitoring of prenatal exposure, the ratio of brain to whole blood methylmercury ranges from 5:1 to 10:1. The mean was used.
- `fetal_bl_vol = fetal_bw*.085`
{L blood}
DOCUMENT: The fetal bl vol was derived from the American Academy of Pediatrics website (American Academy of Pediatrics 2010). It reports fetal blood volume averages 78-86 ml/kg for the term infant. An upper-end number (.085 L/kg) was chosen because there will be pulling into the tissue from the blood.
- `fetal_bw = 3.25`
{kg}
DOCUMENT: The fetal body weight was the mean of male and female full-term infants taken from Chapter 7 (Body Weight Studies) of the Exposure Factors Handbook (EPA, 1997).
- `fish_intake_rate[50] = (general*4.7+consumers*68+women*4.3+women_cons*61.4+childr_14*1.9+childr_14_cons*45.7+anglers_1*7.4+anglers_2*4.9+sub_fisher_1*53.3+sub_fisher_2*58.7)/1000*30`
DOCUMENT: The input of the intake rate of the population of concern is controlled by the chained switch on the interface. Only one population can be "on". This switch receives a value of "1" while all others receive a "0". The proper intake rates are then input in the model by multiplying the switch value (0 or 1) for each possible, and adding them together. For all populations that are "off", the value will be 0, while the population that is chosen will be given the appropriate intake rate. This value is then divided by 1000 to convert from grams to kilograms, and multiplied by 30 to give per month instead of per day.

- fish_intake_rate[90] =
 $(\text{general} * 12.6 + \text{consumers} * 170.8 + \text{women} * 10.9 + \text{women_cons} * 148.8 + \text{childr_14} * 1.3 + \text{childr_14_cons} * 108.4 + \text{anglers_1} * 20.6 + \text{anglers_2} * 13.2 + \text{sub_fisher_1} * 203 + \text{sub_fisher_2} * 110) / 1000 * 30$
DOCUMENT: The input of the intake rate of the population of concern is controlled by the chained switch on the interface. Only one population can be "on". This switch receives a value of "1" while all others receive a "0". The proper intake rates are then input in the model by multiplying the switch value (0 or 1) for each possible, and adding them together. For all populations that are "off", the value will be 0, while the population that is chosen will be given the appropriate intake rate. This value is then divided by 1000 to convert from grams to kilograms, and multiplied by 30 to give per month instead of per day.
- fish_intake_rate[95] =
 $(\text{general} * 32.2 + \text{consumers} * 224.8 + \text{women} * 28.8 + \text{women_cons} * 185.9 + \text{childr_14} * 13.9 + \text{childr_14_cons} * 136.2 + \text{anglers_1} * 24.6 + \text{anglers_2} * 17.9 + \text{sub_fisher_1} * 216.7 + \text{sub_fisher_2} * 170) / 1000 * 30$
DOCUMENT: The input of the intake rate of the population of concern is controlled by the chained switch on the interface. Only one population can be "on". This switch receives a value of "1" while all others receive a "0". The proper intake rates are then input in the model by multiplying the switch value (0 or 1) for each possible, and adding them together. For all populations that are "off", the value will be 0, while the population that is chosen will be given the appropriate intake rate. This value is then divided by 1000 to convert from grams to kilograms, and multiplied by 30 to give per month instead of per day.
- fish_intake_rate[99] =
 $(\text{general} * 82.5 + \text{consumers} * 374.7 + \text{women} * 70.9 + \text{women_cons} * 363.6 + \text{childr_14} * 40.8 + \text{childr_14_cons} * 214.6 + \text{anglers_1} * 82.2 + \text{anglers_2} * 39.8 + \text{sub_fisher_1} * 240 + \text{sub_fisher_2} * 389) / 1000 * 30$
(kg fish per month)
DOCUMENT: The input of the intake rate of the population of concern is controlled by the chained switch on the interface. Only one population can be "on". This switch receives a value of "1" while all others receive a "0". The proper intake rates are then input in the model by multiplying the switch value (0 or 1) for each possible, and adding them together. For all populations that are "off", the value will be 0, while the population that is chosen will be given the appropriate intake rate. This value is then divided by 1000 to convert from grams to kilograms, and multiplied by 30 to give per month instead of per day.
- gap_2 = needed_M_2-MeHg_IN_TROPHIC_LVL_2
UNITS: mg
DOCUMENT: Difference between the mass needed to achieve target concentration and mass already resident in the stock.
- gap_3 = needed_M_3-MeHg_IN_TROPHIC_LVL_3
UNITS: mg
DOCUMENT: Difference between the mass needed to achieve target concentration and mass already resident in the stock.
- gap_4 = needed_M_4-MeHg_IN_TROPHIC_LVL_4
UNITS: mg
DOCUMENT: Difference between the mass needed to achieve target concentration and mass already resident in the stock.
- general = 1
DOCUMENT: This converter is a switch. When this population is chosen, it takes on a value of "1". When not chosen, it has a value of "0".

- hair_to_blood_ratio = 250
(no units)
DOCUMENT: Clarkson et al. 2007 reports a central tendency of total hair mercury to blood methylmercury of 250:1. This is further broken into 80% MeHg and 20% iHg as reported by Phelps, Clarkson, Kershaw, Wheatley (1980) Archives of Environmental Health. Vol 35 (3): pp 161-168).

- ideal_cord:_maternal_ratio = 1.9
DOCUMENT: Stern & Smith (2003) found a central tendency ratio of 1.9 for cord blood to maternal blood methylmercury in a meta-analysis of studies. (This is the ratio found for the meta-analysis that included studies that reported methylmercury concentrations only.)

- ideal_fetal_conc[Population_Intake] = MeHg_blood_conc[Population_Intake]*ideal_cord:_maternal_ratio
{ug per L}

- ideal_M_2_conc = conc_in_M_1*PPF2
UNITS: mg/m³
DOCUMENT: Based on the predator prey factor and the concentration of methylmercury in trophic level 1, this is the target concentration for trophic level 2.

- ideal_M_3_conc = conc_in_M_2*PPF3
UNITS: mg/m³
DOCUMENT: Based on the predator prey factor and the concentration of methylmercury in trophic level 2, this is the target concentration for trophic level 3.

- ideal_M_4_conc = conc_in_M_3*PPF4
UNITS: mg/m³
DOCUMENT: Based on the predator prey factor and the concentration of methylmercury in trophic level 3, this is the target concentration for trophic level 4.

- ideal_tissue_MeHg[50] = body_burden_MeHg[50]/(1+(blood_vol*expected_ratio/bw))
DOCUMENT: Ideal tissue MeHg is the calculated mass of MeHg that should be in TISSUE MeHg in order to attain the expected ratio. It is calculated from the body burden MeHg, expected ratio, bw, and blood vol. The two equations: Body burden MeHg = ideal Blood MeHg + ideal tissue MeHg and expected ratio = (BLOOD MeHg/blood vol)/(TISSUE MeHg/bw) are solved for ideal tissue MeHg, to become: ideal tissue MeHg = body burden MeHg/(1+(blood_vol*expected_ratio/bw)).

