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Contaminant Concentrations in Eggs of Double-crested Cormorants and Forster's Terns from San Francisco Bay: 2002-2012.

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EXECUTIVE SUMMARY

The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) conducted an Exposure and Effects Pilot Study (EEPS) to monitor contaminant exposure and effects in Bay wildlife. Avian egg monitoring is one tool that was piloted in the EEPS and retained as an element of RMP Status and Trends monitoring. Avian eggs from two species have been monitored: Double-crested Cormorants (*Phalacrocorax auritus*), a sentinel species for the open waters of the Bay, and Forster's Terns (*Sterna forsteri*), a sentinel species for shallow-water habitats on the Bay margins, including managed ponds.

Double-crested Cormorant eggs were monitored for a broad suite of persistent, bioaccumulative contaminants in 2002, 2004, and 2006 as a part of the EEPS. For RMP monitoring in 2009 and 2012, cormorant eggs were analyzed for mercury, selenium, polybrominated diethyl ethers (PBDEs), perfluorinated compounds (PFCs; particularly perfluorooctane sulfonate [PFOS]), polychlorinated biphenyls (PCBs), and organochlorine pesticides; in 2012 cormorant eggs were also analyzed for dioxins, dibenzofurans, and coplanar PCBs. Forster's Tern eggs were sampled under EEPS for mercury in 2002 and 2003. In 2009 and 2012, tern eggs were sampled for mercury, selenium, and PBDEs.

The purpose of this report is to present previously unpublished avian egg data from 2006, 2009, and 2012 and the results of spatial patterns and temporal trends analyses using all available data, including data collected annually as part of a Coastal Intensive Site Network (CISNET) study in 1999-2001, and by the RMP in 2002-2004. Statistically significant findings include:

Spatial Patterns (Tables 2 and 3)

- For cormorant eggs, there were several significant relationships indicating higher concentrations for PCBs and PFOS in the South Bay relative to the North Bay. This also was true for mercury, but spatial differences were significant only in 2009, when concentrations at the Don Edwards San Francisco Bay National Wildlife Refuge were significantly higher than at Wheeler Island. For PCBs, Richmond Bridge concentrations were higher than those at Wheeler Island when data for all years were pooled.
- For tern eggs, selenium concentrations were higher in a South Bay site (AB2) compared to the Napa Marsh site. There were statistically significant differences in mercury concentrations indicating higher concentrations in lower South Bay than in South Bay sites, but no significant differences between North Bay and South Bay sites.

Temporal Trends (Tables 2 and 3)

- For cormorant eggs, there were decreasing trends for PBDEs (all sites), dioxin TEQs (all sites), DDT (at North Bay sites), and dieldrin (at the Richmond Bridge only). There were mixed trends for mercury with concentrations decreasing at the

Don Edwards site in South Bay and increasing at the Richmond Bridge site in North Bay. Selenium concentrations increased at the Richmond Bridge. Finally, no trend was observed for PCBs, PFOS, or dioxins.

- For terns, there were too few years of data to assess trends. At nearly all of the sites, there were data for only one or two years.

In addition to analyzing the data for trends, the recent results were compared to ecotoxicological effects thresholds to assess risk. In the most recent dataset (2012), the measured concentrations for PCBs and mercury were higher than effects thresholds at one or more sites, indicating a continued risk to avian species.

Table 1. Contaminants measured in Double-crested Cormorant and Forster's Tern eggs, 2002-2012.

(a) Cormorants

Analyte	**2002**	**2004**	**2006**	**2009**	**2012**
Mercury	X	X	X	X	X
Selenium	X	X	X	X	X
PBDEs	X	X	X	X	X
PCBs	X	X	X	X	X
DDT	X	X	X	X	X
Dieldrin	X	X	X	X	X
PFCs			X	X	X
Dioxins, dibenzofurans, and co-planar PCBs	X	X	X		X

(b) Terns

Analyte	**2002**	**2003**	**2009**	**2012**
Mercury	X	X	X	X
Selenium			X	X
PBDEs			X	X

Table 2. **Summary of statistically significant relationships for contaminants in cormorant eggs.**

Contaminant	Spatial Patterns		Temporal Trends
	Difference among sites within years	Difference among sites for pooled years	
Mercury (ww)	In 2009: DE > WI	Not possible to test	Increasing at RB Decreasing at DE
Selenium (dw)	None	Not possible to test	Increasing at RB
PBDEs (lw)	None	Not possible to test	Decreasing at WI Decreasing at RB Decreasing at DE
PCBs (lw)	In 2012: DE > WI	DE > WI RB > WI	None
DDT (lw)	None	Not possible to test	Decreasing at WI Decreasing at RB
Dieldrin (lw)	None	Not possible to test	Decreasing at RB
PFOS (ww)	In 2009: DE > WI	DE > WI DE > RB	None
Dioxins and Dibenzofurans (lw)	None	Not possible to test	Decreasing at WI Decreasing at RB Decreasing at DE
Coplanar PCBs (lw)	None	Not possible to test	None

Key to site names (Figure 1)
DE = Don Edwards site
RB = Richmond Bridge site
WI = Wheeler Island site

Key to Units
ww = concentration on a wet-weight basis
dw = concentration on a dry-weight basis
lw = concentration on lipid-weight (wet) basis

Table 3 **Summary of statistically significant relationships for contaminants in tern eggs.**

Contaminant	Spatial Patterns		Temporal Trends
	Difference among sites within years	Difference among sites for pooled years	
Mercury (wet wt)	In 2009: A16>HS and EL>HS In 2012: AB2>HS and A7>HS and AB2>A2W	Not possible to test	None at site A16. Trends not calculated at the other sites because fewer than 3 observations.
Selenium (dry wt)	In 2009: AB2>Napa Marsh In 2012: see note*	AB2>Napa Marsh	Trends not calculated because fewer than 3 observations.
PBDEs (lipid wt)	None	None	Trends not calculated because fewer than 3 observations.

* In 2012, there was a significant difference but post-hoc test could not distinguish which stations.

<u>Key to site names (Figure 1)</u>
A16 = Pond A16 in Don Edwards site
AB2 = Pond AB2 in Don Edwards site
A2W = Pond A2W in Don Edwards site
A7 = Pond A7 in Don Edwards site
HS = Hayward Shoreline site
EL = Eden Landing site
Napa Marsh = Napa Marsh site

<u>Key to Units</u>
ww = concentration on a wet-weight basis
dw = concentration on a dry-weight basis
lw = concentration on lipid-weight (wet) basis

I. INTRODUCTION

The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) conducted an Exposure and Effects Pilot Study (EEPS) to monitor contaminant exposure and effects in Bay wildlife. The overall goal was to develop indicators of contaminant exposure and effects for the Bay covering different trophic levels, different levels of biological organization (biochemical, individual, population, and community), and different spatial scales (local and regional).

Avian egg monitoring is one tool that was piloted in the EEPS (Davis et al., 2006) and retained as an element of RMP Status and Trends monitoring. Avian egg monitoring in other aquatic ecosystems has proven to be a highly effective tool for assessment of long-term trends in persistent, bioaccumulative contaminants.

Double-crested Cormorants (*Phalacrocorax auritus*) (hereafter, simply "cormorants") are routinely monitored by the RMP as a sentinel species for the open waters of the Bay. Cormorants forage in a variety of shallow-water habitats (Hatch and Weseloh, 1999), including managed ponds (former salt ponds around the margin of the Bay that were originally tidal marsh), but they primarily hunt in the subtidal shallows and over mudflats and large sloughs when the tide is in. Cormorant eggs were chosen as an exposure indicator for the Bay for several reasons: they are full-time residents in the Bay; they eat Bay fish almost exclusively; they have been the subject of many contaminant studies in the Bay and elsewhere; their eggs are easy to collect at several Bay locations (minimal sampling costs); the colonies and eggs are reliably present (in contrast to fish); and they are known to accumulate a variety of contaminants (Davis et al., 2006).

Forster's Tern (*Sterna forsteri*) (hereafter, simply "terns") eggs were selected as another avian indicator. Recent studies by the U.S. Geological Survey (USGS) have resulted in the establishment of tern eggs as a primary biosentinel species for monitoring of mercury risk to Bay wildlife. This species also feeds primarily on small fish in shallow-water habitats on the Bay margins, including managed ponds. These former salt ponds are now largely managed to support waterbirds such as terns, plovers, ducks and shorebirds. Some managed ponds are shallow and seasonal, drying out in the summer and fall. Others are perennially wet and support fish year round. Forster's Tern, Caspian Tern (*Hydroprogne caspia*), American Avocet (*Recurvirostra americana*), and Black-necked Stilt (*Himantopus mexicanus*) all feed and breed primarily in and around managed ponds, and all have been studied extensively in recent years, particularly regarding methylmercury accumulation and effects. The spatial and habitat coverage of this species (Bay margins and managed ponds) therefore complements that of cormorants (open waters and large sloughs).

Monitoring of a broad suite of persistent, bioaccumulative contaminants in cormorant eggs was performed as a part of EEPS in 2002, 2004, and 2006. Tern eggs were sampled under EEPS for mercury in 2002 and 2003. Cormorant and tern egg monitoring was included as part of the Status and Trends Program with triennial sampling starting in 2009. In 2009 and 2012, cormorant eggs were analyzed for mercury, selenium, polybrominated diethyl ethers (PBDEs), perfluorinated compounds (PFCs), polychlorinated biphenyls (PCBs), organochlorine pesticides, and dioxins (a term used here to include chlorinated dioxins, chlorinated dibenzofurans, and coplanar PCBs). Tern eggs were sampled for mercury, selenium, and PBDEs.

Polycyclic musks, phthalates, nonylphenol, and triphenylphosphate were initially analyzed in cormorant eggs in 2002 and 2004, but were determined not to be high-priority contaminants. Results for these analytes are not presented in this report because they were only measured in two years and future monitoring is not planned.

The objectives of RMP avian egg monitoring are to:

1. evaluate long-term inter-annual trends in concentrations of bioaccumulative contaminants;
2. evaluate risks to Bay birds by comparison of contaminant concentrations in eggs to relevant thresholds, especially the TMDL monitoring target for mercury in bird eggs; and
3. assess spatial variation among Bay segments.

II. METHODS

A. Egg Sampling

Cormorant eggs were collected by the U.S. Fish and Wildlife Service (USFWS) between 7 May and 4 June 2002 from three locations: (1) Wheeler Island, (2) Richmond Bridge, and (3) Don Edwards San Francisco Bay National Wildlife Refuge (hereafter, simply called "Don Edwards") Pond A9/A10 (Figure 1). Eggs were processed and sent to the California Department of Fish and Wildlife's Water Pollution Control Lab for chemical analysis. Two composites with 10 eggs per composite were collected at all three locations.

Tern eggs were sampled by the USFWS between 5 June and 3 July 2002 from four different colonies: (1) Pond A16, and (2) Cargill Pond A1 on Don Edwards; (3) Hayward Shoreline Regional Park; and (4) Knight Island (Figure 1). Five eggs were sampled from each location. Individual tern eggs were dried, homogenized, and analyzed for total mercury (THg) concentrations at the Marine Pollution Studies Laboratory at Moss Landing, California.

