

**Seasonal, interannual, and long-term variation in sport fish
contamination, San Francisco Bay**

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Abstract

This study documents changes in contamination over time at seasonal, interannual, and decadal time scales for sport fish collected in San Francisco Bay. Samples from seven fish species were prepared according to common consumption practices (muscle fillets either with or without skin) and analyzed for trace metals (mercury and selenium) and trace organochlorine contaminants (PCBs, DDTs, chlordanes, and dieldrin). In 2000, sport fish samples exceeded human health screening values for mercury, PCBs, DDTs, selenium, and dieldrin, but did not exceed screening values for chlordanes. On a seasonal time scale, white croaker (Genyonemus lineatus) exhibited significantly lower PCB and lipid concentrations in spring, and a general increase in concentrations in other seasons. When monitoring data were compared among 1994, 1997, and 2000, analysis of variance indicated that concentrations of mercury, PCBs, DDTs, and chlordanes varied significantly among years for several fish species. Interannual variation in DDTs often correlated to changes in sampled fish size or lipid content among years. Interannual variation in mercury and PCBs was evident in striped bass (Morone saxatilis) but absent in shiner surfperch (Cymatogaster aggregata), leopard shark (Triakis semifasciata), and white croaker. The higher interannual variability of striped bass contaminant concentrations may result from migratory behavior and wide home ranges. Chlordanes significantly declined between 1994 and 2000 in white croaker and striped bass. Of the historical data analyzed (1986 – 2000), only DDT concentrations in white sturgeon (Acipenser transmontanus) showed evidence of a significant decline. Neither PCBs nor selenium showed evidence of a trend in white sturgeon. Between 1970 and 2000,

mercury concentrations in striped bass showed no evidence of a trend. The absence of recent trends in mercury may result from the presence of widespread and historic sources, with use reductions occurring in the early 20th century. In contrast to mercury, apparent recent declines in fish tissue DDT and chlordane concentrations may result from use curtailment in the 1970s and 1980s.

Keywords: Fish tissue; Mercury; PCBs; DDT; Chlordane; Selenium; San Francisco Bay;
Temporal trends

Introduction

The San Francisco Bay ecosystem supports considerable sport fishing activity, and local fisherman often eat what they catch (SFEI, 2000). Like many urbanized water bodies, human exposure to contaminants through consumption of contaminated fish has been an ongoing concern for San Francisco Bay. Elevated contaminant concentrations were first documented in fish in 1965 for trace organic contaminants (Risebrough, 1969) and in the early 1970s for mercury (Interagency Committee on Environmental Mercury, 1971). Since that time, a number of grey literature studies determined concentrations of mercury (Hg), selenium (Se), and organochlorines in San Francisco Bay fish in the 1980s and 1990s (CSWRCB, 1980; White et al., 1988; 1989; Rasmussen and Blethrow, 1991; Urquhart and Regalado, 1991; Rasmussen, 1993, 1995), and some published literature studies have documented contaminant concentrations in the same fish species collected

from other regions (e.g., Kennish and Ruppel, 1998; Zlokovitz and Secor, 1999; Gilmour and Riedel, 2000; Burger and Campbell, 2004).

In 1994 the Bay Protection and Toxic Cleanup Program (BPTCP) performed a more extensive study to measure concentrations of contaminants in fish in San Francisco Bay (SFBRWQCB, 1995; Fairey et al., 1997). The BPTCP study indicated that there were six chemicals or chemical groups that were of potential human health concern for people consuming San Francisco Bay-caught fish: PCBs, Hg, DDT, dieldrin, chlordane, and dioxins. As a result of this study, the Office of Environmental Health Hazard Assessment (OEHHA) issued an interim health advisory for people consuming fish from San Francisco Bay (OEHHA, 1997). This interim advisory, still in effect, states that: 1. adults should limit consumption of San Francisco Bay sport fish to, at most, two meals per month; 2. adults should not eat any striped bass over 35 inches (89 cm); and 3. pregnant women or women that may become pregnant or are breast-feeding, and children under 6 should not eat more than one meal per month, and should not eat any meals of shark over 24 inches (61 cm) or striped bass over 27 inches (69 cm).

The Regional Monitoring Program for Trace Substances in the San Francisco Estuary (RMP) is a comprehensive contaminant monitoring program aimed at providing the information needed to manage water quality in San Francisco Bay (Hoenicke et al., 2003; SFEI, 2003). In 1997, the RMP began triennial monitoring of contaminants in San Francisco Bay sport fish. One of the objectives of the RMP fish monitoring element is to track long-term trends in potential human exposure from consuming contaminated fish. The majority of the sampling and analytical effort was allocated toward characterizing concentrations of contaminants in a manner that was comparable with the 1994 sampling

and future sampling years. Data from three rounds of sampling, 1994, 1997, and 2000, are compared in this paper to provide an indication of variation among sample years and possible trends.

There are many potential sources of variation in fish contamination over time. Interannual fluctuations can reflect variability in growth patterns or habits of individual fish species, as well as differences in contaminant availability to a broad range of fish species. Concentrations of mercury and trace organochlorines can be influenced by fish size (Stow, 1995; Tremblay et al., 1998; Amrhein et al., 1999; Gilmour and Riedel, 2000; Davis et al., 2002), which can vary among sampling periods. Additionally, since many legacy organic contaminants are lipophilic, concentrations of PCBs and organochlorine pesticides are often related to tissue lipid content (Reinert et al., 1972; Larsson et al., 1993; Kidd et al., 1998; Amrhein et al., 1999), though the importance of this relationship is in dispute (Stow, 1995; Stow et al., 1997). Long-term trends for particular contaminants may result from regulatory restrictions on use, changes in loading rates, or environmental properties of the contaminant in question (e.g., degradation rate). Declining trends in previously banned contaminants are particularly important to document, as they may suggest that an individual contaminant may be less of a priority for regional management than banned contaminants having stable concentrations.

The objective of this paper is to document changes in San Francisco Bay fish contaminant concentrations over time. Unlike many evaluations of contaminant trends in biota, this paper separately evaluates temporal patterns at multiple time scales: seasonal, interannual, and long-term (a decade or longer). Seasonal variation in organic contaminants was determined in 2000 for white croaker, the sport fish species exhibiting

the highest organic contaminant concentrations in San Francisco Bay studies (Fairey et al., 1997). Interannual variation in contamination of several fish species is evaluated over the three BPTCP and RMP sampling years (1994, 1997, and 2000). The paper statistically evaluates correlations with fish size and lipid content to assess whether these factors may be driving contaminant fluctuation among sampling years. Finally, this paper compares the RMP and BPTCP data set to prior data sets from other programs in order to obtain the most complete assessment possible of long-term trends in San Francisco Bay fish contamination.

Methods

Field methods

The species sampled by the RMP include jacksmelt (*Atherinopsis californiensis*), shiner surfperch (*Cymatogaster aggregata*), white croaker (*Genyonemus lineatus*), striped bass (*Morone saxatilis*), California halibut (*Paralichthys californicus*), leopard shark (*Triakis semifasciata*), and white sturgeon (*Acipenser transmontanus*). Information on the movements and food habits of these species is summarized in Davis et al. (1999). In 1998 and 1999, red rock crabs (*Cancer productus*) and Japanese littleneck clams (*Tapes japonica*) were also collected; results of shellfish contaminant analysis are available elsewhere (Greenfield et al., 2003). In 1997 and 2000, sampling was performed at 6 locations throughout San Francisco Bay (Figure 1). In general, white croaker, shiner surfperch, and jacksmelt were successfully captured at 5-6 sites while other sport fish were collected at 2 - 3 widely dispersed sites (Table 1; Davis et al., 2002; Greenfield et al., 2003). In 1994, sampling was performed at these locations in addition to several other

locations widely distributed throughout San Francisco Bay (Fairey et al., 1997).

Composites contained a specified number of fish that varied according to species (Table 1). Target size classes for collection were based on legal size limits for sport fishing, though not all fish collected were of legal size for human consumption (Table 1).

Fish were collected during the summer months, with additional sturgeon sampling conducted in March and April. White croaker were also collected seasonally from the Oakland Inner Harbor site in 2000 to test for seasonal variation in organochlorine contaminant concentrations. Croaker were collected on March 7-8 (spring), June 16-20 (summer), September 26 (fall) and December 18-19 (winter). Three composites, each containing five fish, were analyzed for PCBs and other trace organic contaminants from each sampling period.

Collection gear included a 16 ft 1.25 in mesh size nylon stretch otter trawl, trammel nets (9 in and 4 in nylon mesh panels), gill nets (0.75 in, 2.25 in, 2.5 in, and 4 in monofilament mesh), and hook and line. A complete description of the field and laboratory sampling methods and a detailed cruise report (Moss Landing Marine Laboratories, 2000) are available from the San Francisco Estuary Institute (SFEI). Total length of each fish was measured in the field to the nearest cm, fish were wrapped in chemically cleaned Teflon sheeting, and frozen on dry ice for transportation to the laboratory. During dissection, the gonad tissue of the 12 croaker composites used in the seasonal study was weighed to determine the gonadal somatic index of each sample ($[\text{gonad tissue mass}/\text{body mass}] * 100$).

