Rapid Changes in Small Fish Mercury Concentrations in Estuarine Wetlands: Implications for Wildlife Risk and Monitoring Programs

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · NOVEMBER 2009

Impact Factor: 5.33 · DOI: 10.1021/es901400c · Source: PubMed

2 AUTHORS:

Collin Eagles-Smith
United States Geological Survey
74 PUBLICATIONS **862** CITATIONS
SEE PROFILE

Joshua Ackerman
United States Geological Survey
73 PUBLICATIONS **1,107** CITATIONS
SEE PROFILE

Environ. Sci. Technol. **2009,** *43,* 8658–8664

Rapid Changes in Small Fish Mercury Concentrations in Estuarine Wetlands: Implications for Wildlife Risk and Monitoring Programs

COLLIN A. EAGLES-SMITH* AND JOSHUA T. ACKERMAN

U.S. Geological Survey, Western Ecological Research Center, Davis Field Station, One Shields Avenue, University of California, Davis, California 95616

Received May 11, 2009. Revised manuscript received September 21, 2009. Accepted October 2, 2009.

Small fish are commonly used to assess mercury (Hg) risk to wildlife and monitor Hg in wetlands. However, limited research has evaluated short-term Hg variability in small fish, which can have important implications for monitoring programs and risk assessment. We conducted a time-series study of Hg concentrations in two small fish species representing benthic (longjaw mudsuckers [*Gillichthys mirabilis*]) and pelagic (threespine sticklebacks [*Gasterosteus aculeatus*]) food-webs within three wetland habitats in San Francisco Bay Estuary. We simultaneously monitored prey deliveries, nest initiation, and chick hatching dates of breeding Forster's terns (*Sterna forsteri*), the most abundant nesting piscivore in the region. Mudsuckers and sticklebacks were the predominant prey fish, comprising 36% and 25% of tern diet, and Hg concentrations averaged (geometric mean ± SE, μg/g dw) 0.44 ± 0.01 and 0.68 ± 0.03, respectively. Fish Hg concentrations varied substantially over time following a quadratic form in both species, increasing 40% between March and May then decreasing 40% between May and July. Importantly, Forster's terns initiated 68% of nests and 31% of chicks hatched during the period of peak Hg concentrations in prey fish. These results illustrate the importance of short-term temporal variation in small fish Hg concentrations for both Hg monitoring programs and assessing wildlife risk.

Introduction

Mercury (Hg) is a globally distributed toxic element that often is found at elevated concentrations in the aquatic environment, and is most problematic when converted to its bioaccumulative and highly toxic methylmercury (MeHg) form (*1*). Microbial MeHg production can be particularly elevated in wetlands because of the unique biogeochemical conditions that stimulate methylation of inorganic Hg by sulfate-reducing bacteria (*2, 3*). The benefits that wetlands provide for fish, wildlife, and aquatic ecosystem health have motivated large-scale efforts to restore wetland habitats (*4*), which may increase MeHg production and contamination to surrounding water bodies (*3*). Thus, tracking temporal changes in Hg bioaccumulation will be important for quantifying the response to altered Hg loading or MeHg production.

* Corresponding author e-mail: ceagles-smith@usgs.gov; tel: 1 + 530-754-8130; fax: 1 +530-752-9680.

Wetland monitoring programs are important for tracking changes in MeHg availability, and many programs utilize small fish as biosentinels to monitor short-term changes in MeHg exposure. Small fish can be valuable bioindicators for monitoring MeHg uptake in local food webs because their low trophic position links them to MeHg production and they are central to the trophic transfer of MeHg through food webs (*5*). Small fish often are prey for larger fish and wildlife, so they also can serve as a principal conduit of MeHg exposure to higher trophic levels (*6*). Because Hg concentrations in small fish can differ among seasons (*5*), it is recognized that interannual monitoring programs should sample within the same season each year (*5, 7*). However, there has been relatively little study of the short-term, within-season variability in small fish Hg concentrations, and any short-term changes in Hg concentrations therefore may be overlooked in monitoring programs.

The interpretation of small fish Hg concentrations can be complicated by the influence of several factors in addition to MeHg production. For example, increases in primary productivity (*8*) or fish growth rates (*9, 10*) can reduce Hg concentrations in fish through biodilution at the base of the food web or growth dilution within fish, respectively. Thus, Hg concentrations in small fish may differ even among similarly sized fish sampled at different times. Cohort effects also can be important, especially if fish spawn over a several month time frame where Hg exposure of different cohorts can vary with ambient MeHg production. Finally, Hg concentrations in small fish can be related to diet and foraging habitat (*11*). The composition and community structure of the invertebrate prey-base often changes substantially over short time frames, particularly for zooplankton which often undergo dramatic seasonal shifts in community structure. Since Hg concentrations typically vary among invertebrate taxa (*12*), shifts in prey-base community structure likely would result in additional variation in fish Hg concentrations over time (*13*).

Short-term variation in small fish Hg concentrations can have significant implications for both monitoring programs and wildlife risk assessment. Piscivorous waterbirds are at particularly high risk to Hg impairment relative to many other wildlife taxa because they forage at a high trophic level and in wetland habitats where MeHg production may be elevated (*14*). Dietary MeHg is rapidly incorporated into body tissues of waterbirds and deposited into eggs (*15*). Consequently, any short-term changes in prey fish Hg concentrations near the time of waterbird reproduction could be critical to evaluating wildlife risk. Waterbird reproduction is highly sensitive to the effects of MeHg and reproduction can be impaired at environmentally relevant exposures (*16, 17*). Therefore, elevated fish Hg concentrations just before or during breeding may cause more harm to wildlife than increased MeHg in prey fish during other times of year. The spring and summer breeding season common of most waterbirds also coincides with ambient environmental conditions that typically enhance MeHg production. Temporal variation in prey fish Hg concentrations among the egg formation, incubation, and chick rearing stages may influence the relative risk to each lifestage. Thus, if short-term changes in prey fish Hg concentrations are common, monitoring programs should focus sampling when wildlife are at greatest risk.

