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Seasonal and annual trends in forage fish mercury concentrations, San Francisco Bay

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HIGHLIGHTS

► First comparison of fish Hg temporal patterns across multiple estuary habitats.
► Surprisingly inconsistent temporal variation among sites and forage fish species.
► Fish Hg showed strong seasonal variation.
► Annual variation was weaker than spatial variation.
► Cannot generalize fish Hg temporal variation across species or regions.

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ABSTRACT

San Francisco Bay is contaminated by mercury (Hg) due to historic and ongoing sources, and has elevated Hg concentrations throughout the aquatic food web. We monitored Hg in forage fish to indicate seasonal and interannual variations and trends. Interannual variation and long-term trends were determined by monitoring Hg bioaccumulation during September–November, for topsmelt (*Atherinops affinis*) and Mississippi silverside (*Menidia audens*) at six sites, over six years (2005 to 2010). Seasonal variation was characterized for arrow goby (*Clevelandia ios*) at one site, topsmelt at six sites, and Mississippi silverside at nine sites. Arrow goby exhibited a consistent seasonal pattern from 2008 to 2010, with lowest concentrations observed in late spring, and highest concentrations in late summer or early fall. In contrast, topsmelt concentrations tended to peak in late winter or early spring and silverside seasonal fluctuations varied among sites. The seasonal patterns may relate to seasonal shifts in net MeHg production in the contrasting habitats of the species. Topsmelt exhibited an increase in Alviso Slough from 2005 to 2010, possibly related to recent hypoxia in that site. Otherwise, directional trends for Hg in forage fish were not observed. For topsmelt and silverside, the variability explained by year was relatively low compared to sampling station, suggesting that interannual variation is not a strong influence on Hg concentrations. Although fish Hg has shown long-term declines in some ecosystems around the world, San Francisco Bay forage fish did not decline over the six-year monitoring period examined.

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1. Introduction

Mercury (Hg) is a globally distributed pollutant that poses serious management concerns because the methylated form (MeHg) bioaccumulates and is toxic to humans and wildlife (U.S. EPA, 1997). Hg pollution varies across multiple time scales, reflecting a range of processes (Wiener et al., 2007). Seasonal variation likely reflects patterns in net Hg methylation in the sediment or water column (Gorski et al., 1999; Heim et al., 2007; Herrin et al., 1998). Interannual fluctuations (i.e., temporary increases or decreases in specific years) can result from temporary perturbations due to management activities, weather patterns, or other environmental changes (Henery et al., 2010). Long-term trends can result from changes in Hg loading or in processes that affect methylation (Braune et al., 2005; Levinton and Pochron, 2008; Monson, 2009; Munthe et al., 2007).

Small fish consumed by piscivorous wildlife (i.e., forage fish) are useful as biosentinels to determine seasonal and interannual variations in MeHg resulting from natural variability or management activities (Wiener et al., 2007). Forage fish have been widely employed in fresh waters to identify changes in Hg exposure due to management perturbations such as reservoir impoundment or lake acidification (e.g., Kelly et al., 1997; Wiener et al., 1990). In addition, sediment and forage fish monitoring has indicated natural seasonal variation in Hg concentrations (e.g., Eagles-Smith and Ackerman, 2009; Fowlie et al., 2008; Gorski et al., 1999; Slotton et al., 1995; Zhang et al., 2012). In freshwater lakes and estuarine wetlands, strong summer increases have been observed, which corresponds to the period of highest risk to embryonic development for some piscivorous bird species (Eagles-Smith and Ackerman, 2009; Gorski et al., 1999). Studies have often been limited in duration to several months, limiting the evaluation of patterns across multiple seasons or years. Comparisons across multiple fish species or multiple sampling locations within large water bodies to determine consistency of seasonal or interannual patterns are also lacking.

San Francisco Bay (the Bay) has elevated mercury (Hg) concentrations in fish and wildlife (Ackerman et al., 2007; Davis et al., 2012; Greenfield et al., 2005; Greenfield and Jahn, 2010), with some evidence of sublethal effects to birds and harbor seals (Herring et al., 2010; Schwarzbach et al., 2006). Consequently, there are substantial efforts to control specific Hg sources through the U.S. federally mandated Total Maximum Daily Load (TMDL) program (Davis et al., 2012). An intensive restoration program is underway to restore wetlands surrounding the Bay, including the conversion of thousands of hectares of historic salt ponds and other isolated habitats to wetlands (Goals Project, 1999; Grenier and Davis, 2010). MeHg production can be relatively high in nearshore managed ponds and wetland habitats due to differences in hydrology and redox conditions (Davis et al., 2003; Grenier and Davis, 2010; Heim et al., 2007; Miles and Ricca, 2010). Consequently, Hg monitoring in Bay biota is underway to evaluate potential short and long-term changes in MeHg exposure and bioaccumulation due to habitat restoration.

The present study seeks to answer the question: how similar are temporal patterns in biosentinel Hg among separate fish species and locations within a single estuary. We report seasonal and interannual variations in Hg concentrations in San Francisco Bay forage fish. Seasonal variation was characterized over three separate monitoring periods, encompassing three species at sixteen separate locations (Fig. 1). Interannual variation and trends were determined by fall monitoring of two species at six sites over six years. We assessed whether temporal patterns were consistent across sites, sampling events (i.e., date), and species and the relative importance of temporal variation versus spatial variation for explaining Hg concentrations.

2. Methods

2.1. Study area, target species, site descriptions, and sampling dates

San Francisco Bay is surrounded by an urbanized region with a population of over seven million and drains approximately 40% of the state of California, USA. A legacy of Hg and gold mining, as well as widespread use of Hg in industrial applications have resulted in elevated Hg concentrations throughout the Bay and its watershed (Conaway et al., 2008; Davis et al., 2012). Hg concentration trends in Bay sediments and biota have been variable, with some surface sediment and sediment core locations indicating declines while other sediment locations and sport fish essentially unchanged over the past several decades (Conaway et al., 2004, 2007; Greenfield et al., 2005; Hornberger et al., 1999).

In this study, temporal Hg trends were evaluated in three San Francisco Bay forage fish species: Mississippi silverside (*Menidia audens*), topsmelt (*Atherinops affinis*), and arrow goby (*Clevelandia ios*). These species were selected based on consistent residence at the chosen sampling locations, usefulness as biosentinels, and having a majority (94%) of whole body Hg composed of MeHg (Greenfield and Jahn, 2010). All sampling was performed by beach seine adjacent to the shoreline.

Four separate sampling efforts were conducted within tidally influenced waters of the Bay or surrounding estuarine ponds. Each sampling effort focused on specific time scales and sampling locations (Table 1, Fig. 1), with the objective of describing temporal variation across a range of habitats (e.g., Bay shoreline, estuarine channel, and adjacent ponds), regions (Lower South Bay through Carquinez Strait), and time scales (seasonal versus annual).

The first effort evaluated seasonal patterns from October 2007 to December 2010, at six-week intervals. Trends were assessed at four stations within Central Bay: Martin Luther King Jr. Regional Shoreline (MLK), Berkeley (BRK), Keller Beach (KEL), and Tiburon (TIB) (Fig. 1). Samples were obtained from BRK, KEL, and TIB as part of long-term sampling performed by US Fish and Wildlife Service (USFWS, Stockton, CA) to characterize fish assemblages in the Bay and in the Sacramento-San Joaquin River Delta (Wichman, 2006). BRK, KEL, and TIB are marine sandy beach sites adjacent to the open waters of Central Bay. MLK was selected to complement the open water sites with a site having greater influence of wetland and watershed processes. MLK is a subtidal mudflat, abutting a 20 ha wetland complex, and enclosed within San Leandro Bay, a small basin with legacy industrial contamination and outlets to Oakland Harbor and Central San Francisco Bay (Daum et al., 2000). MLK was sampled for topsmelt and arrow goby (Mississippi silverside were only intermittently present). BRK, KEL, and TIB were sampled for topsmelt only, as arrow goby (a mudflat inhabitant) and Mississippi silverside (favoring lower salinities) were not present. It was not possible to collect topsmelt at all sampling events, due to their heterogeneous distribution in the Estuary throughout the year. For example, sample collection at TIB began in August, 2008.