Laboratory analysis

Muscle sample preparation was performed using non-contaminating techniques in a clean room environment. Fish fillets were prepared in a fashion similar to the typical culinary preparation for each species (Table 1; Greenfield et al., 2003). Fish samples were dissected and composited in a similar manner as in the previous RMP fish sampling (SFBRWQCB, 1995; Davis et al., 1999). Fillets of muscle tissue were removed in 5 to 10 g portions with Teflon forceps and stainless steel cutting utensils. Equal weight fillets were taken from each fish to composite a total of at least 175 g. All samples were homogenized using either a Büchi Mixer B400[®] or a Brinkman Polytron[®] mixer, both equipped with titanium blades. Sample splits were taken for each analysis after homogenization.

Samples were analyzed in 1994, 1997 and 2000 for Hg, Se, PCBs, organochlorine pesticides, dibenzodioxins, dibenzofurans, and coplanar PCBs. Results for dioxins, furans, and coplanar PCBs are reported elsewhere (Greenfield et al., 2003). Analytical methods were described in SFBRWQCB et al.(1995). Briefly, aliquots analyzed for PCBs and organochlorine pesticides were extracted with methylene chloride:acetone (50:50) using pressurized fluid extraction (PFE) and extracts cleaned using gel permeation chromatography and fractionated using Florisil. Extracts were then analyzed by dual column (DB-5 and DB-17) gas chromatography with electron capture detection. Aliquots for Hg analysis were digested using nitric:sulfuric acid (70:30) and analyzed by a Flow Injection Mercury System.

Forty PCB congeners were measured and summed to obtain "sum of PCB congeners." Concentration of Aroclors 1248, 1254, and 1260 were estimated based on the congener data following Newman et al. (1998); these Aroclors were summed to obtain the "sum of Aroclors" for each sample. Six DDT compounds were summed to derive "sum of DDTs": p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD, and o,p'-DDD (U. S. EPA, 2000). Five chlordane compounds were summed to derive "sum of chlordanes": cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, and oxychlordane. Raw data on all summed and individual contaminant concentrations for 1994, 1997 and 2000, in addition to data on dioxins, coplanar PCBs, and estimated PBDE concentrations, are available at www.sfei.org.

QA measures included analysis of standard reference materials, lab duplicates, and matrix spikes. All data met the data quality objectives specified in the RMP Quality Assurance Project Plan (QAPP) (Lowe et al., 1999). For Hg in 2000, SRM (DORM2 dogfish muscle) recoveries averaged 97.2%, and all were within the $\pm 25\%$ criterion established in the QAPP (Greenfield et al., 2003). For each individual PCB congener in 2000, 95% of the SRM 2974 and SRM 2978 (freeze dried mussel tissue) analyses were within acceptable range ($\pm 35\%$) of the certified concentrations. Similarly, for the organochlorine pesticides, 86% of SRM 2974 and 75% of SRM 2978 analyses were within acceptable range ($\pm 35\%$) of the certified concentrations (Greenfield et al., 2003). Quality assurance results for 1994 and 1997 are reported elsewhere and all data collected in these years met RMP data quality objectives (SFBRWQCB, 1995; Fairey et al., 1997). Quality assurance reports prepared by the analytical laboratories are available from SFEI.

Historical data

In addition to RMP and BPTCP data, there are a number of data sets on Hg contamination in striped bass (filet tissue), and concentrations of Se, sum of PCB Aroclors, sum of DDTs, and sum of chlordanes in white sturgeon (filet tissue). Hg data extend from 1970 to the present. From 1970 to 1972, Hg in striped bass individuals was analyzed by California Department of Fish and Game's Water Pollution Control Laboratory (Interagency Committee on Environmental Mercury, 1971) using the same basic methodologies as the present analyses (sulfuric acid digestion followed by cold vapor atomic absorption spectroscopy). Although standard reference materials were not available at that time, quality assurance measures included duplicates, matrix spikes, reagent blanks, and intercalibration exercises with other laboratories (Dave Crane, California Department of Fish and Game, personal communication). For 18 sets of duplicate fish samples analyzed for Hg at the Water Pollution Control Lab between 1970 and 1972, the relative percent deviation was 9%, indicating reasonably high precision. This included six duplicate analyses of individual striped bass used in our results, which had an RPD of 8%. In 1999, striped bass from Suisun Bay were also analyzed for Hg as part of the CalFed Bay-Delta Mercury Project (Davis et al., 2003). These data were collected and analyzed by the same laboratory as for the RMP and BPTCP studies (California Department of Fish and Game, Moss Landing CA), and therefore have identical methods and quality assurance criteria.

Prior to the RMP and BPTCP, few data were collected on sum of Aroclors, DDTs, or chlordanes in fish from San Francisco Bay. One program that generated a limited data set was the Toxic Substances Monitoring Program (TSMP). The TSMP sampled

sturgeon from Suisun Bay from 1986 to 1992. In each year, the TSMP analyzed a single composite of four to six fillets for each species. Quality assurance measures for the TSMP were comparable to RMP and included reagent blanks, 10 percent sample duplicates, and standard reference materials. Lab results were within 95 percent confidence intervals of reference parameters and duplicate precision was adequate (Rasmussen and Blethrow, 1991; Rasmussen, 1993, 1995). However, reporting limits were relatively high (e.g., 50 ng/g for each PCB Aroclor, as compared to 10 or 25 ng/g for Aroclor equivalents in RMP data). Previous selenium data for white sturgeon were available from the TSMP (1992-1993) and the Selenium Verification Study (1986-1990). Selenium Verification Study samples were individual fillets from fish captured in San Pablo Bay and Suisun Bay. Quality assurance measures indicated adequate accuracy (6% RSD) and precision (6.8% average RSD) (White et al., 1988; White et al., 1989; Urquhart and Regalado, 1991).

Screening values and statistical analysis

U.S. EPA (2000) defines screening values as concentrations of target analytes in fish or shellfish tissue that are of potential public health concern. Exceedance of screening values is an indication that more intensive site-specific monitoring and/or evaluation of human health risk should be conducted. Screening values were taken from a northern California study by Brodberg and Pollock (1999) and were calculated using a consumption rate of 21 g fish/day (following Allen et al., 1996).

In seasonal and interannual comparisons, analysis of variance (ANOVA) was used to evaluate whether individual sampling periods (years or seasons) were significantly higher

than other sampling periods for all samples of a given species. Due to limited sample sizes for other data sets, these ANOVAs were conducted only among RMP and BPTCP sampling years (1994, 1997 and 2000). Spearman rank correlation coefficients were calculated to test for significant increases or decreases in average annual concentrations among all sampling years, including the RMP, BPTCP, and other studies.

Of the species sampled, four species had sufficient sample size to conduct ANOVA among 1994, 1997 and 2000: leopard shark, striped bass, shiner surfperch, and white croaker. Contaminant concentration comparisons among the three RMP and BPTCP sampling periods were performed using standard ANOVAs for unbalanced design (SAS Institute, 1990). Because of the large number of comparisons (16 contaminant-species combinations for temporal comparisons), significance of interannual variation was evaluated using Bonferroni protection ($\alpha = 0.05 / [16]$). For contaminant-species combinations exhibiting significant patterns, Tukey's Studentized Range (HSD) Test was conducted to evaluate among-year differences. ANOVA was also used for the 2000 seasonal comparison of trace organic contaminants in white croaker.

Based on examination of normal scores plots of residuals, contaminant concentration data were sometimes transformed to achieve normality prior to statistical analyses (Draper and Smith, 1998). Square root transformations were performed prior to interannual comparisons of Hg, PCBs, DDTs, and chlordanes. Log transformations were performed prior to seasonal evaluation of PCBs and chlordanes in white croaker and interannual comparisons of lipids. The arcsin (square root) transformation achieved best normal approximation for the gonadal somatic index.

Because of the potential influence of length or tissue lipid content on contaminant concentrations, ANOVAs were also conducted to assess interannual variation in length and lipids of each species. When ANOVA results indicated significant variation in length or lipid content and contaminant concentrations for the same species, stepwise regression was performed with indicator variables (dummy variables). This method makes it possible to determine whether interannual variation in contaminant concentrations results from changes in fish growth attributes (Tremblay et al., 1998). Both forward selection and backwards elimination methods were employed, with $\alpha = 0.05$ required to retain individual predictors; all results reported were consistent among these two methods. For striped bass, all available Hg data sets (the CDFG historic data, RMP data and the Davis et al. (2003) data; log transformed to achieve residual normality) were statistically compared using this method.

Long-term trends of wet weight contaminant concentrations were statistically evaluated by computing the Spearman rank correlation coefficient (r_s) of year versus average contaminant concentration (Daniel, 1990). Previous studies have documented a significant relationship between tissue lipid content and organochlorine concentrations (Reinert et al., 1972; Larsson et al., 1993; Kidd et al., 1998; Amrhein et al., 1999), suggesting that long-term trends in trace organic contaminants may be associated with temporal variation in percent lipid. Therefore, in addition to wet weight trends, trends in lipid corrected concentrations of PCBs, DDTs, and chlordanes in sturgeon were also estimated. Lipid corrected trends were estimated by obtaining the residuals of contaminant versus percent lipid regressions (following Hebert and Keenleyside, 1995), averaging these residuals by year, and conducting Spearman rank correlation coefficient

analysis of the residuals versus year relationship. When contaminants were regressed versus percent lipids, transformations were required to fit the required assumptions of linear regression. PCBs and chlordanes were log transformed. Due to non-normal residual error distribution after common transformations, DDTs were transformed using a modulus power transformation (response variable = $[(DDT + 1)^{-0.5} - 1]/0.5$) (Draper and Smith, 1998).