In this study, we conducted a time series analysis of total Hg (THg) concentrations in two small fish species (longjaw mudsuckers [*Gillichthys mirabilis*] and threespine sticklebacks [*Gasterosteus aculeatus*]) that are common in San

10.1021/es901400c
Published on Web 10/13/2009

Francisco Bay (SFB) wetlands and important in the diets of piscivorous waterbirds. We sampled fish from three different wetland habitats every 2−3 weeks in the spring and summer, and evaluated linear and nonlinear trends in THg concentrations over time. Simultaneously, we documented the chronology of nest initiation and chick hatching for Forster's terns (*Sterna forsteri*, hereafter terns), one of the most numerous breeding piscivorous waterbirds in SFB. We then assessed the temporal overlap between short-term changes in fish THg concentrations and critical wildlife exposure time periods during the egg laying, incubation, and chick rearing stages.

Experimental Section

Study Location and Site Selection. We sampled mudsuckers and sticklebacks from three wetlands that represent some of the most common wetland habitats in SFB. These included a muted-tidal saltmarsh (New Chicago Marsh [NCM]; 37.436°N, 121.967°W); a perennially inundated, breached former salt evaporation pond (Pond A16 [A16], 37.444°N, 121.972°W); and a seasonally flooded, former salt evaporation pond (Pond A8 [A8], 37.425°N, 121.991°W). Each wetland supported colonies of terns, which are at high risk to MeHg impairment in the region (*14*). To link temporal trends in fish THg concentrations and potential wildlife exposure, we selected fixed sampling stations for fish within each wetland that were based upon tern population home ranges determined for radio-marked individuals using each pond during the previous year (2005). Telemetry methodology is described in Ackerman et al. (*18*). We calculated 95% fixed kernel utilization distributions for each of the three ponds separately with ArcView Animal Movement Extension (*19*) using all prebreeding and breeding tern locations from each specific wetland. We excluded locations with error polygons >2.0 ha as well as any locations within 100 m of nesting colonies to reduce bias associated with time spent on colony incubating nests or roosting. We then overlaid 100 × 100 m grid cells onto the tern population's home range within each wetland and randomly selected 3 nonadjacent grid cells within the wetland to place fish sampling stations.

Sample Collection. At each station, we deployed 3 anchored minnow traps for up to 4 days, at approximately 3-week intervals for a period of 4 months from March 22 to July 28, 2006. Traps were baited with canned catfood that was carefully punctured to make a tiny hole that prevented fishes from consuming the food. We stored fish in polyethylene bags on dry ice until return to the laboratory where they were subsequently stored at −20 °C until processing.

Colony-Returned Fish, Nest Initiation, and Chick Hatching. To further link fish sampling with tern diets, we evaluated colony prey returns during the breeding season. Fish often were found at colony locations and were the result of prey deliveries to mates or young. Previous studies have shown that returned fish provided an accurate index of prey consumption by least terns (*Sterna antillarum browni*) in SFB (*20, 21*). We entered tern colonies throughout the region weekly through the breeding season (May−August), and collected all the fish found on the ground within colonies as an estimate of tern diet. Returned fish often were desiccated when collected, making comparisons difficult between sizes of returned fish and live-sampled fish. Therefore, we determined the fresh length of returned fish using linear regression as described in the Supporting Information (SI). During weekly colony visits, we located and marked all tern nests with aluminum tags. We estimated the incubation stage of nests weekly via egg flotation, then determined nest initiation and hatching dates.

Sample Processing and Chemical Determination. We determined THg concentrations in all fish samples on a whole-body basis. Research on several prey fish species in San Francisco Bay has shown that approximately 94% of THg is in the MeHg form (Ben Greenfield, San Francisco Estuary Institute, unpublished data). Prior to THg analysis, each fish was dried at 50 °C for approximately 48 h and homogenized to a fine powder with a Wiley Mill and porcelain mortar and pestle. We analyzed all samples for THg at the U.S. Geological Survey, Davis Field Station Mercury Lab following ref *14*. We provide quality assurance results in SI.

Statistical Analyses. We natural-log transformed THg concentrations to conform to assumptions of heteroscedasticity and normality of residuals (*22*). We evaluated the effects of sampling date and fish length on THg concentrations in each species separately using a mixed-effects repeated measures analysis of covariance model (ANCOVA; PROC MIXED; SAS v9.2; (*23*)). To assess nonlinear changes in THg concentrations we included calendar date as both a linear and quadratic variable (date^2). Fixed factors in the models included date, date^2, standard length (mm), and wetland; whereas station within each wetland was designated as a random variable. We also included wetland × date and wetland × date^2 interactions to determine if THg concentrations varied over time differently in each wetland habitat. Since the interactions were significant for both species (see Results), we then evaluated temporal changes in THg concentrations separately for each wetland. To assess the relative fit of the linear time model in comparison to the nonlinear time (quadratic) model, we compared the two models using the likelihood ratio test (*22*).

We implemented each model using three different scenarios. In the first iteration, we evaluated likely waterbird exposure by including all sampled fish to assess temporal effects across the entire available size range of fish. However, larger fish that were sampled at the start of the study (in March) likely were fish that overwintered in SFB and may have reflected Hg exposure from the previous season. Therefore, in the second iteration we excluded any fish that were large enough to be age-1 (mudsuckers >70 mm; stickleback >40 mm; (*24*)). Lastly, monitoring programs often control for potential size effects on Hg concentrations in their sampling by excluding any fish that are outside a narrow size range. We therefore conducted a third model iteration whereby we excluded any fish that were outside a narrow size range of 50−70 mm for mudsuckers and 30−40 mm for sticklebacks.

We present results as back-transformed least-squares means with standard errors estimated using the delta method (*25*). We standardized all concentrations to the mean size of fish returned to colonies by terns for each fish species using the final model output (68 mm for mudsuckers and 40 mm for sticklebacks, see Results). We present all tissue THg concentrations on a dry weight (dw) basis since variability in moisture content can add variance to the data. However, to facilitate comparison to other studies we provide % moisture estimates for converting from dw to wet weight (mudsuckers: 76.24 ± 0.12%; sticklebacks: 67.89 ± 0.28%).

