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Optimizing Stream Water Mercury Sampling for Calculation of Fish Bioaccumulation Factors

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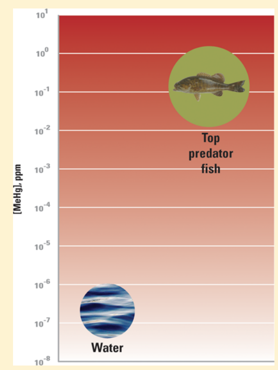
Supporting Information

ABSTRACT: Mercury (Hg) bioaccumulation factors (BAFs) for game fishes are widely employed for monitoring, assessment, and regulatory purposes. Mercury BAFs are calculated as the fish Hg concentration (Hg_{fish}) divided by the water Hg concentration (Hg_{water}) and, consequently, are sensitive to sampling and analysis artifacts for fish and water. We evaluated the influence of water sample timing, filtration, and mercury species on the modeled relation between game fish and water mercury concentrations across 11 streams and rivers in five states in order to identify optimum Hg_{water} sampling approaches. Each model included fish trophic position, to account for a wide range of species collected among sites, and flow-weighted Hg_{water} estimates. Models were evaluated for parsimony, using Akaike's Information Criterion. Better models included filtered water methylmercury (FMeHg) or unfiltered water methylmercury (UMeHg), whereas filtered total mercury did not meet parsimony requirements. Models including mean annual FMeHg were superior to those with mean FMeHg calculated over shorter time periods throughout the year. FMeHg models including metrics of high concentrations (80th percentile and above) observed during the year performed better, in general. These higher concentrations occurred most often during the growing season at all sites. Streamflow was significantly related to the probability of achieving higher concentrations during the growing season at six sites, but the direction of influence varied among sites. These findings indicate that streamwater Hg collection can be optimized by evaluating site-specific FMeHg − UMeHg relations, intra-annual temporal variation in their concentrations, and streamflow-Hg dynamics.



INTRODUCTION

Fish Bioaccumulation Factors (BAFs) are used to develop Total Maximum Daily Load (TMDL) estimates for management of mercury (Hg) loading to freshwater ecosystems in the United States.[1−6] BAFs are also used for wildlife and human exposure assessments as well as for remediation assessments at Superfund and other Hg contaminated sites.[7,8] The United States Environmental Protection Agency (USEPA) recommends site-specific fish BAFs, requiring collection of representative fish and water Hg samples.[1,5] However, empirically based guidelines for fish and water sampling are lacking. The influences of water sample timing and frequency, Hg species (methylmercury [MeHg] and total mercury [THg]), and sample processing (filtered and unfiltered) have not been assessed systematically on a broad geographic scale. Here, we integrate flow-weighted, rating-curve estimated water Hg (Hg_{water}) concentrations from stream sites across the United States with corresponding predatory game fish Hg (Hg_{fish}) data to evaluate different approaches to fluvial Hg sampling for site-specific fish BAF calculations.

This study utilizes fish Hg data, fish and periphyton stable isotope data, water MeHg and THg data, and continuous discharge data from 11 streams across large gradients of geography and environmental condition (e.g., basin area, land cover, methylmercury concentrations, Table 1). These data were used to identify optimal water sampling strategies for computing BAFs for top predator fish by assessing correlations between Hg_{fish} and selected Hg_{water} metrics, while accounting for the influence of fish trophic position. Hg_{water} metrics were selected to evaluate influences, on BAF fluvial Hg data quality, of (1) water-sampling-period duration (i.e., from 30 days to 365 days), (2) different statistical metrics (i.e., mean, median, and percentiles), (3) Hg species (MeHg, THg), (4) sample processing (filtered or whole water), and (5) seasonality and flow condition.

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Table 1. Sampling Sites, Watershed Characteristics, and Selected Chemical Characteristics[a]