The second sampling effort entailed repeated sampling during four seasons: October 2010, January 2011, May 2011, and July 2011. This effort occurred in four Bay locations: Mallard Slough, Alviso Slough (both in Lower South Bay), Eden Landing (South Bay), and Benicia State Park (between San Pablo and Suisun Bays; Fig. 1). These sites were selected to complement ongoing seasonal Hg study in the South Bay region (Ackerman et al., 2011) and to determine regional consistency of seasonal trends across the Bay. All sites are influenced by nearby wetland or historic salt pond complexes. Alviso Slough drains the urbanized and historically Hg contaminated Guadalupe River watershed (Greenfield and Jahn, 2010), Mallard Slough drains treated freshwater discharge from a large publicly operated wastewater treatment plant, Eden Landing drains a historic wetland and recently breached salt pond complex (Miles and Ricca, 2010), and Benicia State Park is a shoreline wetland site largely influenced by the surrounding subtidal embayments (San Pablo and Suisun Bays). Silverside were captured on all dates and stations, and topsmelt were captured at Alviso Slough and Eden Landing only (Table 1).

The third sampling effort focused on seasonal variation in the Napa-Sonoma marsh and managed pond complex in San Pablo Bay, near the Napa River (Table 1, Fig. 1). Historically part of a large wetland complex, the Napa-Sonoma ponds were originally developed for salt extraction,

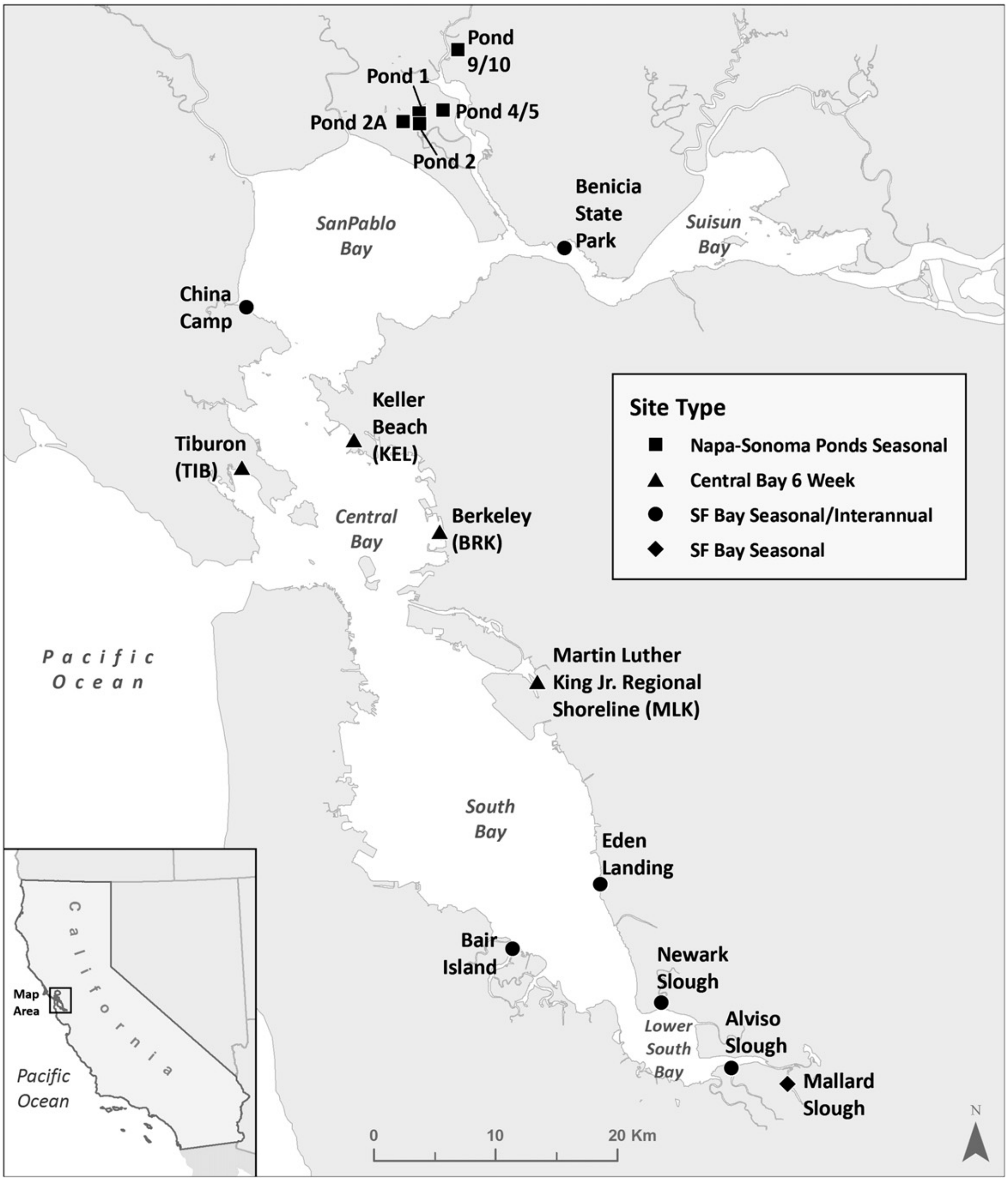

Fig. 1. Study sampling locations. Note: SF Bay Seasonal/Interannual indicates sites that were monitored annually, a subset of which was also monitored seasonally (Table 1).

Table 1
Summary of sampling efforts.

Sampling program and frequency	Species	Stations (Abbreviation)	Dates
1. Central Bay 6 week	Arrow goby	Martin Luther King Jr. Regional Shoreline (MLK)	Nov, 2007–Nov, 2010
1. Central Bay 6 week	Topsmelt	Martin Luther King Jr. Regional Shoreline (MLK)	Nov, 2007–Nov, 2010
1. Central Bay 6 week	Topsmelt	Tiburon (TIB)	Aug, 2008–Oct, 2010
1. Central Bay 6 week	Topsmelt	Berkeley (BRK)	Oct, 2007–Dec, 2010
1. Central Bay 6 week	Topsmelt	Keller Beach (KEL)	Oct, 2007––Dec, 2010
2. San Francisco Bay seasonal	Mississippi silverside	Alviso Slough, Eden Landing, Artesian Slough, and Benicia State Park (SF Bay)	Oct, 2010–July, 2011
2. San Francisco Bay seasonal	Topsmelt	Alviso Slough and Eden Landing (SF Bay)	Oct, 2010–July, 2011
3. Napa-Sonoma Ponds seasonal	Mississippi silverside	Pond 1, Pond 2, Pond 2A, Pond 4/5, Pond 9/10, and Napa River at Kennedy Park	Dec, 2009–July, 2010
4. San Francisco Bay annual	Mississippi silverside	Alviso Slough, Newark Slough, Bair Island, Eden Landing, China Camp, and Benicia State Park	Oct, 2005–Nov, 2010
4. San Francisco Bay annual	Topsmelt	Alviso Slough, Newark Slough, Bair Island, Eden Landing, China Camp, and Benicia State Park	Nov, 2005–Oct, 2010

and are currently either restored to tidal action or managed as waterbird habitat. Sampling occurred on five ponds (Pond 1, Pond 2, Pond 2A, Pond 4/5, and Pond 9/10) and on one site on the Napa River (Kennedy Park). The sites were chosen to represent the spectrum of habitat types in the wetland complex, from a control site on the river (Napa River at Kennedy Park), to managed muted-tidal pond (Ponds 1 and 2), to recently breached fully tidal pond in the process of accreting sediment to become marsh (Ponds 9/10 and 4/5), to fully tidal restored brackish marsh (Pond 2a) (Grenier et al., 2010). Mississippi silverside were collected seasonally on December 2009, March 2010, May 2010, and July 2010.

Finally, annual sampling was performed from 2005 to 2010 at six Bay locations: Alviso Slough, Newark Slough, Bair Island, Eden Landing, China Camp, and Benicia State Park (Table 1, Fig. 1). These sites were chosen for their widespread distribution across the Bay and their location near extant or soon-to-be-restored tidal marshes, enabling long term study on the effect of marshes on Bay margin fish mercury exposure. Alviso Slough, Eden Landing, and Benicia Park are described above; the remaining sites are within tidal channels adjacent to marshes, at the confluence with the Bay. Annual sampling was only performed from September through November, to determine interannual trends while reducing the influence of confounding seasonal variability. Data collected from 2005 to 2007 were reported previously (Greenfield and Jahn, 2010), and are here reanalyzed in combination with new data from 2008 to 2010.

2.2. Sample preparation and analysis

For each date and station combination, four to six composites of five to ten individuals per species were targeted. Target total lengths were 25 to 40 mm for arrow goby, 40 to 80 mm for silverside, and 60 to 100 mm for topsmelt. Fish samples were frozen on the day of collection in a −20 °C laboratory freezer, and analyzed at a later date for total Hg by standard cold vapor atomic absorption (CVAA) spectrophotometry. From 2005 through 2007, laboratory analysis was performed at the River Studies Center at the University of Wisconsin — La Crosse, with analytical methods described in Greenfield and Jahn (2010). Laboratory analyses for all samples collected from 2008 to 2011 were performed at the University of California — Davis. Further analytical and QA methods are described in Supplemental information. All study Hg results are reported on a wet weight basis.