Results

Temporal Changes in Fish Hg Concentrations. We sampled 392 mudsuckers and 232 sticklebacks from the three wetlands habitats between March 22 and July 28, 2006. Mudsucker THg concentrations (geometric mean ± SE μg/g dw) were 0.52 ± 0.01 in A16 and 0.40 ± 0.01 in NCM. Only sticklebacks were captured in A8 and, due to rapid drying and elevated salinity (>80 ppt) in the summer, we only sampled between March and May when fish were present. Stickleback THg concentrations were 0.40 ± 0.02 in A16, 0.51 ± 0.02 in NCM, and 1.57 ± 0.04 in A8. Using the likelihood ratio test to compare the fit of our model containing a quadratic date coefficient against a similar model with a linear date coefficient, we found that the quadratic model better

TABLE 1. Analysis of Covariance for Species and Wetland-Specific Models Evaluating the Effect of Date and Fish Size on Whole-Body Total Mercury Concentrations in All Fish Sampled, Only Age-0 Fish, and Fish within a Limited Size Range (Mudsuckers: 50−70 mm; Sticklebacks 30−40 mm) in San Francisco Bay Wetlands

		all fish			age-0 fish			limited size range		
species and wetland	effect	df	*F*-value	*P*-value	df	*F*-value	*P*-value	df	*F*-value	*P*-value
					mudsucker					
A16	standard length	*1,126*	*4.28*	*0.04*	1,61	0.59	0.45	1,53	2.28	0.14
	date	*1,91.1*	*5.27*	*0.02*	*1,61*	*10.65*	*0.002*	*1,53*	*11.03*	*0.002*
	date^2	*1,124*	*36.29*	*<0.0001*	*1,61*	*33.81*	*<0.0001*	*1,53*	*24.4*	*<0.0001*
NCM	standard length	*1,266*	*34.85*	*<0.0001*	1,64	0.96	0.33	1,46.6	0.97	0.33
	date	*1,265*	*95.54*	*<0.0001*	1,63.7	1.02	0.32	1,46	0.95	0.33
	date^2	*1,266*	*300.31*	*<0.0001*	*1,65.9*	*8.45*	*0.005*	*1,48.9*	*6.38*	*0.01*
					stickleback					
A16	standard length	1,92	3.09	0.08	1,44.3	3.07	0.09	1,37.9	3.86	0.06
	date	*1,91.7*	*10.56*	*0.002*	*1,45.6*	*4.58*	*0.04*	*1,39.1*	*4.02*	*0.05*
	date^2	*1,92*	*35.48*	*<0.0001*	*1,46*	*13.22*	*0.001*	*1,39.8*	*11.02*	*0.002*
NCM	standard length	1,62	0.56	0.46	1,28	2.03	0.07	1,26	0.43	0.52
	date	1,62	1.33	0.25	1,28	2.72	0.11	1,26	2.94	0.1
	date^2	*1,62*	*6.17*	*0.02*	*1,28*	*5.39*	*0.03*	*1,26*	*5.2*	*0.03*
A8	standard length	1,78	0.46	0.50	*1,31*	*11.17*	*0.002*	*1,31*	*11.17*	*0.002*
	date	*1,78*	*12.57*	*0.001*	1,31	0.53	0.47	1,31	0.53	0.47
	date^2	*1,78*	*10.43*	*0.002*	1,31	1.22	0.28	1,31	1.22	0.28

explained the data for both mudsuckers ($n = 392$, $\chi^2 = 206$, $p < 0.0001$) and sticklebacks ($n = 232$, $\chi^2 = 56.8$, $p < 0.0001$). We accordingly evaluated the remaining temporal trends using a quadratic time coefficient. There were significant wetland × date and wetland × date^2 interactions for both mudsuckers (wetland × date: $F_{1,375} = 23.67$, $p < 0.0001$; wetland × date^2: $F_{1,390} = 41.00$, $p < 0.0001$), and sticklebacks (wetland × date: $F_{2,77} = 3.55$, $p = 0.03$; wetland × date^2: $F_{2,76.8} = 3.18$, $p = 0.04$) when simultaneously evaluating the influence of fish size and sampling date on THg concentrations in our initial global model. We subsequently conducted separate analyses for each species in each wetland.

Over the 18-week sampling period there was a consistent temporal trend in THg concentrations for both fish species. In all three wetlands, THg was significantly related to date, following a quadratic function (Table 1) where THg concentrations increased substantially from March to a maximum concentration in May, then declined toward the end of the sampling period in July (Figure 1). In A16, size-normalized THg concentrations increased between mid-March and late May by 27% in mudsuckers and 79% in sticklebacks. Mercury concentrations then declined by 42% in mudsuckers and 47% in sticklebacks by late July. Similar, though less pronounced temporal patterns occurred in NCM.