Tern eggs were sampled by the USFWS between 4 June and 9 July 2003 from Pond A16 and Cargill Pond A1 at Don Edwards, Baumberg Pond B10, and Knight Island (Figure 1). Eight eggs were sampled from Pond A16 and Cargill Pond A1; seven eggs each from Baumberg Pond B10 and Knight Island. Forster's Tern eggs were dried, homogenized, and analyzed for THg concentrations at the Marine Pollution Studies Laboratory at Moss Landing, California.

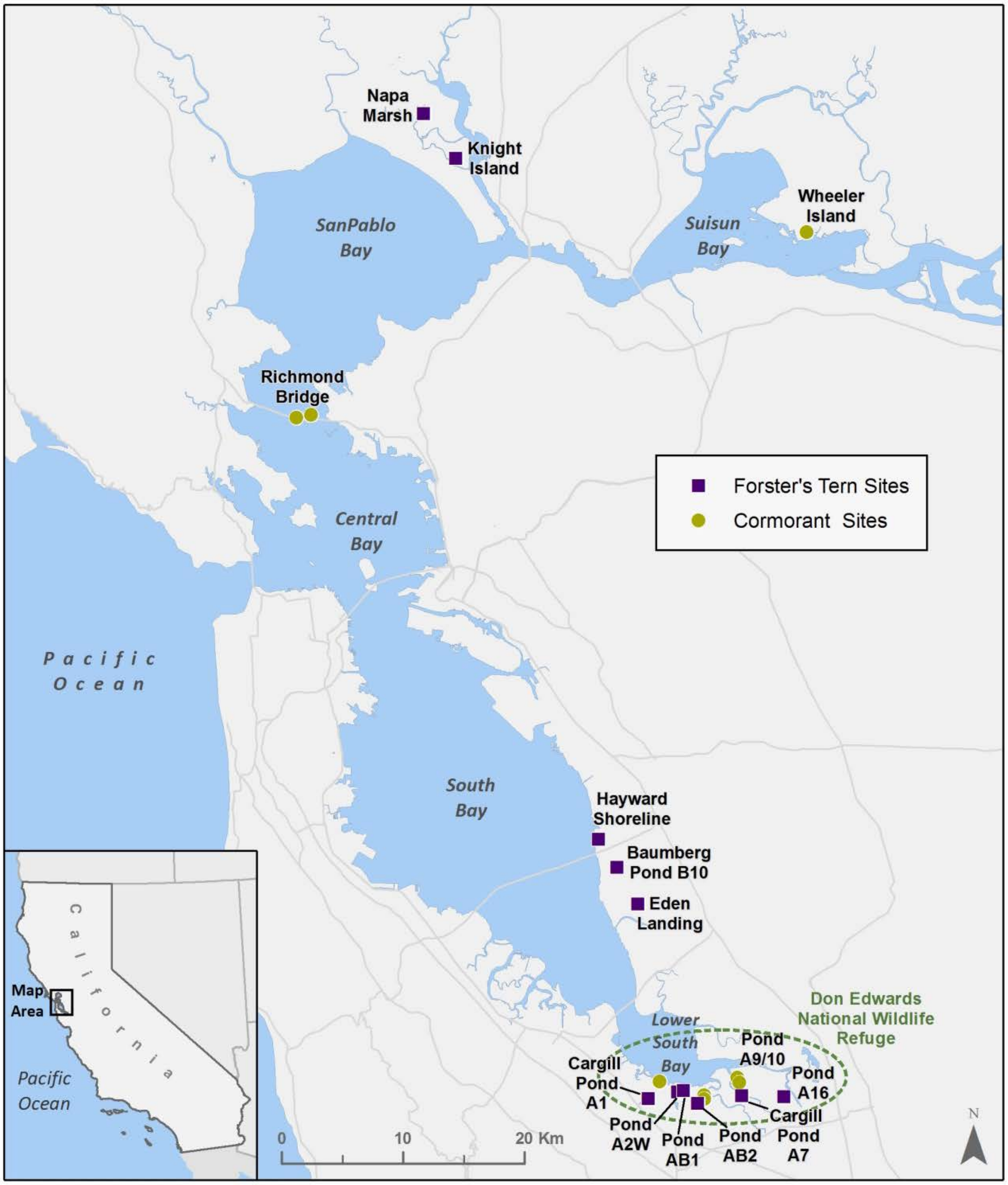
Cormorant eggs were collected by the USFWS between 29 April and 17 June 2004 from Richmond Bridge and Don Edwards Pond A9/A10 (Figure 1). Eggs were not collected from Wheeler Island due to logistical problems. Eggs were processed and sent to the California Department of Fish and Game's Water Pollution Control Lab for chemical analysis. Two composites with 10 eggs per composite were collected at Don Edwards and Richmond Bridge.

Cormorant eggs were collected on 1 May 2006 by the USFWS from Wheeler Island, Richmond Bridge, and Don Edwards Pond A9/A10 (Figure 1). Eggs were processed and sent to the California Department of Fish and Game's Water Pollution Control Lab for chemical analysis (pesticides, PCBS, and PBDEs). Three composites with 7 eggs per composite were collected at each location (3 composites/site), except for eggs from Wheeler Island. For the Wheeler Island site only 18 eggs were collected, so 6 eggs were combined for each composite.

Cormorant eggs were sampled by the USGS Dixon Field Station between 19 March and 27 May 2009 from Wheeler Island, Richmond Bridge, and South Bay PG&E towers (Moffett ponds; Towers 37, 38, and 4/30) (Figure 1). Twenty-one eggs were sampled from each location. Eggs were processed and shipped to AXYS Analytical laboratories in June 2009 for contaminant analyses. Three composites with 7 eggs per composite were collected at each site.

Forster's Tern eggs were sampled by the USGS Dixon Field Station between 12 May and 19 June 2009 from six different colonies: (1) Pond A16, (2) Pond A2W, and (3) Pond AB2 at Don Edwards; (4) Eden Landing Ecological Reserve; (5) Hayward Shoreline Regional Park; and (6) Napa-Sonoma Marsh Wildlife Area (Figure 1). Twenty-one eggs were sampled from each location. Forster's Tern eggs were dried, homogenized, and analyzed for THg concentrations at the USGS Dixon Field Station Environmental Mercury Laboratory. After homogenizing the eggs, equal masses (dried) from each of seven randomly chosen eggs per colony were combined to make three separate composite samples of seven eggs each per colony. Composite aliquots were then sent to the California Department of Fish and Game Moss Landing Marine Lab for selenium determination, and the California Department of Fish and Game Water Pollution Control Laboratory for PBDE analyses.

Figure 1. **Cormorant and tern egg sampling locations in San Francisco Bay, 2002 - 2012.**



Double-crested Cormorant eggs were sampled by the USGS Dixon Field Station between 23 March and 17 May 2012 from Wheeler Island, Richmond Bridge, and Don Edwards Pond A9/A10 (Figure 1). Twenty-one eggs were sampled from each location. Eggs were processed and shipped unopened to AXYS Analytical laboratories in July 2012 for contaminant analyses. Three composites with 7 eggs per composite were collected at each site.

Forster's Tern eggs were sampled by the USGS Dixon Field Station between 30 May and 19 July 2012 from six different colonies: (1) Pond A1, (2) Pond A2W, (3) Pond AB1, (4) Pond AB2, and (5) Pond A7 at Don Edwards; and (6) Hayward Shoreline Regional Park (Figure 1). Twenty-one eggs were sampled from each location. Forster's Tern eggs were dried, homogenized, and analyzed for THg concentrations at the USGS Dixon Field Station Environmental Mercury Laboratory. After homogenizing the eggs, equal masses (dried) from each of seven randomly chosen eggs per colony were combined to make three separate composite samples of seven eggs each per colony. Composite re-homogenized aliquots were then sent to the California Department of Fish and Game Moss Landing Marine Lab for selenium determination, and the California Department of Fish and Game Water Pollution Control Laboratory for PBDE analyses.

B. CHEMICAL ANALYSIS

Table 1 summarizes the contaminants that were measured in cormorant and tern eggs between 2002 and 2012.

Cormorant egg composites were analyzed in 2002, 2004, 2006, 2009, and 2012 for mercury, selenium, PCBs, organochlorine pesticides, and PBDEs. Coplanar PCBs and dioxins/furans were analyzed in composites collected in 2002, 2004, 2006, and 2012. Perfluorinated organic compounds (PFCs) were analyzed in composites collected in 2006, 2009, and 2012. Each composite was also analyzed for percent lipid and percent moisture.

Coplanar PCBs, dioxin/furans, and PFCs were analyzed by AXYS Analytical Services Ltd. (Sidney, B.C., Canada). Coplanar PCBs and dioxin/furan samples were extracted using 1:1 dichloromethane/hexane and analyzed using modified EPA method 1668A and modified EPA method 1613B, respectively. PFC samples were extracted using basic methanol and cleaned up by SPE cartridge before analysis by liquid chromatography/mass spectrometry (LC-MS/MS) using AXYS method MLA-043.

Other organic analyses were performed by the California Department of Fish and Game's Water Pollution Control Laboratory (Rancho Cordova, CA, USA). PCBs, pesticides, and PBDEs were extracted using Hydromatrix and a Dionex Accelerated Solvent Extractor (ASE 200) using a 1:1 acetone/dichloromethane mixture. Extracts were analyzed using a Hewlett-Packard 6890 plus with dual electron capture detectors (GC/ECD).

Selenium was analyzed by hydride generation atomic absorption spectrometry (HGAAS) (CDFG, Selenium Method 2003, 2006), and 2009 digest extracts (EPA Method 3052M) by inductively coupled plasma mass spectrometry (ICP-MS) (EPA Method 200.8). Mercury samples were digested with concentrated nitric acid and analyzed on a Perkin Elmer FIMS (EPA Method 245.5).

Tern egg were analyzed for mercury as composites in 2002 and 2003, and as individual eggs in 2009 and 2012. Tern egg composites were analyzed for selenium (2009, 2012), and PBDEs (2009, 2012). Selenium digest extracts (EPA Method 3052M) were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (EPA Method 200.8). Prior to 2009, mercury samples were digested with concentrated nitric acid and analyzed on a Perkin Elmer FIMS (EPA Method 245.5). In 2009 and 2012 individual egg samples were analyzed by USGS using thermal decomposition, amalgamation, and atomic absorption spectrophotometry (TDA-AAS) (EPA Method 7473). PBDEs were extracted using Hydromatrix and a Dionex Accelerated Solvent Extractor (ASE 200) using a 1:1 acetone/dichloromethane mixture and extracts analyzed using a Hewlett-Packard 6890 plus with dual electron capture detectors (GC-ECD).

A full quality assurance (QA) review was performed on all of the data. There was matrix interference for two Wheeler Island cormorant egg composites that could not be corrected by the laboratory. Surrogate recoveries for the two Wheeler Island composites were 8.1% and 14%. According to the analyzing laboratory procedures, any sample with a surrogate recovery less than 50% is considered an estimated value but is still a valid result. Based on this interpretation, the dieldrin data for Wheeler Island in 2002 were reported as estimated values. The dieldrin data in 2006 for Don Edwards and Richmond Bridge were also reported as estimates. In 2006, p,p'-DDD results for all sampling sites were reported as estimates, as well as the p,p'-DDT results for Don Edwards and Richmond Bridge.

Blank contamination was a problem with 1,2,3,4,6,7,8,9-octachlorodibenzofuran (OCDF) in 2006, with only one concentration for Richmond Bridge being reportable.