site	USGS station name	USGS station number	watershed characteristics: drainage basin area (km^2)	developed land (%)	wetland (%)	chemical characteristics mean, (sd) median min−max [n]: FMeHg (ng/L)[b]	pH	suspended sediment (mg/L)
BEA_{OR}	Beaverton Creek at SW 216th Ave. near Orenco, OR	14206435	96	85.8	0.3	0.04, (0.03), 0.04	7.3, (0.2), 7.3	13, (14), 9
						<0.04−0.23 [46]	7.1−7.9 [69]	1−74 [49]
PIK_{WI}	Pike River at Amberg, WI	04066500	660	4.8	17.9	0.10, (0.06), 0.10	7.7, (0.4), 7.8	27, (13), 27
						<0.04−0.26 [32]	6.9−8.2 [30]	1−50 [32]
EVR_{WI}	Evergreen River below Evergreen Falls near Langlade, WI	04075365	167	4.2	13.4	0.05, (0.04), 0.04	7.9, (0.3), 7.8,	23, (16), 23
						<0.04−0.22 [40]	7.2−8.5 [44]	2−74 [41]
OAK_{WI}	Oak Creek at South Milwaukee, WI	04087204	65	58.9	3.5	0.06, (0.05), 0.05	7.6, (0.2), 7.5	121, (112), 100
						<0.04−0.25 [38]	7.1−8.1 [56]	2−578 [52]
$FB3_{NY}$	Fishing Brook (County Line Flow) near Newcomb, NY	0131199050	66	0.7	9.3	0.14, (0.11), 0.10	6.3, (0.5), 6.3	3, (2), 2
						<0.01−0.45 [41]	5.6−8.0 [43]	1−12 [45]
HUD_{NY}	Hudson River near Newcomb, NY	01312000	493	0.7	9.7	0.09, (0.06), 0.09	6.6, (0.4), 6.7	2, (3), 1
						<0.04−0.24 [32]	5.6−7.3 [37]	1−16 [45]
$MC3b_{SC}$	McTier Creek near New Holland, SC	02172305	79	4.7	8.2	0.12, (0.06), 0.11	5.0, (0.6), 5.0	10, (12), 7
						<0.04−0.24 [49]	3.3−5.9 [50]	1−58 [49]
$ER1_{SC}$	Edisto River near Cottageville, SC[c]	02174175	5341	5.9	16.0	0.31, (0.16), 0.32	6.3, (0.5), 6.4	16, (32), 8
						0.04−0.69 [25]	5.0−7.7 [99]	1−206 [97]
STM_{FL}	St. Mary's River at Boulogne, FL[d]	02231220	3311	5.0	35.6	0.38, (0.22), 0.33	4.8 (1.3), 4.3	91, (49), 100
						<0.04−1.03 [38]	2.9−7.5 [37]	2−193 [33]
WEK_{FL}	Little Wekiva River near Longwood, FL	02234998	115	77.3	13.2	0.08, (0.09), 0.05	7.2, (0.3), 7.2	19, (35), 6
						<0.04−0.44 [39]	6.9−8.7 [40]	1−163 [34]
SNT_{FL}	Santa Fe River near Fort White, FL	02322500	2592	6.2	17.9	0.20, (0.23), 0.09	7.2, (0.4), 7.3	57, (82), 5
						<0.04−0.93 [31]	5.7−7.9 [30]	0−235 [29]

[a]Statistics for chemical characteristics are calculated from samples collected within the period of study over all sites (earliest year was set at 2002 for sites with longer periods of record). FMeHg, filtered methylmercury. [b]Nondetects for FMeHg were converted to half the detection limit of 0.04 ng/L prior to calculating statistics. [c]Water collections and discharge measurements were made at Edisto River near Givhans, SC (012175000), located 10.6 km downstream of the fish collection site near Cottageville, SC. [d]Water collections and discharge measurements were made at St. Mary's River at Macclenny, FL (02231000), located 47.5 km downstream of the fish collection site near Boulogne, FL.

■ MATERIALS AND METHODS

Study Areas. Game fish, periphyton and water samples, and continuous discharge data were collected from 11 sites in five states (Table 1). The 11 study sites were part of a broader study of mercury cycling and bioaccumulation in streams.[9−14] They are described here, briefly (Table 1), and in greater detail elsewhere.[9,10] Five sites are in the southern United States (Florida and South Carolina) and six are in the north (New York, Oregon, and Wisconsin). Drainage basin areas range from 64 to 5341 km^2, and wetland amounts range from less than 1% to 36% of basin area. Three sites occupy developed watersheds (mostly urban); the rest are in relatively undeveloped, forested, and mixed-land use watersheds. Atmospheric deposition from distant sources is the primary source of mercury to all 11 sites.[11,12] Environmental characteristics of the sites varied widely, with a large range of pH and measured FMeHg. However, most sites had relatively low to moderate suspended sediment concentrations (Table 1).

Analytical Approach. Previous work has shown a strong linkage between Hg_{fish} and trophic position.[13−17] Thus, we constructed and compared a series of two-variable regression models of Hg_{fish}, in which each model included trophic position and a metric of Hg_{water}. Fish trophic positions were calculated from fish-tissue nitrogen stable isotope ratios ($\delta^{15}N$) that were adjusted for isotopic differences in $\delta^{15}N$ of periphyton (the presumptive food web base) among sites. Hg_{water} concentration

Table 2. Game Fish Species Collected, Collection Dates, and Statistics for Fish Total Length, Trophic Position, and Mercury (Hg) Concentration[a]

	fish sample characteristics					
site	scientific name; common name	total length (mm) median (min−max)	fish collection date	number	trophic position mean (min−max)	Hg (mg/kg) mean (min−max)
BEA_{OR}	*Oncorhynchus clarkii* cutthroat trout	293 (218−334)	7/16/2003	5	2.5 (2.0−2.9)	0.078 (0.041−0.128)
PIK_{WI}	*Salmo trutta* brown trout	247 (237−275)	8/27/2003	12	3.0 (2.7−3.2)	0.091 (0.041−0.143)
EVR_{WI}	*S. trutta* brown trout	350 (302−404)	6/04/2003	11	3.0 (2.6−3.3)	0.087 (0.048−0.126)
OAK_{WI}	*Lepomis cyanellus* green sunfish	114 (101−139)	6/03/2003	10	2.0 (1.7−2.3)	0.070 (0.046−0.105)
$FB3_{NY}$	*Salvelinus fontinalis* brook trout	272 (257−281)	11/15/2007	5	3.6 (3.4−3.7)	0.315 (0.230−0.392)
HUD_{NY}	*Micropterus dolomieu* smallmouth bass	262 (220−328)	9/4/2007	9	3.5 (3.3−3.7)	0.476 (0.374−0.630)
$MC3b_{SC}$	*Ameiurus* spp. bullheads	163 (132−189)	4/15/2008	5	3.6 (3.2−3.7)	0.414 (0.294−0.490)
$ER1_{SC}$	*M. salmoides* largemouth bass	280 (200−300)	12/11/2007	7	3.7 (3.3−4.1)	0.524 (0.386−0.694)
STM_{FL}	*M. salmoides* largemouth bass	480 (390−517)	4/24/2003	8	4.1 (3.7−4.7)	1.313 (0.910−1.562)
WEK_{FL}	*M. salmoides* largemouth bass	282 (260−340)	11/13/2003[b]	8	3.0 (2.9−3.1)	0.337 (0.252−0.512)
SNT_{FL}	*M. salmoides* largemouth bass	368 (300−475)	4/23/2003	15	3.6 (3.1−4.1)	0.441 (0.216−0.976)