Results

General contamination patterns in 2000

In the summer of 2000, Hg concentrations were highest in leopard shark, intermediate in white sturgeon and striped bass, and lowest in jacksmelt and shiner surfperch (Table 2). PCBs, DDTs, and chlordanes were all highest in white croaker and shiner surfperch and lowest in leopard shark and California halibut (Table 2). Screening value exceedances have been reported previously (Fairey et al., 1997; Davis et al., 2002; Greenfield et al., 2003) and will be briefly updated here. Of all fish samples collected and analyzed in 2000, 90% exceeded screening values for PCBs (sum of Aroclors; 72 exceedances of 80 samples total), 38% exceeded screening values for Hg (51 exceedances of 134 samples total), 18% exceeded screening values for dieldrin (15 of 80 samples), and 4% exceeded screening values for DDTs (3 of 80 samples). None of the 80 samples analyzed for chlordanes exceeded human health screening values.

Seasonal variation

In white croaker samples (skin-on fillets) significant variation in PCB concentration was explained by sampling period (ANOVA $R^2 = 0.69$; $p = 0.019$). Concentrations were significantly lower ($p < 0.05$) in spring (mean = 115 ng/g), as compared to summer (mean = 277 ng/g) and fall (mean = 314 ng/g) (Figure 2b). White croaker also exhibited significant seasonal variation in chlordane concentrations (ANOVA $R^2 = 0.61$; $p = 0.048$). As with PCBs, concentrations were relatively low in spring (mean = 4.2 ng/g), as compared to other sampling seasons (mean = 13.1 ng/g; Figure 2d). White croaker did not exhibit significant seasonal variation in DDT concentrations (ANOVA $R^2 = 0.23$; $p = 0.54$), though concentrations were relatively low in spring for two of the three composites (Figure 2c).

Croaker exhibited highly significant seasonal variation in percent lipid ($R^2 = 0.87$; $p = 0.0006$) and gonadal somatic index ($R^2 = 0.98$; $p < 0.0001$). Similarly to PCBs and chlordanes, tissue lipid concentrations were significantly lower in spring (mean = 1.6 percent) than in other seasons (mean = 5.7 percent; Figure 2a). The gonadal somatic index was significantly greater in winter and spring (means of 7.4 and 6.4, respectively) than summer and fall (both means of 1.2; Figure 2e).

Interannual variation

Of the four species with multiple samples in 1994, 1997, and 2000, only striped bass exhibited statistically significant variation in PCB concentrations between 1994 and 2000 (Table 3). PCB concentrations in striped bass were significantly higher in 1994 than they

were in 1997 and 2000. Significant interannual variation in DDT concentrations was observed for striped bass, shiner surfperch, and white croaker (Table 3). The direction of changes in DDT over time varied among species. In both shiner surfperch and white croaker, DDT concentrations were significantly higher in 1997 than in 1994 or 2000. In contrast, striped bass exhibited significantly elevated DDT concentrations in 1994 as compared to the other two years.

Unlike the other contaminants, sum of chlordanes exhibited a possible decrease in concentrations among the three years for several species sampled since 1994. Significantly lower chlordane concentrations in 2000 were observed for striped bass and white croaker. For both species, 2000 was significantly lower than 1994 and 1997. Striped bass also exhibited a significant decline from 1994 to 1997. A nonsignificant declining trend was observed in leopard shark chlordanes ($R^2 = 0.49$; Bonferroni corrected $p = 0.07$; $n = 19$) (Figure 3).

Significant variation among years in length or percent lipid was not evident in striped bass or leopard shark. Length or lipid did significantly vary for shiner surfperch and white croaker (Table 3). Stepwise regression analysis was conducted to test whether variation in length or lipid content was associated with the significant temporal variation in chlordanes in white croaker or DDTs in croaker or shiner surfperch. For DDT concentrations in shiner surfperch, there was a significant positive effect of length (partial $R^2 = 0.09$; $p = 0.019$; $N = 43$) and a significant positive effect for samples collected in 1997, as compared to 1994 and 2000 (partial $R^2 = 0.32$; $p < 0.0001$). Once length effects were taken into account, there was no significant relationship between percent lipid and DDTs in shiner surfperch. These results indicate that, once length effects are taken into

consideration, shiner surfperch still exhibit elevated DDT concentrations in 1997. Scatter plots of the data show elevated 1997 concentrations at a given length or lipid content (Figures 4a and 4b).

For DDT concentrations in white croaker, there was a significant positive effect of both length (partial $R^2 = 0.23$; $p < 0.0001$; $N = 53$) and percent lipid (partial $R^2 = 0.40$; $p < 0.0001$). There was also a statistically significant but very weak negative effect for samples collected in 2000, as compared to other years (partial $R^2 = 0.04$; $p = 0.017$). Graphical analyses suggest that the significantly elevated concentrations in 1997 may result from the fact that 1997 fish were higher in lipid content than other years (Figure 4d).

For chlordane concentrations in white croaker, there was a significant positive effect of both length (partial $R^2 = 0.15$; $p = 0.0001$; $n = 53$) and percent lipid (partial $R^2 = 0.30$; $p < 0.0001$). There was also a statistically significant negative effect for samples collected in 2000 (partial $R^2 = 0.13$; $p = 0.001$) and a significant but weak negative effect for samples collected in 1997 (partial $R^2 = 0.05$; $p = 0.018$). These results indicate that when possible length and lipid effects are accounted for, croaker filet samples collected in 1997 and 2000 have lower chlordane concentrations than samples collected in 1994.

Striped bass was the only species to exhibit significant interannual variation for all four contaminant classes, including Hg (Table 3). Hg concentrations in striped bass were significantly higher in 1997 than they were in 1994 and 2000. Backwards elimination stepwise regression was conducted to evaluate interannual variation in the length versus Hg relationship for striped bass. Data were used from 1970, 1971, 1972, 1994, 1997, 1999, and 2000, with a separate indicator variable for each year. The final model had an

R^2 of 0.35 and retained two variables: length and the indicator variable for 1997. The model indicated a statistically significant relationship between length and Hg for all years ($p < 0.0001$) and a significant increase in Hg concentration for 1997 ($p = 0.0001$) as compared to all other years (Figure 5).

Long-term trends

Of the five contaminant versus species combinations, DDTs in sturgeon exhibited a significant downward trend ($p < 0.02$; Table 4). No other combination was statistically significant, although a negative Spearman rank correlation coefficient (r_s) was observed for all contaminants except Hg in striped bass (Table 4).

In most cases, graphical analysis of trend plots supported results of the Spearman rank correlation coefficient analysis. DDT concentrations in white sturgeon do appear to be declining (Figure 6).

When contaminant data were corrected for lipid content, significant patterns were not observed for PCBs, DDTs, or chlordanes in white sturgeon. Wet weight sturgeon chlordanes concentrations showed no clear trend (Figure 7a). For these fish, chlordanes concentrations were significantly related to percent lipid (linear regression of log transformed data; $n = 13$; $R^2 = 0.53$; $p = 0.0033$). When the residuals of the log chlordanes versus log lipid relationship were plotted, a non-significant declining trend was observed ($r_s = -0.64$; $p = 0.10$; Figure 7b).

For sturgeon Se concentrations, median concentrations were similar in all years with the exception of elevated concentrations in 1990 (Figure 8). In 1990, the median wet weight Se concentration was $3.6 \mu\text{g/g}$.

Discussion

Consistent with previous studies of fish contamination in San Francisco Bay (Fairey et al., 1997; Davis et al., 2002), contaminant concentrations in 2000 varied widely among fish species. As in 1994 and 1997, the large and long-lived leopard shark, striped bass, and white sturgeon had relatively high Hg concentrations in 2000. Additionally, in 2000, the fattiest fish species, white croaker and shiner surfperch, had the highest concentrations of PCBs, DDTs, and chlordanes, as these trace organic contaminants tend to accumulate in species with higher tissue lipid content (Stow et al., 1997; Davis et al., 2002).

In San Francisco Bay, fish contaminant concentrations fluctuated at seasonal and interannual time scales, but didn't generally exhibit long-term trends. Analysis of variance indicated seasonal variation in trace organic contaminants in white croaker and interannual fluctuations for many contaminant-species combinations. A long-term decline was apparent in DDT in white sturgeon but was not apparent for other contaminants in sturgeon or striped bass.

Seasonal variation

Seasonal variation in trace organic contaminants in white croaker filet tissue was significant. Samples from croaker collected in the spring were less contaminated with PCBs and chlordanes than samples from other seasons. This seasonal variation should be

taken into account in evaluation of human health risks from consumption of white croaker, as exposure will be lower in the spring. Furthermore, if health agencies want a worst-case assessment of potential human exposure to trace organic contaminants, white croaker should not be sampled during the spring.