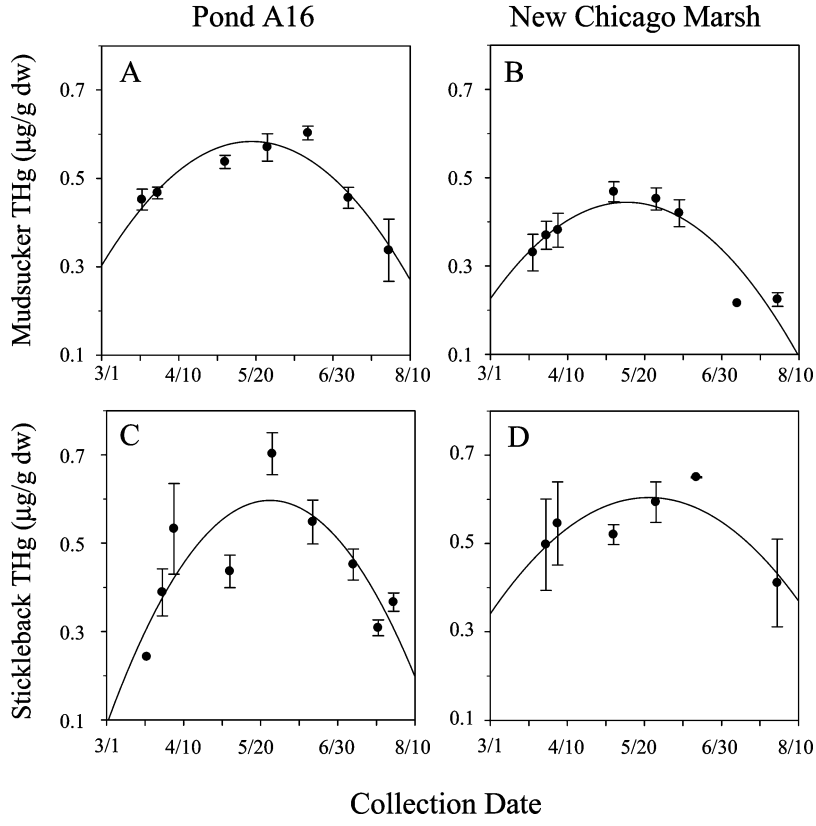

FIGURE 1. Short-term variation in whole-body total mercury (THg) concentrations in longjaw mudsuckers (A, B) and threespine sticklebacks (C, D) from two wetlands in San Francisco Bay, CA. THg concentrations are length-corrected for the average size of fish returned to colonies by Forster's terns (mudsuckers: 68 mm; sticklebacks: 40 mm).

Mudsucker THg concentrations in NCM increased 42% between March and mid-May, then declined 53% by late July. Stickleback THg concentrations in NCM were more variable, increasing 33% between March and May and declining 37% from May to late July. Total Hg concentrations were substantially elevated in A8 and increased by 18% between March and April, followed by a 19% decrease by mid-May which was the final sampling interval when stickleback were present in that wetland.

Based on the quadratic model parameters, we categorized the peak THg concentration period as occurring between May 1 and June 10 (Figure 1). Total Hg concentrations during the peak time period were significantly higher than during the nonpeak period in mudsuckers from both A16 (ANCOVA: $F_{1,121.8} = 8.62$, $p = 0.004$) and NCM (ANCOVA: $F_{1,262.9} = 252.42$, $p < 0.0001$), and in stickleback from A16 (ANCOVA: $F_{1,88.3} = 23.56$, $p < 0.001$; SI Figure S1). There was a trend toward higher THg concentrations during the peak time period in stickleback from NCM, but the difference was not statistically significant (ANCOVA: $F_{1,77} = 3.38$, $p = 0.07$).

Live-caught mudsuckers and sticklebacks from our sampling stations ranged in size from 25 to 117 mm (mean ± SE = 78.6 ± 0.9 mm) and 26 to 54 mm (mean ± SE = 40.9 ± 0.4 mm), respectively. A wide range of sizes was captured during each sampling event, but average length declined over time (mudsuckers: $r^2 = 0.20$, $p < 0.0001$; sticklebacks: $r^2 = 0.16$, $p < 0.0001$) in mudsuckers and stickleback from 88.4 ± 1.3 to 62.8 ± 1.8 and 44.3 ± 0.6 to 36.4 ± 0.8, respectively. Variability in THg concentrations associated with fish age and size are important considerations and we conducted subsequent iterations of the model after removing fish that were outside specified size ranges. In the second model iteration where we excluded all age-1 fish from the data set to prevent the confounding effect of annual Hg carryover, THg concentrations still followed a strong quadratic pattern with date (Table 1) for mudsuckers and sticklebacks in all wetlands except the ephemeral salt pond (A8) which only supported fish for a limited time period. There were no significant relationships between fish THg concentrations and fish size in any of the wetlands for either species after excluding age-1 fish (Table 1). In the final model iteration where we used only a very narrow size range of fish, we again found that the quadratic date factor was significantly related to fish THg concentrations for mudsuckers and sticklebacks in all wetlands except A8 (Table 1). The size limits we applied effectively eliminated the influences of fish length on THg concentrations that were present when our full data set was used, but our overall results of THg concentrations related quadratically to date remained unchanged.

Colony Returned Fish. We collected and identified 799 fish (14 species) that were returned to colony by terns. Mudsuckers and sticklebacks together accounted for 61% of the colony returns (36% and 25%, respectively). The remainder of colony returns consisted of 12 other species, of which only a few comprised >5% of the total sample (12% topsmelt, *Atherinops affinis*; 11% Mississippi silversides, *Menidia audens;* and 6% yellowfin goby, *Acanthogobius flavimanus*). Thus, the fish species that we focused our time series on were appropriate for assessing exposure and risk to terns.

The allometric relationship was strong between dry weight and standard length for fresh fish (SI). Forster's terns delivered mudsuckers ranging in size from 35 to 124 mm (mean ± SE = 68.3 ± 1.1 mm) and sticklebacks from 21 to 55 mm (mean ± SE = 40.2 ± 0.3 mm).

Tern Nest Initiation and Chick Hatching Dates. During weekly colony visits, we found 715 tern nests initiated between April 22 and July 25, 2006. Overall, 68% of tern nests were initiated between May 1 and June 10 when THg concentrations peaked in fish (Figure 2). Since Hg in eggs is primarily in the albumen which is synthesized from dietary protein approximately 7 days prior to egg laying (*26*−*28*), we adjusted nest initiation dates 7 days earlier for comparison to fish THg concentrations. Using this time frame, 78% of eggs were developed during the time period when parents were exposed to peak THg concentrations in prey fish. We also determined chick hatching dates for 444 successful nests (range: May 23 to August 16) and found that 31% of chicks hatched during the time period of peak fish THg concentrations (Figure 2).

Discussion

We documented high variability in small fish THg concentrations during a short time period when waterbirds breed. Across three distinct wetland habitats, fish THg concentrations increased rapidly by an average of 40% during a 2-month period to a maximum in May, and then quickly declined by 39% during the subsequent 2-month period. We found this relationship in both mudsuckers and sticklebacks even though they represented different components of the food web. Length was weakly correlated with THg concentrations, and we found similar temporal trends in fish THg concentrations even when we excluded age-1 fish from our analysis and when we constrained our sample to fish within a very narrow size range. The similarity in temporal patterns of THg concentrations in both fish species and among wetlands suggests that this was not likely a site-specific phenomenon. The reasons for this short-term fluctuation in fish THg concentrations are unclear, but may be due to a combination of temporal changes in MeHg production, changes in wetland primary production, and fish demography and growth.