[a]Fish Hg concentrations are expressed on wet-weight basis. [b]Several specimens were also collected 11/19/2003.

metrics were obtained from rating-curve estimates of daily Hg_{water} concentrations. The rating-curve estimation approach, explained in detail below, integrates streamflow measurements, seasonality, and sampled Hg concentrations. Previous work has demonstrated a strong link between Hg_{fish} and aqueous MeHg (both FMeHg,[13,14,16,17] and unfiltered MeHg [UMeHg][18]). Thus, we used rating-curve estimates of FMeHg to select the best time period metrics and statistical metrics and then used those time periods and statistics to evaluate UMeHg and filtered total Hg (FTHg), both also derived from rating-curve estimates.

Sites in this study were selected to take advantage of a unique national data set, which includes fish and lower food web mercury concentrations and stable isotope ratios, frequently collected Hg_{water} species concentrations, and continuous discharge data across a large geographic scale. This broad geographic scale, and corresponding variety of environmental settings and food webs among sites, precluded the targeting of a single top predator fish species (or several species with similar diets and trophic positions) among sites. This potential limitation was overcome by explicitly including fish trophic position as an explanatory variable in the approach employed here. This approach is intended to identify Hg_{water} metrics, representing methodological differences in sample timing (i.e., from 30 days to 365 days prior to fish sampling), processing (i.e., filtration vs whole water), analysis (i.e., MeHg vs THg), and calculation (i.e., mean, median, or other statistic), which can explain variability in Hg_{fish}, after accounting for variability explained by trophic position. We use rating-curve estimates of FMeHg daily concentrations to determine site-specific optimal timing and flow conditions, where optimal conditions are defined as those under which the defined optimal Hg concentration statistic is likely to occur. The results of this national-scale evaluation are intended to provide a general starting point for smaller (local to regional) scale BAF water-sampling optimization efforts. Other environmental factors (e.g., pH, dissolved organic carbon, system productivity) that are known to influence bioaccumulation[16,19] are not included in the BAF calculation and consequently are not addressed here. In addition, we do not address the various fish sampling considerations that could potentially influence BAF calculation.

Predatory Game Fish Data. Predatory game fish were collected as described elsewhere.[13,14] The presumed top predator species at each site was collected (Table 2). Where multiple species were available in sufficient numbers (at least five specimens), trout (Salmonidae) or black bass (*Micropterus* spp.) were selected for this evaluation. When multiple sample events were available, we focused on the event with the most collected specimens. Each specimen was field-processed as axial muscle (i.e., skinless standard fillets, detailed elsewhere[20]). Samples were analyzed for THg (MeHg comprises >95% of Hg in predatory fish[21]) at the Trace Element Research Laboratory (Texas A & M University, College Station, Texas), using USEPA Method 7473.[22] Accuracies in blind submissions of standard reference materials are provided elsewhere.[23,24] Fish tissue samples were submitted for $\delta^{15}N$ analysis to the USGS Isotope Laboratory (Reston, VA; samples from FL, OR, and WI sites) or to the Stable Isotope Geochemistry Laboratory at Florida State University's National High Magnetic Field Laboratory (Tallahassee, FL; samples from NY and SC sites). Analysis method details and quality assurance results are provided elsewhere.[23,24]

Trophic Position Data. Base N-adjusted trophic position[25] was calculated for fish from each site, as

$$\text{Trophic position} = (\delta^{15}N_{fish} - \delta^{15}N_{base})/3.4$$

where $\delta^{15}N_{fish}$ is the mean $\delta^{15}N$ of fish samples, and mean $\delta^{15}N_{base}$ is the mean $\delta^{15}N$ of periphyton samples. Periphyton was used instead of a common lowest trophic-level consumer, as previously used,[13,14,23,24] because a consistent primary consumer taxon or feeding guild was not collected across all 11 sites. However, preliminary trophic position results were compared for four species at the two sites that had a common primary consumer, and the differences in mean trophic position calculated from the two base organism groups were minimal (0.0−0.1‰). Three composite periphyton samples per substrate type were collected on two or four dates from each of 10 sites and on a single date from one site. Samples were collected from rock, woody snag, and (or) depositional substrates, depending on their availability across the study reach. We address the potentially large seasonal and flow variation of $\delta^{15}N_{periphyton}$[26,27] by limiting periphyton sampling to base flow conditions during the growing season and by using values averaged over multiple collection dates for most sites. Samples were collected, processed, and analyzed for $\delta^{15}N$ as detailed elsewhere.[23,24,26] Base $\delta^{15}N_{periphyton}$ for each site was calculated as the grand mean of composites from each site from similar substrate type calculated over all periphyton collection dates. Resulting temporal variation was small for most sites[23,24] (Supporting Information SI1).

