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APPLICATION OF ECOSYSTEM-SCALE FATE AND BIOACCUMULATION MODELS TO PREDICT FISH MERCURY RESPONSE TIMES TO CHANGES IN ATMOSPHERIC DEPOSITION

CHRISTOPHER D. KNIGHTES,*† ELSIE M. SUNDERLAND,‡ M. CRAIG BARBER,† JOHN M. JOHNSTON,† and ROBERT B. AMBROSE, JR.†

†U.S. Environmental Protection Agency, Office of Research and Development, Ecosystem Research Division, 960 College Station Road, Athens, Georgia 30605

‡Harvard School of Engineering and Applied Sciences, 29 Oxford Street, Cambridge, Massachusetts 02138, USA

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Abstract—Management strategies for controlling anthropogenic mercury emissions require understanding how ecosystems will respond to changes in atmospheric mercury deposition. Process-based mathematical models are valuable tools for informing such decisions, because measurement data often are sparse and cannot be extrapolated to investigate the environmental impacts of different policy options. Here, we bring together previously developed and evaluated modeling frameworks for watersheds, water bodies, and food web bioaccumulation of mercury. We use these models to investigate the timescales required for mercury levels in predatory fish to change in response to altered mercury inputs. We model declines in water, sediment, and fish mercury concentrations across five ecosystems spanning a range of physical and biological conditions, including a farm pond, a seepage lake, a stratified lake, a drainage lake, and a coastal plain river. Results illustrate that temporal lags are longest for watershed-dominated systems (like the coastal plain river) and shortest for shallow water bodies (like the seepage lake) that receive most of their mercury from deposition directly to the water surface. All ecosystems showed responses in two phases: A relatively rapid initial decline in mercury concentrations (20–60% of steady-state values) over one to three decades, followed by a slower descent lasting for decades to centuries. Response times are variable across ecosystem types and are highly affected by sediment burial rates and active layer depths in systems not dominated by watershed inputs. Additional research concerning watershed processes driving mercury dynamics and empirical data regarding sediment dynamics in freshwater bodies are critical for improving the predictive capability of process-based mercury models used to inform regulatory decisions.

Keywords—Models Response times Ecosystem Mercury Fish

INTRODUCTION

In the United States, fish consumption advisories are in place for more than 38% of the nation's total lake acreage and more than 26% of the total river miles (http://www.epa.gov/waterscience/fish/advisories/2006/tech.html). Most of these advisories (~80% in 2006) provide warnings about consuming fish with high levels of mercury found in 993,427 lake acres and 117,564 river miles across the country. Control strategies for anthropogenic mercury emissions are intended to reduce both human and ecological exposure. Evaluating the effectiveness of these strategies requires a variety of data concerning how different ecosystems will respond to changes in atmospheric mercury deposition. Process-based mathematical models are valuable tools for informing such decisions, because measurement data often are sparse and cannot be extrapolated to investigate the environmental impacts of different policy options. As stated in a recent National Research Council report [1], environmental models are critical to the regulatory decision-making process, because the spatial and temporal scales linking environmental controls and environmental quality generally do not allow an observational approach to understand the relationship between economic activity and environmental quality. In addition, environmental models are useful for understanding key research needs and prioritizing future data collection efforts. Here, we explicitly couple process-based mathematical models for watershed and water body mercury dynamics (including speciation) and for food web bioaccumulation to predict temporal changes in fish mercury levels across five diverse freshwater ecosystem types. Such applications are crucial for developing policy advice and refining models that can be used to anticipate the potential timing and magnitude of changes in fish mercury levels resulting from declines in atmospheric deposition. This type of modeling application complements other empirically based studies on this topic [2] by synthesizing our best-available knowledge of mercury dynamics into a mathematical decision-support tool.

Individuals are exposed to methylmercury (MeHg) mainly by consuming freshwater and marine fish and shellfish [3,4]. Depending on the physical and biogeochemical characteristics of a given lake, methylating microbes convert a small but variable fraction of atmospherically deposited mercury in water and sediments to MeHg [5,6]. Some of this MeHg enters the base of the food web, bioaccumulates in higher-trophic-level organisms, and may result in negative health effects in humans and wildlife that consume fish. While our understanding of factors controlling methylation and bioaccumulation in lakes has advanced during recent years [7], ecosystem-scale modeling applications still must be calibrated with site-specific data [8]. Recently, an expert panel on recovery of mercury-contaminated fisheries concluded that variability in ecosystem properties (watershed size and topography, land-cover characteristics, temperature, organic carbon content of sediments,

* To whom correspondence may be addressed (knightes.chris@epa.gov).
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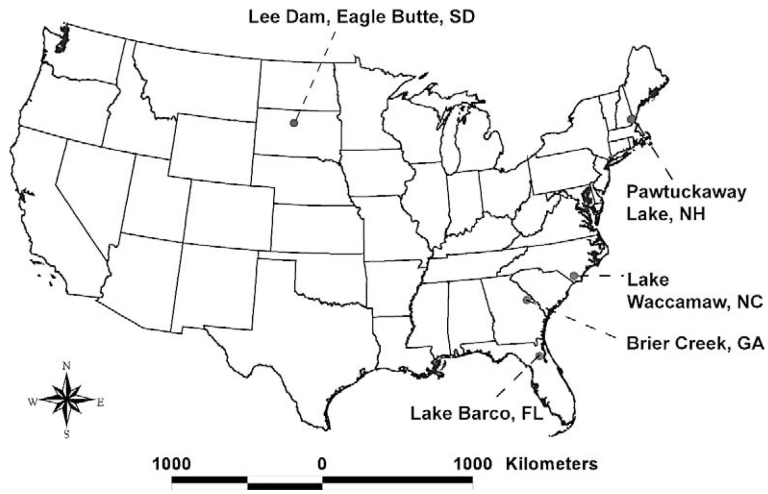

Fig. 1. Ecosystem modeling case-study locations within the United States.

and lake stratification) exerts a strong influence over the magnitude and timing of changes in fish mercury concentrations resulting from reductions in mercury inputs [7]. Accordingly, in the present study, we investigate responses of fish mercury levels across five freshwater ecosystems (Fig. 1) with variable watershed sizes and sediment properties that span a range of latitudes across the United States and have diverse land-cover characteristics (Fig. 2). These sites include a farm pond in South Dakota (USA), a seepage lake in Florida (USA), a stratified drainage lake in New Hampshire (USA), a large drainage lake in North Carolina (USA), and a coastal plain river in Georgia (USA).

Evaluation and underlying formulation of all modeling frameworks applied here have been described in detail in previous studies [8–14]. Here, we go beyond previous ecosystem-scale modeling efforts by coupling results from watershed, water body, and bioaccumulation models to forecast mercury dynamics across multiple ecosystems. Previous modeling studies generally have focused on mercury dynamics in a single water body and rarely have included a mechanistic representation of food web bioaccumulation or watershed loading [15–18].