- ideal_tissue_MeHg[90] = body_burden_MeHg[90]/(1+(blood_vol*expected_ratio/bw))
DOCUMENT: Ideal tissue MeHg is the calculated mass of MeHg that should be in TISSUE MeHg in order to attain the expected ratio. It is calculated from the body burden MeHg, expected ratio, bw, and blood vol. The two equations: Body burden MeHg = ideal Blood MeHg + ideal tissue MeHg and expected ratio = (BLOOD MeHg/blood vol)/(TISSUE MeHg/bw) are solved for ideal tissue MeHg, to become: ideal tissue MeHg = body burden MeHg/(1+(blood_vol*expected_ratio/bw)).

- ideal_tissue_MeHg[95] = body_burden_MeHg[95]/(1+(blood_vol*expected_ratio/bw))
DOCUMENT: Ideal tissue MeHg is the calculated mass of MeHg that should be in TISSUE MeHg in order to attain the expected ratio. It is calculated from the body burden MeHg, expected ratio, bw, and blood vol. The two equations: Body burden MeHg = ideal Blood MeHg + ideal tissue MeHg and expected ratio = (BLOOD MeHg/blood vol)/(TISSUE MeHg/bw) are solved for ideal tissue MeHg, to become: ideal tissue MeHg = body burden MeHg/(1+(blood_vol*expected_ratio/bw)).

- $\text{ideal_tissue_MeHg}[99] = \text{body_burden_MeHg}[99]/(1+(\text{blood_vol}*\text{expected_ratio}/\text{bw}))$
{ug}
DOCUMENT: Ideal tissue MeHg is the calculated mass of MeHg that should be in TISSUE MeHg in order to attain the expected ratio. It is calculated from the body burden MeHg, expected ratio, bw, and blood vol. The two equations: $\text{Body burden MeHg} = \text{ideal Blood MeHg} + \text{ideal tissue MeHg}$ and $\text{expected ratio} = (\text{BLOOD MeHg}/\text{blood vol})/(\text{TISSUE MeHg}/\text{bw})$ are solved for ideal tissue MeHg, to become: $\text{ideal tissue MeHg} = \text{body burden MeHg}/(1+(\text{blood_vol}*\text{expected_ratio}/\text{bw}))$.
- $\text{IHg_conc_in_hair}[\text{Population_Intake}] = \text{IHg_in_1CM_HAIR}[\text{Population_Intake}]/\text{mass_of_1_cm_hair}$
{ug IHg per kg hair}
DOCUMENT: ug IHg per kg of hair. Used in calculation of total hair mercury.
- $\text{IHg_def_rate} = .9$
{no units}
DOCUMENT: Set to help achieve a 80-90% loss through the defecation pathways (both MeHg and IHg together).
- $\text{IHg_hair_fraction} = .0296$
DOCUMENT: Fraction was determined by back-calculating the fraction of TISSUE IHg needed to generate the correct amount of inorganic mercury in hair to achieve the ideal ratio between total mercury in hair and blood methylmercury.
- $\text{intake_conc} = (\text{conc_in_M}_3*\text{troph_M}_3\text{_intake}+\text{conc_in_M}_4*\text{troph_M}_4\text{_intake})/100$
UNITS: mg/kg
DOCUMENT: Feeds into human disposition sector. Allows user to define proportion of diet for a population that comes from trophic levels 3 and 4.

This can be used in two ways:

As written, a population, on average, may consume a certain proportion of its fish intake at trophic level 3, and the rest at trophic level 4. The sliders are set to reflect the proportion of each trophic level consumed.

If interested in the impact of consumption of a particular fish species whose trophic level falls between 3 and 4, the sliders can be set to equal that trophic level (eg. troph M 3 intake slider set at 60% and troph M 4 intake set at 40% is equivalent to intake of a species at trophic level 3.4).
- $\text{mass_of_1_cm_hair} = .0173$
{kg hair}
DOCUMENT: According to Omega Laboratories (<http://www.omegalabs.net/abouthairtesting/hairtestingfaq/hairtestingfaq.aspx>) about 90 to 120 strands of hair (1.5 inches long) make up a 60 mg sample. With estimates of 100,000 to 150,000 strands of hair per head (for those who are not bald), I calculated (using 105 strands for 60 mg and 100,000 strands per head) that the average head would have 18.7 g hair for the first centimeter of growth. this is 0.0173 kg.
- $\text{MeHg_absorption_fraction} = .95$
DOCUMENT: According to Miettinen et al (1971), approximately 95% of ingested MeHg is absorbed.
- $\text{MeHg_blood_conc}[\text{Population_Intake}] = \text{BLOOD_MeHg}[\text{Population_Intake}]/\text{blood_vol}$
{ug MeHg per L blood}
- $\text{MeHg_conc_in_hair}[\text{Population_Intake}] = \text{MeHg_IN_1_CM_HAIR}[\text{Population_Intake}]/\text{mass_of_1_cm_hair}$
{ug MeHg per kg hair}
DOCUMENT: Mass of MeHg in 1 cm hair.

- MeHg_def_fraction = .4
{unitless}
DOCUMENT: Set to help achieve a 80-90% loss through the defecation pathways (both MeHg and IHg together).

- MeHg_ingestion[Population_Intake] = fish_intake_rate[Population_Intake]*intake_conc*convert_units
{ug MeHg per month}
DOCUMENT: Calculates the MeHg ingested based on the kg fish intake for the population multiplied by the fish tissue concentration.

kg fish per month X ug MeHg per kg fish gives units of ug MeHg per month.

- MeHg_tissue_conc[Population_Intake] = TISSUE_MeHg[Population_Intake]/bw
{ug per kg}
DOCUMENT: Gives ug methylmercury per kg tissue. Used in calibration process to determine if the model was achieving the desired ratio between blood and tissue.

- MeHg_tissue_gap[Population_Intake] =
ideal_tissue_MeHg[Population_Intake]-TISSUE_MeHg[Population_Intake]
{ug MeHg}
DOCUMENT: MeHg tissue gap is the difference between TISSUE MeHg and ideal tissue MeHg. This converter informs the BI to Tissue MeHg Transfer flow (in addition to the MeHg Absorption flow). If the number is positive, it is the amount needed to move from BLOOD MeHg to TISSUE MeHg to attain the expected ratio. If it is negative, it is the amount needed to move from TISSUE MeHg to BLOOD MeHg to attain the ratio.

- monthly_hair_MeHg[Population_Intake] =
MeHg_blood_conc[Population_Intake]*hair_to_blood_ratio*mass_of_1_cm_hair*.8
{ug}
DOCUMENT: Calculates amount of mercury in 1 cm of hair (from entire scalp) based on the ratio of hair concentration to blood concentration (250:1). This is multiplied by .8 because a portion of the hair mercury is inorganic, and is calculated separately through the inorganic flow. Total hair mercury is then calculated by adding MeHg and IHg in hair. (80% is the estimated content of MeHg in hair, Phelps, Clarkson, Kershaw, Wheatley (1980) Archives of Environmental Health. Vol 35 (3): pp 161-168).

- needed[Population_Intake] = ideal_fetal_conc[Population_Intake]*fetal_bl_vol
{ug MeHg}
DOCUMENT: Calculates the mass of methylmercury needed to achieve the ideal ratio between cord blood and maternal blood.