Research on croaker in southern California indicates that they spawn in January and February, and have lower body condition during spawning. This suggests that energy normally used for somatic tissue is transferred to reproductive tissue development and allocated toward spawning behavior (Love et al., 1984). In our study, the seasonal variation in trace organic contaminant concentrations corresponded with similar variation in lipid concentrations. There are several possible mechanisms that could explain reduced contaminant and lipid content of the spring croaker samples. The increased gonadal somatic index suggests that energetic resources were allocated toward reproductive activity. Lipids may have been transferred from the sampled filet tissue towards the gonads or other organs, followed by transfer of the associated contaminants. In female fish, some of the contaminants may have been lost during spawning (Larsson et al., 1993), though this loss is negligible in many fish species (Niimi, 1983; Madenjian et al., 1998). Alternatively, cooler temperatures during the winter may have resulted in lower feeding rates, followed by decline of lipid content in the sampled muscle tissue, and repartitioning of the contaminants to lipid storage areas.

Interannual variation

In San Francisco Bay fish, interannual variation was apparent for almost every contaminant monitored. Examples include elevated striped bass Hg in 1997, elevated

striped bass PCBs in 1994, and elevated DDTs in both shiner surfperch and white croaker in 1997. The existence of this interannual variation suggests that popular sport fish should continue to be analyzed for contamination every few years. For all of the contaminants discussed in this report, portions of the San Francisco Estuary are on a regulatory list of impaired water bodies, indicating that the contaminants present potential hazards to wildlife or human uses of the water body (SFBRWQCB, 2001). Fish contaminant concentrations must be accurately estimated because regulatory guidelines for allowable contaminant loading into San Francisco Bay are often determined using current and target concentrations in fish (e.g., Johnson and Looker, 2003).

Interannual variation in trace organic contaminants sometimes correlated with variation among years in fish lipid content. For example, white croaker captured in 1997 had elevated lipid content, corresponding to elevated concentrations of DDTs. Previous studies vary in the strength of the relationship between organochlorine concentrations and tissue lipid content. Trace organochlorine contaminants are partitioned in fatty tissue (Reinert et al., 1972) and may be positively correlated with tissue lipid content in examinations of filet tissue (Kidd et al., 1995) and whole body samples (Larsson et al., 1993; Amrhein et al., 1999). A laboratory study indicated higher bioaccumulation factors in fattier fish of a given species, when dietary lipid régime was held constant (Dabrowska et al., 1999). However, some studies show no significant effect of lipid content on contaminant concentrations, when length effects are accounted for (Stow, 1995; Stow et al., 1997). In our study, lipid concentrations were significantly related to organochlorine pesticides in white croaker and shiner surfperch filet tissue. This correlation could result from increased retention of environmental contaminants by fattier fish, differential

partitioning of lipids and contaminants to tissues not measured (Amrhein et al., 1999), or a positive association between lipid content and fish trophic position (Kidd et al., 1998). Regardless of the mechanism, correlation with lipid concentrations should continue to be assessed when evaluating variation among sampling years.

Interannual fluctuations were particularly apparent for striped bass, which exhibited significant interannual variation in all contaminant classes, but did not exhibit spatial variation among sampling locations (Davis et al., 2002; Greenfield et al., 2003). Striped bass had significantly higher Hg concentrations in 1997, suggesting that Hg bioavailability may have been higher that year. Striped bass PCB concentrations were lower after 1994 but there was no significant variation in lipid content among the three years and striped bass sampled in 1994 (when PCBs were higher) were actually smaller than other sampling years (Greenfield et al., 2003). Continued monitoring is important for striped bass, which is the most popular sport fish in the region (SFEI, 2000), and exhibited significant interannual variation in all contaminants. The lower interannual variation for white croaker, leopard shark, and shiner surfperch suggests that these species would be more sensitive indicators of long-term trends.

When length effects were accounted for, striped bass Hg concentrations were significantly higher in 1997 than other years sampled by the RMP and BPTCP. Possible explanations for the observed interannual variation in striped bass Hg and trace organic contaminant concentrations include variation in movement patterns, diets, or populations sampled. In San Francisco Bay, striped bass exhibit seasonal migration, large home ranges, and variable movement patterns (Calhoun, 1952). Different bass subpopulations are exposed to different contaminant concentrations in the Hudson River (Zlokovitz and

Secor, 1999) and possibly in San Francisco Bay (Davis et al., 2002). Another possible explanation for 1997 increases in bass Hg is that the amount of bioavailable Hg in the Estuary varied among years. In January of 1997, there was a flood event, which may have flushed bioavailable Hg into the Estuary, evidenced by increases in water methylmercury concentrations at Sacramento River monitoring sites (Domagalski, 1998, 2001). Although concentrations were not elevated in other Estuary fish species, striped bass exhibit considerable upstream migration (Calhoun, 1952), which may expose them to elevated Hg in the Sacramento-San Joaquin Delta.

Long-term Trends

When multiple data sets were combined for San Francisco Bay, most contaminants did not exhibit long-term trends over the past several decades. The patterns of individual contaminants may stem from methodological differences among data-sets, the date when contaminant use was curtailed, the present loading rate, or differences in environmental degradation rates.

PCBs showed no recent trend in white sturgeon despite evidence of recent declines in sediments (Venkatesan et al., 1999) in addition to declining trends in bivalves since the late 1980s (Gunther et al., 1999). For PCBs, the apparent lack of trend may partially result from analytical differences among data sets. The TSMP had relatively high detection limits (50 ng/g wet weight for each Aroclor) and non-detects were treated as zero values. This may have resulted in higher concentrations in the late 1980s than were reported. Additionally, the sample sizes in the TSMP for PCBs and other trace organic contaminants were quite small, generally consisting of one composite of four to six sturgeon for each year. Nevertheless, a

separate study of liver contaminant concentrations in starry flounder and white croaker also shows no significant PCB trends in most San Francisco Bay locations between 1984 and 1991 (Stehr et al., 1997). Other potential explanations for the apparent lack of PCB decline in fish include continued loading to the watershed from local sources or slow declines in sediment due to very slow degradation rates (Davis, In press).

Risebrough (1995) previously observed that PCB concentrations in shiner surfperch collected by the BPTCP (1994 median of 160 ng/g) were close to an order of magnitude lower than samples collected in 1965 (ranging from 400 to 1200 ng/g). It is likely that the 1970s ban of PCB production led to an initial rapid decline followed by a much more gradual decrease, approximating steady-state conditions (Risebrough, 1995; Schmitt and Bunck, 1995; Stow et al., 1999). Available evidence did not indicate further declines in fish PCBs since the mid-1980s, and it will likely take decades for significant further reductions of PCBs to occur in San Francisco Bay sediments and water (Davis, In press).

The apparent decline of DDTs, combined with the low frequency of screening value exceedances in 2000, suggest that DDTs may be of lower management concern relative to other contaminants. Most DDT use was curtailed in the early 1970s, but bivalves, sediments, and fish still exhibited decreasing DDT concentrations in the 1980s and early 1990s (Gunther et al., 1999; Venkatesan et al., 1999; this study). DDT concentrations in shiner surfperch have declined almost two orders of magnitude since 1965 sampling (Risebrough, 1969), and have continued to decline from the 1980s through the present. The significant decline in DDTs may be explained by higher degradation rates (Howard, 1991; Mackay et al., 1992) or lower loading rates for DDTs than other trace

contaminants, hypotheses currently being evaluated using mass balance models for San Francisco Bay (following Davis, In press).

Interannual variation ANOVAs indicated significant declines in chlordane concentrations since 1994 for white croaker and striped bass, and a nonsignificant declining trend for leopard shark. For chlordanes in white sturgeon, graphical analysis of lipid-corrected concentrations suggested possible declines since the mid-1980s. If chlordane concentrations in fish are indeed decreasing, this may be a result of the recent use history of this suite of compounds. Overall chlordane use in California exhibited a dramatic increase in 1986 and 1987 (when compared to the previous decade), followed by an abrupt decline in 1988, when banned in the U.S. (Shigenaka, 1990). In contrast, PCB sale and production was banned by 1979 and a primary source of mercury to the region (mining operations) was reduced by the early 20th century (Nriagu, 1994; Alpers and Hunerlach, 2000). In general, after a suite of compounds is banned, contamination in fish and wildlife exhibits an initial rapid decline followed by a much more gradual decrease (Risebrough, 1995; Schmitt and Bunck, 1995; Stow et al., 1999). In three sampling periods since 1994, chlordanes declined in three of four fish species. However, since the 1980s, sturgeon declines were not statistically significant and a separate study of starry flounder and white croaker generally did not observe declining liver tissue chlordane concentrations in the 1980s (Stehr et al., 1997). The observation of apparent declines in the 1990s but not the 1980s (Stehr et al., 1997) may indicate that chlordanes entered a rapidly declining phase shortly after use curtailment in the late 1980s. PCBs were banned in the 1960s and 1970s, and are not likely to still be in a rapidly declining phase (Risebrough, 1995). When compared to PCBs, chlordanes have higher water

solubility, creating the potential for volatilization (Mackay et al., 1992), and higher degradation rates (Howard, 1991). The relative importance of degradation, volatilization, and source reduction is currently being compared by mass balance modeling of chlordane fate in the Estuary (following Davis, In press).