Streamflow Data. Hg_{water} samples were collected at 11 sites near USGS streamgages, nine of which have at least 25 years of streamflow record. Two of these streamgages ($ER1_{SC}$ and STM_{FL}) were located downstream of the fish collection sites (Table 1). Two sites ($FB3_{NY}$ and $MC3b_{SC}$) were sampled near streamgages operating from 2007 to 2009. Estimates of daily mean streamflows at these two sites were extended back to 2004 using continuous streamflow records at nearby long-term (greater than 30 years of record) streamgages[28] and using the program, Maintenance Of Variance Extension, Type 1 (MOVE.1).[29] Continuous (15-min) streamflow data were computed for all streamgages using standard USGS stage/discharge techniques[30] and were stored in the USGS National Water Information System database.[31]

Water Hg Data. Hg_{water} sampling was conducted approximately monthly for 2−4 years, with additional samples collected during selected high flow events, providing 25−49 samples collected across the hydrograph.[28,32] Trace-metal clean sampling and processing, and Hg laboratory analyses of FMeHg, FTHg, and particulate MeHg (PMeHg), were conducted as described in detail elsewhere.[11] Rating-curve estimates of daily FMeHg, PMeHg, and FTHg concentrations were computed using S-LOADEST software.[11,33] The rating-curve approach relates aqueous concentrations to flow and seasonal terms, using maximum likelihood regression to properly account for censored (less-than detect) data. Hg_{water} concentrations were estimated for each day within the period of interest by applying the regression coefficients (β) to the daily streamflow. The rating-curve model used herein [11] is

$$\log[C] = \beta_0 + \beta_1\log[Q^*] + \beta_2\log^2[Q^*] + \beta_3\sin(2\pi t) + \beta_4\cos(2\pi t)$$

where C = measured water concentration, Q^* = daily mean centered streamflow, sine and cosine terms model seasonality, and t = time (years). Statistics (mean, median, minimum, maximum, and percentiles) of estimated daily Hg_{water} values were generated for fish-collection antecedent periods (up to and including fish-collection date, Table 2) of 30, 60, 90, 120, 150, 180, and 365 days. Daily UMeHg values were calculated as the sum of daily FMeHg and PMeHg values. Several sites did not have a full year of water and discharge measurements prior to the fish collection date; in these cases, the water time period encompassed, but was allowed to progress beyond, the fish collection date (Supporting Information SI2). Herein we use the abbreviation Hg_{water} to refer in general to water-borne-Hg metrics, including all combinations of Hg species, filtration, sampling periods, and statistical measures.

Data Analysis. Models of Hg_{fish} were developed from a combination of trophic position and rating-curve estimated Hg_{water} data. Models were generated with different Hg species (MeHg or THg), water sample processing approaches (filtered, FMeHg or unfiltered, UMeHg), statistics (mean, median, percentiles), and time periods (30 days to 365 days). Models were generated with Distance-based Linear Model (DISTLM) analysis, using the PRIMER-E computer program, PERMANOVA.[34−36] DISTLM uses permutations of a Euclidian-distance-based resemblance matrix to model the relation between a response variable and one or more environmental variables. Hg_{fish} was $\log_{10}$ transformed, and Hg_{water} metrics were fourth-root transformed to approximate normal distributions. Trophic position was included as the first explanatory variable input to each model, and Hg_{water} metrics were added using the 'BEST' procedure.[36] Models were evaluated on the basis of Akaike's Information Criterion (AIC).[37] AIC measures the lack of model fit relative to the number of explanatory variables included and penalizes models having too many variables (indicated by a high 'lack of fit'). The most parsimonious model is that with the lowest AIC. Thus, AIC of each two-variable model (i.e., including both trophic position and one Hg_{water} metric) was compared with AIC of the one-variable model (i.e., including only trophic position) and was deemed superior to the one-variable trophic position model only if the resulting AIC was lower by at least one AIC unit. AICs were then compared among the successful two-variable models to identify the better Hg_{water} metric(s). By these means, we derived a set of useful water sampling 'choices' (timing, statistic, filtration, Hg species) that were most highly correlated with Hg_{fish}, while accounting for the broad range of fish trophic positions across the data set.

Site-specific influences of seasonality and flow conditions on the probability of collecting the optimal Hg_{water} samples were determined in the following way. First, we used the Hg_{water} species, sampling period, filtration method, and statistic that produced the best 2-variable models (i.e., with lowest AIC) to establish site-specific targeted concentration ranges. These targeted concentration ranges were interpreted as the range of Hg_{water} concentrations that are most closely associated with Hg_{fish} exposure for each site. Second, the percentage of days per month that rating-curve-estimated concentrations fell within the targeted concentration range was calculated, and the monthly pattern was evaluated, to determine whether site-specific Hg_{water} sampling could be optimized by selecting particular times of the year. Third, binary logistic regression[38] was used to determine whether flow condition could predict the optimal Hg_{water} sample timing. A dependent variable for the logistic regression was created for each site by coding the rating-curve estimated Hg_{water} concentration for each day as 0 or 1 depending upon whether or not it fell within the targeted concentration range. The logistic regression's independent variable was the daily mean flow ($\log_{10}$ transformed). This analysis generated, for each site, a probability of achieving the targeted concentration across the range of flow conditions that occurred at that site over the selected time period. A nonsignificant regression ($p > 0.05$) indicated no relation between site-specific flow conditions and the probability that a water sample has a concentration that is within the targeted range. For sites having significant regressions, the sign of the logistic regression coefficient indicated whether the targeted concentration range was more likely to occur during higher flows or during lower flows (i.e., positive or negative sign, respectively).