2.3. Data analysis

Linear models were constructed to evaluate temporal variation at seasonal or annual scales using the linear model function in R version 2.15 (R Development Core Team, 2012). The four sampling efforts occurred on different time frames and frequencies (Table 1); therefore, separate analyses were performed across the entire time range of each sampling effort. Total Hg was $\log_{10}$ transformed prior to analysis to improve normality and variance homoscedasticity of residuals. Potential input parameters included sampling date (categorical), station, and fish total length. Interaction terms were also evaluated to evaluate potential changes in the relationship between fish length and Hg over time (date∗length) or across stations (length∗station), as well as whether different stations exhibited different interannual variations or trends (date∗station). For the six-week seasonal evaluations (i.e., MLK, BRK, KEL, and TIB stations), each site-species combination was evaluated individually, due to the inconsistent seasonal coverage across sites; a station effect and a date∗length interaction were not included. Parameters were retained based on statistical significance of addition to the full model ($p<0.05$); the final model contained only significant parameters.

The squared semipartial correlation (hereafter, sr^2) was determined for each significant parameter. Calculated as the difference in R^2 resulting from removing that parameter from the full model, the sr^2 indicates the amount of added variation that parameter explains after all other parameters are accounted for. For base terms (i.e., date, station, and length), the sr^2 was determined based on the full model, prior to adding any interaction terms.

Spatial and temporal patterns were plotted, including concentration averages and confidence intervals (CI). When length was a significant predictor, plotted concentrations were corrected to a standardized length, based on the model length coefficient. To aid in visual comparison of concentration means across sampling events, error bars (CI) were constructed based on 95% confidence for a pairwise difference between means with unknown mean and unknown standard deviation; i.e., $CI=(t_{0.915,\ df=n-1})*SD/\sqrt{N}$, where SD and N are specific to each sampling event (Austin and Hux, 2002; Goldstein and Healy, 1995).

3. Results

All models included date in the final model structure ($p<0.05$), indicating that temporal variation was present at all time scales examined. Date alone explained much more variation in the individually examined six-week Central Bay sites (squared semipartial correlation [sr^2] ranging from 0.57 to 0.93) than the remaining evaluations (sr^2 from 0.04 to 0.12). A date∗station interaction was present in all of the annual and seasonal evaluations of multiple stations (sr^2 from 0.11 to 0.36), except for the 2011 examination of topsmelt at Alviso Slough and Eden Landing (Table 2).

3.1. Seasonal variation in Central Bay, 2007 to 2010

Arrow goby at MLK and topsmelt at all four sites exhibited strong variation across sampling dates. Date was included, with high sr^2, in the models for both species and all stations, as was length for all

Table 2
Linear model results for each sampling effort. N = number composite samples included in analysis. Model structure includes all significant parameters and interactions included in model. sr^2 = squared semipartial correlation. NS = not significant ($p>0.05$).

Sampling effort	N	Dates [a]	Stations	Model structure	Model R^2	Date sr^2	Length sr^2	Station sr^2	Date∗station sr^2
MLK arrow goby 6 week	95	23	1	Date + length	0.75	0.65	0.02		
MLK topsmelt 6 week	101	21	1	Date + length	0.60	0.57	0.12		
TIB topsmelt 6 week	34	9	1	Date	0.93	0.93	NS		
BRK topsmelt 6 week	57	15	1	Date + length	0.89	0.71	0.04		
KEL topsmelt 6 week	58	17	1	Date	0.72	0.72	NS		
SF Bay silverside seasonal	78	4	4	Date∗station	0.82	0.08	NS[b]	0.56	0.11
SF Bay topsmelt seasonal	44	4	2	Date + station	0.77	0.12	NS[b]	0.65	NS
Napa-Sonoma marsh silverside seasonal	131	4	6	Date∗station + length	0.83	0.10	0.16	0.18	0.36
SF Bay silverside annual	115	6	6	Date∗station + length	0.76	0.05	0.05	0.60	0.11
SF Bay topsmelt annual	130	6	6	Date∗station + length	0.78	0.04	0.15	0.36	0.16

[a] Only dates with $N\geq2$ included.
[b] $0.05<p<0.08$.

combinations except topsmelt at TIB and at KEL (Table 2). Length corrected arrow goby sampled at MLK exhibited a clear seasonal pattern from 2008 to 2010 (Fig. 2a). In each year, concentrations were lowest in the early spring (i.e., March or April), and then increased and peaked in July (2008) or September (2009 and 2010).

Concentrations in topsmelt at all stations exhibited seasonal periodicity that was generally distinct from arrow goby at MLK. Length corrected topsmelt geometric mean concentrations at MLK were elevated in winter (December, 2008, late November, 2009, and January, 2010). Summer concentrations varied among years, with elevated concentrations in July, 2008 and July, 2009 but low concentrations in July, 2010 (Fig. 2b). For the remaining stations, topsmelt concentrations peaked during late winter to early spring of every monitored year (Fig. 2c–e). Annual peak geometric average topsmelt concentrations

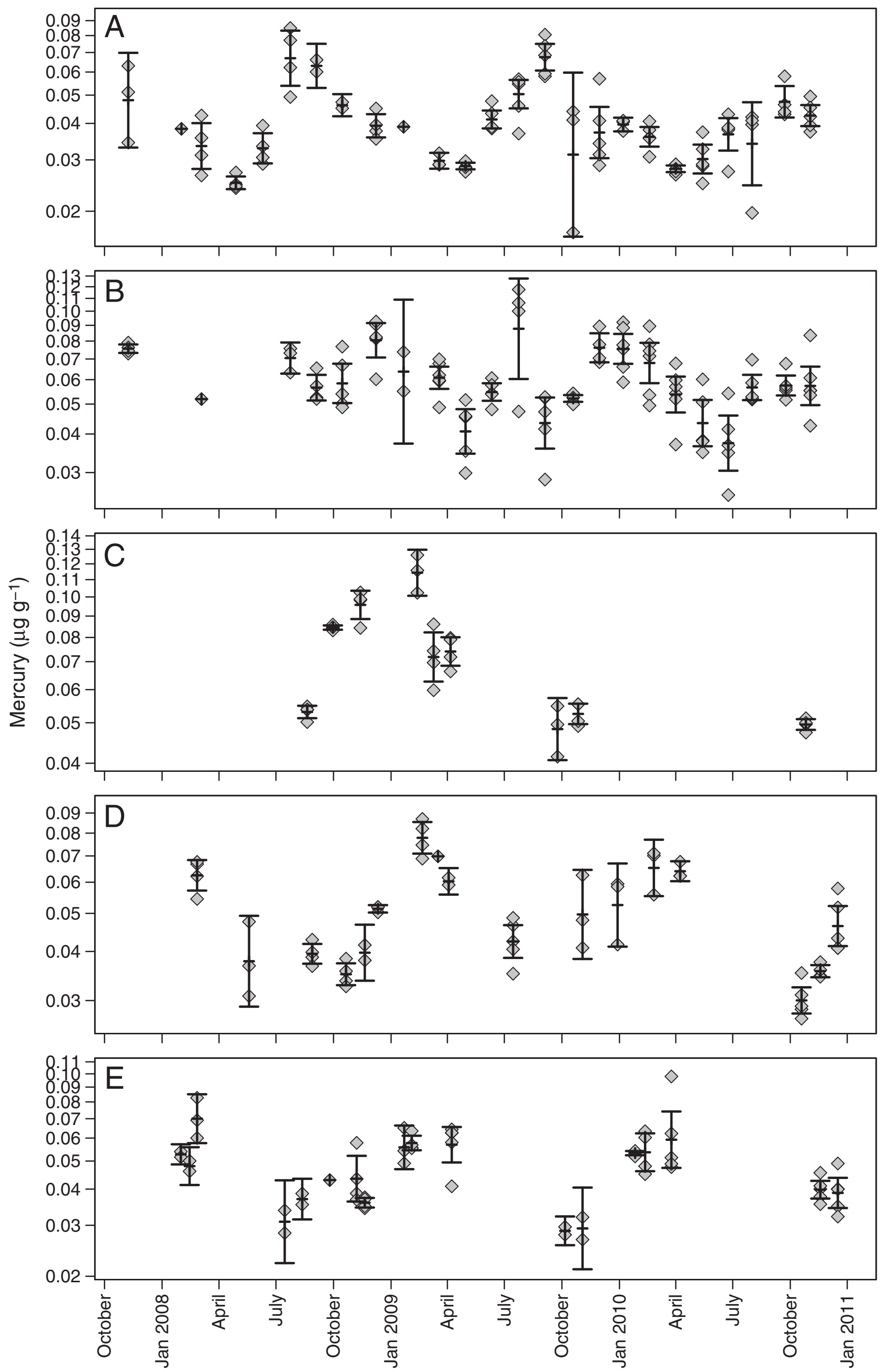

Fig. 2. Temporal variation in Hg concentrations at six-week collection intervals from late 2007 to 2010. Points are composite sample results and error bars indicate approximate 95% significant differences in means. Note log scale. a. Martin Luther King Jr. Regional Shoreline (MLK) arrow goby, length corrected. b. MLK topsmelt, length corrected. c. Tiburon topsmelt. d. Berkeley topsmelt, length corrected. e. Keller beach topsmelt.

were highest in February for TIB in 2009; KEL in 2008 and 2009; and BRK (length corrected) in all three years. Similarly, peak concentrations for KEL in 2010 were in March.