Although atmospheric fate and transport modeling is beyond the scope of the present study, we use 2001 results for both wet and dry deposition from the Community Multi-scale Air Quality Model (CMAQ) [19] to estimate baseline atmospheric deposition rates for all ecosystems. We apply a systematic, 50% load reduction to investigate temporal responses in ecosystems. Because all ecosystem models are based on first-order relationships, magnitudes of atmospheric load reductions determine the magnitude of change in fish mercury levels but do not affect the relative timing of modeled responses (times required for fractions of total declines at steady state to be achieved). Accordingly, this analysis provides insight regarding response times of freshwater ecosystems to declines in mercury deposition, key sources of uncertainty affecting the timing of changes in mercury concentrations across a variety of ecosystems, and the importance of ecosystem response times and associated uncertainties for informing policy analysis.

MATERIALS AND METHODS

Model descriptions

The U.S. Environmental Protection Agency (EPA) has developed, tested, and evaluated a set of publicly available watershed, water body, and food web models that describe the speciation, transport, and bioaccumulation of mercury as a function of the physical, chemical, and biological properties of different ecosystems (http://www.epa.gov/ceampubl/). These models are used both as research tools to better understand processes that drive mercury cycling in terrestrial and aquatic systems and as regulatory support tools for Superfund risk assessments and total maximum daily load determinations [9,20,21].

Watershed models

We used the U.S. EPA Region 4 Watershed Characterization System Mercury Loading Model (WCS-MLM) to estimate watershed loading of mercury in systems with large watershed to water surface area ratios (coastal plain river and farm pond). For all other systems, we used the simple watershed loading function incorporated in the Spreadsheet-based Ecological Risk Assessment for the Fate of Mercury (SERAFM) model (described below) based on the Revised Universal Soil Loss Equation and runoff coefficients for different watershed land-use types [8]. The WCS is a Geographic Information Systems–based modeling system for calculating soil particle transport and pollutant fate in watersheds [22]. The MLM in WCS was adapted from the IEM-2M (Indirect Exposure Model, Ver 2) model used in the 1997 U.S. EPA Mercury Report to Congress [23]. The WCS-MLM calculates long-term average hydrology and sediment yield and simulates mercury transport in a distributed subwatershed network. Examples of previous WCS-MLM applications include the development of mercury total maximum daily loads in the middle and lower Savannah River, Canoochee River, and Ogeechee River watersheds (all GA, USA) [24,25].

Water body models

We simulated the aquatic cycling of mercury in each ecosystem using two water body modeling frameworks (SERAFM and WASP7). The Water Quality Analysis Simulation Program (WASP) has been used for a variety of regulatory [26,27] and research [28,29] applications over the past several decades. An enhancement of the original WASP [10,11], WASP7 provides a dynamic, mass-balance framework for modeling the fate and transport of a variety of contaminants in surface water systems. The WASP7 mercury module simulates three mercury species (Hg(0), Hg(II), and MeHg) as well as three solids

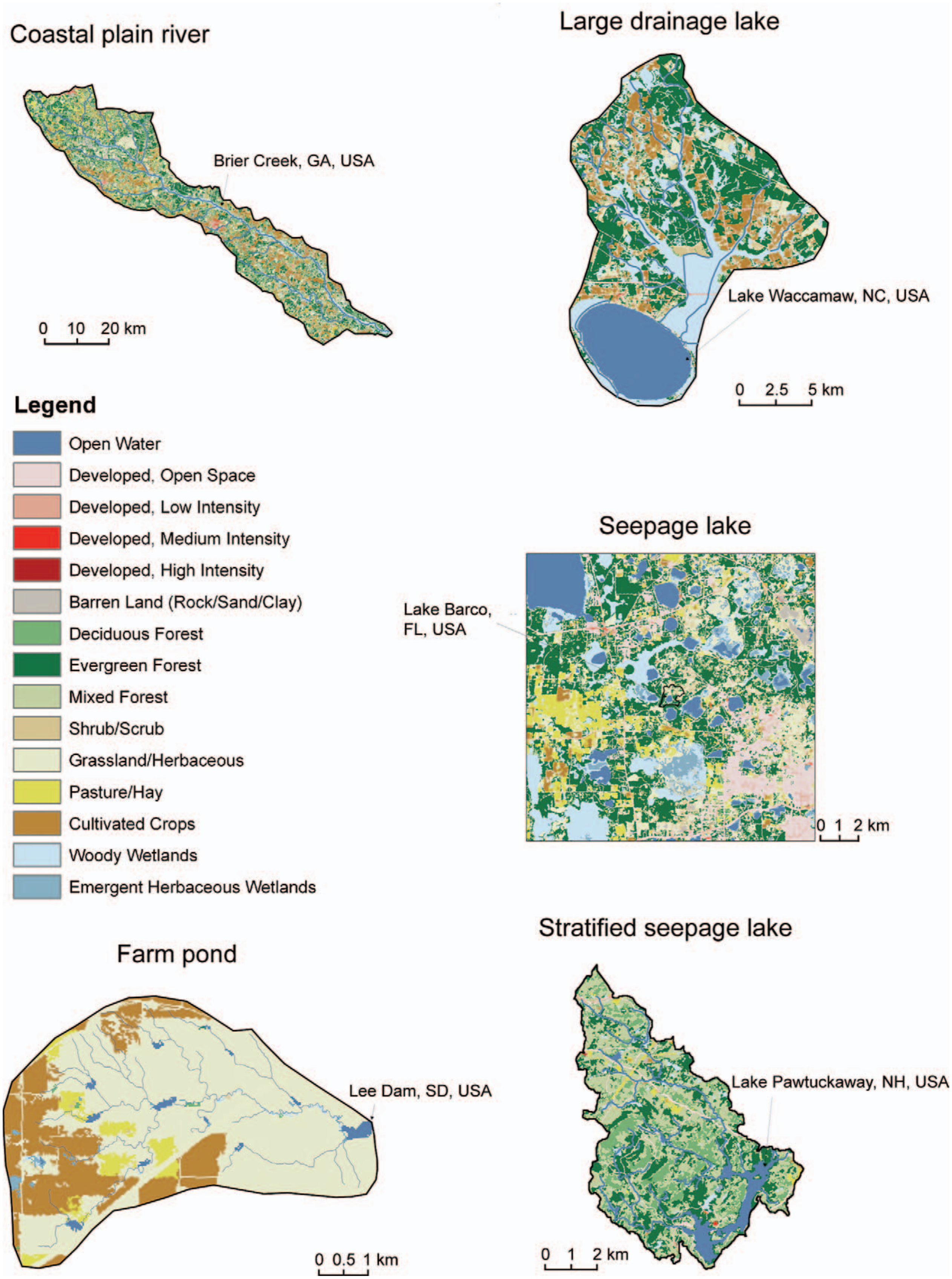

Fig. 2. Watershed land-cover characteristics for each of the case-study ecosystems. Data are from the 2001 National Land Cover Database (NLCD; http://www.mrlc.gov/index.asp), which also were used to parameterize watershed mercury loading models for each ecosystem.