- needed_M_3 = biomass_of_M_3*ideal_M_3_conc
UNITS: mg
DOCUMENT: The mass of methylmercury needed in the trophic level 3 stock based on the target concentration and the biomass of trophic level 3.

- needed_M_4 = biomass_of_M_4*ideal_M_4_conc
UNITS: mg
DOCUMENT: The mass of methylmercury needed in the trophic level 4 stock based on the target concentration and the biomass of trophic level 4.

- needed_M_2 = ideal_M_2_conc*biomass_of_M_2
UNITS: mg
DOCUMENT: The mass of methylmercury needed in the trophic level 2 stock based on the target concentration and the biomass of trophic level 2.

- PPF2 = 7+bloom_growth_dilution
 UNITS: Unitless
 DOCUMENT: PPF is the predator prey factor. It is the "unitless factor by which methylmercury concentrations in trophic level [2] organisms exceed those in the trophic level [1] organisms upon which they prey". Hg Study Report to Congress Vol VII, p 6-5.

 Detailed analysis of the derivation of PPF can be found in Hg Study Report to Congress Vol III, Appendix D. (pg D-6 for PPF2). The suggested value of 6.3 was adjusted to 7 to increase model fit.

 The bloom growth dilution factor adjusts the PPF to simulate the effects of nutrient status on bioaccumulation.

- PPF3 = 7+bloom_growth_dilution
 UNITS: Unitless
 DOCUMENT: PPF4 is the predator prey factor. It is the "unitless factor by which methylmercury concentrations in trophic level 4 organisms exceed those in the trophic level 3 organisms upon which they prey". Hg Study Report to Congress Vol VII, p 6-5.
 PPF3 is the ratio of methylmercury concentration of trophic level 3 over trophic level 2. These values are derived from several studies and represent a mean value.

 Detailed analysis of the derivation of PPF can be found in Hg Study Report to Congress Vol III, Appendix D. (pg D-7 for PPF3).

 A PPF3 of 6.3, the suggested average in the Study Report was begun with. This value was adjusted to reduce mean error for all sites. The final adjusted value was 7.0. (Range from cited studies: 2.6-15.5.)

 The bloom growth dilution factor adjusts the PPF to simulate the effects of nutrient status on bioaccumulation.

- PPF4 = 4.5+bloom_growth_dilution
 UNITS: Unitless
 DOCUMENT: PPF is the predator prey factor. It is the "unitless factor by which methylmercury concentrations in trophic level 4 organisms exceed those in the trophic level 3 organisms upon which they prey". Hg Study Report to Congress Vol VII, p 6-5.




 Detailed analysis of the derivation of PPF can be found in Hg Study Report to Congress Vol III, Appendix D. (pg D-8 for PPF4)

 The suggested PPF of 5 was adjusted to 4.5 for better model fit.

 The bloom growth dilution factor adjusts the PPF to simulate the effects of nutrient status on bioaccumulation.

- rate_constant_convert_to_IHg = 0.00155*30
 {no units}
 DOCUMENT: This rate was calibrated by adjusting so that the half-time in the body and the ratio between blood and tissue methylmercury came closest to matching literature values.

- sub_fisher_1 = 1
 DOCUMENT: This converter is a switch. When this population is chosen, it takes on a value of "1". When not chosen, it has a value of "0".

- $sub_fisher_2 = 0$
DOCUMENT: This converter is a switch. When this population is chosen, it takes on a value of "1". When not chosen, it has a value of "0".
- $tissue_to_urine_transfer_rate = .001*30$
{no units}
DOCUMENT: This rate was set to help achieve the goal of having an 80-90% loss through the defecation pathways (MeHg + IHg).
- $total_body_burden[Population_Intake] =$
 $body_burden_IHg[Population_Intake]+body_burden_MeHg[Population_Intake]$
{ug Hg}
DOCUMENT: This converter was used in evaluating the half-time of Hg in the body. It includes all the stocks except Hg in HAIR and FETAL BLOOD.
- $total_conc_in_hair[Population_Intake] =$
 $IHg_conc_in_hair[Population_Intake]+MeHg_conc_in_hair[Population_Intake]$
{ug Hg per kg hair}
- $troph_M_3_intake = 0$
DOCUMENT: Links to slider on interface page. User inputs the proportion of the diet of the target population that is TL3.
- $troph_M_4_intake = 100$
DOCUMENT: Links to slider on interface page. User inputs the proportion of the diet of the target population that is TL4.
- $weighted_TL = (3*troph_M_3_intake+4*troph_M_4_intake)/100$
- $women = 1$
DOCUMENT: This converter is a switch. When this population is chosen, it takes on a value of "1". When not chosen, it has a value of "0".
- $women_cons = 1$
DOCUMENT: This converter is a switch. When this population is chosen, it takes on a value of "1". When not chosen, it has a value of "0".
- $bloom_growth_dilution = GRAPH(mean_productivity_index)$
 (0.00, 2.00), (18.4, 1.88), (36.8, 0.245), (55.3, 0.155), (73.7, 0.065), (92.1, 0.00), (111, 0.005), (129, 0.00), (147, 0.00), (166, 0.00), (184, 0.00), (203, 0.00), (221, 0.00), (239, 0.00), (258, 0.00), (276, 0.00), (295, -0.025), (313, -0.075), (332, -0.15), (350, -0.175)
DOCUMENT: This converter represents the effects of nutrients on bioaccumulation. In eutrophic systems, the methylmercury is spread through a larger number of algal cells. This effect is called bloom dilution (Chen & Folt, 2005). Primary consumers then intake less methylmercury per unit algae consumed than in more oligotrophic systems. In addition, the algae in high-nutrient systems tend to produce more biomass per unit consumed than in nutrient-poor systems (Karimi et al., 2007), so consumers in eutrophic systems consume less for a given amount of biomass produced. This effect is called growth dilution. These two factors lead to eutrophic systems having lower predator prey factors than oligotrophic systems. This graphical function is used to adjust the predator prey factor to reflect this.
- $diffusion = GRAPH(water_temp)$
 (0.00, 0.3), (3.00, 0.345), (6.00, 0.41), (9.00, 0.48), (12.0, 0.565), (15.0, 0.635), (18.0, 0.73), (21.0, 0.795), (24.0, 0.845), (27.0, 0.895), (30.0, 0.935)
- $seasonal = GRAPH(count)$
 (1.00, 0.395), (2.10, 0.4), (3.20, 0.4), (4.30, 0.4), (5.40, 0.335), (6.50, 0.215), (7.60, 0.255), (8.70, 0.8), (9.80, 0.8)
(10.9, 0.8), (12.0, 0.405)
DOCUMENT: Simulates the seasonal pattern of decline, death, and sloughing of periphyton mats

Appendix B

DATA SOURCES

References for Table 2

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- Georgia Spatial Data Infrastructure. 2009. Georgia GIS clearinghouse.
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<http://waterdata.usgs.gov/nwis>. Accessed 9/23/2011
- [USEPA] US Environmental Protection Agency. 2011. STORET/WQX: STORET database access. <http://epa.gov/storet/dbtop.html>. Accessed: 10/26/2010.
- [USEPA] US Environmental Protection Agency Region 4. 2003. Total Maximum Daily Load (TMDL) for total mercury in fish tissue residue in Spring Creek (HUC 03150104) including listed segment.