3.2. Seasonal variation in San Francisco Bay, 2011

For both silverside and topsmelt, there was a significant effect of date and station but not length. Station explained a greater proportion of the total variation in fish Hg than date (Table 2). For example, median silverside concentrations at Alviso Slough (0.27 μg g^{-1}) were more than four times those at Benicia State Park (0.06 μg g^{-1}). Silverside exhibited moderately different seasonal patterns among stations (date∗station $sr^2=0.11$). In particular, the lowest concentrations at Mallard Slough were in July 2011, while the lowest concentrations at Benicia State Park occurred in October 2010 (Fig. 3, top panels). Silverside were absent from Alviso Slough in July, but seasonal differences among stations were still present in an analysis excluding Alviso Slough (date∗station $sr^2=0.22$; N = 62). For topsmelt, seasonal variations were consistent between Alviso Slough and Eden Landing, with concentrations lowest in October and highest in July at both stations (Fig. 3, bottom panels). The increase in median topsmelt concentrations from October to January was consistent with the seasonal pattern found at Central Bay stations.

3.3. Seasonal variation in North Bay Ponds, 2010

Hg in Mississippi silverside from North Bay Ponds was influenced by date, station, and length, but the seasonal pattern was divergent across stations (date∗station $sr^2=0.36$, Table 2). In particular, Pond 2 Hg exhibited much greater seasonal variation than other stations (Fig. 4), with a dramatic decrease from December, 2009 (median = 0.20 μg g^{-1}) to March (0.14 μg g^{-1}) and May, 2010 (0.045 μg g^{-1}). In contrast, Pond 4/5 and Kennedy Park exhibited increases from December to March (Fig. 4).

3.4. Interannual variation

For both silverside and topsmelt, there were significant effects of date, station, length, and a date∗station interaction (Table 2). For Mississippi silverside, the variability explained by sampling station ($sr^2=0.60$) was much greater than that accounted for by date (i.e., year; $sr^2=0.05$), fish length ($sr^2=0.05$), and a date∗station interaction ($sr^2=0.11$), indicating that the majority of variability in silverside Hg resulted from differences among sampling locations. Station was also most important for topsmelt ($sr^2=0.35$), which had somewhat more variability explained by length ($sr^2=0.15$) and date∗station interaction ($sr^2=0.16$) than silverside. As reported previously (Greenfield and Jahn, 2010), concentrations were highest in Lower South Bay stations, and lowest in China Camp and Benicia State Park.

There was an overall lack of directional trend over the six sampling years, with the exception of increasing silverside Hg concentrations over time at Alviso Slough (Fig. 5). Interannual patterns were generally inconsistent across stations for silverside (Fig. 5) and topsmelt (Fig. 6). However, silverside concentrations in 2006 were lower than other years at Alviso Slough, Newark Slough, and China Camp (Fig. 5). Topsmelt

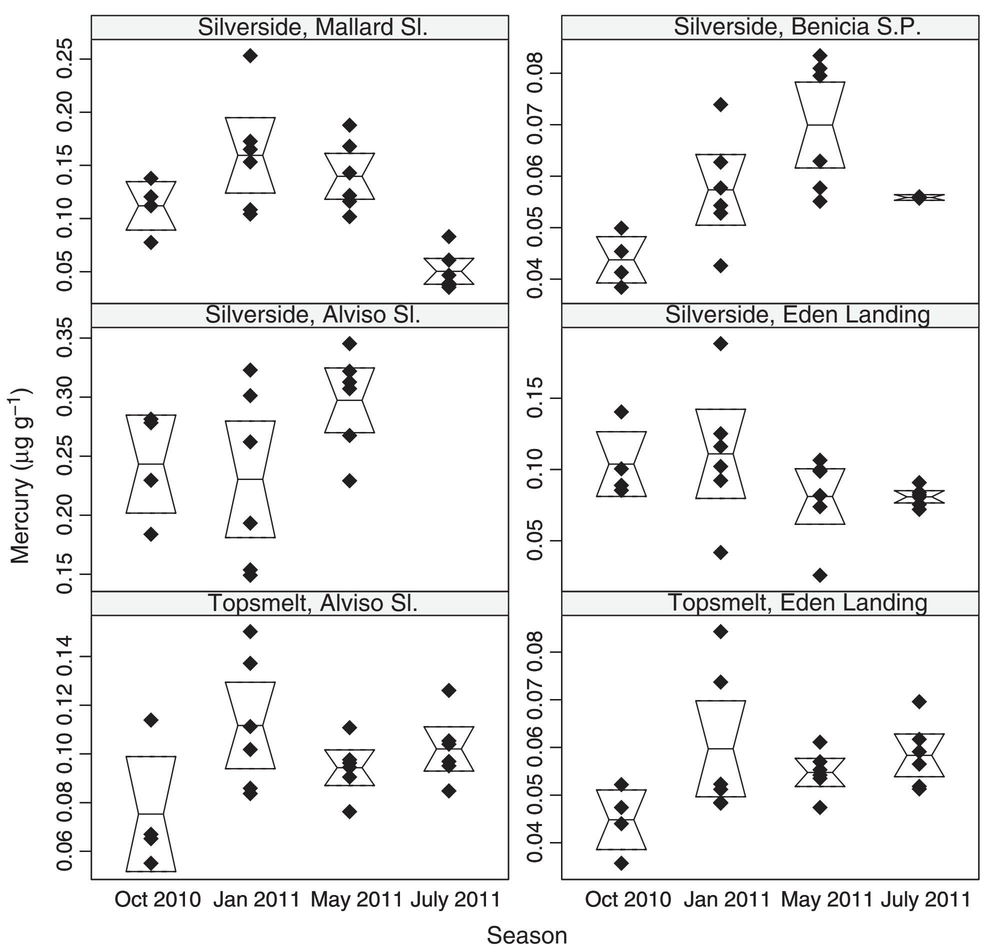

Fig. 3. Seasonal variation in silverside and topsmelt Hg at four San Francisco Bay monitoring stations. In this and all following plots, points are composite sample results, boxes indicate approximate 95% significant differences in means, and y-axis scales vary among subplots.