types (silt, sand, and biotic solids) [21]. In general, WASP7 is easily linked with hydrodynamic and sediment transport models that can provide flows, depths, velocities, temperature, and sediment fluxes. The SERAFM model is an updated version of the IEM-2M model used by the U.S. EPA to assess cycling of mercury released from coal-fired utilities in the 1997 Mercury Study Report to Congress [23]. Details regarding the development and evaluation of SERAFM can be found elsewhere [8]. We applied a dynamic version of SERAFM to predict mercury concentrations in sediments and water for three principal species (Hg(0), Hg(II), and MeHg) in the epilimnion and hypolimnion of lakes as well as a surface sediment layer. The SERAFM model includes watershed mercury loading algorithms based on the Revised Universal Soil Loss Equation, enhanced capability to represent lake stratification and mixing, current information on speciation of Hg(II), photo-reactions, reaction rates for methylation and demethylation in water and sediments, and partitioning of Hg(II) and MeHg to different types of suspended solids. Transformation processes among species in the model generally are represented by first-order rate constants for methylation of Hg(II) to MeHg in water and sediments, demethylation of MeHg to Hg(II) in water and sediments, biotic reduction and photo-reduction of Hg(II) to Hg(0) in water only, photo-oxidation and dark oxidation of Hg(0) to Hg(II) in water, and photo-degradation of MeHg to Hg(0) in water [8,20]. In other applications, SERAFM has been used to model particulate and dissolved total mercury and MeHg in water and sediments (e.g., Steamboat Creek, NV, USA, and constructed wetland mesocosms) [20]. Model evaluation conducted as part of those applications indicated that SERAFM reproduces observed seasonal patterns in mercury and MeHg concentrations in western streams and constructed wetlands. Comparison of the present work to WASP applications at the Carson River (NV, USA) suggests similar capability [30–32]. Because results from the two water body models were comparable for all ecosystems investigated here, we use the results interchangeably throughout the discussion.

Bioaccumulation

We used the Bioaccumulation and Aquatic System Simulator (BASS) model to simulate changes in food web mercury dynamics in each ecosystem. The BASS is a well-established model that describes contaminant dynamics (including mercury) using algorithms that account for species-specific terms affecting uptake and elimination of mercury, such as diet composition and growth dilution among different age classes of fish [12,13]. For example, fish mercury intake is modeled as a function of gill exchange and dietary ingestion, and the model partitions mercury internally to water, lipid, and nonlipid organic material. The structure of BASS is generalized and flexible, allowing users to simulate both small, short-lived species (daces and minnows) and large, long-lived species (bass, perch, and trout) by specifying either monthly or yearly age classes for any given species. The community's food web is defined by identifying one or more foraging classes for each fish species based on body weight, body length, or age. The dietary composition of each foraging class is then specified as a combination of benthos, incidental terrestrial insects, periphyton/attached algae, phytoplankton, zooplankton, and/or other fish species [12].

For all case-study ecosystems, BASS project files were constructed for fish communities using an auxiliary BASS model software component that can generate BASS parameterizations for most eastern U.S. fish species using internal databases and genera-based default assignments [13]. All BASS simulations were performed using the BASS Food and Gill Exchange of Toxic Substances (FGETS) simulation option that simulates fish growth and chemical bioaccumulation within age-structured fish communities [33]. The default and site-specific ecological, morphological, and physiological parameters as well as the dietary compositions and initial conditions of each species are presented in *Supporting Information,* Table S1 (http://dx.doi.org/10.1897/08-242.S1).

Changes in biomass of phytoplankton and zooplankton are simulated from ingestion or photosynthesis, respiration, mortality resulting from fish consumption, and nonconsumptive mortality and dispersal. For benthos, phytoplankton, and zooplankton, which can be conceptualized as populations of organisms possessing similar body sizes, the rate coefficients for each of the above processes and fluxes are estimated using temperature-dependent allometric relationships. The BASS model estimates internally a physiologically based carrying capacity for phytoplankton and zooplankton based on projected daily oxygen consumption and the community's prevailing dissolved oxygen content. Bioaccumulation factors calculated for each nonfish compartment are based on empirically determined values calculated from MeHg concentrations in water, chemical exchange rates, and growth rates.

Site descriptions

Sites investigated include a seepage lake with a negligible watershed (Lake Barco, FL, USA), a coastal plain river (Brier Creek, GA, USA), a large drainage lake (Lake Waccamaw, NC, USA), a stratified drainage lake in the Northeast (Pawtuckaway Lake, NH), and a shallow, well-mixed farm pond in the Midwest (Lee Dam, Eagle Butte, SD, USA). Atmospheric deposition rates vary across case-study ecosystems from 8.5 $\mu g/m^2/year$ (farm pond) to 19.8 $\mu g/m^2/year$ (coastal plain river). All sites have previously measured mercury levels in fish that exceed the U.S. EPA's tissue residue criterion for protection of human health of 0.3 $\mu g/g$ (http://www.epa.gov/waterscience/fish/advisories/2006/tech.pdf). Qualitative descriptions of each ecosystem, land-use types, and food webs used to parameterize the bioaccumulation model for each ecosystem are given below. For detailed parameterization used for bioaccumulation modeling, mercury-specific physicochemical constants, and watershed modeling characterization for each ecosystem and all models, see *Supporting Information,* Tables S1, S2, and S3 (http://dx.doi.org/10.1897/08-242.S1, http://dx.doi.org/10.1897/08-242.S2, and http://dx.doi.org/10.1897/08-242.S3, respectively). Data regarding watershed land-use characterization and water body geochemical characteristics of each system are summarized in Table 1 and Figure 1.

Coastal plain river. Brier Creek is a coastal plain river surrounded by a watershed located in the Savannah River basin in Georgia (Fig. 1). We divided the Brier Creek watershed into 11 subwatersheds representing all the major tributaries (Fig. 2). Land uses in the Brier Creek watershed include a mix of urban areas, agricultural pasture and croplands, grassland, forest, wetlands, and upland scrubland (Table 1 and Fig. 2). The fish community for Brier Creek used to parameterize the food web model consists of bluegill sunfish (*Lepomis macrochirus*), grass pickerel (*Esox americanus*), shiners (*Notropis* spp.), pirate perch (*Aphredoderus sayanus*), redbreast sunfish (*Lepomis auritus*), and tesselated darter (*Etheostoma olmstedi*) [34].

Table 1. Overview of ecosystem case-study site characteristics[a]

Type	Farm pond	Seepage lake	Stratified drainage lake	Bay lake	Coastal plain river
Site	Lee Dam (SD, USA)	Lake Barco (FL, USA)	Pawtuckaway Lake (NH, USA)	Lake Waccamaw (NC, USA)	Brier Creek (GA, USA)
Location	45.120°N, 100.702°W	29.676°N, 82.009°W	43.073°N, 71.152°W	34.287°N, 78.509°W	32.783°N, 81.433°W
Watershed (km^2)	4.2	0.81	50	220	2,190
Lake Area (km^2)	0.20	0.12	3.6	35	9.9
Land use (%)		NA			
Urban	5		4	4	7
Forest	1		81	37	32
Wetland	1		4	25	8
Riparian	2		4	10	12
Upland	91		6	24	41
Hydraulic residence time (years)	NA	32	0.45	0.29	0.03
Inflow/outflow (m^3/year)	0	1.7×10^4	4.05×10^7	1.2×10^8	$3.3–7.4 \times 10^8$
Water pH	9.0	4.5	6.5	4.3	NA
DOC (mg/L)	27.0	0.8	5.5	25.9	5.0–8.0
TSS (mg/L)	1.01	0.66	0.8	11	4–16
Avg. depth (m)	2.0	4.8	5.0	2.3	0.3–2.0
Trophic status	Eutrophic	Oligotrophic	Dystrophic	Mesotrophic	NA
Stratification	No	No	Yes	No	No
Sediment organic carbon (%)	2	2	1	5	3–6
Models applied	WCS, SERAFM, WASP, BASS	SERAFM, WASP, BASS	SERAFM, WASP, BASS	SERAFM, WASP, BASS	WCS, WASP, BASS

[a] BASS = Bioaccumulation and Aquatic System Simulator; DOC = dissolved organic carbon; NA = not applicable; SERAFM = Spreadsheet-based Ecological Risk Assessment for the Fate of Mercury; TSS = total suspended solids; WASP = Water Quality Analysis Simulation Program; WCS = Watershed Characterization System.