[USEPA] US Environmental Protection Agency Region 4. 2003. Total Maximum Daily Load (TMDL) for total mercury in fish tissue residue in Talking Rock Creek (HUC 03150102) including listed segment.

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http://www.wvdhhr.org/fish/Data/Data_for_2010_Advisory-waterbody.pdf.

Accessed: 9/25/2011.

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<http://wvgis.wvu.edu/data/data.php>. Accessed: 8/15/2011.

Fish Tissue Data

Calibration Sites†	TL	species	year	QL mm	length mm	sample Hg	sample mean**
Floyds Fork		spotted bass	1999	280	289	0.164	
	3.5	rock bass	2004	180	191	0.194	0.179
		*channel catfish	1999	410	216	0.053	
	3	black redhorse	2004		349	0.138	0.138
Tygarts Creek	4	sauger	2002	300	432	1.140	1.140
Mud River	4	LMB	2004	300	358	0.366	0.366
		channel catfish	2004	410	444	0.122	
		channel catfish	2005	410	513	0.160	
	3.5	channel catfish	2005	410	513	0.179	
		freshwater drum	2002	300	358	0.243	0.201
		*black crappie	2005	200	267	0.303	
		*flathead catfish	1999	510	305	0.166	
		black crappie	2005	200	263	0.303	
		bluegill	1999	150	196	0.091	
		longear sunfish	1999	150	140	0.180	
	3	black redhorse	2002		376	0.057	0.085
		black redhorse	2002		368	0.076	
		*smallmouth buffalo	2002		450	0.039	
		bluegill	2004	150	184	0.068	
Mayfield Creek	3.5	channel catfish	2000	410	419	0.247	0.247
Salt River		spotted bass	1999	280	330	0.277	
	3.5	northern hogsucker	1999		275	0.131	0.179
		freshwater drum	1999	300	279	0.129	
	3	longear sunfish	1999	150	121	0.073	0.073
Nolin River	3.5	rock bass	2001	180	190	0.170	0.170
Slate Creek	4	SMB	2004	280	310	0.190	0.190

*outlier

**excluding outliers

†all calibration sites are in
Kentucky

Abbreviations: TL - trophic level; QL - Quality Length; Hg - mercury
Mercury measurements in mg/kg

Evaluation Sites	TL	species	year	QL mm	length mm	sample Hg	sample mean**	
Spring Creek Georgia	3.5	redeye bass	2002		260	0.380	0.262	
		redeye bass	2002		260	0.300		
		spotted bass	2002	280	225	0.320		
		spotted bass	2002	280	215	0.150		
		shadow bass	2002		190	0.160		
	3	bluegill	2002	150	180	0.310	0.123	
		green sunfish	2002	150	146	0.080		
		green sunfish	2002	150	150	0.050		
	Talking Rock Creek Georgia	4	striped bass*	2002	510	450	0.130	0.271
			striped bass*	2002	510	405	0.060	
3.5		redeye bass	2002		235	0.500		
		redeye bass	2002		224	0.150		
		redeye bass	2002		233	0.420		
		spotted bass	2002	280	330	0.660		
		spotted bass	2002	280	285	0.260		
		spotted bass	2002	280	335	0.150		
		spotted bass	2002	280	275	0.120		
		channel catfish	2002	410	445	0.030		
shadow bass		2002		159	0.150			
3		bluegill	2002	150	166	0.080	0.065	
		bluegill	2002	150	184	0.100		
		bluegill	2002	150	185	0.070		
		redbreast sunfish	2002		165	0.050		
	redbreast sunfish	2002		164	0.050			
redbreast sunfish	2002		175	0.040				

Abbreviations: TL - trophic level; QL - Quality Length; Hg - mercury
 *outlier
 **excluding outliers
 Mercury measurements in mg/kg

Evaluation Sites	TL	species	year	QL mm	length mm	sample Hg	sample mean**
Big Creek	3.5	channel catfish	2002	410	495	0.260	0.260
Indiana	3	longear sunfish	2002	150	142	0.120	0.12
		longear sunfish	2002	150	143	0.120	
Muscatatuck River	3.5	spotted bass	2002	280	279	0.330	0.330
Indiana	3	longear sunfish	2002	150	132	0.085	0.097
		longear sunfish	2002	150	143	0.076	
		redeer sunfish	2002	150	180	0.130	
North Fork Forked	4	largemouth bass	2007	300	338	0.361	0.426
Deer River		largemouth bass*	1998	300	493	0.520	
Tennessee		largemouth bass	1998	300	371	0.490	
		channel catfish*	1998	410	566	0.360	
	3.5	channel catfish	2007	410	437	0.144	0.162
		spotted bass	2007	280	318	0.180	
		spotted bass	2002	280	257	0.368	
Little Kanawha	3.5	channel catfish	2008	410	372	0.041	0.174
West Virginia		channel catfish	2002	410	441	0.138	
		channel catfish	2002	410	387	0.193	
		channel catfish	2008	410	313	0.079	
		channel catfish	2002	410	492	0.225	
		bluegill	2002	150	152	0.018	
	channel catfish	2002	410	437	0.148		
Middle Island Creek	3.5	channel catfish	2002	410	374	0.200	0.179
West Virginia		channel catfish	2002	410	499	0.188	



*outlier

**excluding outliers










Abbreviations: TL - trophic level; QL - Quality Length; Hg - mercury
Mercury measurements in mg/kg