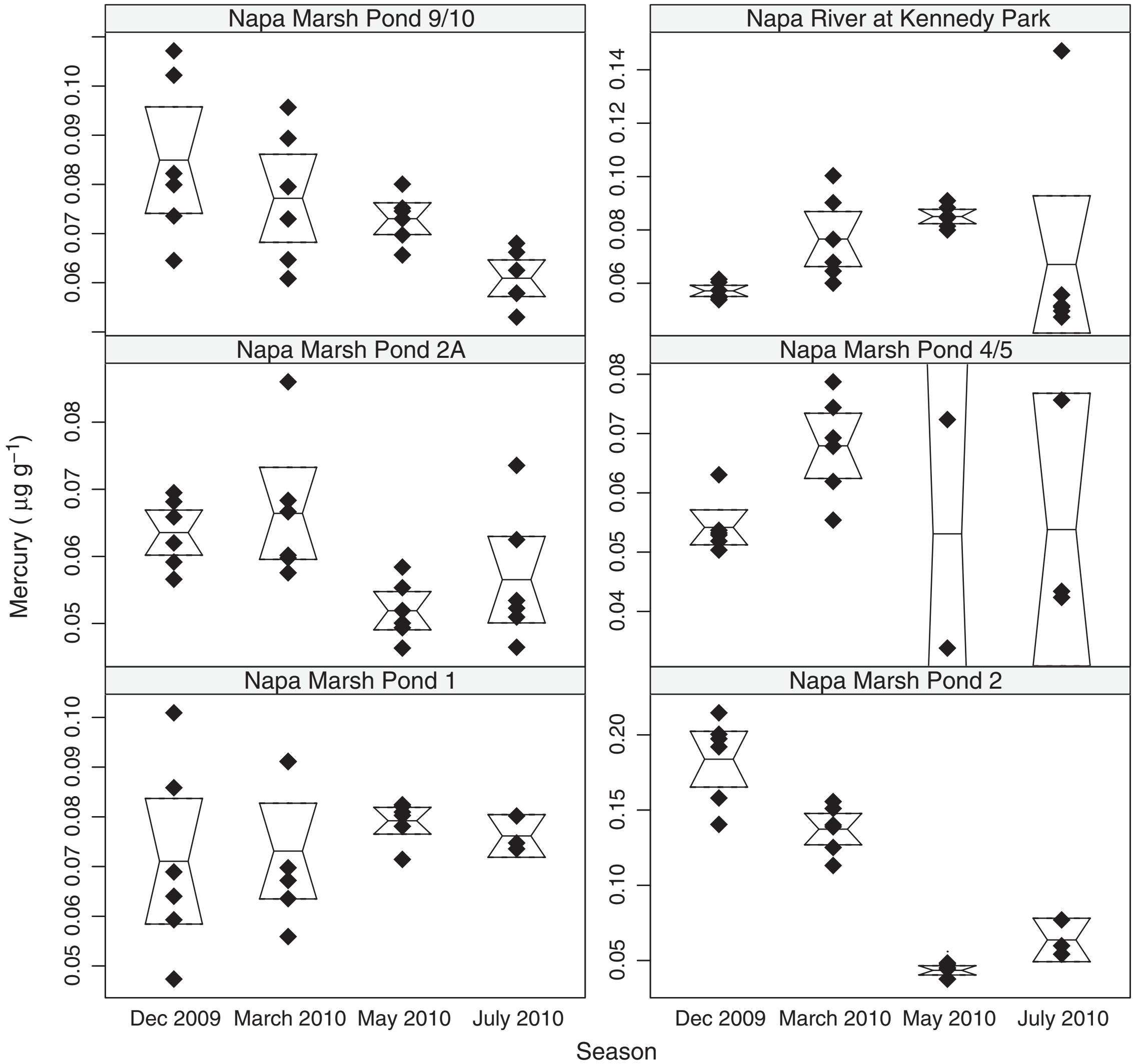

Fig. 4. Seasonal variation in length corrected silverside Hg at Napa-Sonoma ponds.

exhibited qualitatively similar interannual variation at Newark Slough and Eden Landing (Fig. 6). At Eden Landing, silverside concentrations in 2005 were much higher than other years. Outliers were evident, with silverside samples from China Camp (2006) and Benicia State Park (2008) and a topsmelt sample from Alviso Slough (2009) three to four times the remaining samples.

4. Discussion

Consistent with previous studies (e.g., Eagles-Smith and Ackerman, 2009; Fowlie et al., 2008; Gorski et al., 1999; Slotton et al., 1995; Ward and Neumann, 1999; Zhang et al., 2012), we found significant seasonal variation in fish Hg. However, we also observed a striking lack of consistency in temporal patterns across different sites and species, at both seasonal and interannual scales. These results indicate that even within a single estuary, temporal patterns of wildlife Hg exposure and risk (e.g., Eagles-Smith and Ackerman, 2009), should not be extrapolated across regions, habitats, or predator species.

4.1. Seasonal variation

In the three-year examination of Central Bay sites, strong seasonal variation was evident across the sampling years. Examinations of seasonal patterns in biota Hg often demonstrate consistent patterns of seasonal variation across species (Eagles-Smith and Ackerman, 2009; Zhang et al., 2012). In contrast, we found that arrow goby and topsmelt collected at the same site (MLK) exhibited distinct seasonal patterns, with arrow goby Hg highest in late summer and early fall, while topsmelt Hg concentrations were elevated in early spring and variable in the summer. Topsmelt Hg concentrations also tended to increase during late winter and early spring in the other Central Bay sites (2008 to 2010) and Alviso Slough and Eden landing (2010 to 2011), suggesting a consistent pattern for this species across sites. Unlike topsmelt, silverside exhibited notable spatial variation in seasonal patterns; for example, North Bay Pond 2 silverside exhibited much stronger seasonal variation than other stations.

The differences in seasonal and interannual patterns of MeHg exposure among topsmelt, silverside, and arrow goby may stem from differing seasonal changes in MeHg concentrations in the contrasting habitats and spatial scales utilized by these species, resulting from spatial differences in net MeHg production. Arrow gobies are sedentary burrow dwellers, indicating a highly localized exposure area (Emmett et al., 1991; Goals Project, 2000; Prasad, 1958). In contrast, topsmelt exhibit onshore and offshore movements with the tides, suggesting a broader sampling of the Central Bay bentho-pelagic food web (Greenfield and Jahn, 2010; Visintainer et al., 2006).

Available data on seasonal variation in estuarine wetland and mudflat MeHg generally supports the seasonal pattern observed in arrow goby. The mudflats at MLK, and other arrow goby mudflat habitats,

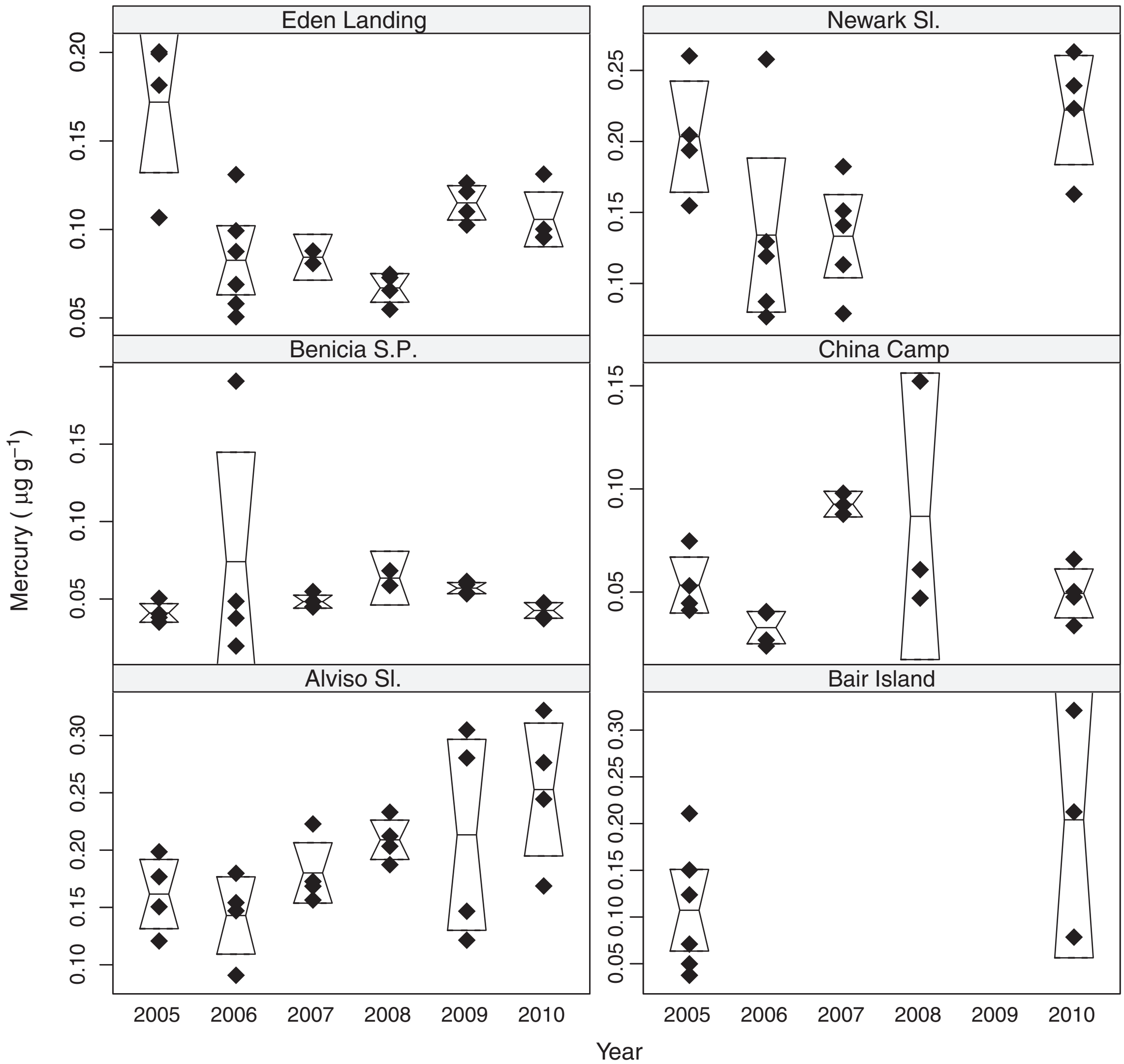

Fig. 5. Interannual variation in length corrected silverside Hg at San Francisco Bay stations.