Farm pond. Eagle Butte is located in the north–central portion of South Dakota on the Cheyenne River Sioux Tribal Lands (Fig. 1). The modeled site (Lee Dam) is a shallow, well-mixed farm pond surrounded mainly by grassland and cultivated cropland with some woody wetlands and pasture with predominantly clay loam soils (Fig. 2). The food web of Lee Dam is predominantly a northern pike (*Esox lucius*) and yellow perch (*Perca flavescens*) community, but it also includes subdominant black crappie (*Pomoxis nigromaculatus*), largemouth bass (*Micropterus salmoides*), and spottail shiner (*Notropis hudsonius*).

Seepage lake. Lake Barco is a small seepage lake within the Katherine Ordway Preserve near the southern toe of the Trail Ridge physiographic region approximately 35 km east of Gainesville (FL, USA) (Fig. 1). The preserve is protected from direct human impacts, although some recreational fishing does take place. Land use surrounding Lake Barco is a combination of evergreen forest and mixed shrub/grassland (Fig. 2). Lake Barco remains isothermal throughout the year, and groundwater inflow accounts for between 5 and 14% of annual hydrological inputs [35]. To account for this inflow, we calculate groundwater mercury inputs from reported annual discharge ($\sim 1.76 \times 10^4$ m^3/year) and an unfiltered mercury concentration of approximately 2.8 $\mu g/m^3$ based on other studies [36,37]. The fish community modeled in Lake Barco consists of bluegill sunfish, lake chubsucker (*Erimyzon sucetta*), largemouth bass, mosquitofish (*Gambusia holbrooki*), redear sunfish (*Lepomis microlophus*), and warmouth sunfish (*Lepomis gulosus*) [38].

Stratified lake. Pawtuckaway Lake is a medium-sized, stratified drainage lake in Nottingham (NH, USA) (Fig. 1). Dissolved oxygen levels in the hypolimnion typically fall below 1 mg/L during seasonal stratification [39]. The watershed land use is a mix of deciduous and coniferous forest (Fig. 2) and stony to silty loam soils [40]. The fish community modeled consists of black crappie, brown bullhead (*Ameiurus nebulosus*), chain pickerel (*Esox niger*), common shiner (*Luxilus cornutus*), fallfish (*Semotilus corporalis*), largemouth bass, pumpkinseed sunfish (*Lepomis gibbosus*), redbreast sunfish, smallmouth bass (*Micropterus dolomieu*), white perch (*Morone americana*), and yellow perch [41] (http://www.wildlife.state.nh.us/Fishing/fishing_forecast/Locations_Southeast.htm).

Drainage lake. Lake Waccamaw is a large drainage lake in southeastern North Carolina that is a popular destination for recreational fishing. The area surrounding Lake Waccamaw is typical of the region: flat terrain with ubiquitous wetlands and waterways (Fig. 2). Historically, the largest releases of mercury in the region were from a mercury cell chloralkali operation approximately 25 km east–northeast of Lake Waccamaw that closed in the mid-1990s. The fish community modeled for Lake Waccamaw consists of black crappie, bluegill sunfish, largemouth bass, redbreast sunfish, redear sunfish, white catfish (*Ameiurus catus*), white crappie (*Pomoxis annularis*), and yellow perch (http://www.landbigfish.com/fishingspots/showcase.cfm?ID=82).

Model calibration

We developed mass balances for mercury in each system based on a comprehensive synthesis of all available empirical data for each ecosystem, including physical characteristics (lake area, watershed size, and depth), mercury concentrations, and rate constants for methylation, demethylation, oxidation, and reduction that were calibrated to observed mercury concentrations and fluxes and/or constrained within measured ranges reported in other studies (Tables 1–3). We performed extensive sensitivity analyses on physically realistic ranges of rate constants to examine their impact on modeled response

Table 2. Annually averaged rate constants (1/d) used to parameterize ecosystem models

Description	Lee Dam (SD, USA)	Lake Barco (FL, USA)	Pawtuckaway Lake (NH, USA)	Lake Waccamaw (NC, USA)	Brier Creek (GA, USA)
Type	Farm pond	Seepage lake	Stratified drainage lake	Bay lake	Coastal plain river
Methylation (water)[a] Hg(II) → MeHg	0.00	0.00	0.00[b] 0.01[c]	0.002	0.001
Demethylation (water)[d] MeHg → Hg(II)	0.04	0.04	0.05[b] 0.05[c]	0.05	0.05
Methylation (sediment)[e] Hg(II) → MeHg	0.015	0.02	0.02	0.02	0.0005
Demethylation (sediment)[e] MeHg → Hg(II)	0.70	0.25	0.62	0.50	0.005
Oxidation (water)[f] Hg(0) → Hg(II)	1.45	1.59	1.59	1.45	0.001
Reduction (water)[g] Hg(II) → Hg(0)	0.07	0.04	0.20	0.06	0.10[h] 0.03–0.05[i]
Photodegradation (water)[j] MeHg → Hg(0)	0.04	0.00	0.01	0.01	0.05[h] 0.015–0.025[i]

[a] Water-column methylation rates from Eckley and Hintelmann [6], Gilmour and Henry [47], and U.S. Environmental Protection Agency [48].
[b] Epiliminion.
[c] Hypolimnion.
[d] Water-column demethylation rates estimated from water-column dissolved organic carbon concentrations using relationships reported by Matilainen and Verta [49].
[e] Net methylation rates for sediments were calibrated to the observed percentage methylmercury (MeHg) values and rate constant ranges as reported in literature [5,50–52].
[f] Water-column oxidation from Amyot et al. [53] and Lalonde et al. [54].
[g] Water-column reduction rates from Mason et al. [55] and O'Driscoll et al. [56,57].
[h] Water surface.
[i] Water column.
[j] Photodegradation rate in water from Sellers and Kelly [58].

times. These results are presented in later sections; however, our analysis suggests that for most systems, variability in rate constants across the ranges considered in the present study based on previous experimental and empirical work did not have a large impact on the timing of changes in fish mercury levels.

Model simulations

For all case-study ecosystems, we ran each model with fixed inputs until steady state was achieved using baseline wet and dry atmospheric deposition rates from the CMAQ (Table 3). We then simulated the effects of a hypothetical, 50% decline in atmospheric mercury deposition to explore the temporal response of each ecosystem to a future atmospheric load reduction. For all simulations, we ran the coupled watershed, water body, and bioaccumulation models in a time-dependent mode for several hundred years or until steady state (defined as a change in concentration of $<0.01\%$ per year) was achieved with a time step of 0.2 d or less.