MeHg production generally increases as temperatures begin to rise, surface sediments become anoxic, and there is adequate labile organic carbon (*3, 29*). These conditions are common during spring and summer in the shallow, productive, saline wetlands of SFB (*30*). MeHg can bioaccumulate in small fishes within a span of a few weeks (*31*). Thus, the increase in fish THg concentrations that we detected between March and May could have resulted from enhanced MeHg production and availability in the food web. However, fish THg concentrations declined across wetlands after 20 May, even though temperatures continued to increase. MeHg production may have declined during this period due to sulfide production (*32*), or the extremely high rate of primary production during summer (*30*) may have reduced Hg concentrations at the base of the food web via biodilution. However, even a complete cessation of MeHg production is unlikely to have resulted in reduced fish THg concentrations during this short time period because MeHg elimination rates are slow in fish (*33, 34*) and, depending on the wetland sampled, we found a 20−50% decrease in fish THg concentrations within approximately 2 months of peak THg concentrations.

For THg concentrations in fish to decline as rapidly as we detected, factors in addition to changes in MeHg production or availability were likely important. Changes in the demography and growth rates of fish that we sampled may have altered exposure profiles and bioaccumulation rates. Mudsuckers spawn between December and June (*24*) with the heaviest spawning occurring in March to May, and sticklebacks spawn between March and July (*24*). Thus, when our study was initiated in early spring, we were likely sampling a greater proportion of older fish that overwintered locally, compared to those fish that were collected later in the study, during and after spawning. Indeed, the mean length in mudsuckers and sticklebacks declined over the course of our study, suggesting that we sampled a larger proportion of young-of-year fish later in the season. However, the negative linear trends of fish length with date were weak, indicating a wide range of ages was sampled throughout the

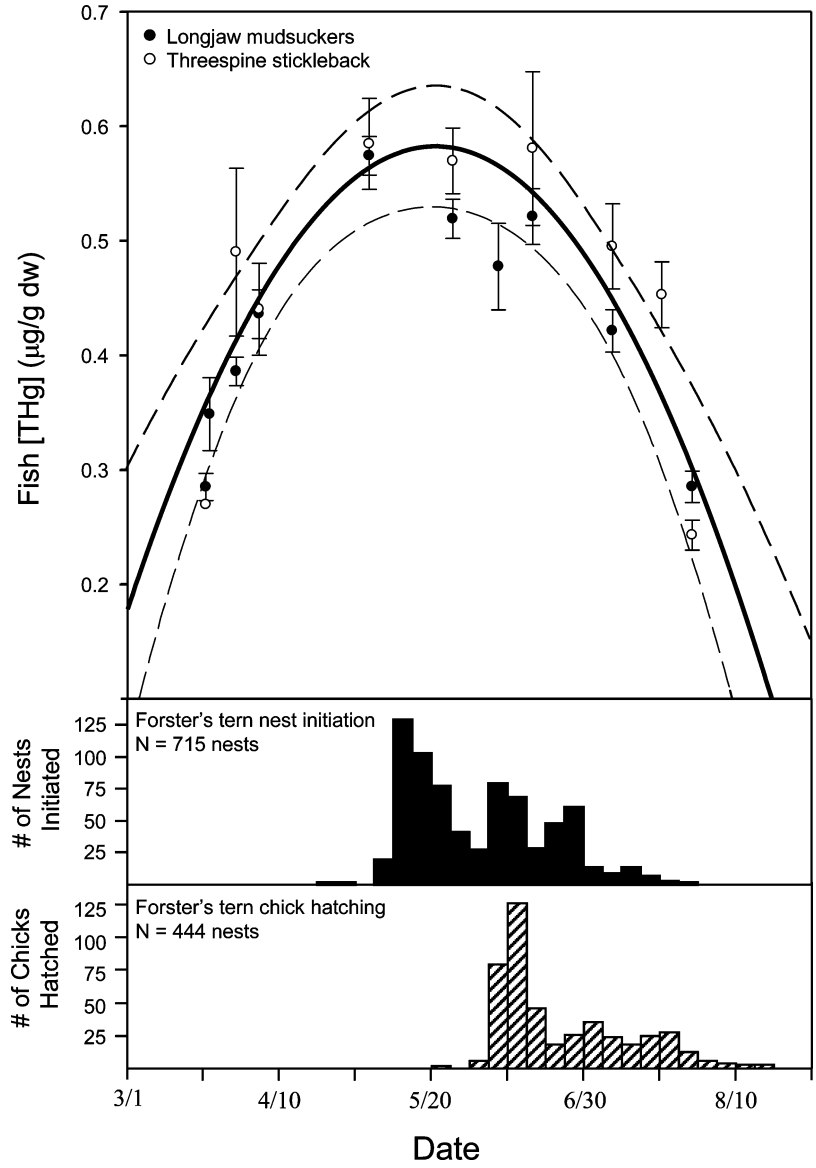

FIGURE 2. Relationship between the temporal trend in whole-body prey fish total mercury (THg) concentrations and the timing of Forster's tern nest initiation and chick hatching. Fish THg concentrations are statistically corrected for wetland effects, and are standardized to the average size of fish returned to colonies by Forster's terns (mudsuckers: 68 mm; sticklebacks: 40 mm).

study. Our results were similar when we excluded age-1 fish or restricted our sample to a very narrow size range of fish. These results indicate that the seasonal trend in fish THg concentrations we observed was not driven by size-related factors, nor confounded by Hg carryover from fish that were exposed during the previous season.