Appendix C

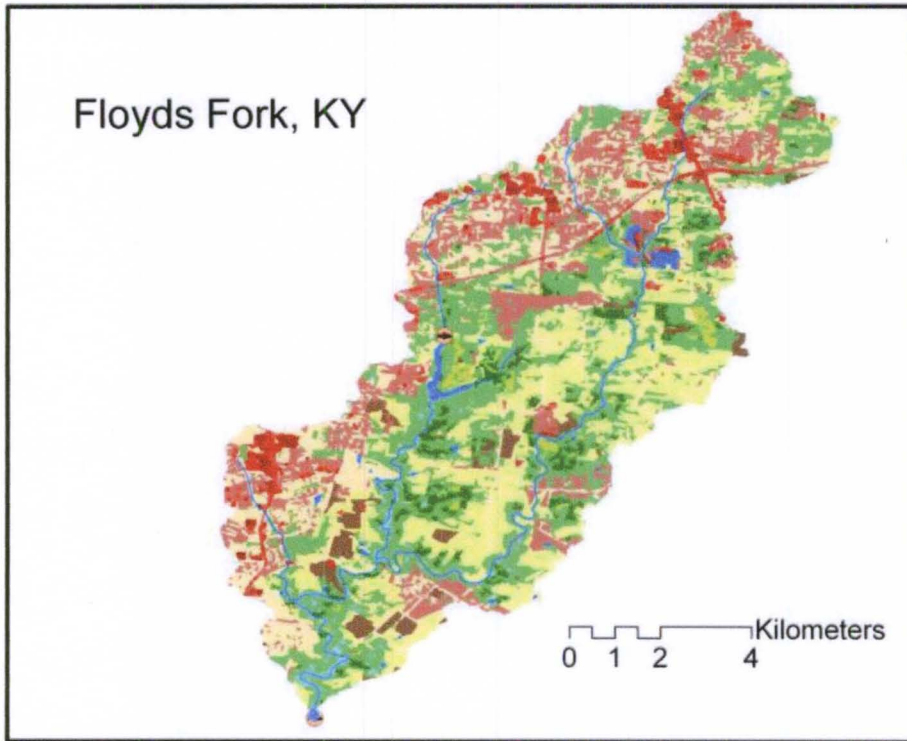
Legend

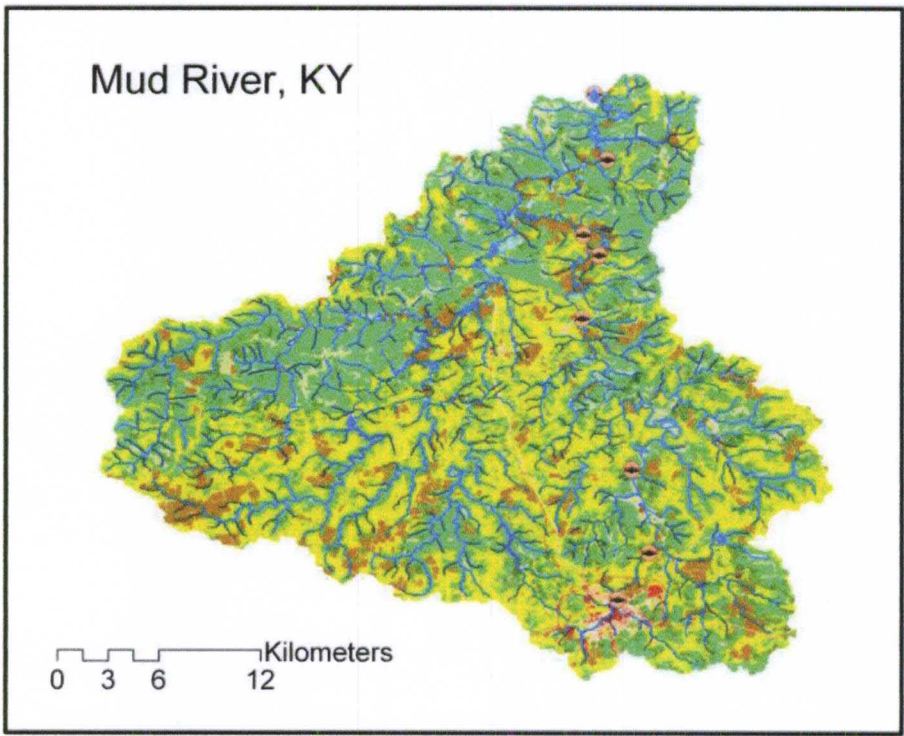
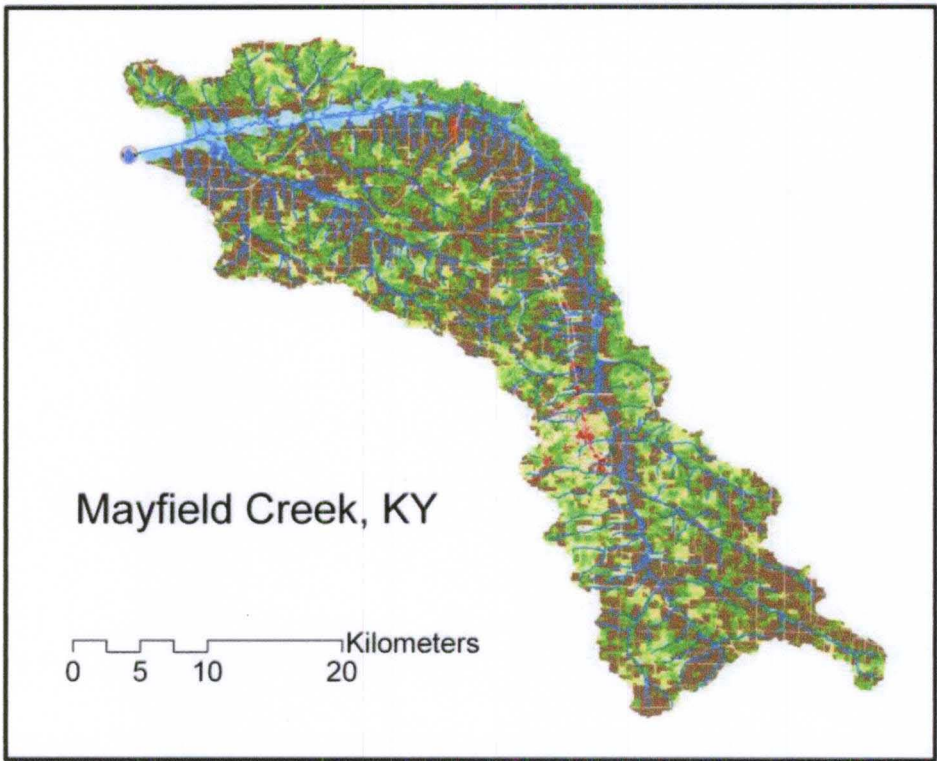
-  Fish Sampling Station
-  Water Sampling Station
-  Streams