Sensitivity analyses

We analyzed the sensitivity of response times to changes in parameter values by systematically reducing and increasing model parameter values by increments of 5% within the range of physically realistic values. Key parameters investigated were active sediment layer depth, sediment burial and settling rates, water-column oxidation, reduction and evasion rates, and water and sediment methylation and demethylation rates. This analysis was not performed for Brier Creek, because watershed inputs account for virtually all mercury inputs to sediments and the water column.

RESULTS

Annual budgets, calculated as the sum of total inputs (atmospheric and watershed) minus outputs (evasion, outflow, and burial) from each ecosystem, suggest that none of the systems modeled were at steady state when empirical data were collected (Table 3). To compare temporal responses across ecosystems, models were run with fixed inputs until they reached steady state. Running the models to steady state before systematically lowering inputs allowed us to isolate the ecosystem characteristics (size of watershed, hydrology, and food web structure) that govern responses to changes in atmospheric deposition. Although the models were all calibrated to observed data regarding mercury concentrations in water and sediments as well as the physical and biological characteristics of each system, it was possible to evaluate the performance using independent data concerning fish mercury concentrations. Observational data, however, also are inherently uncertain, and measured fish mercury concentrations represent only a snapshot of biological concentrations across species, fish sizes, and age classes (as partially represented by the error bars on observed fish concentrations in Fig. 3).

Figure 3 shows independent observed and model-predicted fish mercury concentrations for each system. For three of the systems (stratified lake, seepage lake, and farm pond), modeled fish mercury concentrations fell within the error bars of measured values, which suggest the models reasonably represented the mercury dynamics. The coupled models underpredicted fish mercury concentrations in the drainage lake (Lake Waccamaw) and overpredicted concentrations in the coastal plain river (Brier Creek). These differences, however, can be explained by uncertainty in the observational data used to evaluate and calibrate the models. For example, measured mercury concentration data were only available for chain pickerel at one segment of the coastal plain river, but the dominant, top predator in the system (and species modeled) was grass pickerel. In the drainage lake, measured sediment mercury concentration data used to calibrate the initial simulations were much lower than would be expected in a system affected by a nearby chloralkali facility, and this likely explains the underprediction of fish mercury in this system (Table 3).

Table 3. Empirically constrained present-day (ca. 2000–2005) concentrations (mean [range]), fluxes, and reservoirs of mercury in each case-study ecosystem

Description	Lee Dam (SD,USA)	Lake Barco (FL,USA)	Pawtuckaway Lake (NH,USA)	Lake Waccamaw (NC,USA)	Brier Creek (GA,USA)
Type	Farm pond	Seepage lake	Stratified drainage lake	Bay lake	Coastal plain river
Hg water (ng/L)	6.9 (0.5–100)	1.03	2.3 (0.71–3.8)[a] 20.7 (6.9–34)[c]	4.8 (1.1–18.4)	6.0–8.3[b]
Reservoir Hg water (g)	1.5	0.58	168	107	130
Hg sediment (ng/g)	44.1 (28–95)	160 (152–186)	290	22.8 (28.1–95.0)	6.4–37.0
Reservoir Hg sediment	108.7	250.16	16,790	18,869	5,500
MeHg water (ng/L)	1.0 (0.4–2.9)	0.02	0.2 (0.1–0.2)[a] 2.9 (2.4–3.4)[c]	0.5 (0.1–5.0)	0.7–1.4
MeHg water (%)	14	2	8[a] 14[c]	10	9–23
MeHg sediment (ng/g)	0.4 (0.1–1.7)	5.0 (1.9–6.9)	7	0.1 (0.03–0.2)	0.04–5.7
MeHg sediment (%)	0.9	3.1	2.4	0.6	1–15
Atmospheric Hg (g/year)	1.7	1.08	62	604	197
Watershed Hg (g/year)	12.7	0.05[d]	188	951	5,300
Evasion Hg(0) (g/year)	3.7	0.19	64	106	1,349
Outflow Hg (g/year)	0.0	0.02[d]	98	161	2,604
Burial Hg (g/year)	1.4	0.10	420	9	1,300
Empirical Hg flux[e] (g/year)	+9.3	+0.82	−332	+1,280	+244

[a] Epilimnion.
[b] Brier Creek data represent ranges across reaches.
[c] Hypolimnion.
[d] Groundwater flow.
[e] Net flux is calculated as the sum of total inputs (atmospheric an d watershed) minus outputs (evasion, outflow, and burial) from each ecosystem at the point in time that empirical data were collected and indicate the present state of each ecosystem accumulating (+) or losing (−) mercury. Data sources: Lee Dam from U.S. Environmental Protection Agency (EPA) Region 8 (D. Hoff, personal communications), Lake Barco from Harris and Hutchinson [59], Lake Pawtuckaway from Kamman and Engstrom [40] and from Kamman et al. [39], Lake Waccamaw from Riggs et al. [60] and from North Carolina Department of Environment and Natural Resources (D. Owens, personal communications), and Brier Creek from U.S. EPA [61].

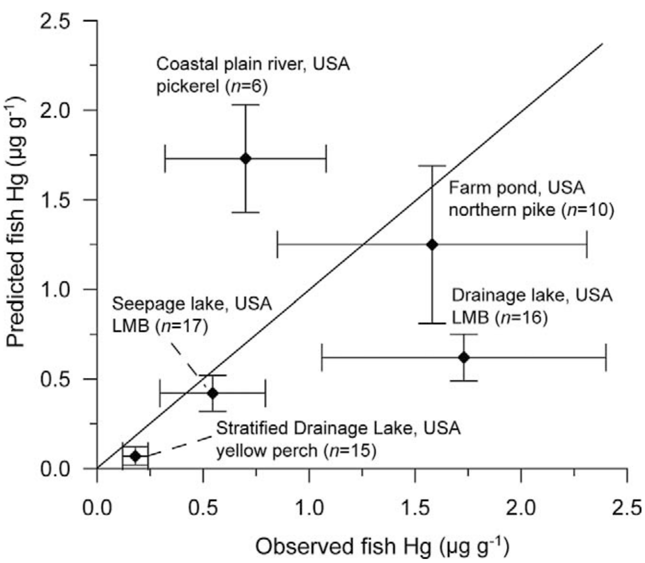

Fig. 3. Comparison of predicted and observed fish mercury concentrations (n indicates number of observed samples) from case-study ecosystems. Error bars represent standard deviations of observed fish mercury concentrations (horizontal) and modeled variability in fish mercury (vertical). All data are weight normalized to the age-class weight corresponding to empirical samples available (age of 2 years for all systems except Brier Creek, GA, USA, which was age 4 years). Coastal plain river pickerel has measured data for chain pickerel (*Esox niger*) and observed data for grass pickerel (*Esox americanus*). Largemouth bass (LMB) data for the coastal plain river (Brier Creek) were for grass pickerel, and observed concentrations were for chain pickerel from one location along the river (no other data were available).