Hg concentrations in striped bass showed no apparent trend from the early 1970s to the late 1990s. Trends in watershed loading of Hg are likely to be weak because of the widespread and historic sources (Nriagu, 1994; Domagalski, 1998; Alpers and Hunerlach, 2000; Domagalski, 2001). A major use of Hg in the region occurred over a century ago, and loading was reduced in the early 20th-century (Nriagu, 1994). Between 1850 and 1900, large amounts of Hg were extracted from mines in the watershed of San Francisco Bay. Much of this Hg was used to amalgamate gold in gold mining operations in the Sierra Nevada (Nriagu, 1994; Alpers and Hunerlach, 2000). As these wide-spread and poorly regulated historic mercury and gold mining operations remain a significant source of Hg to the watershed (Nriagu, 1994; Domagalski, 2001), it may take decades or even centuries before the source inputs are successfully curtailed. Furthermore, the active sediment layer within the Estuary and erosion of buried sediments in the northern Estuary may provide continuous sources of total Hg to the overlying water column (Jaffe et al., 1998; Fuller et al., 1999). Our failure to detect a trend in fish contrasts with the long-term decreases observed in sediment Hg concentrations since the 1950s (Hornberger et al., 1999). Fluctuation in Hg bioavailability to fish likely stems from interannual variation in a number of factors: fish ecology, watershed loading (Domagalski, 1998, 2001), contaminated sediment exposure (Jaffe et al., 1998; Fuller et al., 1999), and net methylmercury production rates (e.g., Gilmour et al., 1992).

Although sturgeon Se concentrations were elevated in 1990 relative to other years, long-term directional trends were absent. Recent trends in bioavailable Se may be obscured by changes in food web uptake and local discharge. The 1986 invasion of Potamocorbula amurensis bivalves into the Estuary has increased Se contamination in the benthic food web because P. amurensis bioaccumulate Se to higher concentrations than native bivalves (Linville et al., 2002). Bivalves are a major dietary component of North Bay sturgeon (McKechnie and Fenner, 1971; Urquhart and Regalado, 1991), creating the potential for increased dietary uptake. However, Se loads from local oil refineries in San Francisco Bay and the Sacramento-San Joaquin River Delta were considerably lower in 1999 than 1986-1992, due to stricter regulation on local discharge (Luoma and Presser, 2000). A major source of Se is agricultural runoff, and future management of the San Joaquin River and watershed could significantly impact loading of Se to the San Francisco Estuary (Luoma and Presser, 2000). Continued long-term monitoring of sport fish contamination trends will help ascertain the cumulative effect of changes in bioavailability and loading of Se and other legacy contaminants.

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Table Captions:

Table 1. Attributes and locations of fish sampled in the summer of 2000. Numbers in the location cells indicate number of composite samples collected. When two numbers are present in a cell, the second number indicates individual fish that were analyzed at that site for Hg.

Table 2. Summary statistics for Hg and organochlorines, for all San Francisco Bay fish captured in the summer of 2000. Data are medians for each fish species, wet weight (ND = Not detected). For organics, ‘ Σ ’ indicates ‘sum of.’

Table 3. Results of analysis of variance for variation in fish contaminant concentration (wet weight) or growth attribute among the years 1994, 1997, and 2000. Model R^2 values are presented. Boldface values are statistically significant with Bonferroni correction ($\alpha < 0.02$ in all cases). The first numeric column presents sample size (total number of fish composites across all years) for Hg, followed by sample size for all other contaminants and growth attributes.

Table 4. Results of spearman rank correlation coefficient (r_s) analysis between sampling year and annual mean contaminant concentration in selected fish species. N = number of sampling years for which comparable data were available.

Tables

Table 1:

Species	Number of fish per composite	Legal size (cm)	Size range collected (cm)	Tissue sampled ^a	Number of composites analyzed					
					South Bay Bridges	Oakland Harbor	San Leandro Bay	S.F. Waterfront	Berkeley	San Pablo Bay
Jacksmelt	5	No Limit	24-30	ms	3	3	-	3	3	3
Shiner Surfperch	20	No Limit	8-15	ms	3	3	3	3	3	3
White Croaker	5	No Limit	21-30	ms	3	3	-	3	3	3
Striped Bass	2-3	> 46	45-78	m	3, 9	-	-	-	3, 11	3, 12
Leopard Shark	3	> 91	86-134	m	2, 12	-	-	-	2, 11	2, 9
California Halibut	3	> 56	51-98	m	-	-	-	2, 6	-	1, 4
White Sturgeon	3	117 – 183	115-182	m	2, 6	-	-	-	-	2, 6

a ms = muscle with skin; m = muscle without skin

Table 2.

	Length	Hg	Lipid	Σ Aroclors	Σ PCB Congeners	Σ DDTs	Σ Chlordanes	Dieldrin
	(cm)	($\mu\text{g/g}$ wet)	%	(ng/g wet)	(ng/g wet)	(ng/g wet)	(ng/g wet)	(ng/g wet)
Screening Value		0.30		20		100	30	2
California Halibut	70	0.21	0.4	24	22	6.0	ND	ND
Jacksmelt	27	0.06	1.4	39	34	21	1.2	ND
Leopard Shark	98	0.83	0.4	20	13	5.1	ND	ND
Shiner Surfperch	11	0.08	2.6	207	135	37	8.1	ND
Striped Bass	52	0.28	1.1	48	36	23	1.2	ND
White Croaker	27	0.21	4.0	278	191	61	9.4	ND
White Sturgeon	132	0.29	0.7	52	43	13	1.3	ND

Table 3.

Species	Sample Size	Contaminant				Attribute	
	(Hg, All others)	Mercury	PCBs	DDTs	Chlordanes	Length	% Lipid
White croaker	54, 54	0.06	0.07	0.23*	0.26*	0.13	0.44*
Shiner surfperch	44, 44	0.10	0.11	0.36*	0.12	0.54*	0.55*
Striped bass	64, 29	0.47*	0.67*	0.41*	0.73*	0.31	0.03
Leopard shark	45, 19	0.02	0.22	0.24	0.49	0.01	0.35

* Bonferroni corrected $p < 0.02$

Table 4.

Contaminant	Species	Data Range	N	r_s	p-value	Data Sources
PCBs	Sturgeon	1986-2000	8	-0.38	$p > 0.2$	1, 2
DDTs	Sturgeon	1986-2000	8	-0.86	$p < 0.02$	1, 2
Chlordanes	Sturgeon	1986-2000	8	-0.50	$p > 0.2$	1, 2
Mercury	Striped Bass	1970-2000	7	0.11	$p > 0.2$	1, 3-5
Selenium	Sturgeon	1986-2000	10	-0.49	$p > 0.1$	1, 6

Data sources: 1. RMP and BPTCP data (Fairey et al., 1997; Davis et al., 2002), and the present study. 2. TSMP data (Rasmussen and Blethrow, 1991; Rasmussen, 1993, 1995). 3. Interagency Committee on Environmental Mercury (1971). 4. CDFG, unpublished data. 5. CalFed data (Davis et al., 2003). 6. Selenium Verification Study (White et al., 1988; 1989; Urquhart and Regalado, 1991).

Figure Captions:

Figure 1. Sampling locations for 2000 RMP fish contamination monitoring.

Figure 2. Seasonal variation in attributes of white croaker composite samples collected from Oakland Inner Harbor in 2000. Triangles are concentrations in each composite sample analyzed. a) Tissue lipid content (%). b) PCBs (as sum of congeners; ng/g wet). c) DDTs (ng/g wet). d) Chlordanes (ng/g wet). e) Gonadal somatic index ([gonad mass/whole body mass] * 100).

Figure 3. Change in chlordanes (ng/g wet) over consecutive RMP sampling periods. Points are concentrations in each sample analyzed. Bars indicate median concentrations. Capital letters indicate statistically significant difference in years by ANOVA ($p < 0.10$; Bonferroni corrected for multiple comparisons). a) Leopard shark. b) Striped bass. c) Shiner surfperch. d) White croaker.

Figure 4. Total DDTs (ng/g wet) versus length (cm) and lipids (%) in selected fish species. Data taken from 1994 (circles), 1997 (squares) and 2000 (triangles). a) Length versus DDTs in shiner surfperch. b) Lipids versus DDTs in shiner surfperch. c) Length versus DDTs in white croaker. d) Lipids versus DDTs in white croaker.

Figure 5. Mercury concentrations in striped bass in the 1970s and 1990s. Gray bars indicate annual median concentrations. To correct for variation in fish length, all plotted

data have been calculated for a 55 cm fish using the residuals of a length vs log(Hg) relationship. Asterisk above 1997 indicates significant difference from overall length versus mercury regression (see text). Data were obtained from CDFG historical records (1970-1972), a CalFed-funded collaborative study (1999), and the Regional Monitoring Program (1994, 1997 and 2000). Note log scale on y-axis.