Growth rates in fish generally decline as size increases (*35, 36*), and are directly related to water temperature, assuming food availability and fish activity are similar (*37*). Thus, the smaller fish that we sampled later in the season may have had higher growth rates due to their age and higher water temperatures. Rapid fish growth can result in reduced Hg concentrations through growth dilution (*9, 10*). In fact, growth dilution accounted for 30−40% of the reduction in yellow perch Hg concentrations following a whole-lake nutrient enrichment experiment (*9*). Thus, we speculate that the reduction in fish Hg concentrations that we documented from May to July may have been driven by a combination of reduced MeHg production and elevated growth rates of younger fish. Other factors such as changes to the prey community structure or fish diet shifts may also have contributed to the observed short-term changes in fish THg concentrations (*11, 13*), though we have no supporting data to elucidate these factors. Clearly, the factors influencing short-term temporal trends in small fish THg concentrations are complicated, and further study should focus on the possible mechanisms driving these patterns.

Implications for Wildlife Risk. Regardless of the mechanisms driving the trends we observed in fish THg concentrations, these results have important implications for interpreting risk to wildlife, as well as for water quality monitoring programs. Reproduction is thought to be the most sensitive end point of Hg toxicity in waterbirds (*38*). Among the most critical exposure periods for waterbirds is when maternal Hg is deposited into eggs during egg formation (*16*). Methylmercury in eggs is known to impair hatchability (*16, 17*) and may also influence early chick survival (*39*). Most of the Hg in avian eggs is in the albumen (*17, 28*) and albumen synthesis in seabirds occurs within approximately 4−7 days prior to egg laying (*26*). Additionally, albumen proteins are typically derived exogenously from dietary sources acquired only a few days before egg laying (*26, 27*). Thus, there is a very narrow, critical exposure period of approximately 7 days over which dietary Hg is deposited into eggs. In our study, tern nest initiation began in late April when THg concentrations in fish were peaking. In fact, 62% of all nests were

initiated during the peak in prey fish THg concentrations. If we adjust nest initiation dates 7 days earlier to when birds were forming and depositing Hg into eggs, then 74% of clutches were exposed to peak THg concentrations in prey fish. Thus, most nesting terns were exposed to peak THg concentrations in prey during the critical period of egg formation. Previous studies have documented high Hg concentrations in tern eggs in SFB (*40*) that may be impairing egg hatchability (*41*). Hg concentrations in adult tern liver and blood increased by 3−5 times from prebreeding to breeding in just 6 weeks (*14*), suggesting that short-term variation in prey Hg levels likely propagated rapidly into waterbirds upon their arrival into SFB estuary.

Another critical exposure period for terns is the fledgling stage after chicks hatch and before they begin to fly (about 28 days; (*42*)). As chicks approach fledging, their body growth and feather growth slow, thus Hg depuration (into feathers) and dilution (via body growth) pathways become less available, and Hg concentrations begin to increase (*43*). Given the decline in fish THg levels toward the end of the nesting season, the risk to fledging chicks may be relatively lower than to eggs, because Hg exposure declines in their common prey fish. Correspondingly, Ackerman et al. (*42*) found no effect of Hg levels on survival of postfledgling terns during July and August. Instead, Hg is most likely to impair tern reproduction via maternally derived Hg, such as egg hatchability or early chick growth and survival, when Hg is still high in prey fish.

Implications for Monitoring Programs. In the United States, over 5,500,000 ha of lakes and 1,400,000 km of rivers had fish-consumption advisories issued in 2006 due to elevated fish Hg concentrations. These included 23 statewide freshwater advisories and 12 statewide coastal advisories (*44*). Many of these advisories were based on Hg concentrations in large sport fish that are consumed by humans, but small fish monitoring also has become more widespread because large fish Hg levels often do not reflect local or annual changes in Hg bioaccumulation (*5*). In California, Total Maximum Daily Load (TMDL) Hg monitoring targets have been established for small fish to protect wildlife from deleterious effects (*45*). In addition, the development of a national monitoring network will rely heavily on Hg measurements in small fish as a component of evaluating yearly changes to MeHg production, export, and risk to wildlife (*7*). Although incorporating small fish into monitoring programs may be beneficial, our results indicate that strategic design and implementation of these monitoring programs is critical to ensure relevance to wildlife and comparability across sampling sites and years. Sampling designs should conform to a very narrow time window (a few weeks), and should be repeated during the same time window each year. If they are not, then Hg concentrations within a site can vary by up to 79% over just 30 days as we observed in our study. Thus, if too much time passes between sampling events, comparisons of Hg concentrations in small fishes among sites and years may not be robust.

Additionally, if assessing wildlife risk is a goal of monitoring programs, then fish sampling should occur during or just before critical life-history phases for wildlife, such as egg-laying and chick rearing in waterbirds. In our study, risk to wildlife would have been greatly underestimated if monitoring was restricted to sampling during the early spring or late summer. Instead, the peak exposure of Hg in fish overlapped with peak egg laying, exacerbating Hg risk to waterbirds in SFB. Finally, monitoring programs should conduct high-resolution time series studies initially, to understand how Hg varies seasonally, and then incorporate additional time-series studies at regular intervals in subsequent years to calibrate comparisons among years.

Acknowledgments

This research was funded by the CALFED Ecosystem Restoration Program and USGS Western Ecological Research Center. We thank J. Yee, M. Ricca, K. Aceituno, R. Keister, T. Adelsbach, S. Stoner-Duncan, J. Henderson, C. Johnson, T. Maurer, and C. Marn for assistance. U.S. Fish and Wildlife Service, California Department of Fish and Game, and San Francisco Bay Bird Observatory graciously provided logistical support. This manuscript was improved with comments from by A.K. Miles, M. Marvin-DiPasquale, J. Wiener, A.R. Stewart, and three anonymous reviewers. The use of trade, product, or firm names in the publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Supporting Information Available

Details of methods for estimating fresh length of colony returned fish based on dry weight and the allometric regressions for each species, details of quality assurance data, and a figure showing differences in THg concentrations between peak and nonpeak time periods. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Wiener, J. G.; Krabbenhoft, D. P.; Heinz, G. H.; Scheuhammer, A. M. Ecotoxicology of mercury. In *Handbook of Ecotoxicology*; Hoffman, D. J., Rattner, B. A., Burton, G. A., Cairns, J., Eds.; Lewis: Boca Raton, FL, 2003; pp 409−463.