In 2009, one dieldrin result for Wheeler Island was not reportable due to blank contamination. PBDE 138 concentrations for 2009 were not reportable due to poor accuracy.

In 2012, p,p'-DDD, PCB 156 and PCB 174 concentrations were not reportable due to poor accuracy. No QA issues were identified for the analysis of the tern egg composites.

C. DATA ANALYSIS

Due to the small sample sizes and the lack of information on the distributions of the data, results were analyzed using non-parametric methods. The Kruskal-Wallis test was used to determine spatial differences among sites. Tests were run treating each sampling year separately. All sites were then combined to determine if there were significant differences among sampling years. If no statistically significant temporal differences were found among years the data were combined and the Kruskal-Wallis test was run to investigate spatial differences on the aggregated data. If the null hypothesis stating that the sample distributions were from the same population was rejected ($p < 0.05$), then all pairwise comparisons were examined using Dunn's test with a family error rate of 0.05. The Kendall rank correlation test was used to investigate temporal trends.

Tables 2 and 3 summarize the results of the statistical analyses for spatial and temporal trends.

For organic contaminants, statistical tests for spatial patterns or temporal trends were run on concentrations expressed as lipid weight, except for PFCs which were analyzed using wet-weight (ww) concentrations. Concentrations expressed as wet weight were used to make comparisons to effects thresholds.

Toxic Equivalents (TEQs) for dioxins/furans and co-planar PCBs were calculated using World Health Organization toxic equivalency factors (TEFs) (WHO, 2005). To calculate TEQs, the concentration of each chemical in a mixture is multiplied by its TEF and is then summed with all other chemicals to report the total toxicity-weighted concentration.

III. RESULTS AND DISCUSSION

A. POLYCHLORINATED BIPHENYLS (PCBS)

Background and Prior Work

PCBs are persistent, cancer-causing chemicals that were domestically manufactured from 1929 until their production and sale were banned in 1979. PCBs were used in hundreds of industrial and commercial applications including electrical, heat transfer, and hydraulic equipment; as plasticizers in paints, plastics, and rubber products; in pigments, dyes, and carbonless copy paper; and many other industrial applications.

The first study of contaminants in Bay cormorant eggs showed high PCB concentrations in eggs from the Richmond Bridge and elevated activity of a liver enzyme biomarker (cytochrome P450 measured via an EROD assay) in embryos sampled in 1994 and 1995, suggesting that PCB exposure in the embryos was sufficient to cause low rates of embryo mortality (Davis et al., 1997; Davis, 1997).

A subsequent study in 1999-2001 (CISNET) also indicated that PCBs approached a known threshold for toxic effects (Davis et al., 2004). Custer et al. (1999) found reduced hatchling mass in cormorants at 13.6 ug/g ww in eggs, and Kubiak et al. (1989) found reduced hatching success at 23 ug/g ww in terns. Yamashita et al. (1993) found high proportions of dead and deformed embryos (24%) at a location (Tahquamenon Island - the cleanest location they sampled) with PCB concentrations (as sum of congeners) in the 3.6-5.0 ug/g range. Yamashita et al. concluded that PCBs (via their large contribution to dioxin toxic equivalents) were likely associated with occurrence of live-deformed cormorant embryos across the four locations they sampled. PCB concentrations found in the CISNET study had a maximum of 3.8 ug/g fww in a composite sample from 2001, at the low end of the observed effects concentrations observed by Yamashita et al. (1993) and Custer et al. (1999). The CISNET study also found significant differences between PCB concentrations at the Richmond Bridge and Don Edwards sites, suggesting that distinct regional differences in PCB concentrations exist, and that cormorants are effective indicators of this spatial variation.

Spatial Patterns

Considering the entire dataset from 1999-2012, PCBs (sum of congeners) ranged from a low of 11 ug/g lipid weight (lw) at Wheeler Island in 2009 to a high of 143 ug/g lw at Don Edwards Pond A9/10 in 2006 (Figure 2). Spatial differences within each year (2002, 2004, 2006, 2009, and 2012) were investigated and a statistically significant difference was found between sites for 2012 (Kruskal-Wallis: $H = 6.49$, $df = 2$, $p = 0.039$) with concentrations significantly greater in the South Bay (Don Edwards) than at Wheeler Island (Dunn's Test: $z = 2.53$, $p = 0.011$).

There was no statistically significant difference among years (2002-2012, all sites combined; Kruskal-Wallis: $H = 6.24$, $df = 4$, $p = 0.182$); therefore, data were pooled and significant differences between sites were found (Kruskal-Wallis: $H = 12.85$, $df = 2$, $p = 0.002$) with post-hoc pairwise comparisons indicating PCB concentrations at Wheeler Island were significantly lower than at Richmond Bridge (Dunn's Test: $z = 3.34$, $p = 0.001$) and Don Edwards (Dunn's Test: $z = 2.90$, $p = 0.004$).

Higher PCB concentrations at the Richmond Bridge site are likely due to its proximity to urban and industrial land uses, especially the Richmond Harbor area, a known PCB hot spot (SFBRWQCB, 2008). Urban runoff and in-Bay PCB hotspots are two of the main pathways for entry of PCBs into the Bay food web (Davis et al., 2006; SFBRWQCB, 2008). The PCB concentrations observed at the Richmond Bridge and Wheeler Island locations suggest distinct regional differences in food web contamination, and that cormorants are effective indicators of this spatial variation.

Temporal Trends

The cormorant egg PCB time series (Figure 2) exhibits a great deal of variation. Concentrations at the Richmond Bridge site were relatively high from 2000 to 2004 (with a maximum of 100 ug/g lw in 2002), but lower in 1999, 2006, 2009, and 2012. Wheeler Island concentrations were highest in 2002 (76 ug/g lw), but lower in 2006, 2009, and 2012. However, Kendall's rank correlation test indicated that there were no significant trends in PCB concentrations at Don Edwards ($z = 1.31$, $p = 0.189$, $tau = 0.290$), Richmond Bridge ($z = -0.88$, $p = 0.377$, $tau = -0.153$), or Wheeler Island ($z = -1.21$, $p = 0.225$, $tau = -0.302$). Given the high variance in the time series, the lack of trends is not a surprise. Changes in foraging area are a possible explanation for the high inter-annual variation observed.

Comparison to Effect Thresholds

PCB concentrations over the 14-year period of record have been occasionally above the lowest observed effects concentration of 3.6 ug/g reported by Yamashita et al. (1993). Five Richmond Bridge samples (one in 2001, two in 2002, one in 2004, and one in 2006), and one Don Edwards sample in 2012 exceeded the lower range of the effects threshold (3.6 ug/g fww, Figure 3). This suggests that PCB concentrations in cormorant eggs were at a level that could be having effects on embryos such as mortality and beak deformity. Mortality and developmental effects directly impact individuals, but also may cause effects at the population level. Because egg volumes were not measured for eggs collected by the RMP (from 2002-2012), we do not have the information necessary to convert the wet-weight data to fww for these comparisons, but fww values are estimated to be about 5% lower than ww values.

Figure 2. **PCB concentrations (ug/g lw) in cormorant egg composites from San Francisco Bay, 1999-2012.** Some data are from sites monitored during the Coastal Intensive Site Network (CISNET) study (Davis et al., 2004) (orange circles).

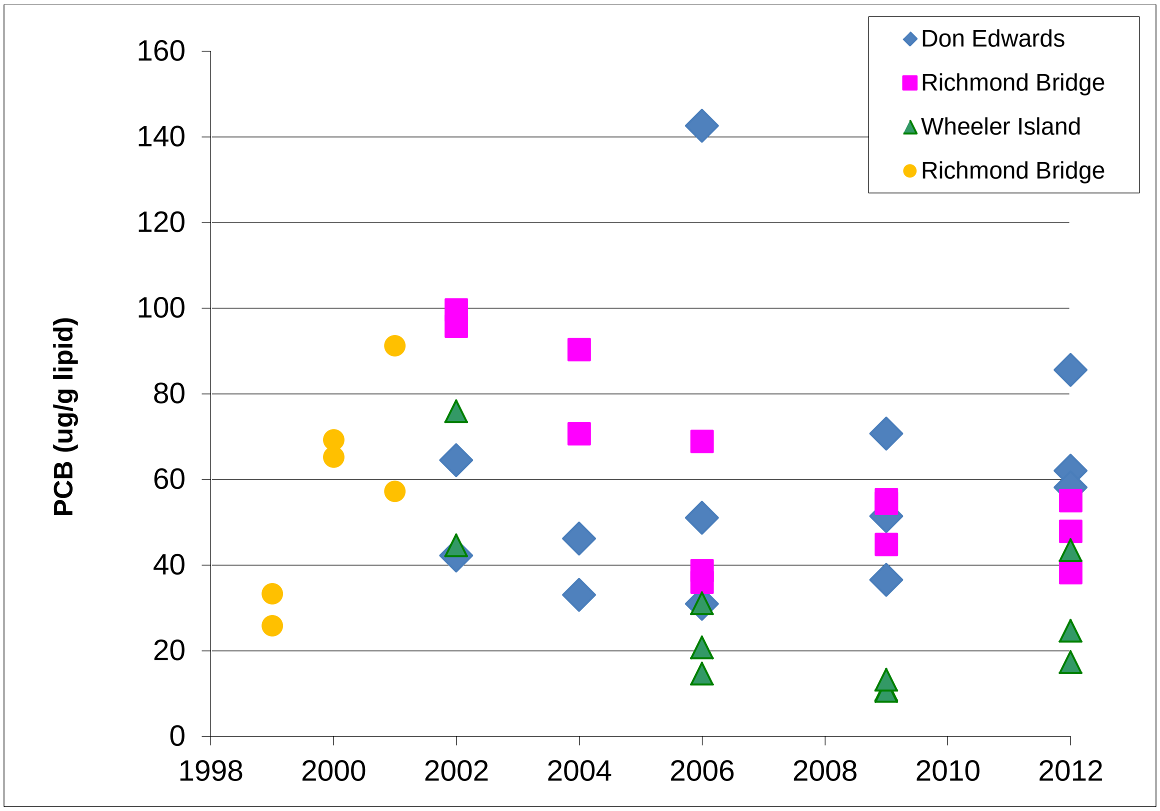
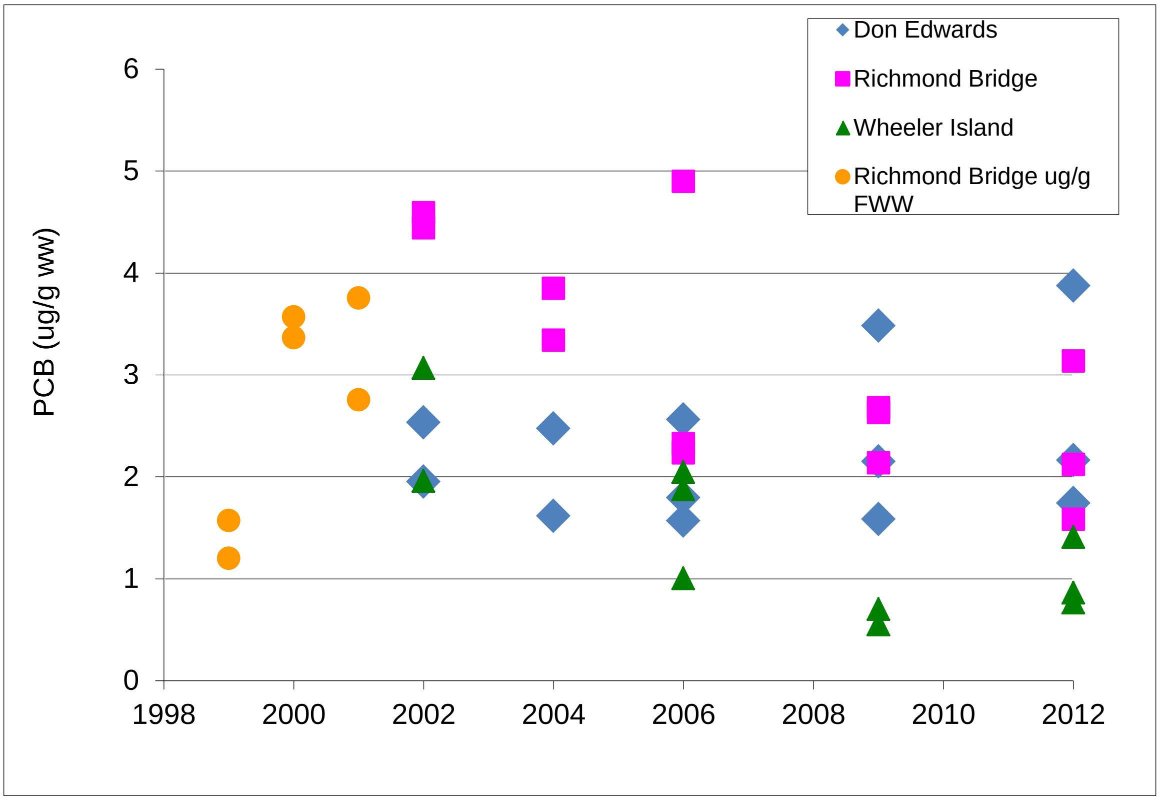