are adjacent to emergent tidal wetlands, which often exhibit summer increases in MeHg production and export. Mitchell et al. (2012) describe summer increases in water column concentrations and net export from an estuarine wetland draining the Chesapeake Bay, and Best et al. (2008) found that fragmentation and leaching of two abundant wetland plant species (*Spartina foliosa* and *Salicornia virginica*) cause late spring and summer peaks in MeHg release from the China Camp tidal marsh (Fig. 1) to San Francisco Bay. There may also be increased summer MeHg production within the mudflats themselves, associated with elevated temperatures and increasing in situ activity of sulfate reducing bacteria. For example, MeHg concentrations are seasonally elevated in spring and summer within intertidal mudflat surface sediment and sediment-dwelling polychaetes (*Nereis diversicolor*) of the Scheldt Estuary, Belgium (Muhaya et al., 1997).

Rather than being determined by mudflat MeHg fluctuations, topsmelt Hg is likely influenced by pelagic water column processes and exchange with offshore sediments, since topsmelt appear to spend some time in pelagic and offshore habitats (Greenfield and Jahn, 2010; Visintainer et al., 2006). Consistent with the topsmelt Hg pattern, Conaway et al. (2003) describe higher water column MeHg concentrations in February (2000) than July (1999, 2000) in North Bay (i.e., San Pablo Bay to the Sacramento-San Joaquin River Delta), although they show no significant seasonal pattern in Central or South Bay. Luengen and Flegal (2009) also observe a spring increase in Bay water column MeHg concentrations, following a phytoplankton bloom. These limited findings, in combination with our forage fish data, suggest that the timing of MeHg production peaks may differ between the Bay water column (spring peak) and intertidal wetlands (summer peak).

Seasonal variability should be considered in sampling design, with long-term trend or spatial studies focusing on a narrow and consistent sampling season (Wiener et al., 2007), and evaluations of MeHg risk to piscivorous wildlife focusing on developmental periods for sensitive life stages (Eagles-Smith and Ackerman, 2009; Herring et al., 2010). Changes over time accounted for half to nearly all (57% to 93%) of the variation in forage fish Hg that we sampled every six weeks. Similarly, Eagles-Smith and Ackerman (2009) found Hg in longjaw mudsucker (*Gillichthys mirabilis*) and three-spined stickleback (*Gasterosteus aculeatus*) from managed wetlands to increase 40% during the summer months of 2006. Mercury monitoring in multiple seasons is warranted when there are multiple predator species of concern or uncertainty regarding the most sensitive periods.

The contrasting patterns observed among forage fish species and locations in this study underscore a need to know what prey species and habitats are favored by piscivorous wildlife. Seasonal patterns in topsmelt Hg concentrations contrasted with arrow goby and also with longjaw mudsucker and three-spined stickleback sampled in South Bay managed ponds (Eagles-Smith and Ackerman, 2009), indicating

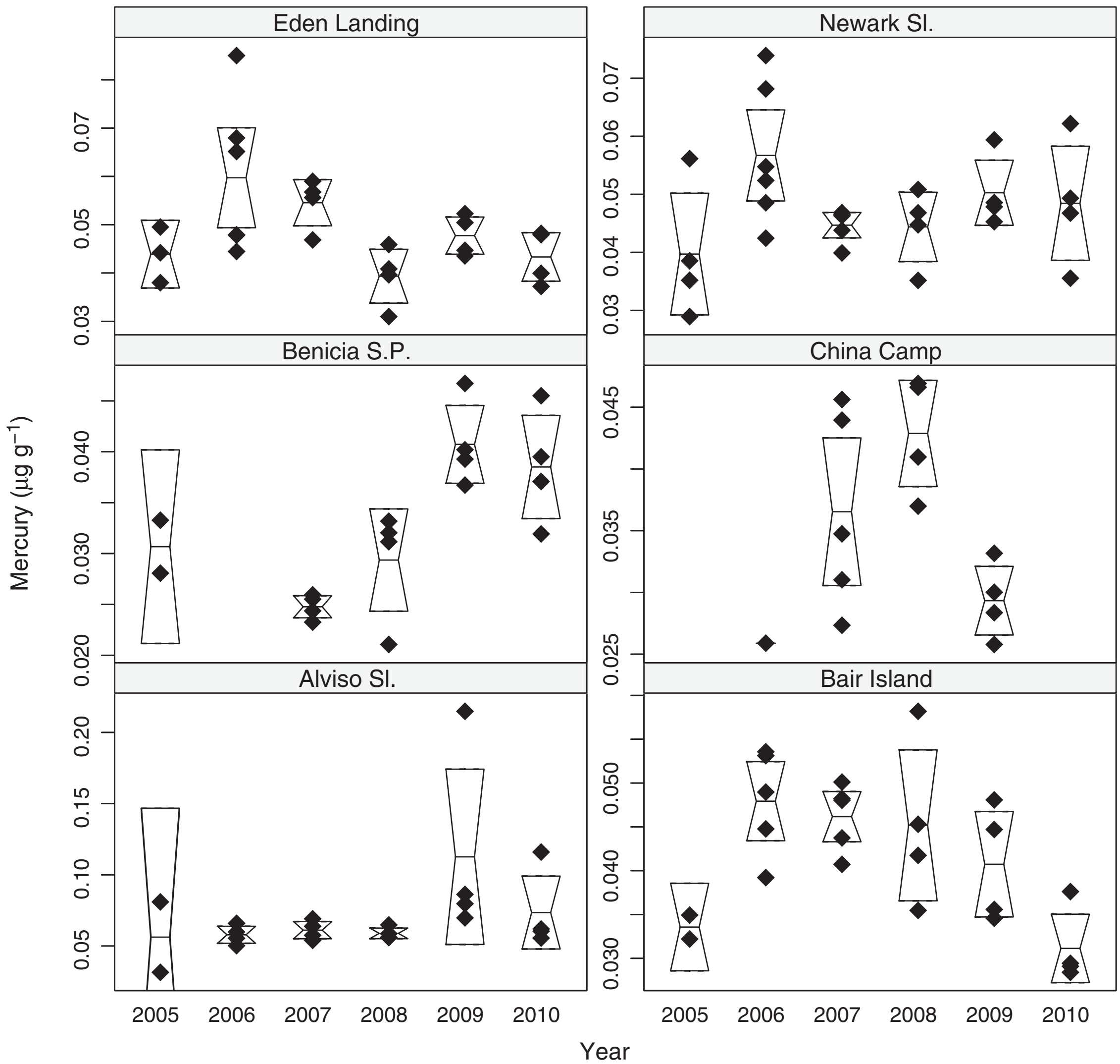

Fig. 6. Interannual variation in length corrected topsmelt Hg at Bay stations.

species-specific temporal risk patterns for piscivorous birds. For example, Forster's tern (*Sterna forsteri*) predominantly consumes the wetland fish species (Eagles-Smith and Ackerman, 2009), whereas California Least tern (*Sterna antillarum browni*, a federally endangered bird) largely consumes topsmelt and other Atherinopsidae (Elliott, 2005; Elliott et al., 2007). Arrow goby appears to be a component of the diet of mudflat feeding birds, including greater yellowleg (*Tringa melanoleuca*) and long-billed dowitcher (*Limnodromus scolopaceus*) (Goals Project, 2000; Reeder, 1951).

The unique MeHg bioaccumulation pattern in silverside from North Bay Pond 2 indicates that site-specific biogeochemical conditions can develop in these isolated ponds. Pond 2, like several of the North Bay Ponds, is fairly hydrologically isolated, lacking major inflows or outflows, and exhibiting muted tidal action. Silverside in Pond 2 exhibited the strongest temporal fluctuation among all sites and species examined, with a more than fourfold concentration decline between December, 2009 and May, 2010. Possible mechanisms to explain this variation include seasonal differences in net MeHg production or variations in trophic status causing biodilution.