(2) Marvin-DiPasquale, M.; Agee, J. L.; Bouse, R.; Jaffe, B. Microbial cycling of mercury in contaminated pelagic and wetland sediments of San Pablo Bay, California. *Environ. Geol.* **2003**, *43*, 260–267.

(3) Hall, B. D.; Aiken, G. R.; Krabbenhoft, D. P.; Marvin-DiPasquale, M.; Swarzenski, C. M. Wetlands as principal zones of methylmercury production in southern Louisiana and the Gulf of Mexico region. *Environ. Pollut.* **2008**, *154*, 124–134.

(4) Mitsch, W. J. Applying science to conservation and restoration of the world's wetlands. *Water Sci. Policy* **2005**, *51*, 13–26.

(5) Wiener, J. G.; Bodaly, R. A.; Brown, S. S.; Lucotte, M.; Newman, M. C.; Porcella, D. B.; Reash, R. J.; Swain, E. B.; Monitoring and evaluating trends in methylmercury accumulation in aquatic biota. *In Ecosystem Responses to Mercury Contamination: Indicators of Change*; Harris, R., Krabbenhoft, D. P., Mason, R., Murray, M. W., Reash, R., Saltman, T., Eds.; CRC Press: Boca Raton, FL, 2007; pp 87−122.

(6) Scheuhammer, A. M.; Atchison, C. M.; Wong, A. H. K.; Evers, D. C. Mercury exposure in breeding common loons (*Gavia immer*) in Central Ontario, Canada. *Environ. Toxicol. Chem.* **1998**, *17*, 191–196.

(7) Mason, R. P.; Abbot, M. L.; Bodaly, R. A.; Bullock, O. R., Jr.; Driscoll, C. T.; Evers, D.; Lindberg, S. E.; Murray, M.; Swain, E. B. Monitoring the response to changing mercury deposition. *Environ. Sci. Technol.* **1995**, *39*, 14A–22A.

(8) Pickhardt, P. C.; Folt, C. L.; Chen, C. Y.; Klaue, B.; Blum, J. D. Algal blooms reduce the uptake of toxic methylmercury in freshwater food webs. *Proc. Natl. Acad. Sci.* **2002**, *99*, 4419–4423.

(9) Essington, T. E.; Houser, J. N. The effect of whole lake nutrient enrichment on mercury concentration in age-1 yellow perch. *Trans. Am. Fish. Soc.* **2003**, *132*, 57–68.

(10) Swanson, H. K.; Johnston, T. A.; Schindler, D. W.; Bodaly, R. A.; Whittle, D. M. Mercury bioaccumulation in forage fish communities invaded by rainbow smelt (*Osmerus mordax*). *Environ. Sci. Technol.* **2006**, *40*, 1439–1446.

(11) Eagles-Smith, C. A.; Suchanek, T. H.; Colwell, A. E.; Anderson, N. L.; Moyle, P. B. Changes in fish diets and food web mercury bioaccumulation induced by an invasive planktivorous fish. *Ecol. Appl.* **2008**, *18*, A213–A226.

(12) Kainz, M.; Lucotte, M.; Parrish, C. C. Methylmercury in zooplankton-the role of size, habitat, and food quality. *Can. J. Fish. Aquat. Sci.* **2002**, *59*, 1606–1615.

(13) Stewart, A. R.; Saiki, M. K.; Kuwabara, J. S.; Alpers, C. N.; Marvin-DiPasquale, M.; Krabbenhoft, D. P. Influence of plankton mercury dynamics and trophic pathways on mercury concentration of top predator fish of a mining-impacted reservoir. *Can. J. Fish. Aquat. Sci.* **2008**, *65*, 2351–2366.