Figure 6. Long-term patterns in white sturgeon total DDT concentrations (ng/g wet wt.). Each data point represents a composite sample of 2 to 6 sturgeon. Data were obtained from the Toxic Substances Monitoring Program (1986 through 1992) and the Regional Monitoring Program (1994 through 2000).

Figure 7. Long-term patterns in white sturgeon chlordane concentrations (sum of 5 chlordanes). Each data point represents a composite sample of 2 to 6 sturgeon. Data source as in Figure 6. a) Wet weight chlordane concentrations (ng/g). b) Lipid-corrected chlordane concentrations. The y-axis is the residual variation in chlordane concentrations from a chlordane versus tissue lipid regression.

Figure 8. Long-term patterns in white sturgeon selenium concentrations. Gray bars represent median concentrations. Data were obtained from the Selenium Verification Study (1986 through 1990), the Toxic Substances Monitoring Program (1986 through 1993) and the Regional Monitoring Program (1994 through 2000).

Figures (following pages):

Figure 1.

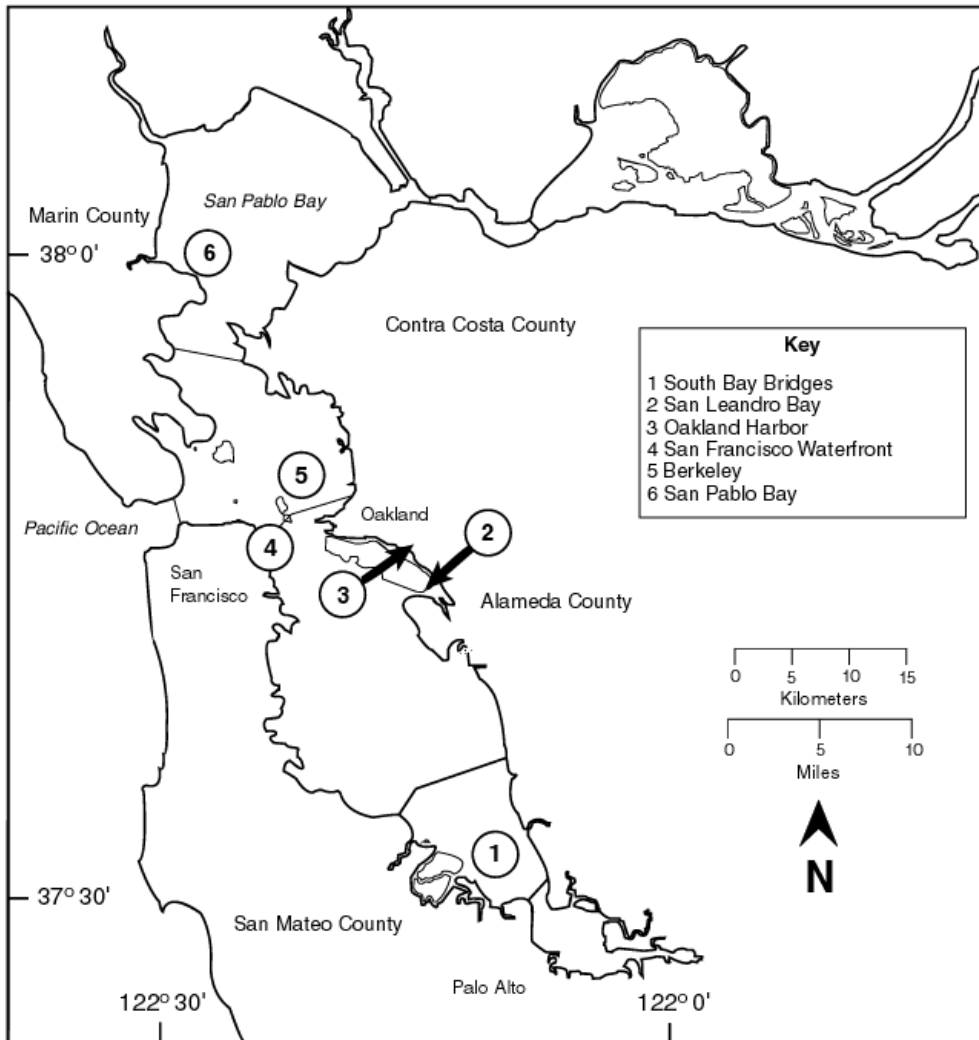


Figure 2

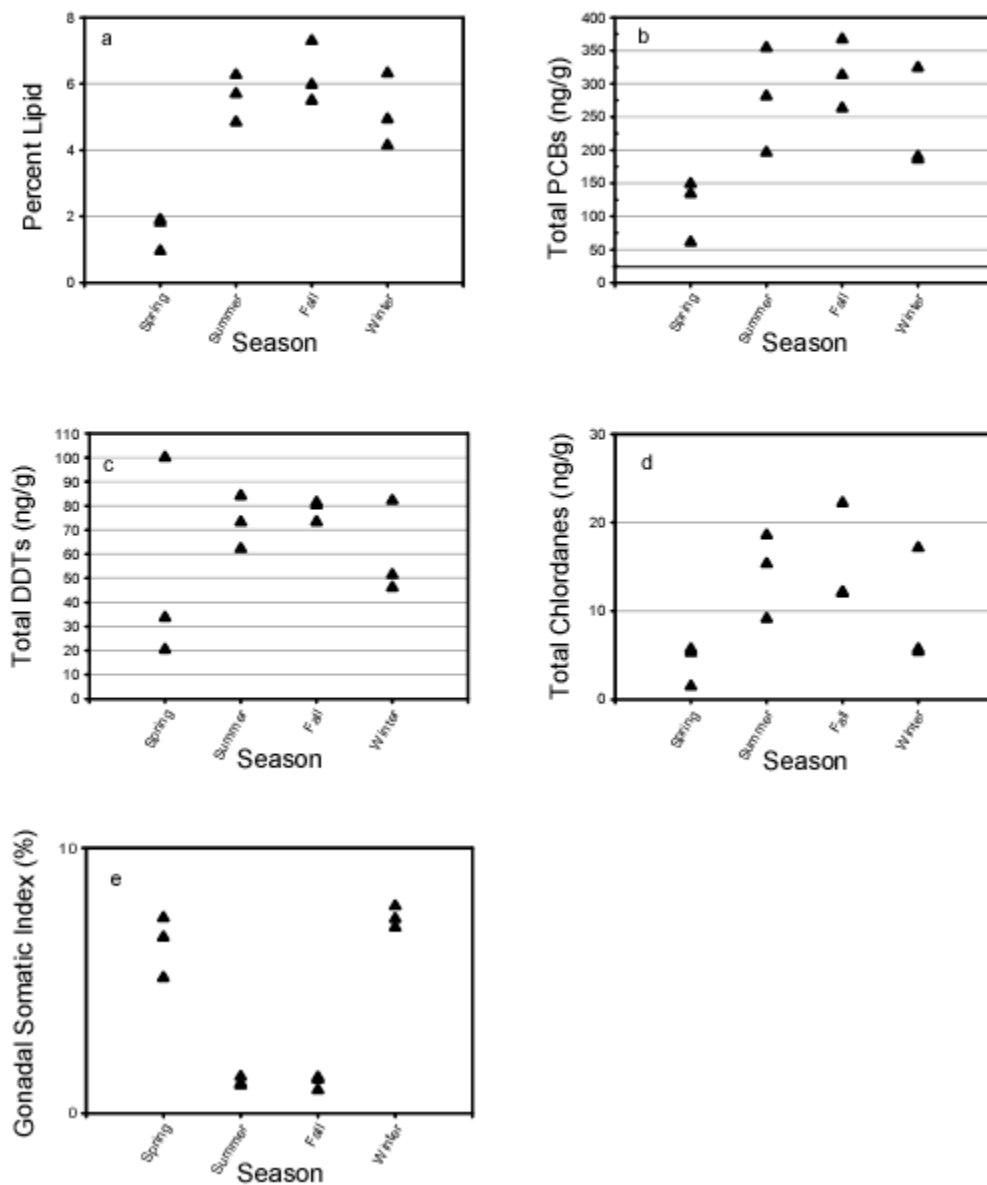


Figure 3

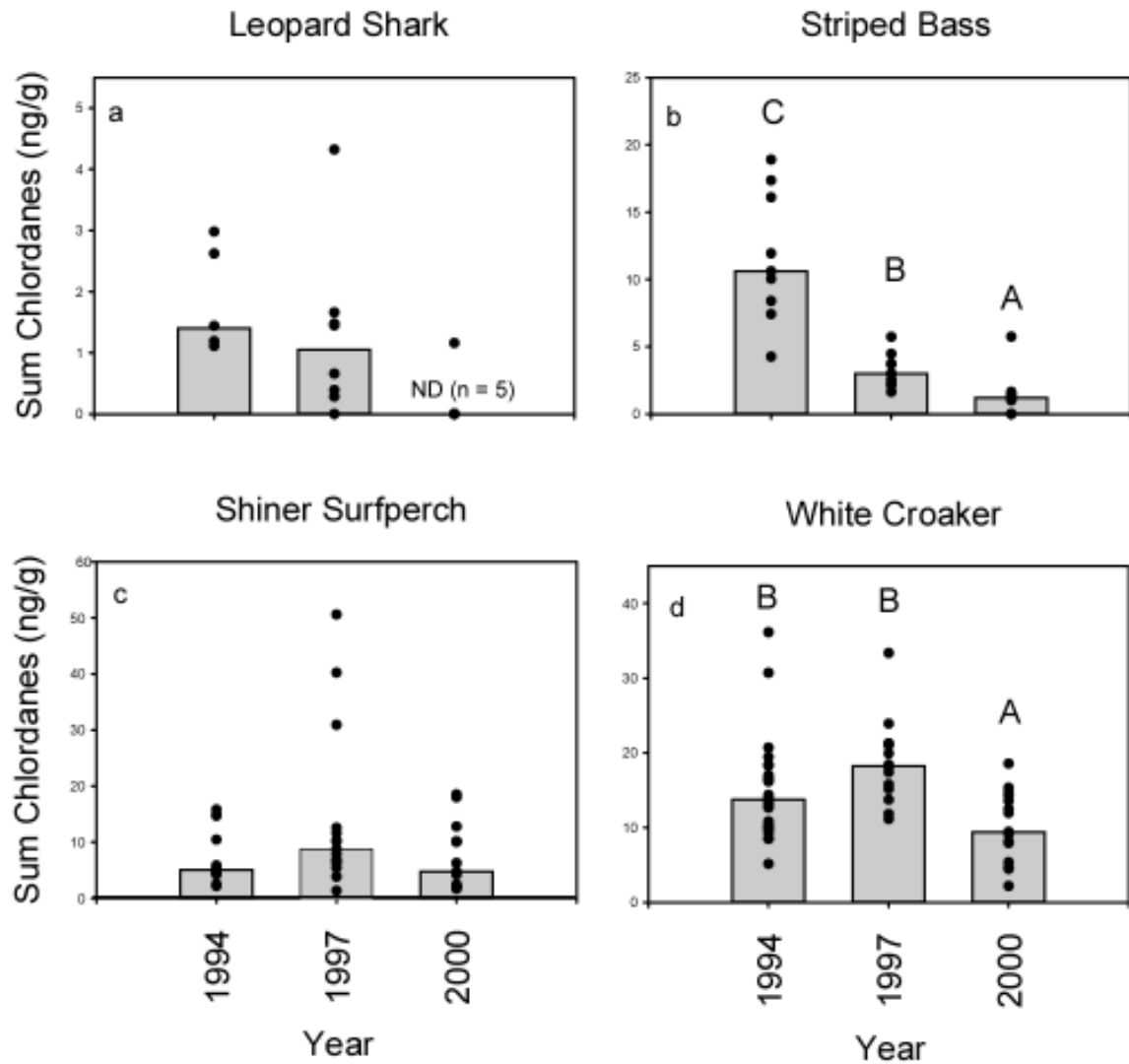


Figure 4

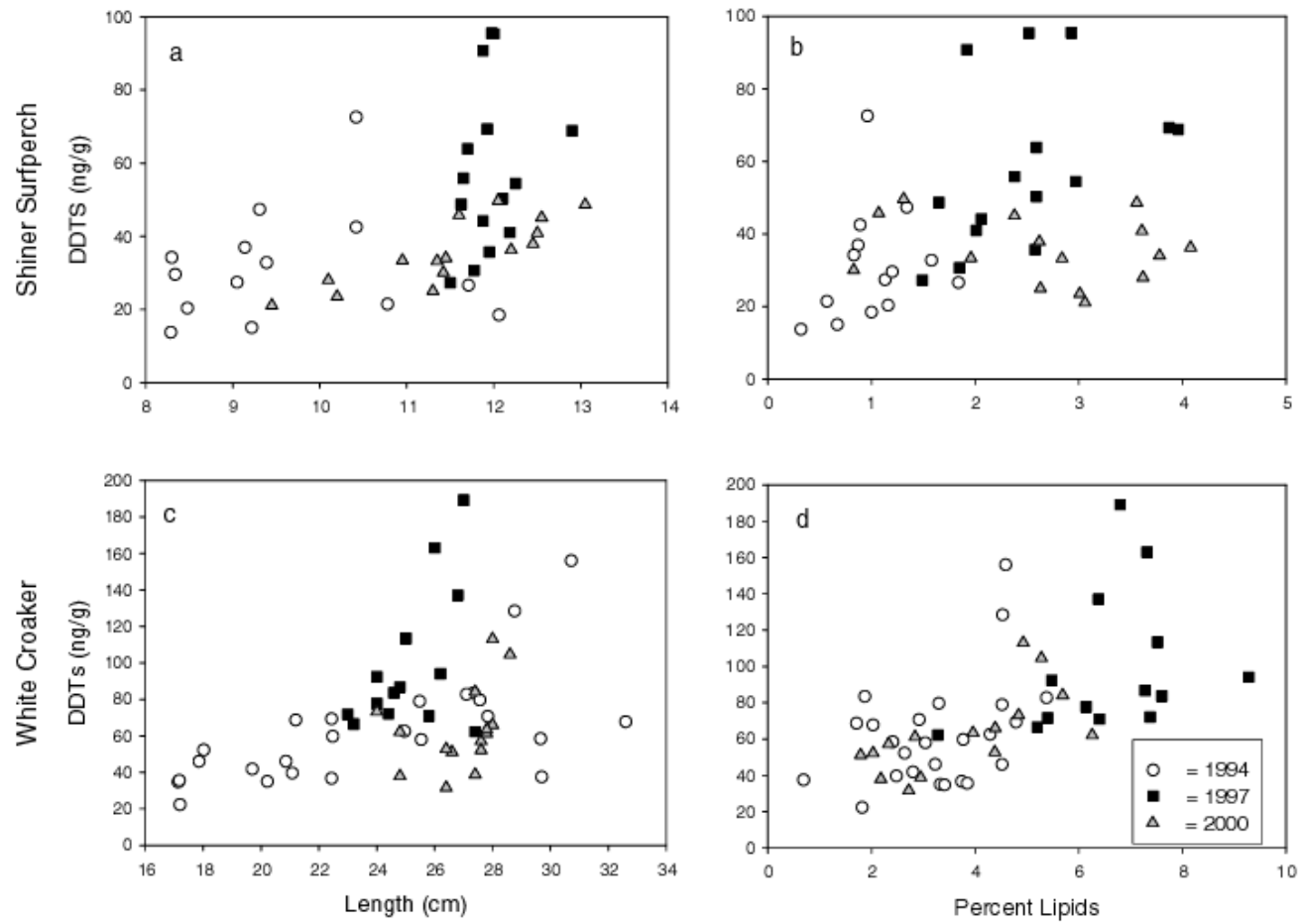


Figure 5.