Seasonal variation in small fish Hg is likely driven by seasonal patterns in water MeHg concentrations, which also vary among study systems. For example, maximum MeHg concentrations in Florida Everglades wetlands and Venice Lagoon mudflats peak in midsummer (Bloom et al., 2004; Hurley et al., 1998). Lavaca Bay, Texas exhibited highest sediment to water column MeHg fluxes in late winter (Gill et al., 1999), and in Davis Creek Reservoir, California, and Devil's Lake, Wisconsin, fall destratification resulted in substantial food web MeHg uptake (Herrin et al., 1998; Slotton et al., 1995).

4.2. Interannual variation

Interannual variation, though significant, explained limited variation in fish Hg compared to previously documented (Greenfield and Jahn, 2010) spatial differences among sampling stations. Both silverside and topsmelt exhibited interannual variation in Hg concentrations that differed among sites, suggesting an influence of local conditions on temporal Hg patterns.

Site specific differences in Hg patterns may be associated with the hydrologic management of former salt ponds adjacent to South Bay sites including Alviso Slough, Bair Island, and Newark Slough (Miles and Ricca, 2010). These ponds are currently managed for wildlife as part of a long-term restoration project. This project could potentially alter biotic MeHg exposure due to the high sediment MeHg concentrations in some of the salt ponds and the potential for hydrologic modification, including cycles of wetting and drying, to increase MeHg production or release (Grenier and Davis, 2010). In Eden Landing, silverside were elevated in 2005 compared to other years, which could have been due to pond management activities. The 2005 elevated silverside concentrations at the Eden Landing site could have resulted from short term exposure to MeHg released from the Eden Landing pond complex, as they transitioned from hydrologically isolated ponds having elevated sediment MeHg production to ponds with a greater hydrological connection to the South Bay (Miles and Ricca, 2010; South Bay Salt Pond Restoration Project, 2006).

At Alviso Slough, decreases in fall dissolved oxygen and consequent increases in MeHg production may have caused the increases in silverside Hg from 2005 to 2010, and topsmelt high outlier results in 2009 and 2010. The time period of increasing fish Hg corresponded with reported fish kills in the Guadalupe River draining to Alviso Slough in 2008, 2009, and 2010 (City of San Jose et al., 2011). The fish kills occurred around the time we collected fish, and are believed to be related to low dissolved oxygen levels in the river channel (R. Schlipf, SFRWQCB, *pers. comm.*). Also during this time period, compliance monitoring of outfall water from one of the salt ponds that drains to Alviso Slough (Pond A7) indicated an annual increasing rate of hypoxic water between 2005 and 2009, which pond managers attribute to periodic algae blooms within the pond (United States Fish and Wildlife Service and United States Geological Survey, 2012). Hypoxic conditions are often associated with increased MeHg production in aquatic systems, due to activity of sulfate reducing bacteria (Gilmour et al., 1992; Watras et al., 1995).

Consistent regional, long-term directional trends for Hg in forage fish were not apparent over the six-year study duration. With the exception of Alviso Slough, most stations did not exhibit increases or decreases over time, and spatial differences were greater than temporal variation. Fish Hg has exhibited long-term declines in many ecosystems (Levinton and Pochron, 2008; Munthe et al., 2007), but this declining trend is inconsistent among water bodies and may be reversing in recent years (Monson, 2009). In San Francisco Bay, PCBs and legacy pesticides have declined but Hg concentrations have exhibited no consistent upward or downward trends in Bay biota (Greenfield et al., 2005; Gunther et al., 1999; Stephenson et al., 1995). This is likely due to continued atmospheric and fluvial inputs in addition to disturbance of legacy deposits, resulting in stable concentrations of total Hg in sediment and projected rates of change on the order of decades to centuries (Davis et al., 2012; Yee et al., 2011).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.12.009.

References

Ackerman J, Marvin-DiPasquale M, Slotton D, Herzog M, Eagles-Smith C. The effects of wetland restoration on mercury bioaccumulation in the south bay salt pond restoration project: using the biosentinel toolbox to monitor changes across multiple habitats and spatial scales. 2010 annual report. Davis, CA: USGS; 2011. p. 11. [http://www.southbayrestoration.org/documents/technical/].

Ackerman JT, Eagles-Smith CA, Takekawa JY, Demers SA, Adelsbach TL, Bluso JD, et al. Mercury concentrations and space use of pre-breeding American avocets and black-necked stilts in San Francisco Bay. Sci Total Environ 2007;384:452–66.

Austin PC, Hux JE. A brief note on overlapping confidence intervals. J Vasc Surg 2002;36:194–5.

Best EPH, Hintelmann H, Dimock B, Bednar AJ. Natural cycles and transfer of mercury through pacific coastal marsh vegetation dominated by *Spartina foliosa* and *Salicornia virginica*. Estuaries Coasts 2008;31:1072–88.

Bloom NS, Moretto LM, Scopece P, Ugo P. Seasonal cycling of mercury and monomethyl mercury in the Venice Lagoon (Italy). Mar Chem 2004;91:85–99.

Braune BM, Outridge PM, Fisk AT, Muir DCG, Helm PA, Hobbs K, et al. Persistent organic pollutants and mercury in marine biota of the Canadian Arctic: an overview of spatial and temporal trends. Sci Total Environ 2005;351:4-56.

City of San Jose, Santa Clara Valley Water District, EOA Inc. Follow-up evaluation of stormwater pump station discharges in San Jose; 2011. p. 41.

Conaway CH, Black FJ, Grieb TM, Roy S, Flegal AR. Mercury in the San Francisco Estuary: a review. Rev Environ Contam Toxicol 2008;194:29–54.

Conaway CH, Ross JRM, Looker R, Mason RP, Flegal AR. Decadal mercury trends in San Francisco Estuary sediments. Environ Res 2007;105:53–66.

Conaway CH, Squire S, Mason RP, Flegal AR. Mercury speciation in the San Francisco Bay estuary. Mar Chem 2003;80:199–225.

Conaway CH, Watson EB, Flanders JR, Flegal AR. Mercury deposition in a tidal marsh of south San Francisco Bay downstream of the historic New Almaden mining district, California. Mar Chem 2004;90:175–84.

Daum T, Lowe S, Toia R, Bartow G, Fairey R, Anderson J, et al. Sediment contamination in San Leandro Bay, CA. Richmond, CA: San Francisco Estuary Institute, San Francisco Bay Regional Water Quality Control Board, California Department of Fish and Game, and Port of Oakland; 2000. p. 52. [http://www.sfei.org/node/2103].

Davis JA, Looker RE, Yee D, Marvin-Dipasquale M, Grenier JL, Austin CM, et al. Reducing methylmercury accumulation in the food webs of San Francisco Bay and its local watershed. Environ Res 2012;119:3-26.

Davis JA, Yee D, Collins JN, Schwarzbach SE, Luoma SN. Potential for increased mercury accumulation in the Estuary food web. San Franc Estuary Watershed Sci 2003;1(1). [Article 4. http://escholarship.org/uc/item/9fm1z1zb].

Eagles-Smith CA, Ackerman JT. Rapid changes in small fish mercury concentrations in estuarine wetlands: implications for wildlife risk and monitoring programs. Environ Sci Technol 2009;43:8658–64.

Elliott ML. Diet, prey, and foraging habits of the California least tern (*Sterna antillarum browni*). San Francisco State University; 2005. p. 89.

Elliott ML, Hurt R, Sydeman WJ. Breeding biology and status of the California least tern *Sterna antillarum browni* at Alameda Point, San Francisco Bay, California. Waterbirds 2007;30:317–25.

Emmett RL, Hinton SA, Stone SL, Monaco ME. Distribution and abundance of fishes and invertebrates in west coast estuaries, Volume II: species life history summaries. ELMR Report No 8 NOAA/NOS Strategic Environmental Assessments Division, Rockville, MD; 1991. p. 329.

Fowlie AR, Hodson PV, Hickey MBC. Spatial and seasonal patterns of mercury concentrations in fish from the St. Lawrence River at Cornwall, Ontario: Implications for monitoring. J Great Lakes Res 2008;34:72–85.

Gill GA, Bloom NS, Cappellino S, Driscoll CT, Dobbs C, McShea L, et al. Sediment—water fluxes of mercury in Lavaca Bay, Texas. Environ Sci Technol 1999;33:663–9.

Gilmour CC, Henry EA, Mitchell R. Sulfate stimulation of mercury methylation in fresh-water sediments. Environ Sci Technol 1992;26:2281–7.