Fish age classes, lengths, or weights typically are used to normalize mercury data before evaluating model performance, allowing modeled values to be compared to some central concentration value from measurements (Fig. 3). Such relationships between mercury levels and weights/lengths are highly variable across species, as indicated by the raw data shown in Figure 4. One advantage of using a mechanistic bioaccumulation model, such as BASS, to forecast future fish mercury concentrations for policy determinations is that species-specific properties can be simulated to characterize expected variability in mercury concentrations across age classes of different fish species. In addition, overall model performance tends to improve when compared directly to raw data and modeled length and weight classes of fish (Fig. 4).

Response times

Modeled changes of mercury concentrations in water, sediment, and fish showed an initially rapid (years to decades) decline in mercury concentrations (20–60% of steady-state values); followed by a more gradual approach toward steady state that requires additional decades to centuries (Fig. 5 and Table 4). Predatory fish mercury response times were longest for the farm pond with a large watershed (Lee Dam) and most rapid for the drainage lake (Lake Waccamaw).

Predatory fish mercury concentrations in watershed-dominated systems (Brier Creek and Lee Dam) and the stratified lake (Pawtuckaway) exhibited a delayed initial response to declines in loading. In the watershed-dominated systems, this delay was the result of continued mercury inputs from the watershed after the decline in atmospheric deposition. In the stratified lake, this lag reflected the time for changes in epilimnion mercury concentrations to be reflected in the hypo-

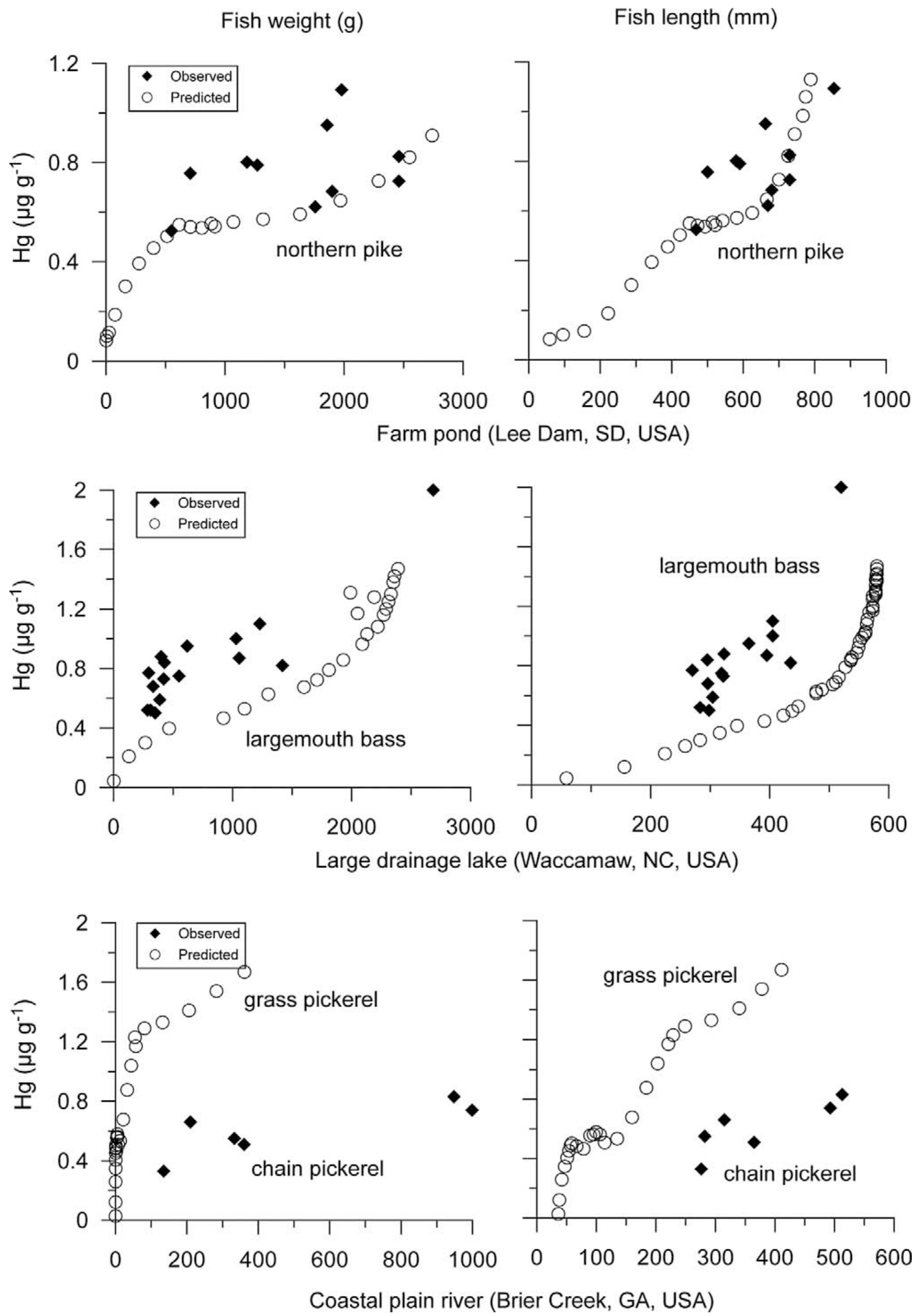

Fig. 4. A comparison between modeled and measured fish mercury concentrations as a function of fish length and weight.

limnion and sediments through turnover of the lake and settling of suspended sediments. In contrast, both the seepage lake (Barco) and the drainage lake (Waccamaw) exhibited relatively consistent declines in mercury concentrations over time.

Despite faster relative declines in water and sediment mercury concentrations, predatory fish levels responded more slowly in the seepage lake (Barco) than in the drainage lake (Waccamaw) (Table 4). The higher trophic position of fish species modeled in the seepage lake (largemouth bass) compared to the drainage lake (yellow perch) caused the overall response time of the top predator fish in the system to be delayed relative to that of the shorter food web. These results suggest that lakes with longer, more complex food chains will exhibit a slowed response to declines in atmospheric deposition relative to those with simpler, shorter food chains.

Water body controls on ecosystem response times

For each system, we computed a sensitivity term, S, as the relative change in modeled response times of water and sediments divided by the relative change in model parameter values (see Table 5 for details). Comprehensive numerical results for all sensitivity runs can be found in *Supporting Information,* Table S4 (http://dx.doi.org/10.1897/08-242.S4). Results show

Table 4. Response times (years) reported as a percentage of steady-state values (defined as a change in concentration of <0.01% per year) achieved in water, sediment, and fish after atmospheric deposition reduction

% Steady state	Farm pond	Seepage lake	Stratified drainage lake	Bay lake	Coastal plain river
Water					
−20%	5	4	0.8[a]/0.8[b]	0.3	6
−40%	27	11	0.8[a]/0.8[b]	0.6	13
−60%	76	22	0.8[a]/0.8[b]	15	27
−80%	200	41	0.8[a]/27[b]	45	54
Sediment					
−20%	6	4	9	10	6
−40%	28	11	19	22	11
−60%	76	22	34	40	25
−80%	200	41	60	70	51
Fish[c]					
−20%	22–25	10–12	<1–5	<1–2	10–11
−40%	67–70	23–29	<1–11	<1–5	15–16
−60%	100	45–67	<1–56	14–18	28–30
−80%	100	100	28–100	48–55	57–58

[a] Epilimninon.
[b] Hypolimnion.
[c] The bioaccumulation model was run for only 100 years. Ranges shown represent the variability among young-of-the-year fish and oldest fish with maximum mercury concentrations.

that the modeled temporal response of the farm pond (Lee Dam) is dictated by watershed inputs of mercury. For this system, changes in chemical rate constants and physical parameters affecting water body dynamics do little to affect the overall responsiveness of this system. We did not perform sensitivity analysis on the water body model parameters for the coastal plain river, because the dynamics of this system were clearly dominated by watershed processes and the system was segmented into a number of stream reaches for loading scenarios, confounding analyses of ecosystem level results.