RESULTS AND DISCUSSION

Game Fish Hg and Trophic Position. Mean wet weight fish Hg concentrations (Table 2) ranged from 0.070 mg/kg in green sunfish (*Lepomis cyanellus*) from Oak_{WI}, an urban site, to 1.313 mg/kg in largemouth bass (*Micropterus salmoides*) from STM_{FL}, a large river with abundant wetlands (Table 1).

Detailed fish Hg, isotope, and field data are reported elsewhere.[23,24] Exceedences of USEPA's 0.3 mg/kg human health advisory level[5] occurred in bass species at all five sites from which they were collected (four southern sites and one northern site, HUD_{NY}) as well as in bullheads (*Amieurus* spp.) from $MC3b_{SC}$ and brook trout (*Salvelinus fontinalis*) from $FB3_{NY}$. Mean Hg_{fish} concentrations in trout and sunfish from the other four sites were below the wildlife critical value of 0.1 mg/kg for piscivorous mammals.[39]

Mean trophic position (Table 2) ranged from 2.0 for green sunfish from OAK_{WI} to 4.1 for largemouth bass from STM_{FL}. The median trophic position among all 11 samples was 3.0. Trophic positions for trout and bass were similar to those used in USEPA guidance documents for BAF calculation;[1,5] medians among sites were 3.0 (trout) and 3.6 (bass); these corresponded with the discrete trophic levels (i.e., trophic positions rounded to whole numbers) of 3 and 4 for trout and bass, respectively, that are presented in the guidance documents.[1,5]

Evaluation of Antecedent Time Periods and FMeHg Statistics. Mean annual FMeHg concentrations, derived from the daily rating curve-estimates, ranged from 0.039 ng/L at BEA_{OR}, a relatively small stream in a developed watershed with low percentage of wetland cover, to 0.426 ng/L at STM_{FL}, a relatively large river in an undeveloped watershed with high percentage of wetland cover (Supporting Information SI2, Table 1). Daily rating-curve estimates of FMeHg (Supporting Information SI2) and daily discharge measurements are provided in previous papers.[11,28,32] DISTLM models, with trophic position as the first explanatory variable, and rating-curve estimated mean FMeHg concentration calculated over 365 days as the second explanatory variable, accounted for 84.5% of the variation in Hg_{fish} among the 11 sites (Table 3).

Table 3. Regression Coefficients (R^2) and Akaike Information Criteria (AIC) from Distance Based Linear Models (DISTLM) of Game Fish Mercury Concentrations from 11 Sites[a]

	statistic	
number of days	mean	median
365	**84.5 (−19.2)**	80.4 (−16.6)
180	82.6 (−17.9)	81.3 (−17.1)
150	82.3 (−17.7)	83.0 (−18.2)
120	81.9 (−17.5)	81.4 (−17.2)
90	80.9 (−16.9)	80.2 (−16.5)
60	79.5 (−16.1)	79.5 (−16.1)
30	79.4 (−16.1)	79.4 (−16.1)

[a]Models are based on trophic position and either mean or median concentrations of filtered methylmercury (FMeHg). Statistics are based on rating-curve estimates of daily FMeHg concentrations and were calculated over 30-day to 365-day periods prior to fish collection. Trophic position is included in each model, explains 79.4% of the total variation in game fish Hg, and has an AIC of −18.1. Bold results indicate model for which AIC is lower by at least one unit than AIC of the trophic position model, indicating model parsimony.

Trophic position accounted for most of the variability (79.4%), as expected, given the broad range of fish trophic positions (2.0−4.1, Table 2) among sites, and corresponding with the strong positive relation between mercury and organism trophic position reported elsewhere.[13−17] The 365-day mean FMeHg explained an additional 5.1% of variation in Hg_{fish}, above that accounted for by trophic position. In contrast, neither the median for any time period, nor any mean calculated over the shorter time periods produced successful (i.e., parsimonious) models, based on similar or elevated AIC values for these 2-variable models as compared with the single-variable (trophic position only) model (Table 3).

Because the model that included Hg_{water} calculated over a 365-day period performed best, the remaining analyses focused on this period. Because the mean performed better than the median, and the mean is influenced by higher concentrations, we also evaluated models that incorporated higher FMeHg concentration statistics. Results (Figure 1) indicate that FMeHg concentration percentiles from 80th to 100th (i.e., maximum) produced Hg_{fish} models that were better than the one-variable trophic position model (i.e., had markedly lower AIC). As with the median, the AIC of the two-variable models using 70th or 75th percentiles were higher than, or similar to, the AIC of the one-variable trophic position model. Thus, spatial variation in Hg_{fish} across these 11 sites is most closely related to spatial variation of the higher concentrations of FMeHg that occur during the year at each site. Although AIC indicated that the 85th and 90th percentiles produced the best models (Figure 1), the minimal differences in AIC (i.e., < 1) among the 80th, 85th, 90th, and 95th percentiles indicate that a sampling program generally targeting higher concentrations for BAF calculation would provide FMeHg concentrations that are similarly representative of fish exposure.