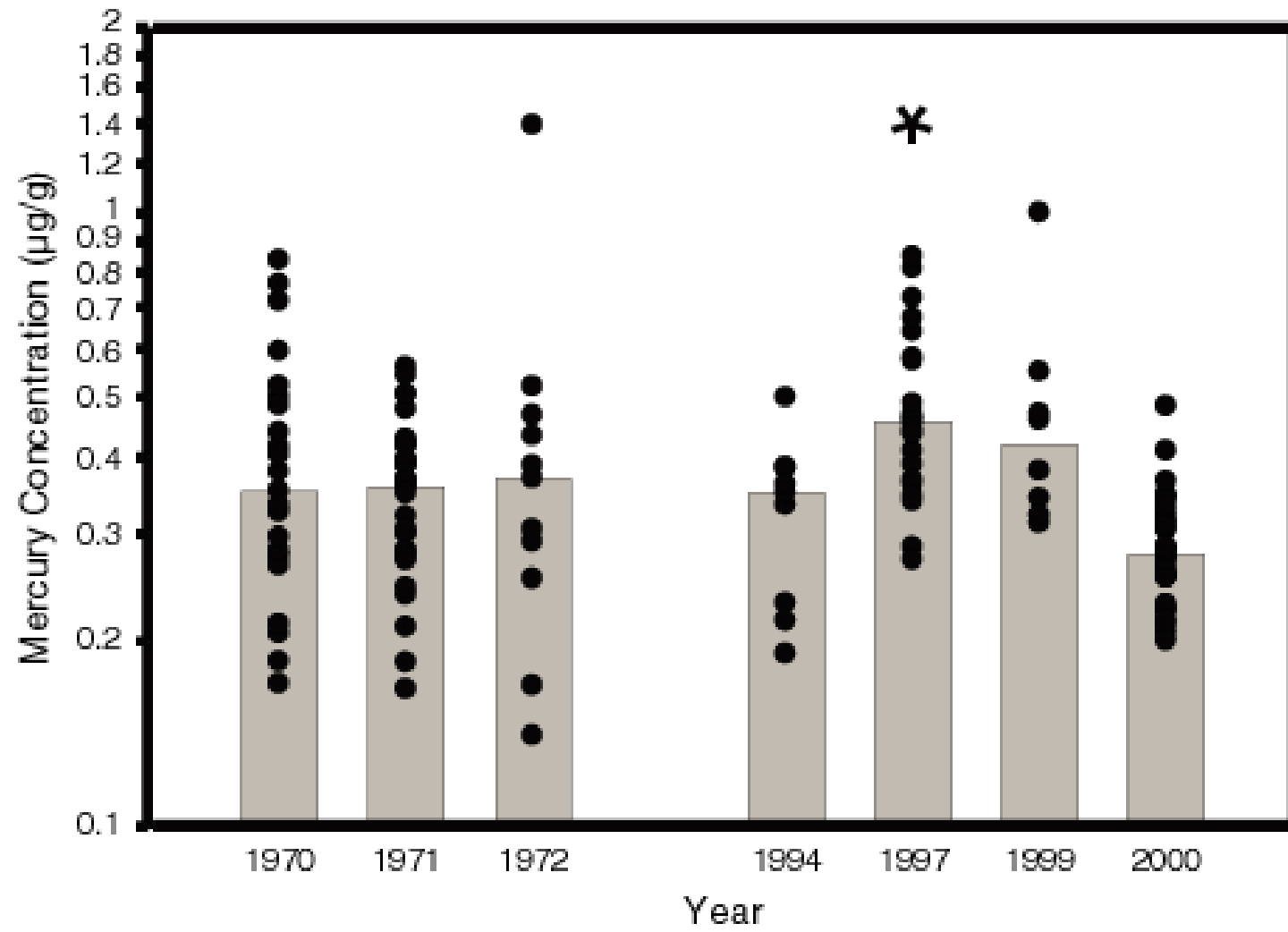


Figure 6

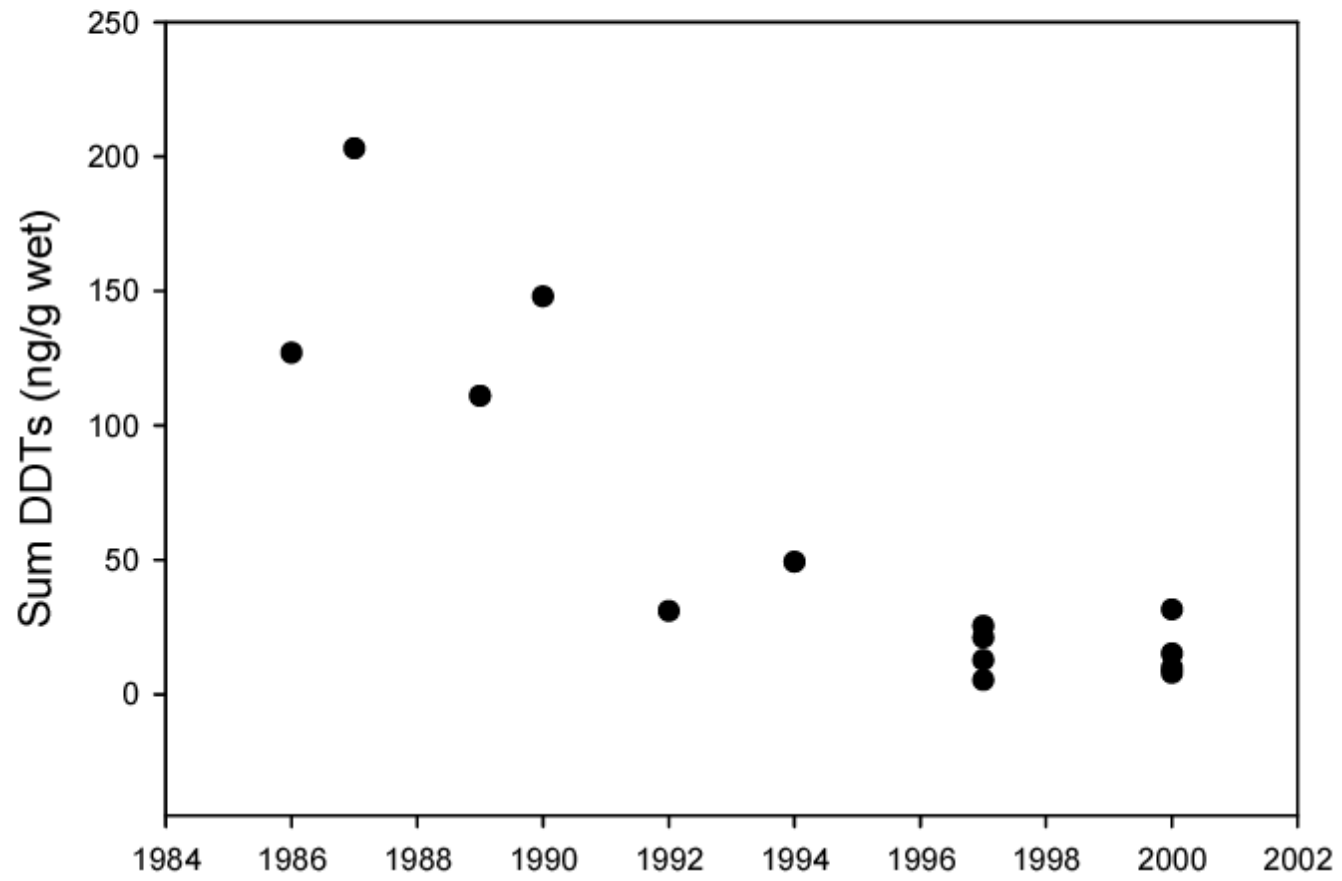


Figure 7

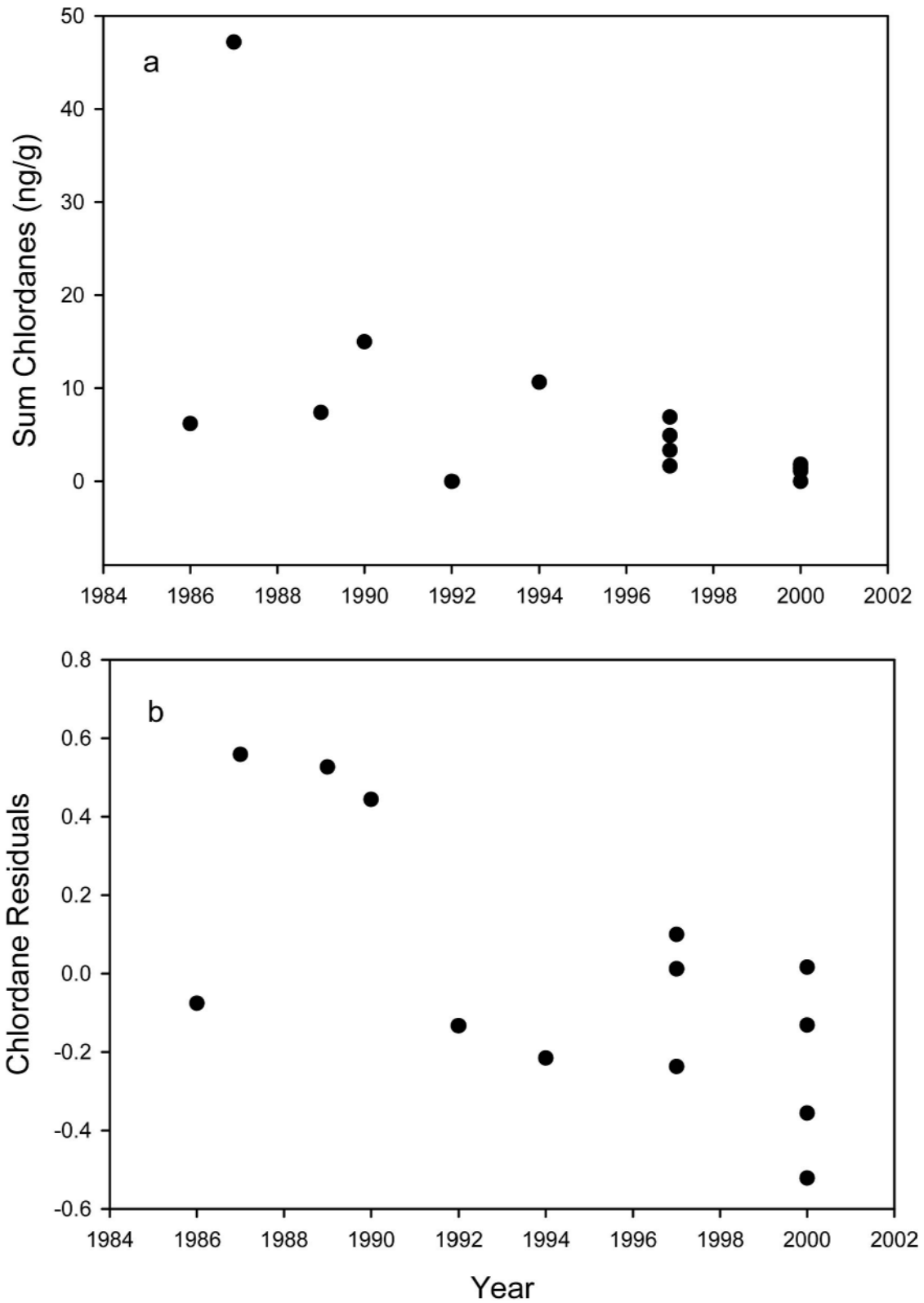


Figure 8