Changes in active sediment layer depth had the largest impact on modeled response times in the seepage lake (Barco). For example, with a 25% increase in active sediment layer depth, the time needed for water-column mercury concentrations to reach 90% of steady-state values with atmospheric deposition increased by 30 years. The seepage lake also was sensitive to other model terms affecting loss of mercury from the water column, including decreases in evasion rates, increases in water-column Hg(0) oxidation, and water-column Hg(II) reduction rates (Table 5). Generally, response times were longer when evasion rates and Hg(II) reduction rates were lowered and Hg(0) oxidation rates were increased.

Response times of the stratified lake (Pawtuckaway) were affected by both active sediment layer depth and demethylation rates (Table 4). For example, a 25% increase in the active sediment layer depth resulted in an approximately 25-year increase in time needed for sediments to reach 90% of steady-state values but almost no change in water-column response times. Changes in water-column demethylation rates affected water-column response times but had little effect on sediment responses. Overall, response time in the stratified lake was most sensitive to changes in burial rates. Response times for water and sediments to reach 90% of steady-state values more than doubled (from 28 to ~60 years) with a 50% reduction in burial rates and reached 180 years with a 90% reduction in burial rate.

Similar to both the seepage lake and the stratified lake, the response time for the drainage lake (Waccamaw) was affected by relatively small changes in both burial rates and active sediment layer depth (Table 5). Lowering the burial rate increases the response times of both water and sediments. Small changes in active sediment layer depth result in more than proportional increases or decreases in response times in this system. For example, a 25% increase in active sediment layer depth increased the time needed to reach 95% of steady-state values in sediments (baseline, 130 years) up to 272 years and that to reach 90% of steady-state values in water (baseline, 75 years) up to 125 years. These results reinforce the importance of accurate characterization of active sediment layer depths across a variety of lake types and the potential significance of water-column demethylation as a process contributing to mercury removal in some lake systems.

DISCUSSION

Many recent modeling studies have assumed an instantaneous and linear response in fish mercury levels to changes in atmospheric deposition [42,43]. In contrast, our modeling results show that in the absence of additional environmental changes, the time needed to achieve reductions in concentrations that are proportional to reductions in atmospheric deposition will take a minimum of decades and a maximum of centuries. Rapid reductions in fish mercury of 20 to 60% of steady-state values, however, are expected in most systems during the first several decades after atmospheric deposition is reduced, which is a substantial portion of the ultimate benefits achieved from declines in mercury loading.

Our results also show that systems with a large fraction of their mercury inputs from watershed sources (as opposed to direct deposition to the water surface) respond more slowly to changes in atmospheric inputs (Fig. 5 and Table 4). One exception to this pattern may be large, deep systems (like the Great Lakes). Similar results have been reported in the Mercury Experiment To Assess Atmospheric Loading (METAALICUS) study from a lake in northern Ontario (Canada), where changes in fish mercury concentrations over the first several years of the experiment were almost entirely attributable to changes in direct deposition of mercury to the water surface [2]. Mesocosm experiments by Orihel et al. [44] also showed a linear and rapid response in fish mercury concentrations when isotopically labeled mercury was added directly to the water column in a boreal lake.

Sensitivity analyses of our modeling results show that key water body factors driving the temporal responses of freshwater ecosystems to declines in mercury deposition include those processes affecting mercury loss from the water column through evasion, sediment burial rates, and active sediment layer depths. The relative importance of each of these controls varies considerably across different system types. Future empirical studies interested in the responsiveness of a given lake to loading reductions therefore should carefully characterize these terms for any modeling application.

Implications for policy assessments

In the United States, Executive Order 12866 requires a cost–benefit analysis for all significant regulatory actions, which are defined as any ''highly influential'' decision and/or decisions with an economic impact of greater than $100 million [45]. Although we are not advocating the application of economics to ecological assessments or debating appropriate