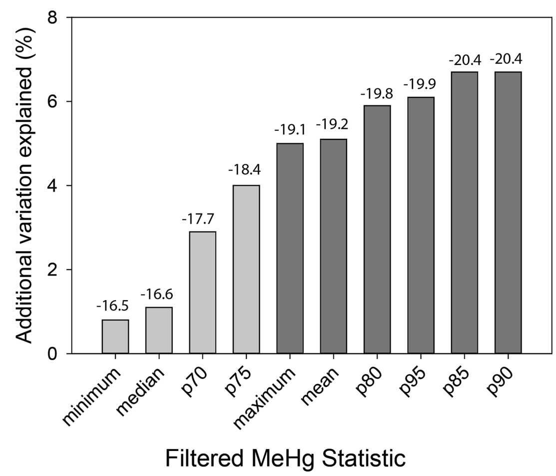

Figure 1. Comparison of DISTLM results for 2-variable models of game fish mercury based on trophic position and each of the 10 statistics shown for filtered methylmercury (FMeHg) concentrations to examine the influence of statistic used on additional variance explained above the trophic position-only model. FMeHg statistics are based on rating-curve estimates of FMeHg daily concentrations for 365 days prior to fish collection for each of 11 sites. Dark bars indicate statistics for which Akaike's Information Criterion (AIC) is smaller than AIC of the trophic position model (−18.1) by at least one AIC unit, indicating model parsimony. AIC values are shown above bars.

Filtration Influences. The 90th percentile concentrations of FMeHg and UMeHg (the latter calculated from estimates of FMeHg and PMeHg, Supporting Information SI2), derived from rating-curve estimates and calculated over 365 days, were used to evaluate whether or not filtration (i.e., FMeHg) provided an advantage over analysis of whole-water samples, i.e., UMeHg) on model results. Using UMeHg to obtain the 90th percentile statistic calculated over 365 days produced a parsimonious two-variable model and accounted for a similar amount of additional variation (i.e., above the one-variable trophic position model) as the corresponding FMeHg statistic (Figure 2). Rating-curve estimated aqueous MeHg was

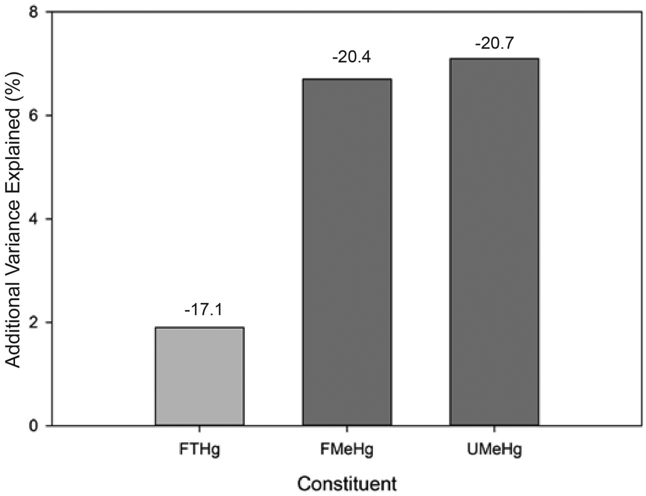

Figure 2. Comparison of DISTLM results for 2-variable models of game fish mercury based on trophic position and 90th percentile concentrations of filtered total mercury (FTHg), filtered methylmercury (FMeHg), or unfiltered methylmercury (UMeHg) to examine the influence of sample processing and mercury species on additional variance explained above the trophic position-only model. Statistics were calculated from rating-curve estimates of daily concentrations across 365 days prior to fish collection. Data are based on results from 11 sites. Dark bars indicate statistics for which Akaike's Information Criterion (AIC) is smaller than AIC of the trophic position model (−18.1) by at least one AIC unit, indicating model parsimony. AIC values are shown above bars.

primarily in the dissolved form (i.e., FMeHg) at most sites, and PMeHg made up more than 35% of annual mean UMeHg at only one of the 11 sites (Supporting Information SI2). Accordingly, significant savings of time and expense might be achieved using MeHg from unfiltered water samples for calculation of BAFs where streamwater MeHg occurs primarily in the dissolved form.

Hg Species Influence (FTHG). Substituting the 90th percentile of rating-curve daily estimates of FTHg (Supporting Information SI2) for FMeHg substantially reduced the explanatory power of the model (Figure 2). The two-variable model with trophic position and FTHg was no better than the single-variable trophic position model, according to AIC results. This result is consistent with the substantially greater potential of MeHg than THg to bioconcentrate and biomagnify[14,40−42] and the generally low correlation between MeHg and THg concentrations in surface water systems.[11,14] These findings indicate that THg would be inferior to either FMeHg or UMeHg as a Hg_{water} metric in BAF calculations.

Optimal Water Sampling Regime. The region- and site-specific nature of temporal variation in FMeHg and flow dynamics[11,12] preclude broadly applicable recommendations for sampling month, season, and (or) flow conditions, but the following observations may help optimize site-specific sampling regimes. For this purpose, a site-specific targeted concentration range was calculated on the basis of the 80th percentile to maximum concentration calculated over the 365-day period prior to (and including) the fish collection date. This is because the 80th percentile to the maximum represented a range of suitable models (better than the others, and with minimal AIC difference among these statistics, as stated previously). This site-specific target range (Table 4) was used to assess monthly patterns and for coding daily values for the subsequent logistic regression models. At all 11 sites in this study the 80th percentile and higher FMeHg concentrations occurred most frequently (at least 50% of days) during a one to three month period (Table 4, Figure 3), and these periods occurred within the growing season at all sites. Higher FMeHg concentrations did not occur during winter months at eight sites (including all six northern sites and two of the four southern sites) and occurred relatively infrequently during winter months at the remaining three sites (Figure 3). Thus, an optimized water sampling program for these sites would avoid winter months and target the growing season. Knowledge of site-specific