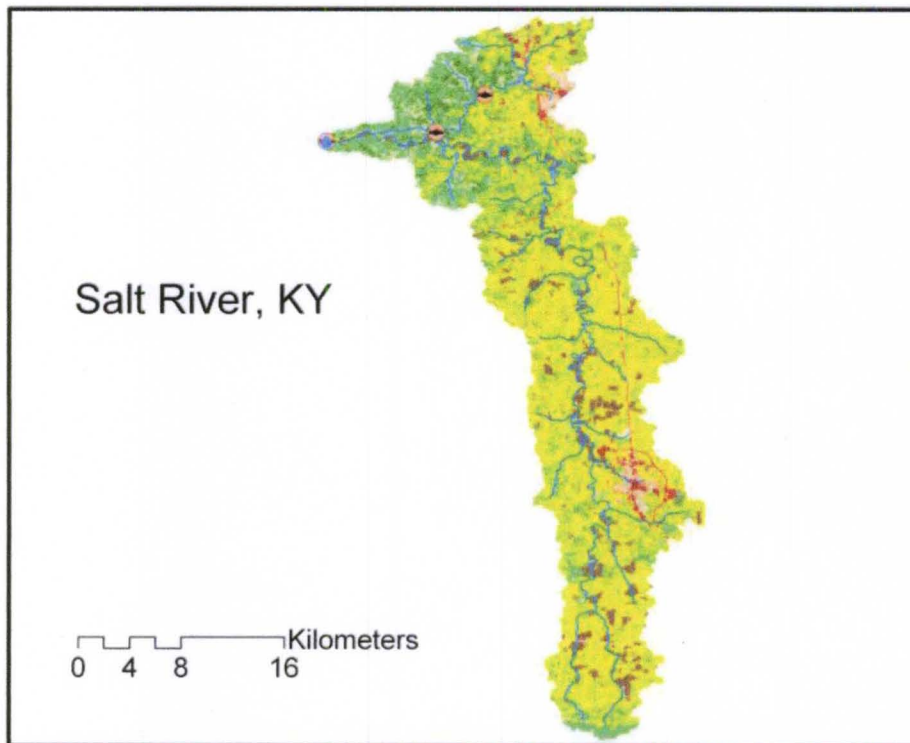
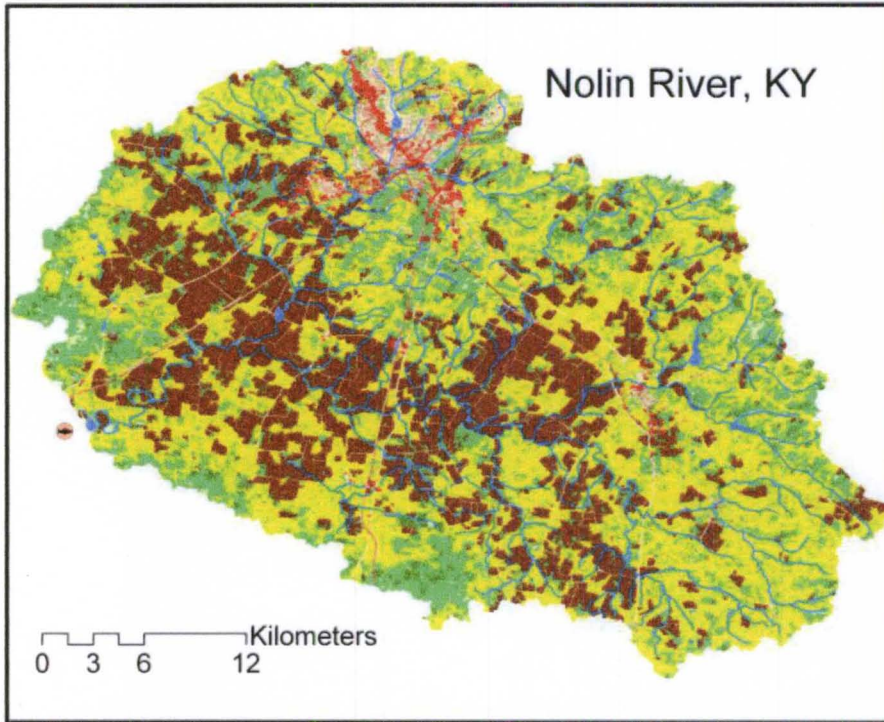
Land Cover

-  Open Water
-  Developed, Open Space
-  Developed, Low Intensity
-  Developed, Medium Intensity
-  Developed, High Intensity
-  Barren Land
-  Deciduous Forest
-  Evergreen Forest
-  Mixed Forest
-  Shrub/Scrub
-  Grassland/Herbaceous
-  Pasture Hay
-  Cultivated Crops
-  Woody Wetlands
-  Emergent Herbaceous Wetlands

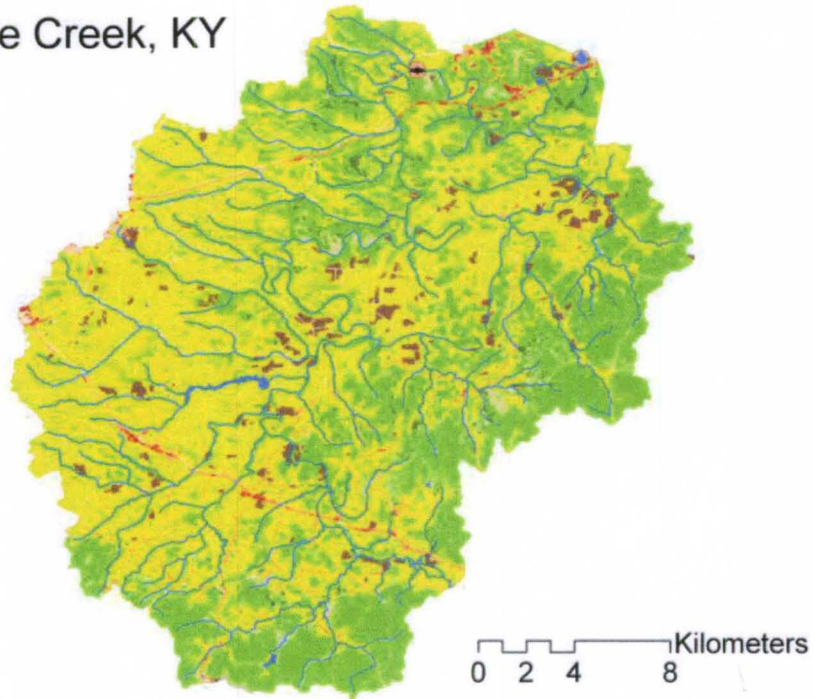
LAND COVER MAPS FOR CALIBRATION AND EVALUATION
BASINS.