(14) Eagles-Smith, C. A.; Ackerman, J. T.; De La Cruz, S. W. D.; Takekawa, J. Y. Mercury bioaccumulation and risk to three waterbirds foraging guilds is influenced by foraging ecology and breeding stage. *Environ. Pollut.* **2009**, *157*, 1993–2002.
(15) Heinz, G. H.; Hoffman, D. J.; Klimstra, J. D.; Stebbins, K. R. Rapid increases in mercury concentrations in the eggs of mallards fed methylmercury. *Environ. Toxicol. Chem.* **2009**, *28*, 1979–1981.
(16) Evers, D. C.; Savoy, L. J.; DeSorbo, C. R.; Yates, D. E.; Hanson, W.; Taylor, K. M.; Siegel, L. S.; Cooley, J. H.; Bank, M. S.; Major, A.; Munney, K.; Mower, B. F.; Vogel, H. S.; Schoch, N.; Pokras, M.; Goodale, M. W.; Fair, J. Adverse effects from environmental mercury loads on breeding common loons. *Ecotoxicology* **2008**, *17*, 69–81.
(17) Heinz, G. H.; Hoffman, D. J.; Klimstra, J. D.; Stebbins, K. R.; Kondrad, S. L.; Erwin, C. A. Species differences in the sensitivity of avian embryos to methylmercury. *Arch. Environ. Contam. Toxicol.* **2009**, *56*, 129–138.
(18) Ackerman, J. T.; Eagles-Smith, C. A.; Takekawa, J. Y.; Bluso, J. D.; Adelsbach, T. L. Mercury concentrations in blood and feathers of pre-breeding Forster's terns in relation to space use of San Francisco Bay habitats. *Environ. Toxicol. Chem.* **2008**, *27*, 897–908.
(19) Hooge, P. N.; Eichenlaub, B. *Animal movement extension to Arcview: version 1.1*; Alaska Biological Science Center, U.S. Geological Survey: Anchorage, AK, 1997.
(20) Atwood, J. L.; Kelly, P. R. Fish dropped on breeding colonies as indicators of Least Tern food habits. *Wildl. Bull.* **1984**, *96*, 34–47.
(21) Elliott, M. L. Diet, Prey, and Foraging Habits of the California Least Tern (*Sterna antillarum browni).* MS Thesis. San Francisco State University, San Francisco, CA, 2005.
(22) Zar, J. H. *Biostatistical Analysis*; Prentice-Hall: Upper Saddle River, NJ, 1999.
(23) *SAS Institute. SAS_ version 9.1.2.*; Cary, NC, 2005.
(24) Moyle, P. B. *Inland fishes of California*; University of California Press: Berkeley, CA, 2002.
(25) Williams, B. K.; Nichols, J. D.; Conroy, M. J. *Analysis and Management of Animal Populations: Modeling, Estimation, and Decision Making*; Academic Press: San Diego, CA, 2002.
(26) Astheimer, L. B. Egg formation in Cassin's Auklet. *Auk* **1986**, *103*, 682–693.
(27) Hobson, K. A. Reconstructing avian diets using stable-carbon and nitrogen isotope analysis of egg components: patterns of isotopic fractionation and turnover. *Condor* **1995**, *97*, 752–762.
(28) Kennamer, R. A.; Stout, J. R.; Jackson, B. P.; Colwell, S. V.; Brisbin, I. L., Jr.; Burger, J. Mercury patterns in wood duck eggs from a contaminated reservoir in South Carolina, USA. *Environ. Toxicol. Chem.* **2005**, *24*, 1793–1800.
(29) Lambertsson, L.; Nilsson, M. Organic Material: The primary control on mercury methylation and ambient methyl mercury concentrations in estuarine sediments. *Environ. Sci. Technol.* **2006**, *40*, 1822–1829.
(30) Thebault, J.; Schraga, T. S.; Cloern, J. E.; Dunlavey, E. G. Primary production and carrying capacity of former salt ponds after reconnection to San Francisco Bay. *Wetlands* **2008**, *28*, 841–851.
(31) Harris, R. C.; Russ, J. W.; Amyot, M.; Babiarz, C. L.; Beaty, K. G.; Blanchfield, P. J.; Bodaly, R. A.; Branfireun, B. A.; Gilmour, C. C.; Graydon, J. A.; Heyes, A.; Hintelmann, H.; Hurley, J. P.; Kelly, C. A.; Krabbenhoft, D. P.; Lindberg, S. E.; Mason, R. P.; Paterson, M. J.; Podemski, C. L.; Robinson, A.; Sandilands, K. A.; Southworth, G. R.; St. Louis, V. L.; Tate, M. T. Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. *Proc. Natl. Acad. Sci.* **2007**, *104*, 16586–16591.
(32) Benoit, J. M.; Gilmour, C. C.; Mason, R. P.; Heyes, A. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment porewaters. *Environ. Sci. Technol.* **1999**, *33*, 951–957.
(33) Trudel, M.; Rasmussen, J. B. Bioenergetic and mercury dynamics in fish: a modeling perspective. *Can. J. Fish. Aquat. Sci.* **2006**, *63*, 1890–1902.
(34) Van Walleghem, J. L. A.; Blanchfield, P. J.; Hintelmann, H. Elimination of mercury by yellow perch in the wild. *Environ. Sci. Technol.* **2007**, *41*, 5895–5901.
(35) Snyder, R. J. Migration and life histories of the threespine stickleback: evidence for adaptive variation in growth rate between populations. *Env. Biol. Fishes* **1991**, *31*, 381–388.
(36) Wright, H. A.; Wooton, R. J.; Barber, I. Interpopulation variation in early growth of threespine sticklebacks (*Gasterosteus aculeatus*) under laboratory conditions. *Can. J. Fish. Aquat. Sci.* **2004**, *61*, 1832–1838.
(37) Allen, J. R. M.; Wooton, R. J. The effect of ration and temperature on the growth of the three-spined stickleback (*Gasterosteus aculeatus L.*). *J. Fish Biol.* **1982**, *20*, 409–422.
(38) Scheuhammer, A. M.; Meyer, M. W.; Sandheinrich, M. B.; Murray, M. W. Effects of environmental methylmercury on the health of wild birds, mammals, and fish. *Ambio* **2007**, *36*, 12–18.
(39) Ackerman, J. T.; Takekawa, J. Y.; Eagles-Smith, C. A.; Iverson, S. A. Mercury contamination and effects on survival of American avocets and black-necked stilt chicks in San Francisco Bay. *Ecotoxicology* **2008**, *17*, 103–116.
(40) Ackerman, J. T.; Eagles-Smith, C. A. Integrating toxicity risk in bird eggs and chicks: using chick down feathers to estimate mercury concentrations in eggs. *Environ. Sci. Technol.* **2009**, *43*, 2166–2172.
(41) Ackerman, J. T.; Eagles-Smith, C. A. *A Dual Life-Stage Approach to Monitoring the Effects of Mercury Concentrations on the Reproductive Success of Forster's Terns in San Francisco Bay*; Administrative Report; U. S. Geological Survey, Western Ecological Research Center: Davis, CA, 2008; 47 pp.
(42) Ackerman, J. T.; Eagles-Smith, C. A.; Takekawa, J. Y.; Iverson, S. A. Survival of postfledging Forster's terns in relation to mercury exposure in San Francisco Bay. *Ecotoxicology* **2008**, *17*, 789–801.
(43) Kenow, K. P.; Gutreuter, S.; Hines, R. K.; Meyer, M. W.; Fournier, F.; Karasov, W. H. Effects of methyl mercury exposure on the growth of juvenile common loons. *Ecotoxicology* **2003**, *12*, 171–182.
(44) U.S. EPA. *2005/2006 National Listing of Fish Advisories Fact Sheet*; EPA-823-F-07-003; Office of Water: Washington, DC, 2007; http://www.epa.gov/waterscience/fish/advisories/2006/tech.pdf.
(45) Wood, M. L.; Foe, C.; Cooke, J.; Louie, S. J.; Bosworth, D. H. Regional Water Quality Control Board - Central Valley Region, Sacramento-San Joaquin Delta Estuary TMDL for Methylmercury; Staff Report, February 2008; http://www.waterboards.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/delta_hg/staff_report_feb09/tmdl_full_rpt.pdf.

ES901400C