Table 4. Targeted Methylmercury (FMeHg) Concentration Range, Months during Which FMeHg Concentration Is within the Targeted Range at Least 50% of the Time and Flow-Based Logistic Regression Results Across the Growing Season[a]

			logistic regression model for growing season		
site	targeted FMeHg concentration range (ng/L)	months with FMeHg concentration in targeted range ≥50% of days	coefficient[b]	p	direction of influence
Northern Sites					
BEA_{OR}	0.047−0.051	May−June	**+5.50**	<0.0001	positive
PIK_{WI}	0.132−0.196	May−June	**+8.33**	<0.0001	positive
EVR_{WI}	0.084−0.133	July−August	+1.25	0.422	ns
OAK_{WI}	0.084−0.093	June−July	+0.08	0.791	ns
$FB3_{NY}$	0.207−0.285	June−July	−0.28	0.361	ns
HUD_{NY}	0.149−0.175	July and September	**−4.17**	<0.0001	negative
Southern Sites					
$MC3b_{SC}$	0.174−0.204	May−July	+0.09	0.860	ns
$ER1_{SC}$	0.385−0.623	August−September	**+3.27**	<0.0001	positive
STM_{FL}	0.709−0.741	May−June	**−12.11**	<0.0001	negative
WEK_{FL}	0.220−0.431	August	**+42.79**	<0.0001	positive
SNT_{FL}	0.396−0.816	March−April	+49.49	0.145	ns

[a]Growing season is defined here as May through October for northern sites (184) and March through November for southern sites (274−275). The targeted FMeHg concentration range represents the 80th percentile to maximum of daily values for the 365-day period prior to fish collection for each site. [b]Significant coefficients are indicated with bold font.

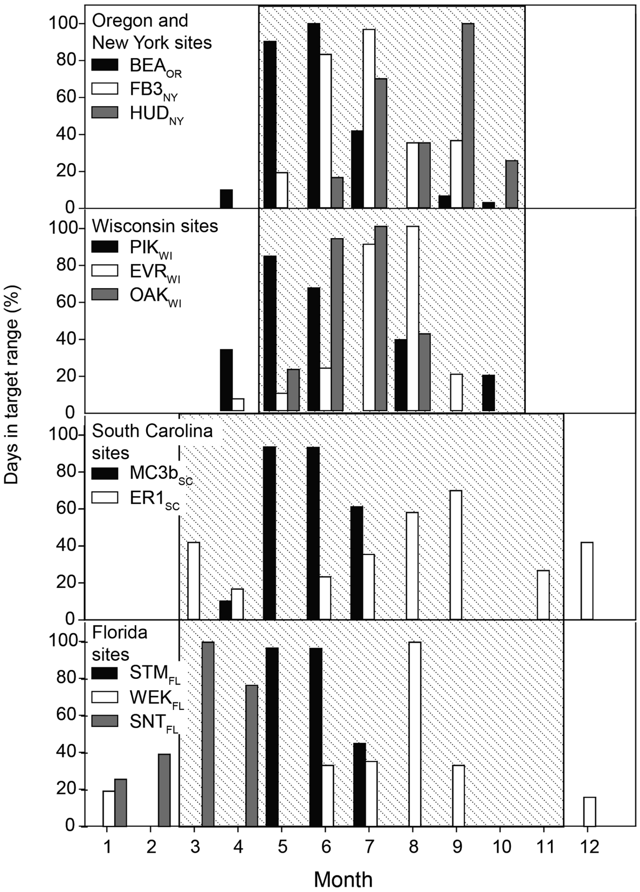

Figure 3. Percentage of days during which rating-curve estimates of daily filtered methylmercury concentrations were within the targeted concentration range within each month. Site-specific targeted concentration ranges are based on the 80th percentile to maximum concentrations calculated over the 365-day period prior to fish collection. The months shown cover the same time period. The hatched areas approximate the growing season. Site names are given in Table 1, and targeted concentration ranges are listed in Table 4.

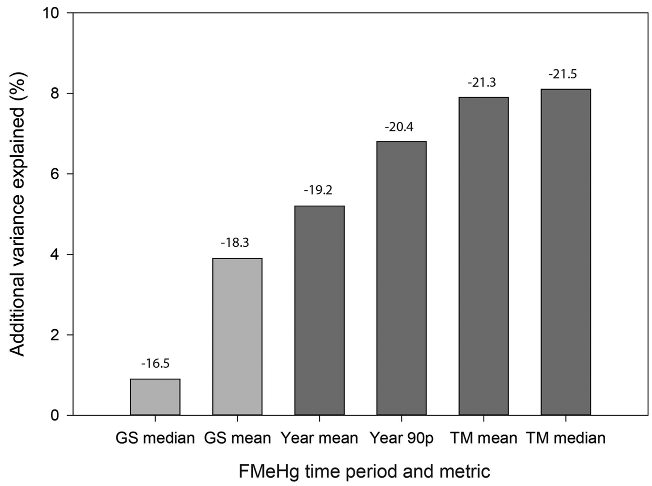

Figure 4. Comparison of DISTLM results for 2-variable models of game fish mercury concentration based on trophic position and rating-curve estimates of filtered methylmercury (FMeHg) concentrations for the growing season (GS), a full year, and a set of targeted months (TM), to examine the influence of particular time periods within a year on additional variance explained above the trophic position-only model. Data are based on results from 11 sites. Dark bars indicate statistics for which Akaike's Information Criterion (AIC) is smaller than AIC of the trophic position model (−18.1) by at least one AIC unit, indicating model parsimony. AIC values are shown above bars. Year 90p = 90th percentile concentration for the year prior to fish collection. Site-specific targeted months are given in Table 4.