Figure 3. **PCB concentrations (ug/g ww) in cormorant egg composites from San Francisco Bay, 1999-2012.** Data collected during the San Pablo Bay Coastal Intensive Site Network study (Davis et al., 2004) (orange circles) are presented in fresh wet weight (fww).



B. MERCURY

Background and Prior Work

Mercury is a contaminant of primary concern in San Francisco Bay. Mercury, in the form of methylmercury, is a mutagen, teratogen, and carcinogen that accumulates in organisms and biomagnifies through food chains (Eisler, 2000). Mercury is measured as total mercury, but is primarily present as methylmercury in avian eggs.

The CISNET study (Davis et al., 2004) and a study by Schwarzbach and Adelsbach (2003) examined concentrations of mercury in cormorant eggs from the Bay in 1999-2001. Maximum mean mercury concentrations of 0.55 ug/g fww were found in cormorant eggs collected from Wheeler Island (Suisun Bay) in 2000 (Schwarzbach and Adelsbach, 2003). Davis et al. (2006) reported additional mercury data for 2002 and

2004. Mercury concentrations ranged from 0.17 ug/g ww at Richmond Bridge in 1999 to 1.2 ug/g ww at Don Edwards in 2004.

Two controlled feeding studies that have established accepted thresholds for evaluating risks associated with mercury in wild bird eggs are Heinz (1979), which found low to moderate effects on hatchability of mallard (*Anas platyrhynchos*) eggs with 0.8 ug/g fww, and Fimreite (1971), which found low hatchability in pheasant eggs with concentrations of 0.5 to 1.5 ug/g fww. The sensitivity of cormorant embryos to mercury exposure was evaluated in egg injection experiments by Heinz (2003), which indicated that cormorants are less sensitive to mercury than mallards. This suggests that concentrations below 0.8 ug/g fww in cormorants would not be expected to cause embryo mortality. However, three out of the four Don Edwards composites exceeded 0.8 ug/g fww, suggesting concentrations in the South Bay were high enough to cause possible effects on cormorant reproduction (Davis et al., 2006).

Distinct spatial patterns were found in mercury concentrations, with mean concentrations at Don Edwards (0.87 ug/g ww in 2002 and 1.0 ug/g ww in 2004) being considerably higher than the means for Richmond Bridge (0.45 ug/g ww in 2002 and 0.44 ug/g ww in 2004) (Davis et al., 2006). Longer-term data did not indicate any increasing or decreasing trends in mercury concentrations at the Richmond Bridge site (Davis et al., 2006). Schwarzbach and Adelsbach (2003) found that cormorant eggs were indicators of regional variation in mercury concentrations, with high concentrations in Suisun Bay and San Francisco Bay compared to locations in the Delta.

DOUBLE-CRESTED CORMORANTS

Spatial Patterns

Considering the entire 1999-2012 dataset, mercury concentrations in cormorant eggs ranged from 0.20 ug/g ww at Richmond Bridge in 1999 to 1.34 ug/g ww at Don Edwards in 2006 (Figure 4). Mean concentrations were highest at the Don Edwards site where they were 0.87 ug/g ww in 2002, 1 ug/g ww in 2004, 0.92 ug/g ww in 2006, 0.56 ug/g ww in 2009, and 0.37 ug/g ww in 2012. Spatial differences within each year (2002, 2004, 2006, 2009, and 2012) were investigated and a statistically significant difference was found between sites for 2009 (Kruskal-Wallis: $H = 6.49$, $df = 2$, $p = 0.039$) with concentrations significantly greater in the Lower South Bay (Don Edwards) than at Wheeler Island (Dunn's Test: $z = 2.53$, $p = 0.011$). There was a statistically significant difference between the years (all sites combined; Kruskal-Wallis: $H = 10.38$, $df = 4$, $p = 0.034$); therefore, years could not be pooled to test for spatial differences.

Birds foraging in the lower South Bay appear to be exposed to higher mercury levels in their prey and passing this mercury on to their eggs. Other studies have also found relatively high concentrations of mercury in the South Bay food web: High mercury concentrations have been documented in eggs of other piscivorous bird species, Forster's Terns and Caspian Terns, in this region, as discussed below. Also, mercury concentrations in some sport fish, particularly leopard shark (*Triakis semifasciata*) and striped bass (*Morone saxatilis*), have been relatively high in the South Bay (Davis et al., 2007). Relatively high mercury concentrations have also been found in small fish in the South Bay, especially at Alviso Slough (Greenfield and Jahn, 2010; Gehrke et al., 2011). Mercury concentrations may be higher at the Don Edwards site due to proximity to a known mercury source: the historic New Almaden mercury mine is located in the watershed of the Guadalupe River. The Guadalupe River drains into Alviso Slough, which is adjacent to Ponds A9/A10, and eventually into the Bay. It is also possible that environmental conditions in the South Bay favor net methylation and greater food web accumulation of methylmercury.

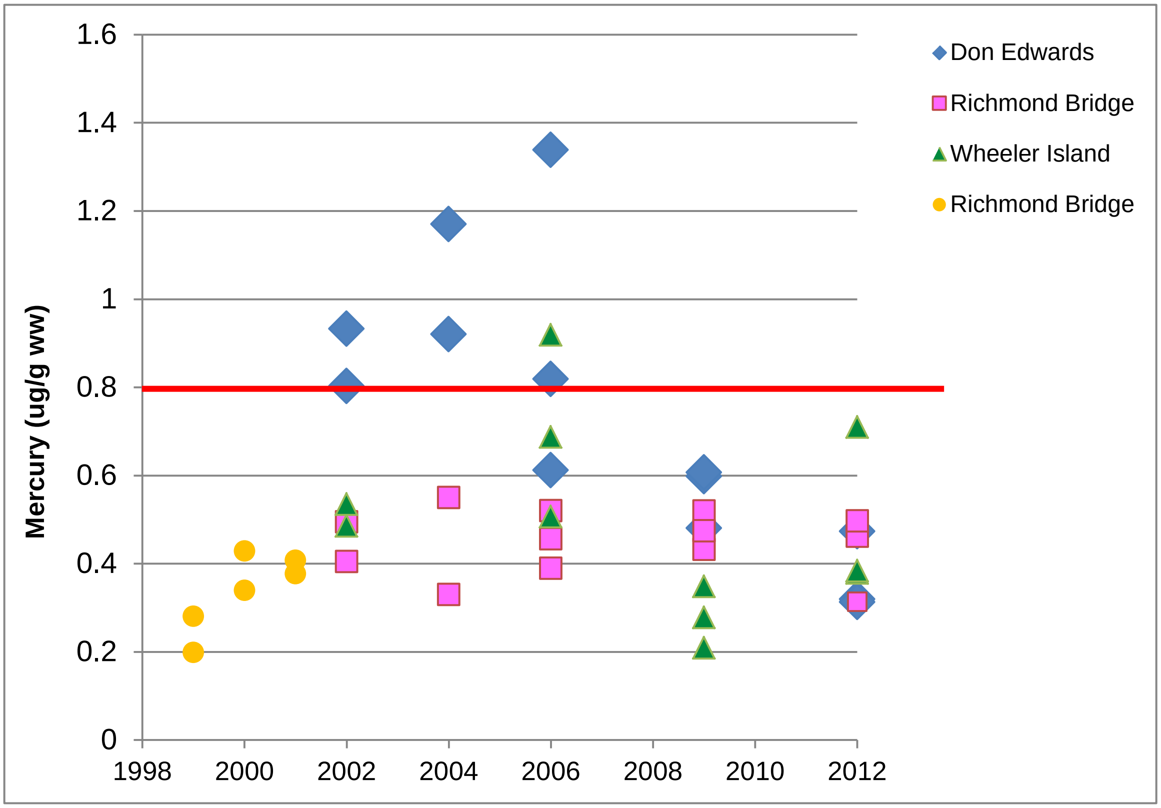
Temporal Trends

Distinct trends in mercury concentrations were not expected due to the large reservoir of mercury in the Bay and its watershed and the lack of any major management action to reduce mercury inputs to the Bay. There was, however, a statistically significant increase in mercury concentrations at Richmond Bridge (Kendall's rank correlation: $z = 2.08$, $p = 0.037$, $tau = 0.360$; Figure 4) over the 14-year sampling period. Concentrations at the Richmond Bridge site were lowest in 1999 (mean 0.24 ug/g ww), and increased fairly steadily to a mean of 0.48 ug/g ww in 2009, before leveling out at 0.42 ug/g ww in 2012, with little inter-annual variation. Mercury concentrations decreased significantly at Don Edwards (Kendall's rank correlation: $z = -3.190$, $p = 0.001$, $tau = -0.705$), and tended to do so at Wheeler Island but not significantly ($z = -0.73$, $p = 0.467$, $tau = -0.181$). Concentrations at the Don Edwards site were highest in 2004 (mean 1.05 ug/g ww), and decreased to a mean of 0.37 ug/g ww in 2012. High inter-annual variance and small datasets for Wheeler Island resulted in low power to detect inter-annual trends.