Goals Project. Baylands Ecosystem Habitat Goals. A report of habitat recommendations prepared by the San Francisco Bay Area Wetlands Ecosystem Goals Project. U.S. Environmental Protection Agency, San Francisco, Calif./S.F. Oakland, CA: Bay Regional Water Quality Control Board; 1999. p. 328. [http://www.sfestuary.org/about-the-estuary/documents-reports/].

Goals Project. Baylands ecosystem species and community profiles: life histories and environmental requirements of key plants, fish and wildlife. In: Olofson PR, editor. San Francisco Bay Area Wetlands Ecosystem Goals Project. Oakland, CA: San Francisco Bay Regional Water Quality Control Board; 2000. p. 435. [http://www.sfestuary.org/about-the-estuary/documents-reports/].

Goldstein H, Healy MJR. The graphical presentation of a collection of means. J R Stat Soc A 1995;158:175–7.

Gorski PR, Lathrop RC, Hill SD, Herrin RT. Temporal mercury dynamics and diet composition on the mimic shiner. Trans Am Fish Soc 1999;128:701–12.

Greenfield BK, Davis JA, Fairey R, Roberts C, Crane D, Ichikawa G. Seasonal, interannual, and long-term variation in sport fish contamination, San Francisco Bay. Sci Total Environ 2005;336:25–43.

Greenfield BK, Jahn A. Mercury in San Francisco Bay forage fish. Environ Pollut 2010;158:2716–24.

Grenier JL, Davis JA. Water quality in South San Francisco Bay, California: current condition and potential issues for the South Bay Salt Pond Restoration Project. Rev Environ Contam Toxicol 2010;206:115–47.

Grenier JL, Greenfield BK, Slotton DG, Ayers SM. North Bay small fish mercury monitoring with a focus on Napa–Sonoma managed ponds and sloughs V.2. Oakland, CA: Aquatic Science Center; 2010. p. 30. [http://www.sfei.org/documents/3624].

Gunther AJ, Davis JA, Hardin DD, Gold J, Bell D, Crick JR, et al. Long-term bioaccumulation monitoring with transplanted bivalves in the San Francisco Estuary. Mar Pollut Bull 1999;38:170–81.

Heim WA, Coale KH, Stephenson M, Choe K-Y, Gill GA, Foe C. Spatial and habitat-based variations in total and methyl mercury concentrations in surficial sediments in the San Francisco Bay-Delta. Environ Sci Technol 2007;41:3501–7.

Henery RE, Sommer TR, Goldman CR. Growth and methylmercury accumulation in juvenile Chinook salmon in the Sacramento River and its floodplain, the Yolo Bypass. Trans Am Fish Soc 2010;139:550–63.

Herrin RT, Lathrop RC, Gorski PR, Andren AW. Hypolimnetic methylmercury and its uptake by plankton during fall destratification: a key entry point of mercury into lake food chains. Limnol Oceanogr 1998;43:1476–86.
Herring G, Ackerman JT, Eagles-Smith CA. Embryo malposition as a potential mechanism for mercury-induced hatching failure in bird eggs. Environ Toxicol Chem 2010;29:1788–94.
Hornberger MI, Luoma SN, van Geen A, Fuller C, Anima R. Historical trends of metals in the sediments of San Francisco Bay, California. Mar Chem 1999;64:39–55.
Hurley J, Krabbenhoft D, Cleckner L, Olson M, Aiken G, Rawlik P. System controls on the aqueous distribution of mercury in the northern Florida Everglades. Biogeochemistry 1998;40:293–311.
Kelly CA, Rudd JWM, Bodaly RA, Roulet NP, St. Louis VL, Heyes A, et al. Increases in fluxes of greenhouse gases and methyl mercury following flooding of an experimental reservoir. Environ Sci Technol 1997;31:1334–44.
Levinton JS, Pochron ST. Temporal and geographic trends in mercury concentrations in muscle tissue in five species of Hudson River, USA, fishes. Environ Toxicol Chem 2008;27:1691–7.
Luengen A, Flegal AR. Role of phytoplankton in mercury cycling in the San Francisco Bay estuary. Limnol Oceanogr 2009;54:23–40.
Miles AK, Ricca MA. Temporal and spatial distributions of sediment mercury at salt pond wetland restoration sites, San Francisco Bay, CA, USA. Sci Total Environ 2010;408:1154–65.
Mitchell CPJ, Jordan TE, Heyes A, Gilmour CC. Tidal exchange of total mercury and methylmercury between a salt marsh and a Chesapeake Bay sub-estuary. Biogeochemistry 2012:1-18.
Monson BA. Trend reversal of mercury concentrations in piscivorous fish from Minnesota Lakes: 1982–2006. Environ Sci Technol 2009;43:1750–5.
Muhaya BBM, Leermakers M, Baeyens W. Total mercury and methylmercury in sediments and in the polychaete *Nereis diversicolor* at Groot Buitenschoor (Scheldt estuary, Belgium). Water Air Soil Pollut 1997;94:109–23.
Munthe J, Bodaly RA, Branfireun BA, Driscoll CT, Gilmour CC, Harris R, et al. Recovery of mercury-contaminated fisheries. Ambio 2007;36:33–44.
Prasad RR. Notes on the habitat and habits of *Clevelandia ios* (Jordan and Gilbert). Proceedings of the National Institute of Sciences of India Part B, Biological sciences, 24. ; 1958. p. 314–24.
R Development Core Team. R: a language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing; 2012 [http://www.R-project.org/].
Reeder WG. Stomach analysis of a group of shorebirds. Condor 1951;53:43–5.
Schwarzbach SE, Albertson JD, Thomas CM. Effects of predation, flooding, and contamination on reproductive success of California Clapper Rails (*Rallus longirostris obsoletus*) in San Francisco Bay. Auk 2006;123:45–60.
Slotton DG, Reuter JE, Goldman CR. Mercury uptake patterns of biota in a seasonally anoxic northern California Reservoir. Water Air Soil Pollut 1995;80:841–50.
South Bay Salt Pond Restoration Project. Pond Breach Dates; 2006. Accessed August 10, 2012 http://www.southbayrestoration.org/monitoring/breachdates.html.
Stephenson MD, Martin M, Tjeerdema RS. Long-term trends in DDT, polychlorinated biphenyls, and chlordane in California mussels. Arch Environ Contam Toxicol 1995;28:443–50.
U.S. EPA. Mercury study report to congress. U.S. Environmental Protection Agency; 1997. [http://www.epa.gov/mercury/report.htm].
United States Fish and Wildlife Service and United States Geological Survey. South Bay Salt Pond Restoration Project 2011 Annual Self-Monitoring Report. Prepared for San Francisco Bay Regional Water Quality Control Board; 2012. p. 169. [http://www.southbayrestoration.org/monitoring/].
Visintainer TA, Bollens SM, Simenstad C. Community composition and diet of fishes as a function of tidal channel geomorphology. Mar Ecol Prog Ser 2006;321:227–43.
Ward SM, Neumann RM. Seasonal variations in concentrations of mercury in axial muscle tissue of largemouth bass. N Am J Fish Manag 1999;19:89–96.
Watras CJ, Bloom NS, Morrison KA, Claas SA, Gilmour CC, Craig SR. Methylmercury production in the anoxic hypolimnion of a dimictic seepage lake. Water Air Soil Pollut 1995;80:735–45.
Wichman L. Regional trends in fish assemblage stability and diversity based on Fall seine and trawl sampling, 1995–2005 September–December. Interagency Ecol Program Newsl 2006;19(1):7-13. [http://www.water.ca.gov/iep/newsletters/2006/IEPNewsletter_Winter2006final6.pdf].
Wiener JG, Bodaly RA, Brown SS, Lucotte M, Newman MC, Porcella DB, et al. Monitoring and evaluating trends in methylmercury accumulation in aquatic biota. In: Harris R, Krabbenhoft DP, Mason R, Murray MW, Reash R, Saltman T, editors. Ecosystem responses to mercury contamination: indicators of change. Pensacola, FL: CRC Press; 2007. p. 87-122.
Wiener JG, Fitzgerald WF, Watras CJ, Rada RG. Partitioning and bioavailability of mercury in an experimentally acidified Wisconsin lake. Environ Toxicol Chem 1990;9:909–18.
Yee D, McKee LJ, Oram JJ. A regional mass balance of methylmercury in San Francisco Bay, California, USA. Environ Toxicol Chem 2011;30:88–96.
Zhang L, Campbell LM, Johnson TB. Seasonal variation in mercury and food web biomagnification in Lake Ontario, Canada. Environ Pollut 2012;161:178–84.