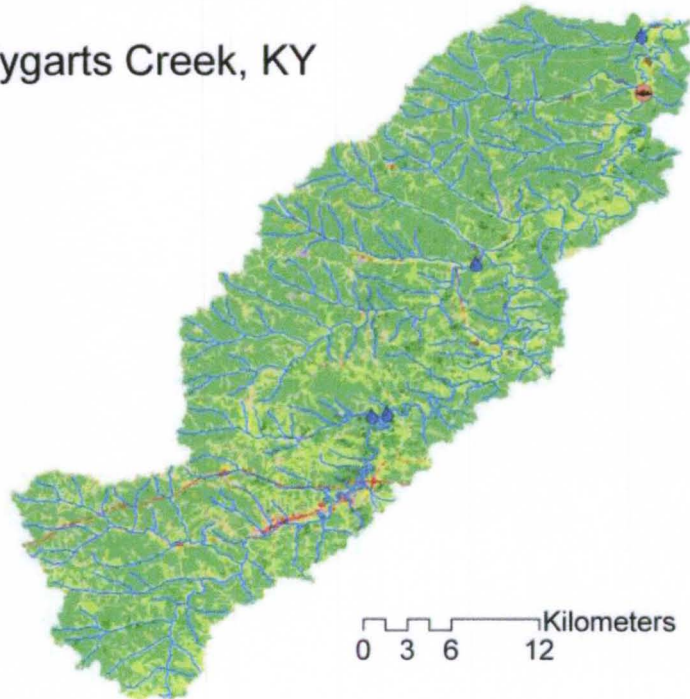




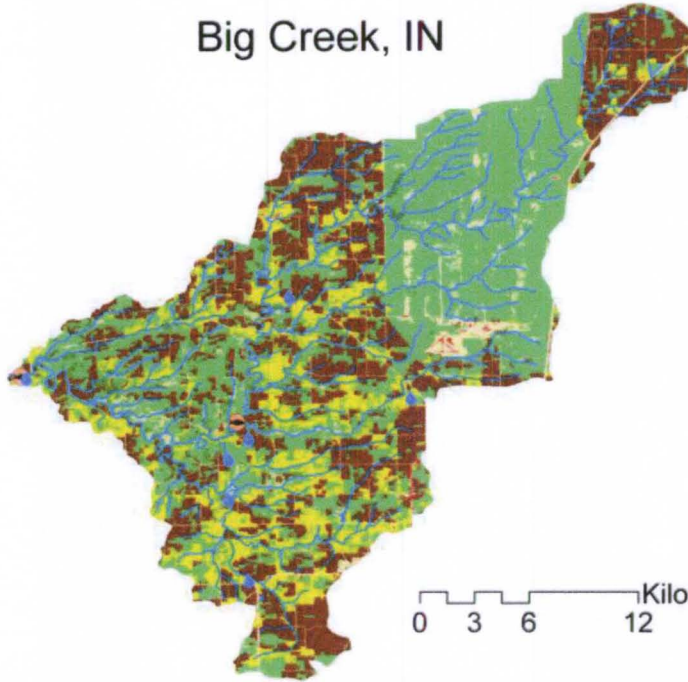
Slate Creek, KY



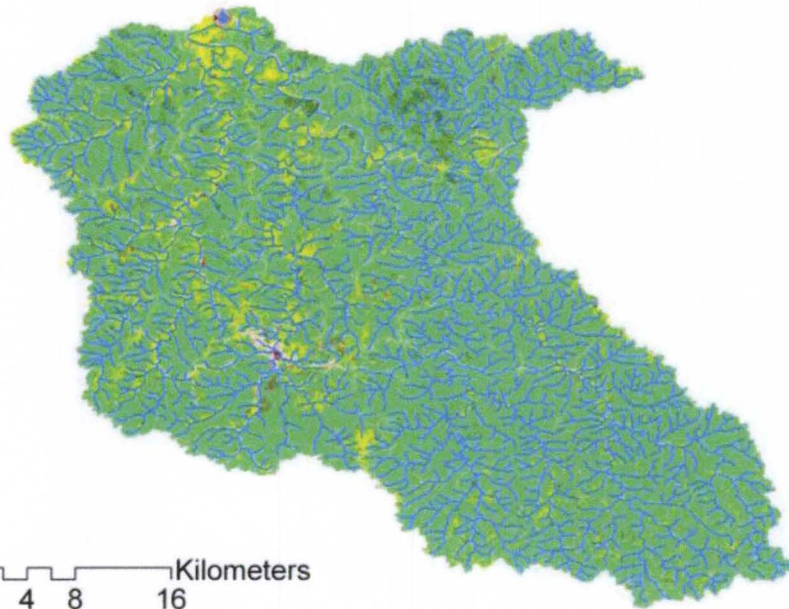
Tygart's Creek, KY



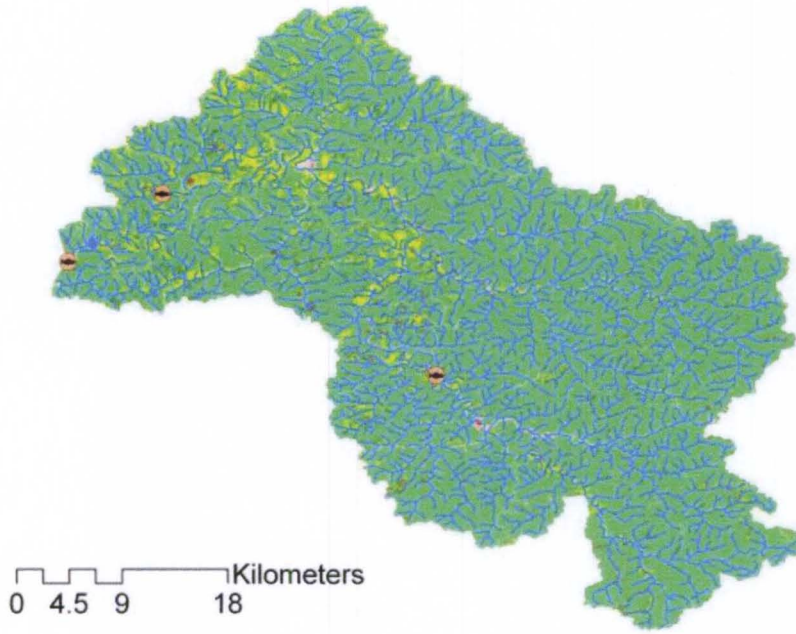
Big Creek, IN



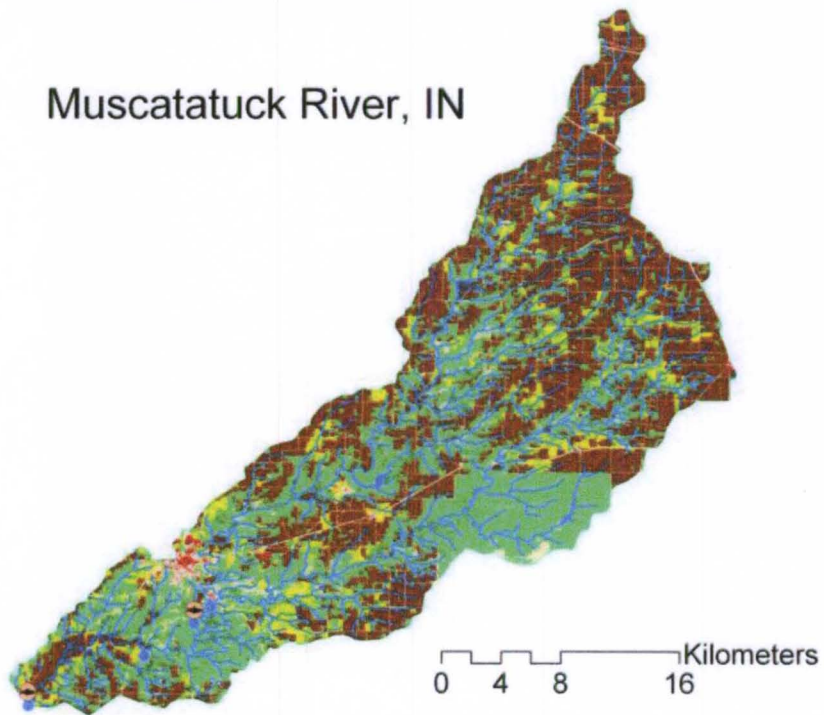
Little Kanawha, WV



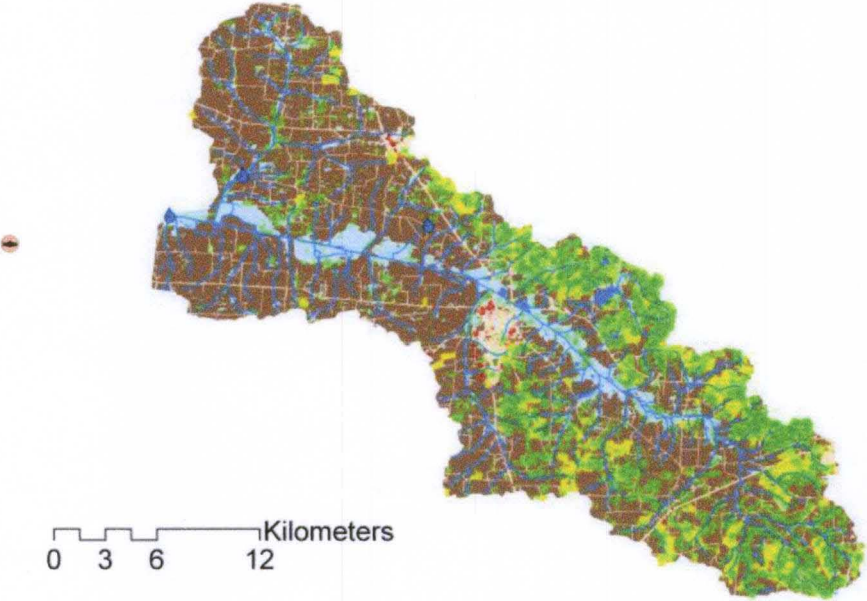
Middle Island Creek, WV



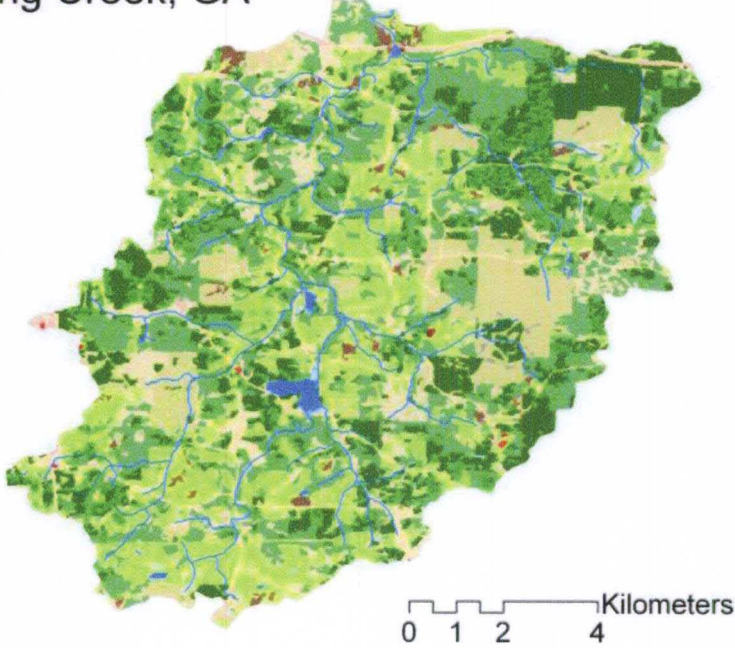
Muscatatuck River, IN

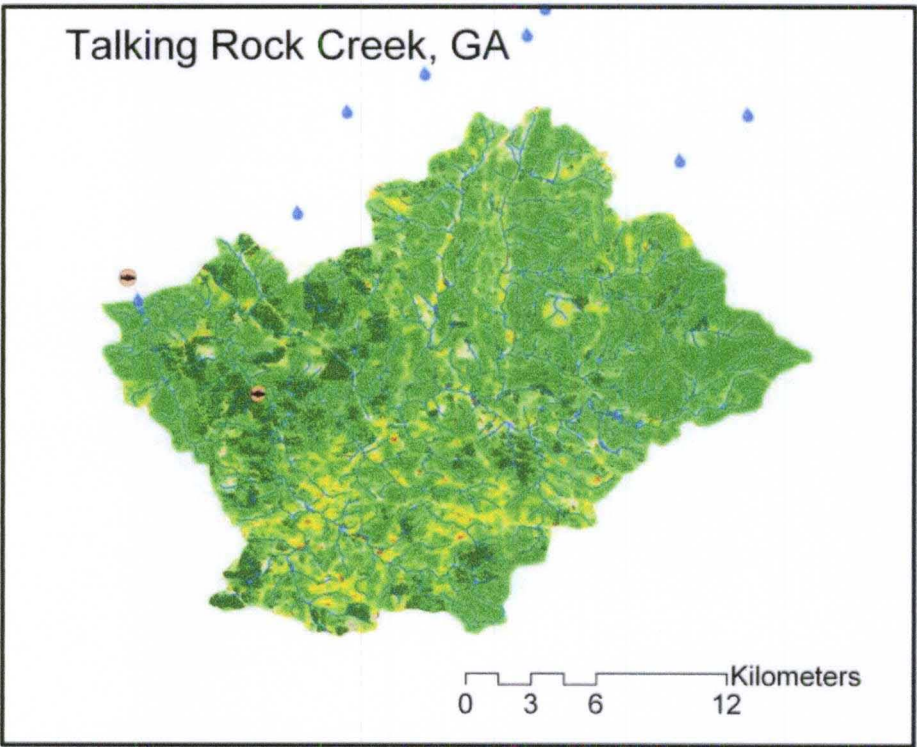


North Forked Deer River, TN



Spring Creek, GA





Appendix D

PERMISSIONS

In regards to the following papers:

Chan C, Heinbokel JF, Myers JA, Jacobs RR. 2011. Development and evaluation of a dynamic model that projects population biomarkers of methylmercury exposure from local fish consumption. *Integr Environ Assess Manag* 7: 624-635.

Chan C, Heinbokel JF, Myers GJ, Jacobs RR. 2012. A dynamic model using monitoring data and watershed characteristics to project fish tissue mercury concentrations in stream systems. *Integr Environ Assess Manag* (DOI: 10.1002/ieam.1302).

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Teaching and Research Experience

Instructor
University of Louisville, Spring 2011
PHEH 500: Introduction to Environmental and Occupational Health

Teaching Assistantship
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PHEH 610: Occupational Safety and Health.

Graduate Teaching Academy
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Research Assistantship
University of Louisville, 2007-2009
Assisting in a study to determine standardized mortality ratios for an occupational cohort.
Duties include data analysis and manuscript preparation.

Computer Programmer
University of Notre Dame, 1982-1984