Comparison to Effect Thresholds

Mercury concentrations in the South Bay were high enough to warrant concern about possible effects on cormorant reproduction. The ecological effect screening benchmark for mercury in avian eggs is 0.5 ug/g fww (RAIS, 2004). This is the same value established as a "monitoring target" in the mercury TMDL (SFBRWQCB, 2006). However, mercury sensitivity varies among bird species (Fimreite, 1971; Barr, 1986; Heinz et al., 2009), and there is evidence that cormorants are not as sensitive to mercury as mallards and that the effects threshold may be closer to 0.8 ug/g fww (Heinz, 2003; Schwarzbach and Adelsbach, 2003). Five of the seven Don Edwards composites exceeded the 0.8 ug/g threshold between 2002 and 2006, as did one Wheeler Island composite in 2006 (Figure 4). All composites were below this threshold in 2009 and 2012.

Figure 4. **Mercury concentrations (ug/g ww) in cormorant egg composites from San Francisco Bay, 1999-2012.** The red line indicates the estimated lowest effects threshold (0.8 ug/g ww) for cormorants. Data from sites monitored during the Coastal Intensive Site Network (CISNET) study (Davis et al., 2004) are shown in orange circles.



FORSTER'S TERNS

Spatial Patterns

In RMP data for 2002 the mean (± standard error) mercury concentration in tern eggs was 1.98 ± 0.53 ug/g ww, and concentrations in individual eggs ranged from 0.41 ug/g at Knight Island to 6.4 ug/g at Pond A16 (Figure 5 - Pond A16 labeled as "Don Edwards"). Mercury concentrations did not differ between the two colonies sampled (Kruskal-Wallis: $H = 1.32$, $df = 1$, $p = 0.251$).

In RMP sampling in 2003, the mean mercury concentration in tern eggs was 1.41 ± 0.27 ug/g, and concentrations in individual eggs ranged from 0.42 ug/g at Knight Island to 2.62 ug/g at Pond A16 (Figure 5). Mercury concentrations did not differ among the four colonies sampled (Kruskal-Wallis: $H = 1.83$, $df = 3$, $p = 0.608$).

In 2009 RMP sampling, the mean mercury concentration in tern eggs was 1.38 ± 0.13 ug/g, and individual egg concentrations ranged from 0.44 ug/g at Pond AB2 to 10 ug/g at Napa Marsh (Figure 5). Mercury concentrations in 2009 differed significantly among the six colonies sampled (Kruskal-Wallis: $H = 12.16$, $df = 5$, $p = 0.033$) with concentrations at Hayward Shoreline being significantly lower than Pond A16 (Dunn's Test: $z = 2.85$, $p = 0.004$) and Eden Landing (Dunn's Test: $z = 2.82$, $p = 0.005$).

In 2012 RMP sampling the mean mercury concentration in tern eggs was 1.86 ± 0.09 ug/g, and individual egg concentrations ranged from 0.37 ug/g at Hayward Shoreline to 3.94 ug/g at Pond AB2 (Figure 5). Mercury concentrations in 2012 varied significantly among the six colonies sampled (Kruskal-Wallis: $H = 32.36$, $df = 5$, $p = <0.0005$) with concentrations at Hayward Shoreline being significantly lower than Pond AB2 (Dunn's Test: $z = 4.96$, $p = <0.0005$) and Cargill Pond A7 (Dunn's Test: $z = 4.26$, $p = <0.0005$), and concentrations at Pond A2W significantly lower than Pond AB2 (Dunn's Test: $z = 3.29$, $p = 0.001$).

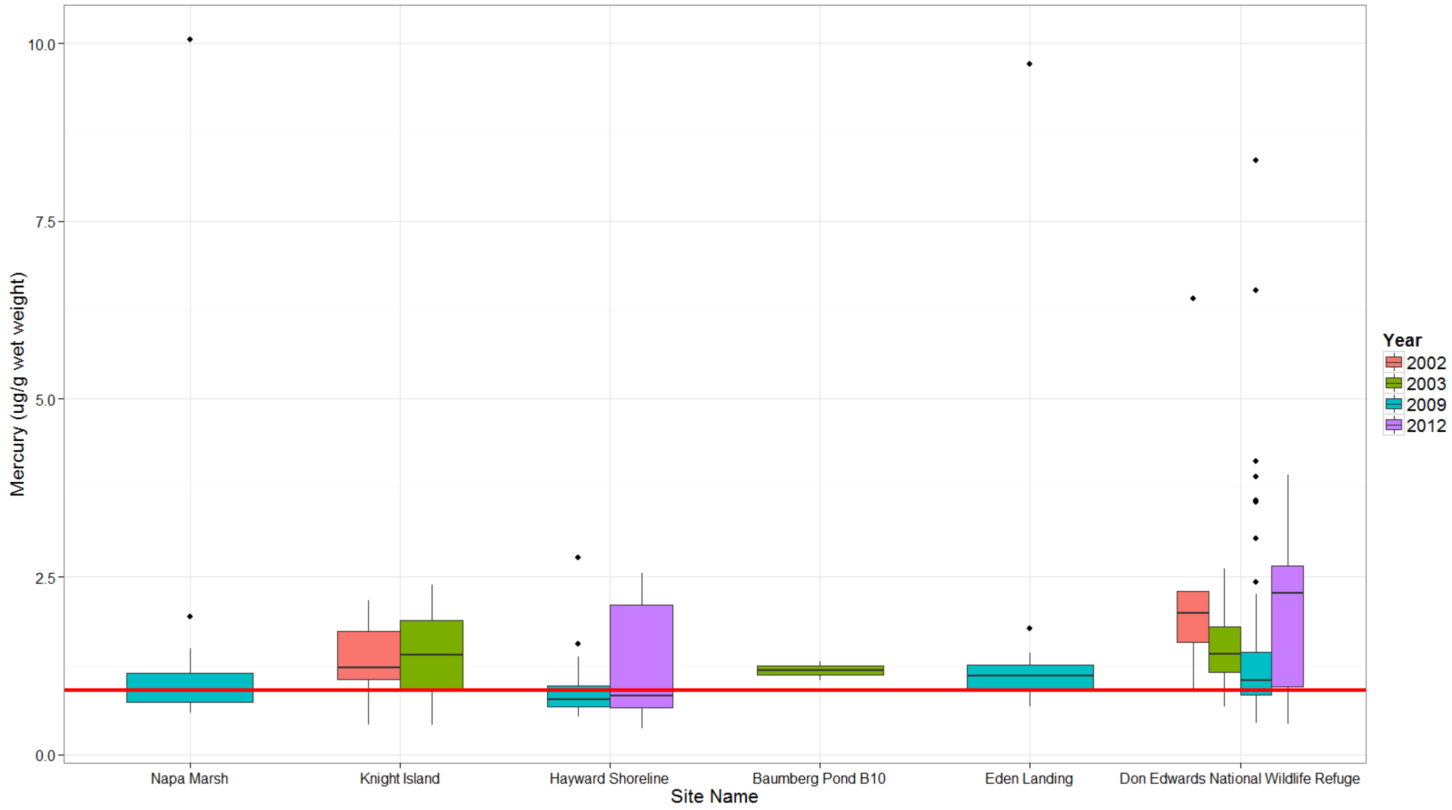
There was a statistically significant difference among the years (all sites combined; Kruskal-Wallis: $H = 22.77$, $df = 3$, $p = <0.0005$), therefore, years were not pooled to test for spatial differences.

Temporal Trends

Insufficient data were collected to assess inter-annual trends at most of the sites based on RMP data. No significant trend was detected at Pond A16 (Kendall's rank correlation: $z = 1.71$, $p = 0.088$, $tau = -0.267$). Other sites were not evaluated as they were sampled for fewer than three years (Figure 5).

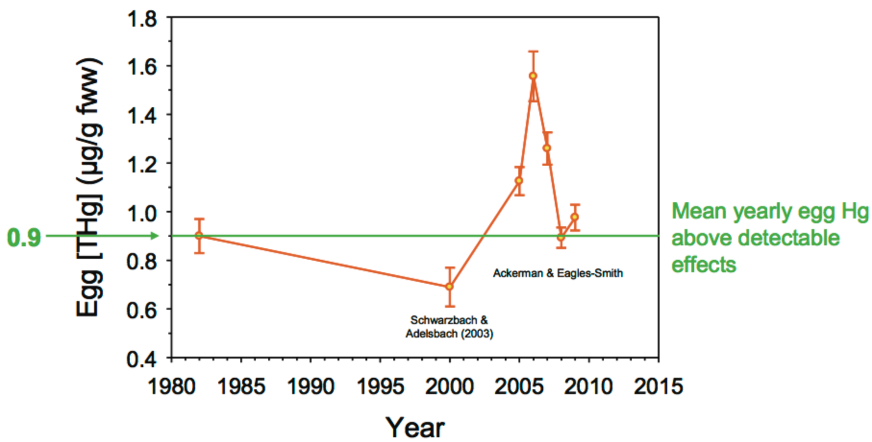
A high proportion of tern egg mercury concentrations were identified as outliers in 2009 relative to the other years sampled (Figure 5). The cause of this pattern is unknown.

Figure 5. **Mercury concentrations (ug/g ww) in individual tern eggs from San Francisco Bay, 2002-2012, based on RMP data.** Red line indicates the lowest effects threshold (0.9 ug/g fww). The bottom, middle, and top lines of each box are the 25th, 50th, and 75th percentiles of the data. Whiskers extend from the top and bottom of the boxes to the highest and lowest values that are within 1.5 times the interquartile range (distance between the 25th and 75th percentiles) of the upper or lower hinge (25th or 75th percentile). Outliers (values that are greater or less than the values spanned by the whiskers) are plotted as points.



Eagles-Smith and Ackerman (2010) combined RMP data with data from other studies to evaluate long-term variation in Bay-wide average mercury concentrations in tern eggs (Figure 6). They compared the egg concentrations to a threshold of 0.9 ug/g fww developed from their extensive studies of effects of mercury on Forster's Terns in the Bay. Their work indicated that at this concentration, egg hatchability was reduced by 10% and nest survival was reduced by 18%. Annual average concentrations have varied considerably, from 0.7 ug/g fww in 2000 to almost 1.6 ug/g fww in 2006.

Figure 6. Variability in tern egg mercury concentrations (ug/g fww) from San Francisco Bay, 1982-2009. Green line indicates the effects threshold (0.9 ug/g fww). Figure from Eagles-Smith and Ackerman (2010). Data for 1982 are from Ohlendorf et al. (1988).



Comparison to Effect Thresholds

Terns appear to face significant risk from methylmercury exposure. Nearly half (48%) of the breeding terns (Eagles-Smith et al., 2009) had blood mercury concentrations exceeding a risk threshold developed for Common Loon (*Gavia immer*) blood of (3 ug/g ww) at which there was a 40% loss in loon reproduction (Evers et al., 2008). Tern hatching success shows evidence of impacts from mercury: fail-to-hatch and abandoned eggs of terns tend to have higher mercury concentrations than randomly sampled eggs sampled from successful nests (Ackerman et al. 2014). Additionally, the likelihood of an embryo being malpositioned in the egg increased with tern egg mercury concentrations (Herring et al. 2010). There is also evidence that mercury affects chick survival shortly after hatching (Ackerman et al. 2008), but not in older, flegded chicks (Ackerman et al., 2008) because of reduced mercury concentrations associated with mass dilution (Ackerman et al. 2011).

Tern hatching success shows evidence of impacts from mercury: fail-to-hatch eggs of terns had higher average mercury concentrations than abandoned eggs and random eggs sampled from successful nests (Eagles-Smith and Ackerman, 2008). In contrast, fledgling tern survival was not related to blood mercury concentration in chicks (Ackerman et al., 2008).