temporal and flow-related variation in FMeHg concentration would allow further optimization by providing information to define a narrower period during which the higher concentrations are most likely to occur at each site, such as the months identified here ('target months') for these sites (Table 4, Supporting Information SI3). Limiting analysis of rating-curve estimated FMeHg daily concentrations to these target months resulted in Hg_{fish} models that were greatly improved over the 365-day 90th percentile model (Figure 4), with R^2 of 87.4 and 87.2, for median and mean, respectively (Figure 4). However, models based on FMeHg calculated across the entire growing season were inferior to both the targeted month models and to the model based on the 365-day mean FMeHg (Figure 4). This suggests that acquiring information regarding temporal variation in FMeHg concentration across the growing season for particular sites or environmental settings can be very useful in optimizing water sampling for BAF calculation.

Daily flow data across the growing season during the 365-day antecedent period were used to evaluate the utility of incorporating information on flows to optimize the timing of water collection. The probability of daily occurrence of the higher FMeHg concentrations (i.e., 80th percentile and higher) during the growing season was significantly related to daily flow at six of the 11 sites (Table 4). This suggests that the use of additional information regarding flow-FMeHg relations can help develop a targeted Hg_{water} sampling strategy for some sites or environmental settings. However, a generalization regarding flow conditions most predictive of higher FMeHg concentrations is not possible because of the differing direction of influence of flow among sites, even those within the same geographic region (Table 4, Supporting Information SI3). For example, the probability of occurrence of the higher FMeHg concentrations was positively related to flow at WEK_{FL} and inversely related to flow at STM_{FL}. The observed differences among sites may be due to differences in stream channel, riparian, and landscape characteristics that influence the extent and timing of hydrologic connection of MeHg source areas to the stream channel.[43]

Implications for Optimizing Water Sampling. We evaluated several key water sampling considerations for calculation of BAF at 11 sites across the contiguous U.S, with the aim of identifying sampling choices that result in Hg_{water} concentration data that best represent the pattern of fish exposure among sites. Our findings are intended to enhance consistent development of BAF for site-specific applications (e.g., tracking temporal changes) and for comparison among sites (e.g., examining spatial patterns). The various water-sampling choices examined in the current study can result in large differences among site-specific BAFs developed with different water sampling methodologies (Supporting Information SI4) and can potentially affect comparisons within and among sites. For example, at BEA_{OR} using the 90th percentile FMeHg yields a log BAF of 6.2, while using the 90th percentile FTHg yields a log BAF of 4.3. Additional investigation is needed to identify the factors driving variation in BAFs among sites in this study and across other environmental settings and spatial extents.[5,44] Standardizing both fish sampling and water sampling methods, and thus, minimizing methodological 'noise', will enhance the ability to discern the 'signal' of important environmental drivers.

Our results suggest several important considerations for optimal BAF Hg_{water} sampling. The sampling choices that result in the better models of spatial variation in Hg_{fish} in this study provide a starting point for more local-scale or regional-scale determination of optimal water sampling designs for BAF calculation. Our results suggest that fluvial Hg sampling should focus on MeHg, because THg did not account for significant variation in Hg_{fish}. Comparable results were obtained for FMeHg and UMeHg, however, indicating that the additional time and expense of filtration for BAF computations may not be required, at least in settings with generally low to moderate suspended sediment concentrations and where MeHg occurs mainly in the dissolved form, as in most sites in the current study[11,28,45] (Table 1, Supporting Information SI1). However, UMeHg-based BAFs may differ substantially from those based on FMeHg in streams with high suspended sediment loads and other settings where the particulate fraction dominates aqueous MeHg concentrations. The spatial pattern of Hg_{fish} in this study was most strongly related to the spatial pattern of the relatively high (80th percentile and higher) MeHg concentrations occurring during the antecedent year, and these site-specific concentrations were most likely to occur during particular months within the growing season. The improvement in performance of elevated-MeHg-concentration metrics for the year, compared with mean and median concentrations, indicated that a sampling approach that targets the higher concentrations may be as effective as sampling across the entire year and then statistically determining the higher percentiles. Indeed, the best models in this study, overall, were generated with mean and median FMeHg calculated over a limited time period of targeted months (i.e., when higher concentrations tend to occur). Knowledge of both site-specific temporal variation in MeHg and the generality of these patterns across particular environmental settings could, thus, be used to establish the timing of higher MeHg concentration periods. Some sites also had a predictable relation between daily streamflow across the growing season and the probability of collecting water samples with higher FMeHg concentrations. This indicates that consideration of the flow regime when determining when to conduct water sampling may help to target the higher concentrations at some sites. However, the relation between flow and the probability of achieving the targeted concentration range varied among sites, even within the same ecoregion. Thus, knowledge of the temporal variation in MeHg concentrations across the year for particular sites or environmental settings and (where continuous discharge data are available) reliable models of the relation between MeHg concentrations under different flow and seasonal conditions (e.g., a rating-curve approach) will aid optimization of fluvial MeHg sampling and BAF calculations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional supporting data tables and figures are presented. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

Disclosure: This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's and U.S. Geological Survey's peer and administrative review policies and approved for publication. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government. The views expressed in this paper are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

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