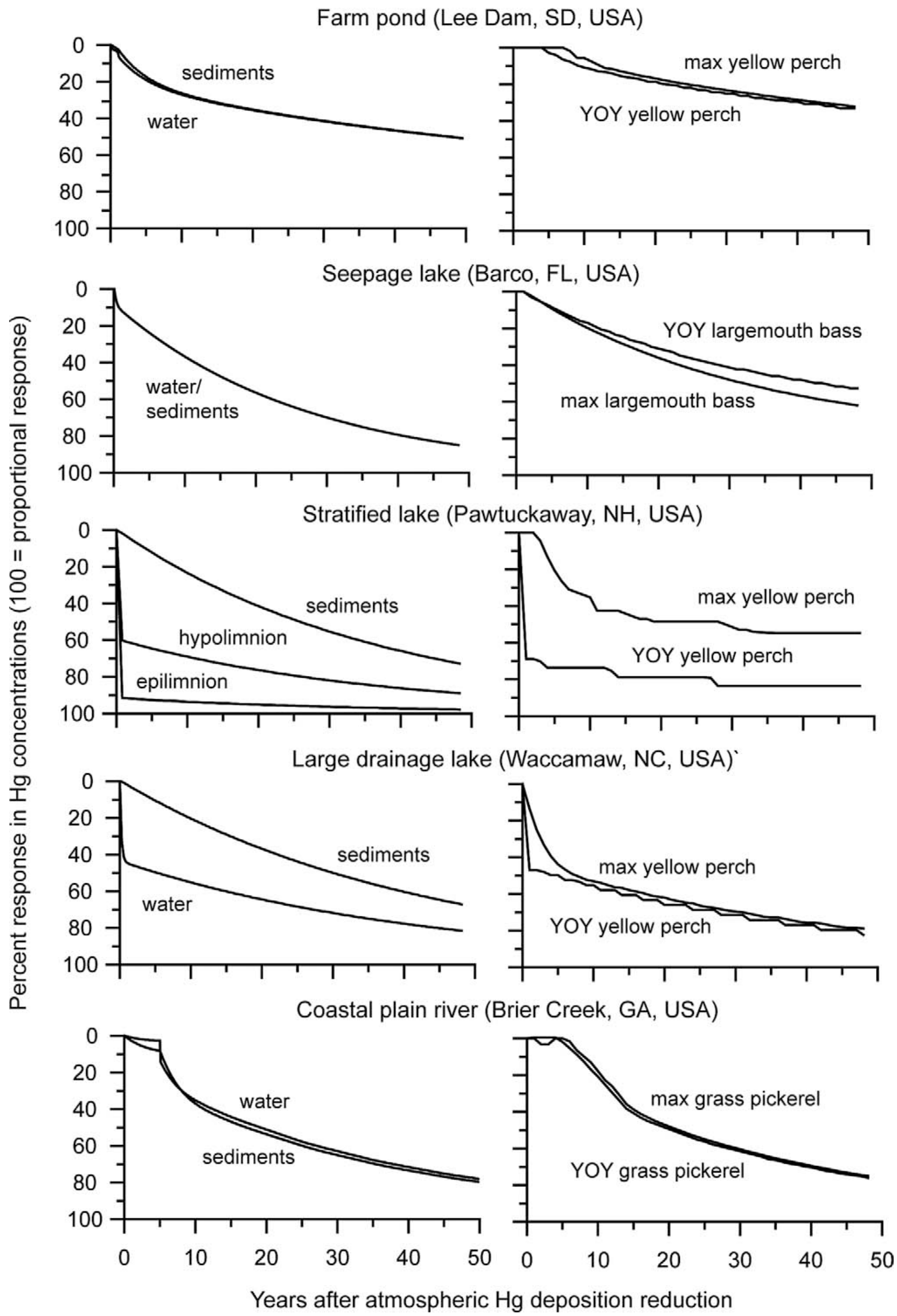

Fig. 5. Relative change (%) in water, sediment, and fish mercury concentrations divided by the relative reduction in atmospheric deposition from case-study ecosystems (100% response = proportionality with atmospheric deposition reductions). Note that watershed-dominated ecosystems (farm pond and coastal plain river) have not reached steady state even after 50 years (Lee Dam, Brier Creek, GA, USA). Fluctuations in fish mercury concentrations represent natural variability in mercury concentrations across different cohorts and age classes of fish. Max = predatory species with maximum Hg concentrations; YOY = young-of-the-year fish.

discount rates for environmental processes (both are beyond the scope of the present study), it is important for the scientific community to recognize that benefits from proposed regulations often are discounted over the time period required to achieve an environmental response. For example, if we construct a hypothetical example in which benefits to human and ecological health associated with a reduction in fish mercury concentrations equivalent to T (%) are valued at some number, V, for each case-study ecosystem described here, and if assume that benefits are achieved in a linear fashion (each percent reduction in fish tissue mercury has a health benefit value at V/T, or B), then we can calculate the net present value (NPV) of fish mercury reductions based the modeled time frame over which each ecosystem responds. The U.S. Office of Management and Budget recommends standard discount rates of 5 to 7% for cost–benefit analyses [19]. Given annual benefits, B,

Table 5. Summary of sensitivities (S) of water and sediment response times for case-study ecosystems to changes in parameter values

Description	Farm pond	Seepage lake	Stratified drainage lake	Bay lake
Active sediment layer depth	$\|S\| < 1$	$\|S\| > 1$[a]	Water, $\|S\| < 1$ Sediment, $\|S\| > 1$[a]	$\|S\| > 1$[a]
Sediment burial rate	$\|S\| < 1$	$\|S\| < 1$	$\|S\| > 1$[a]	$\|S\| > 1$[a]
Settling rate	$\|S\| < 1$	$\|S\| < 1$	$\|S\| < 1$	$\|S\| < 1$
Evasion rate	$\|S\| < 1$	$\|S\| > 1$[a]	$\|S\| < 1$	$\|S\| < 1$
Oxidation rate	$\|S\| < 1$	$\|S\| > 1$	$\|S\| < 1$	$\|S\| < 1$
Reduction rate	$\|S\| < 1$	$\|S\| > 1$[a]	$\|S\| < 1$	$\|S\| < 1$
Methylation rate	$\|S\| < 1$	$\|S\| < 1$	$\|S\| < 1$	$\|S\| < 1$
Demethylation rate	$\|S\| < 1$	$\|S\| < 1$	Water, $\|S\| > 1$[a] Sediment, $\|S\| < 1$	$\|S\| < 1$

[a] Parameter for which the absolute value of the computed model sensitivity, $|S|$, achieves values that are greater than one in at least one instance. The sensitivity, S, is calculated from the relative change in modeled temporal response divided by the relative change in parameter value, or $S = [(t_s - t_o)/t_o]/[(P_s - P_0)/P_0]$, where t_o is the time required to achieve 90% steady state in the initial simulation, t_s is the time required for the sensitivity run, P_s is the parameter value in the sensitivity run, and P_0 is the initial parameter values when $|S| < 1$ model is relatively insensitive to change and $|S| > 1$ model is considered to be sensitive. Numerical results for all sensitivity analyses are available in *Supporting Information,* Table S4 (http://dx.doi.org/10.1897/08-242.S4).

the percentage reduction in fish tissue, Δfish, achieved at time, t, and a discount rate, r, of 5% per year, the NPV of the hypothetical benefits, V, from reductions in fish mercury over time can be calculated as follows:

$$\mathrm{NPV}(V) = \sum_{t=1}^{n} \frac{B \cdot (\Delta \mathrm{fish})_t}{e^{rt}} \tag{1}$$

Note that the cumulative percentage reduction in fish tissue mercury concentrations is denoted $T = \Sigma(\Delta\mathrm{fish})_t$. Our analysis shows that the value of these benefits in present-day dollars (NPV) for each ecosystem ranges between 14% of the original value for the farm pond with a large watershed (Lee Dam) up to 54% for the drainage lake (Waccamaw). Based on the time needed to achieve a decline in top-predator fish concentrations, hypothetical benefits in present dollars for the seepage lake (Barco), the coastal plain river (Brier Creek), and the stratified lake (Pawtuckaway) would be worth 29, 33, and 36%, respectively, of their original values. Across all ecosystems, at the assumed discount rates, the reductions in benefits range from 46 to 87% when converted to NPVs. This example illustrates how near-term changes in fish mercury are weighted much more heavily in economic terms than are those that respond over many decades (Table 4) and the resulting large impact that ecosystem lag times can have on economic assessments. For example, in 2005, when the U.S. EPA promulgated the Clean Air Mercury Rule (CAMR) to regulate emissions of mercury from coal-fired utilities [19], economic benefits of mercury emission reductions calculated by several groups ranged from less than 200 million to more than 1 billion U.S. dollars [42,43,46]. One of the key differences between the U.S. EPA's assessment and others was that the U.S. EPA's benefits were discounted using the modeled temporal lag in response times of freshwater ecosystems to reductions in atmospheric mercury inputs [19,46]. Such examples reinforce the importance of refining and synthesizing the best-available mechanistic research into dynamic modeling tools that may be used to estimate ecosystem response times and inform policy analysis of future regulatory options for controlling mercury releases from anthropogenic sources.

SUPPORTING INFORMATION

Table S1. Default ecological, morphological, and physiological parameters for all species.

Found at DOI: 10.1897/08-242.S1 (171 KB PDF).

Table S2. Land-use specific parameterization, initial conditions, and rate constants for watershed modeling.

Found at DOI: 10.1897/08-242.S2 (30 KB PDF).

Table S3. Mercury specific parameters for water body modeling.

Found at DOI: 10.1897/08-242.S3 (19 KB PDF).

Table S4. Response time to reach a given percentage of final response for each system.

Found at DOI: 10.1897/08-242.S4 (37 KB PDF).

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