The risk to hatching and nesting success was evaluated for RMP data by assessing individual egg mercury concentrations in relation to a threshold value of 0.9 ug/g fww, which is associated with a 10% reduction in hatching success and 18% reduction in nest survival in Forster's Terns (Eagles-Smith and Ackerman, 2010). Because egg volumes were not measured for the individual 2002 and 2003 eggs, we could not convert the wet-weight data to fresh wet weight; however, fww values are estimated to be about 5% lower than ww values. Overall, it is estimated that 62% of eggs sampled (168 of 270) exceeded the 0.9 ug/g fww threshold; on a site-specific basis the frequency of individual eggs exceeding the threshold was as follows: Baumberg Pond B10, 100%; Cargill Pond A7, 86%; Pond AB2, 83%; Eden Landing, 71%; Knight Island, 71%; Pond A16, 71%; Pond AB2, 67%; Cargill Pond A1, 57%; Pond A2W, 55%; Napa Marsh, 43%; and Hayward Shoreline 31%.

C. DDT

Background and Prior Work

DDT is a broad-spectrum insecticide that was widely applied in agriculture, mosquito abatement, residential applications, and other uses in the U.S. from 1939 until 1972. The percent composition of the technical DDT mixture is p,p'-DDT (77%), o,p'-DDT (15%), p,p'-DDE (4%). In the environment, DDT is converted to DDE under aerobic conditions, while it is converted to DDD under anaerobic conditions. DDTs are neurotoxins and classified by USEPA as probable human carcinogens. They are persistent in the environment, lipophilic, and subject to biomagnification in aquatic food webs. Historical use of DDT, including processing at the United-Heckathorn packaging plant in Richmond Harbor between the 1940s and 1960s, has resulted in contamination of the Bay and the associated watersheds. The Central Valley and local watersheds continue to act as a source of DDT loads to the Bay and ultimately to the aquatic food web.

The CISNET and RMP studies measured concentrations of DDT and other organochlorine pesticides in cormorant eggs. DDT concentrations at Wheeler Island appeared to be particularly elevated in 2002 (Davis et al., 2006). The mean concentration for Wheeler Island was more than twice the mean concentration for Don Edwards and more than 1.5 times the mean for the Richmond Bridge in that year. DDT concentrations at Richmond Bridge have varied considerably over time.

Spatial Patterns

Total DDT (sum of o,p'-DDD, o,p'-DDE, o,p'-DDT, p,p'-DDD, p,p'-DDE, and p,p'-DDT) ranged from a high of 194 ug/g lw measured at Don Edwards in 2006, to a low of 8 ug/g lw measured at Wheeler Island in 2009 (Figure 7). No statistically significant spatial differences were found among sampling sites within each year (2002, 2004, 2006, 2009, and 2012). There was a statistically significant difference among the years (all sites combined; Kruskal-Wallis: $H = 15.79$, $df = 4$, $p = 0.003$); therefore, the data could not be pooled and tested for spatial differences.

The mean DDT concentration at Wheeler Island in 2002 appeared to be relatively high (131 ug/g lw). One composite sample from Wheeler Island in 2002 had a particularly elevated DDT concentration (163 ug/g lw). The mean concentration for Wheeler Island in 2002 was more than double the mean concentration for Don Edwards (63 ug/g lw) and more than 1.5 times the mean for the Richmond Bridge (81 ug/g lw) in that year. Wheeler Island is next to a large tidal marsh complex on the north side of Suisun Bay just seaward of the confluence of the Sacramento and San Joaquin rivers. The observation of relatively high concentrations in this region is consistent with its proximity to water and sediment inputs to the Estuary from the Central Valley, a vast agricultural area with a large amount of historical use of DDT (Connor et al., 2004). However, this pattern did not persist over time.

Temporal Trends

DDT concentrations at Richmond Bridge varied considerably over time with a pattern similar to that observed for PCBs. Like PCBs, DDT concentrations were low in 1999, increasing over the next three years, before decreasing from 2004 to 2012 (Figure 7). The overall temporal decline was statistically significant (Kendall's rank correlation: $z = -2.72$, $p = 0.007$, $tau = -0.470$). A statistically significant decline in DDT concentrations was observed at Wheeler Island from 2002-2012 (Kendall's rank correlation: $z = -2.34$, $p = 0.019$, $tau = -0.583$). Additional sampling will be needed to determine whether this is simply inter-annual variation or truly indicative of a long-term decline. A high degree of inter-annual variation and no trend were observed at Don Edwards ($z = -1.31$, $p = 0.189$, $tau = -0.290$). DDTs in resident mussels at National Mussel Watch sites (Treasure Island/Yerba Buena Island and Dumbarton Bridge) in the Bay have decreased over the period of record (1986 – 2009), but only significantly so at Dumbarton Bridge (SFEI, 2014). Trends in DDTs for transplanted mussels and resident clams (combined RMP and SMW data) all show significant declines (SFEI, 2014).

Comparison to Effect Thresholds

Concentrations of DDE in most of the cormorant egg samples were below the threshold for impacts on reproductive success (Figure 8). The lowest concentration of DDE associated with impaired reproduction in cormorants was reported by Weseloh et al. (1983), who found reduced numbers of young produced per active nest associated with colony mean DDE concentrations of 5 ug/g fww. One composite (estimated fww) from Wheeler Island in both 2002 and 2006 exceeded this 5 ug/g fww effects threshold. All other samples were below this threshold and were in the range of 1-4 ug/g fww. Eggshell thinning, a well-known effect of DDE in wild bird populations (Blus, 1996), has a much higher threshold (24 ug/g fww) associated with sufficient thinning to reduce populations of cormorants (Gress et al., 1973). None of the samples approached this threshold.

Figure 7. **Sum of DDT concentrations (ug/g lw) in cormorant egg composites from San Francisco Bay, 1999-2012.** Data from sites monitored during the San Pablo Bay Coastal Intensive Site Network study (Davis et al., 2004) are shown in orange circles.

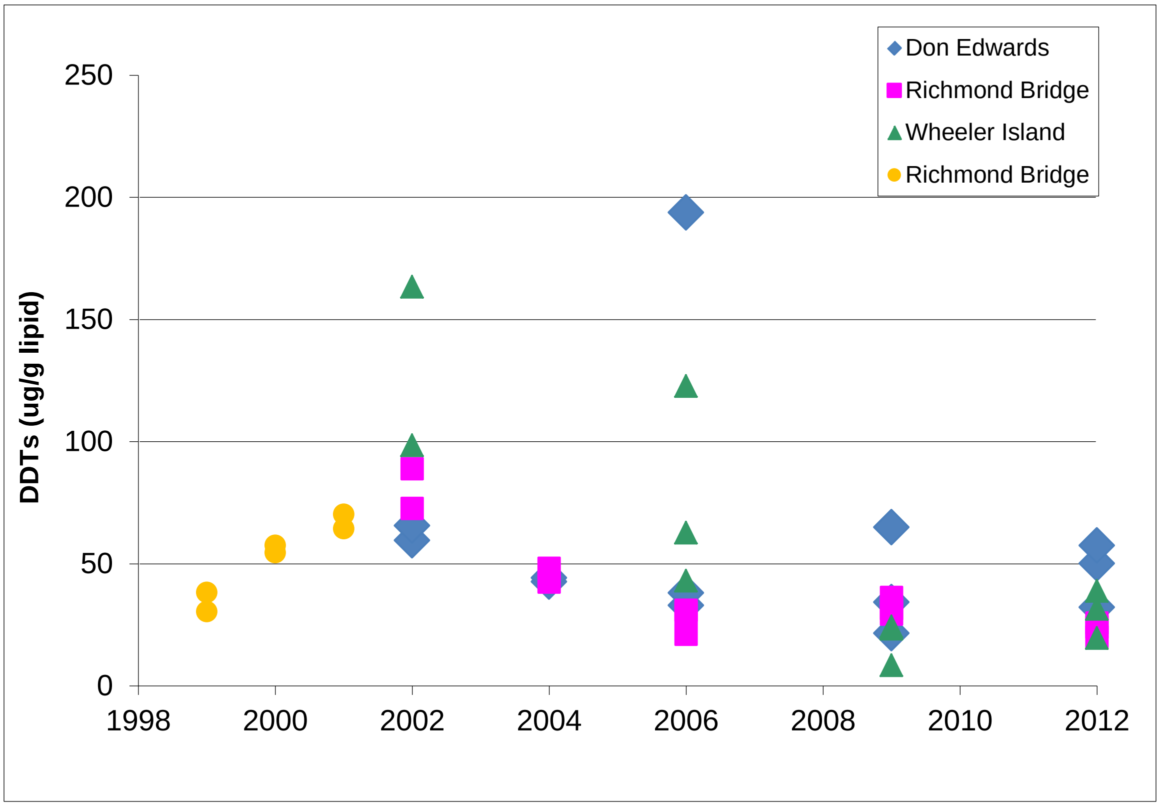


Figure 8. **DDE concentrations (ug/g ww) in cormorant eggs from San Francisco Bay, 1999-2012.** Data from sites monitored during the San Pablo Bay Coastal Intensive Site Network study (Davis et al., 2004) are shown in orange circles and presented as fresh wet weight. The red line indicates the lowest effects threshold for cormorants (5 ug/g fww).

D. DIELDRIN

Background and Prior Work

Dieldrin is an organochlorine insecticide that is a persistent, bioaccumulative, and toxic pollutant. From 1950 to 1974, dieldrin was widely used to control insects on cotton, corn, and citrus crops. Dieldrin also was used to control locusts and mosquitoes, as a wood preservative, and for termite control. Historical use near the Bay included dieldrin processing, packaging, and shipping at the United-Heckathorn facility in Richmond Harbor between the 1940s and 1960s. Dieldrin is no longer produced in the United States due to its harmful effects on humans, fish, and wildlife, and all uses of dieldrin were banned in the United State in 1985 except for subsurface termite control, dipping of nonfood roots and tops, and moth-proofing in a closed manufacturing process.

Dieldrin was measured in the CISNET and RMP pilot studies. There was no statistically significant long-term trend in dieldrin at the Richmond Bridge site, and concentrations appeared erratic over the period of record. The mean concentration was highest in 2000 (560 ng/g lw) and lowest in 2002 (150 ng/g lw).

Walker et al. (1969) found that mallard egg production was reduced by 20% and egg fertility was reduced by 34% at dieldrin concentrations (whole egg) of 45,200 ng/g ww. None of the CISNET study (Davis et al., 2004) or Davis et al. (2006) study composites were anywhere near this threshold.

Spatial Patterns

Concentrations ranged from a low of 14 ng/g lw at Richmond Bridge in 2012 to a high of 1760 ng/g lw at Wheeler Island in 2002 (Figure 9). There were no statistically significant differences among sites for 2002, 2004, 2006, 2009, or 2012. There was a statistically significant difference among the years (all sites combined; Kruskal-Wallis: $H = 18.89$, $df = 4$, $p = 0.001$); therefore, the data could not be pooled and tested for spatial differences.

Although not statistically significant, the mean concentration at Wheeler Island in 2002 (885 ng/g lw) was seven times higher than the mean for the Don Edwards site (122 ng/g lw) due to one composite with an elevated concentration. This sample also had high concentrations of DDTs, PBDEs, and PCBs. Higher concentrations at Wheeler Island are consistent with its location near agricultural areas where the use of pesticides has been historically high.