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Honors and Awards

First Place, Graduate Public Health Student Poster. Research! Louisville. October 2010

Dean's Award (University of Louisville School of Public Health and Information Sciences), May 2007

Delta Omega, Honorary Society in Public Health, 2008

Membership in Professional Societies

American Public Health Association, 2007 – present

Society of Environmental Toxicology and Chemistry, 2008 - present

Certification in Public Health by the National Board of Public Health Examiners, 2008

Publications

Chan C, Heinbokel JF, Myers JA, Jacobs RR. 2012. A dynamic model using monitoring data and watershed characteristics to project fish tissue mercury concentrations in stream systems. *Integr Environ Assess Manag in press.*

Chan C, Heinbokel JF, Myers JA, Jacobs RR. 2011. Development and evaluation of a dynamic model that projects population biomarkers of methylmercury exposure from local fish consumption. *Integr Environ Assess Manag* 7: 624-635.

Chan C, Hughes T, Muldoon S, Aldrich T, Rice C, Hornung R, Brion G, Tollerud D. 2010. Mortality patterns among Paducah Gaseous Diffusion Plant Workers. *J Occup Environ Med* 52: 725-732.

Presentations

Oral Presentations

- “Creation of a Catalog of Environmental Mercury Databases in Kentucky”, Department of Environmental Protection, Frankfort, Kentucky, June 2007
- “Creation of a Catalog of Environmental Mercury Databases in Kentucky”, Kentucky Water Resources Research Institute Annual Symposium, Lexington, Kentucky, March 2008.
- “Water Quality in Public Health”, Area Health Education Centers Summer Conference, Mt Vernon, Kentucky, June 2008.

Poster Presentations

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