Temporal Trends

Dieldrin concentrations were fairly consistent over time except for one very high composite at Wheeler Island. Kendall's rank correlation indicated no statistically significant long-term trend in dieldrin at the Don Edwards ($z = -1.19$, $p = 0.235$, tau = -

0.263), or Wheeler Island (z = -1.52, p = 0.130, tau = -0.426) sites, but a significant decline at Richmond Bridge (z = -2.18, p = 0.029, tau = -0.388). Dieldrin in transplanted bivalves in the Bay has decreased significantly over the period of record (1980 – 2003) (Gunther et al., 1999; Connor et al., 2004).

Comparison to Effect Thresholds

Walker et al. (1969) found that mallard egg production was reduced by 20% and egg fertility by 34% at dieldrin concentrations (whole egg) of 45,200 ng/g ww. All of the current study composites as well as the CISNET composites were well below this threshold (Figure 10).

Figure 9. **Dieldrin concentrations (ng/g lw) in cormorant egg composites from San Francisco Bay, 1999-2012.** Data from sites monitored during the San Pablo Bay Coastal Intensive Site Network study (Davis et al., 2004) are shown in orange circles.

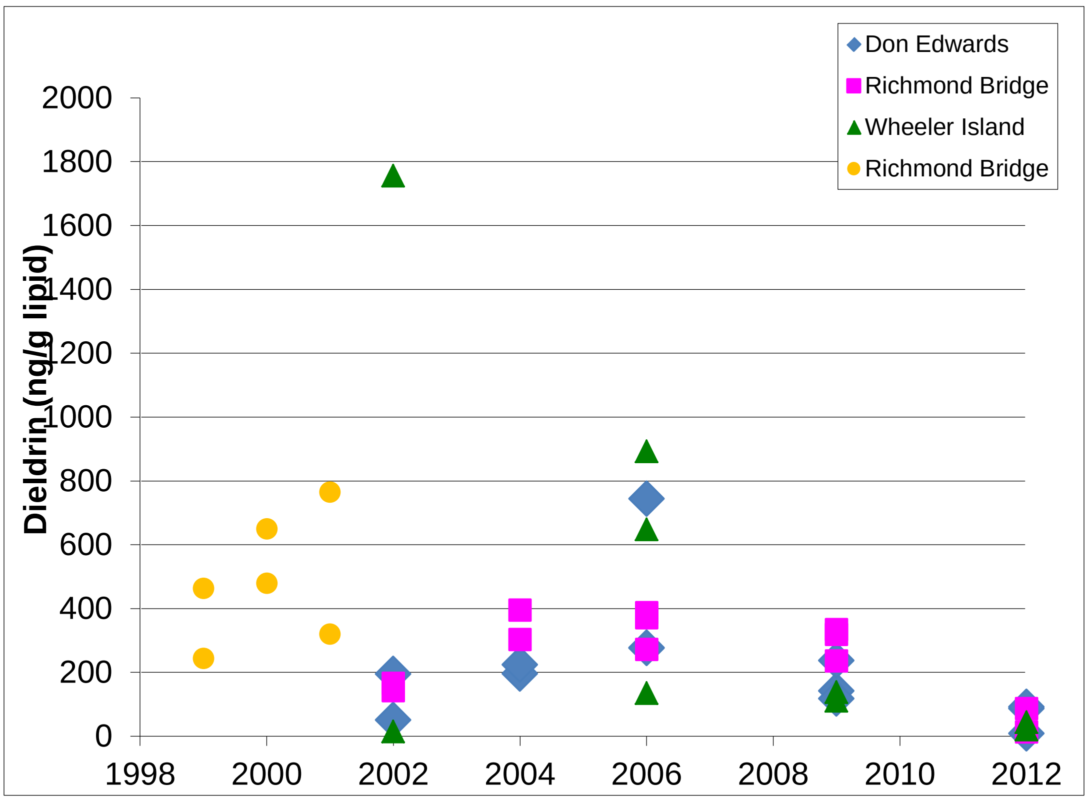
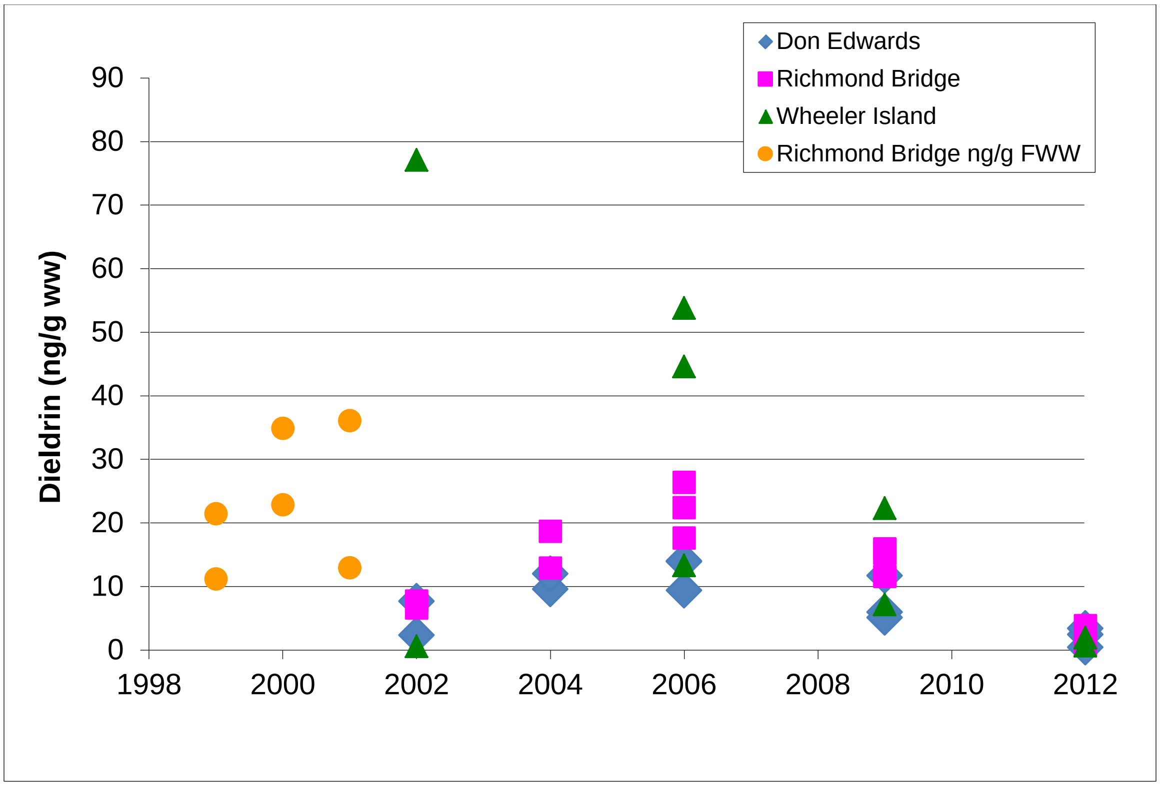


Figure 10. Dieldrin concentrations (ng/g ww) in cormorant egg composites from San Francisco Bay, 1999-2012. Data from sites monitored during the San Pablo Bay Coastal Intensive Site Network study (Davis et al., 2004) are shown in orange circles and presented in fww. The lowest effects threshold level is 45,200 ng/g ww.



E. POLYBROMINATED DIPHENYL ETHERS

Background and Prior Work

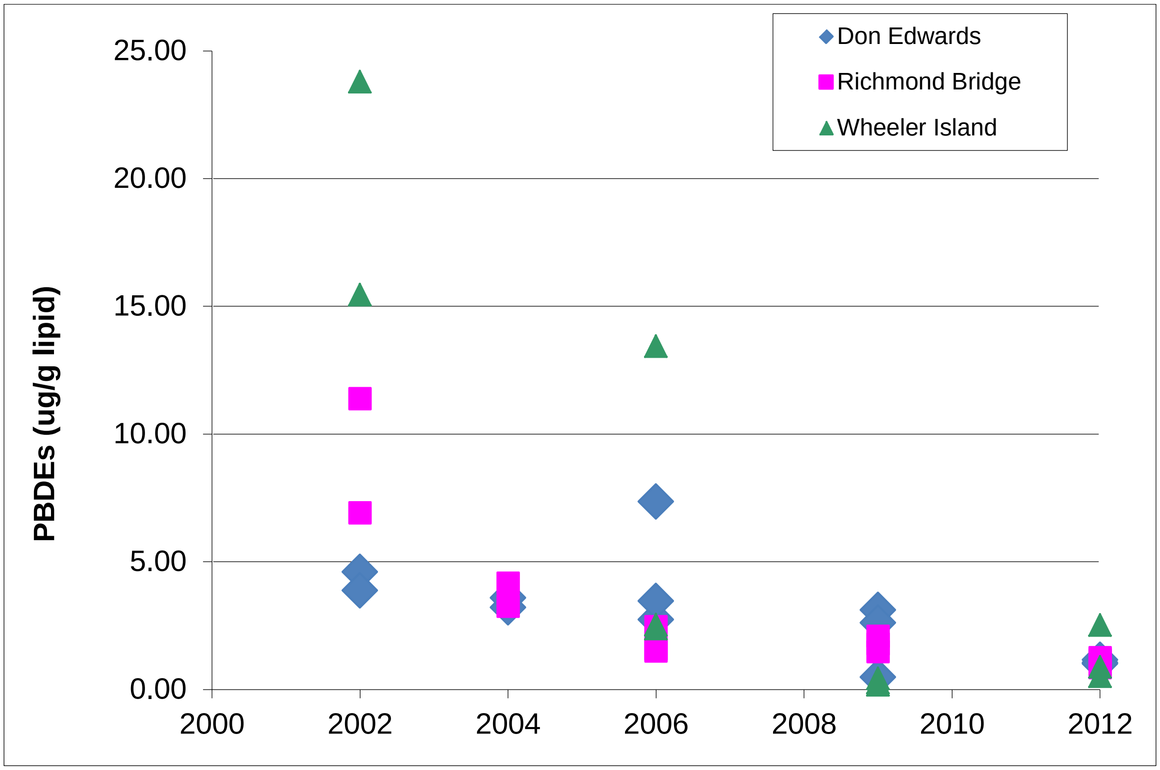
Environmental contamination by brominated flame retardants, especially PBDEs, has attracted the attention of managers and the public due to their persistence, bioaccumulation, and possible adverse effects on humans and Bay wildlife. Prior monitoring studies of PBDEs in the Bay are discussed in the "Comparison to effects thresholds" sections for cormorants and terns below.

DOUBLE-CRESTED CORMORANTS

Spatial Patterns

Concentrations of PBDEs in cormorant eggs varied considerably in space and time among samples collected from the three regions of San Francisco Bay (Figure 11). PBDE concentrations in cormorant eggs ranged from a maximum of 23.8 ug/g lw at Wheeler Island in 2002 to a minimum of 0.17 ug/g lw at Wheeler Island in 2009. Mean concentrations in 2002 at Wheeler Island (19.6 ug/g lw) were more than twice those at the Richmond Bridge mean (9.1 ug/g lw) and almost five times the Don Edwards mean (4.2 ug/g lw). However, due to the small sample sizes and large variances, statistically significant spatial differences within each year (2002, 2004, 2006, 2009, and 2012) were not discernible. There was a statistically significant difference among the years (all sites combined; Kruskal-Wallis: $H = 24.75$, $df = 4$, $p = <0.0005$), so years could not be pooled to test for spatial differences.

Figure 11. PBDE concentrations (ug/g lw) in cormorant egg composites from San Francisco Bay, 2002-2012.



Temporal Trends

PBDE concentrations appear to be contaminants of diminishing concern in San Francisco Bay because of falling concentrations in water and in the food web (Werme, 2012). Trend analysis conducted using Kendall's rank correlation documented statistically significant decreases for all three sampling sites (Don Edwards: $z = -3.06$, $p = 0.002$, $tau = -0.678$; Richmond Bridge: $z = -3.69$, $p = <0.0005$, $tau = -0.816$; Wheeler Island: $z = -2.02$, $p = 0.043$, $tau = -0.503$).

The decline in environmental PBDE concentrations has been attributed to the California Legislature's ban in 2006 on the use of the "penta" and "octa" commercial congener mixes (the more bioaccumulative congeners) (Werme, 2012). Continued monitoring of avian eggs and other biosentinel species (mussels, sport fish) will be essential to confirm the downward trends in the San Francisco Bay, and track the effectiveness of the bans.

Comparison to Effect Thresholds

Although effect thresholds for PBDEs in birds are not available, the seemingly high concentrations in some San Francisco Bay bird egg samples raised concern. A review showed that PBDE concentrations in the eggs of piscivorous birds from the Bay were an order of magnitude higher than those in birds from Chesapeake Bay and the Delaware Bay area (Yogui and Sericano, 2009).

San Francisco Bay appears to have relatively high concentrations of PBDEs compared to other ecosystems worldwide. The cormorant eggs from Wheeler Island in 2002 contained higher PBDE concentrations (15-24 ug/g lw) than are typically found eggs of other fish-eating birds in North America (Sutton et al., 2015). Hites (2004) reviewed two long-term studies on PBDEs in aquatic bird eggs and reported a maximum concentration of 7.51 ug/g lw.

The elevated concentrations at Wheeler Island were unexpected because the Wheeler Island colony is in the least urbanized of the three regions sampled, far from the suspected primary sources of PBDEs (wastewater effluent and urban runoff). RMP bivalve data have also indicated relatively high concentration in the Suisun Bay region. Resident *Corbicula fluminea* collected from the Sacramento and San Joaquin rivers (just above the confluence of the rivers) had relatively high PBDE concentrations with maximum concentrations reaching 0.11 ug/g dry weight (dw) (RMP Data: http://www.sfei.org/rmp/wqt). The evidence suggests a PBDE source near Suisun Bay, either a local source such as a landfill or transport from Central Valley sources into Suisun Bay via Delta outflow.

FORSTER'S TERNS

Spatial Patterns

Across all sites, the mean (± standard error) PBDE concentration in Forster's Tern eggs in 2009 was 1.44 ± 0.12 ug/g lw, and concentrations in individual eggs ranged from 0.67 ug/g lw at Napa Marsh to 2.35 ug/g lw at Eden Landing (Figure 12). PBDE concentrations did not vary significantly among colonies (Kruskal-Wallis: $H = 5.19$, $df = 5$, $p = 0.394$).

Across all sites, the mean PBDE concentration in Forster's Tern eggs in 2012 was 1.56 ± 0.17 ug/g lw, and concentrations in individual eggs ranged from 0.69 ug/g lw at Cargill Pond A7 to 3.57 ug/g lw at Hayward Shoreline (Figure 12). PBDE concentrations in 2012 did not vary significantly among the six colonies (Kruskal-Wallis: $H = 8.77$, $df = 5$, $p = 0.119$).

When the data for both years were combined there were no significant differences among sites (Kruskal-Wallis: $H = 10.2$, $df = 8$, $p = 0.251$).

Temporal Trends

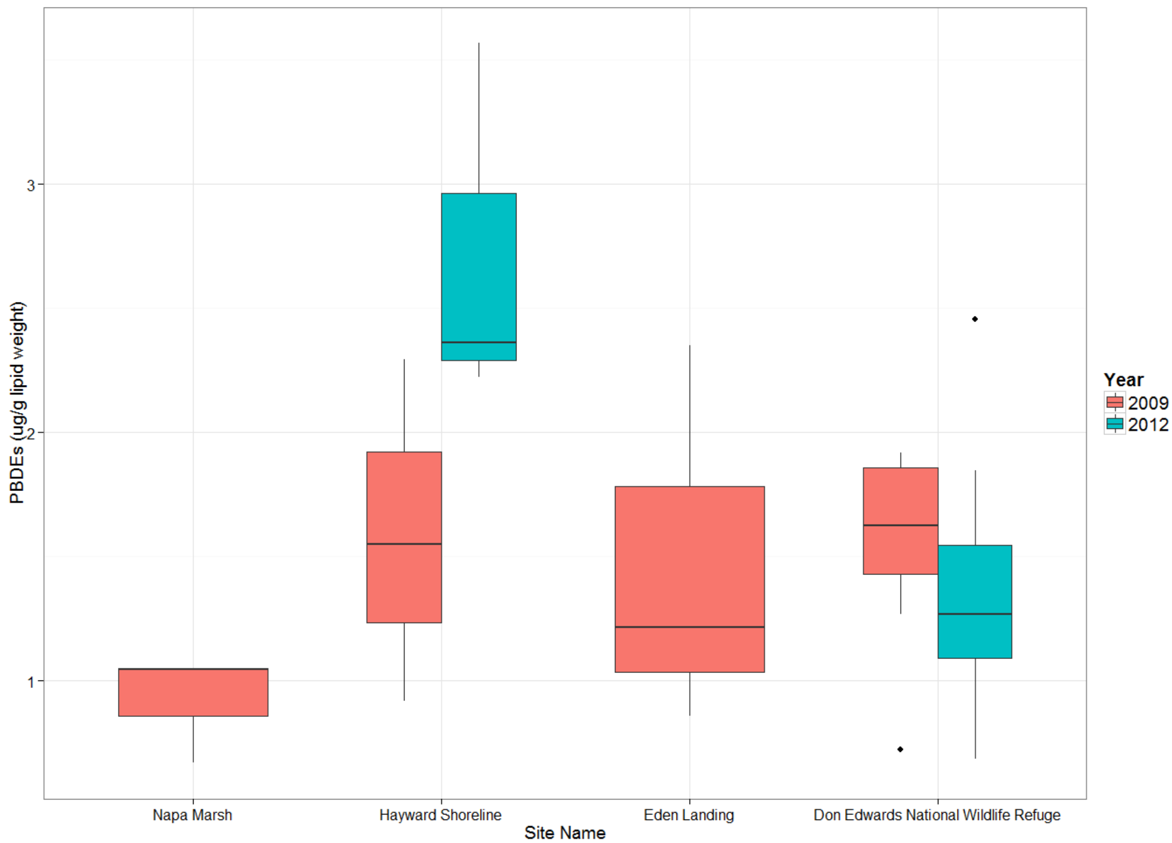
Insufficient data have been collected to assess inter-annual trends based on RMP data, because sites have been monitored for less than three years (Figure 12).

Comparison to Effect Thresholds

Effect thresholds for PBDEs in terns are not available, but recent embryotoxicity studies with American kestrels (*Falco sparverius*) suggest the lowest-observed-adverse-effect-level (LOAEL) for pipping and hatching success to be 1.8 µg penta-BDE/g egg on a ww basis (~32 µg/g lw) (McKernan et al., 2009, 2010). The PBDE concentrations in tern eggs from RMP monitoring were well below this threshold. However, tern samples collected in 2002 and 2003 from Eden Landing in the San Francisco Bay had the highest PBDE concentrations (62 and 63 ug/g lw) ever recorded in wildlife (She et al., 2008), and they exceeded this LOAEL. This observation of some of the highest concentrations of PBDEs anywhere in the world raised concern for possible impacts on terns in the Bay (Shaw and Kannan, 2009).

Information on the relative sensitivity of terns to PBDEs was needed to assess the risk these chemicals pose to terns and other species of waterbirds that nest in San Francisco Bay. Therefore, a study was undertaken in 2010 by Rattner et al. (2011) with three objectives: (1) determine embryonic survival, pipping and hatching success of common terns (*Sterna hirundo*) to air cell-administered PBDE (DE-71 formulation); (2) examine embryos and hatching terns for evidence of sublethal effects including deformities, growth, hepatic, thyroid and immune organ histopathology, and biochemical effects; and (3) compare responses and the relative sensitivity of common terns to results found in other similarly tested avian species (chicken, mallard and kestrel) controls. The findings suggest common tern embryos, and perhaps other tern species, are no more sensitive (and are probably less sensitive) to PBDEs than are American kestrel embryos, and are similarly sensitive as chickens and mallard embryos (Rattner et al., 2011).

Figure 12. **PBDE concentrations (ug/g lw) in tern egg composites from San Francisco Bay, 2009 and 2012.** The bottom, middle, and top lines of each box are the 25th, 50th, and 75th percentiles of the data. Whiskers extend from the top and bottom of the boxes to the highest and lowest values that are within 1.5 times the interquartile range (distance between the 25th and 75th percentiles) of the upper or lower hinge (25th or 75th percentile). Outliers (values that are greater or less than the values spanned by the whiskers) are plotted as points.



F. SELENIUM

Background and Prior Work

Selenium is an essential element in bird diets, but it can also be toxic. Selenium exposure can cause reproductive deformities and impair hatching of bird embryos.

Davis et al. (2006) found selenium concentrations in cormorant eggs ranged from 2.0 ug/g dw in 1999 at the Richmond Bridge site to 3.4 ug/g dw at Don Edwards in 2002. In 2002, mean selenium concentrations at Don Edwards were about 1.5 times higher than at Wheeler Island, in contrast to other RMP findings that have indicated higher selenium concentrations in Suisun Bay than in the South Bay (Davis et al., 2006).

The USFWS has established guidelines for interpreting the ecological risk associated with concentrations of selenium in various environmental matrices (Beckon et al. 2000). For avian eggs, risks to sensitive species are not likely for concentrations lower than 6 ug/g dw. These guidelines are lower than a guideline of less than 8 µg/g dw suggested as a threshold for risks to sensitive species by Ohlendorf and Heinz (2011). The maximum selenium concentration found by Davis et al. (2006) was 3.4 ug/g dw at Don Edwards, and the maximum concentration observed in a composite sample of cormorant eggs in the CISNET study was 3.0 ug/g dw, both of which were well below the 6 or 8 µg/g concentration of concern. Schwarzbach and Adelsbach (2002) observed similar concentrations in cormorant eggs from the Bay region collected in 2000 and 2001, with a mean of 2.6 ug/g dw in 8 eggs, and concluded selenium contamination was not a cause for concern in populations of this species in San Francisco Bay.

DOUBLE-CRESTED CORMORANTS

Spatial Patterns

Selenium concentrations ranged from 1.9 ug/g dw in 1999 at the Richmond Bridge site to 8.7 ug/g dw at Don Edwards in 2009 (Figure 13). Due to small sample sizes statistically significant spatial differences within each year (2002, 2004, 2006, 2009, and 2012) were not discernible. There was a statistically significant difference among the years (all sites combined; Kruskal-Wallis: $H = 15.17$, $df = 4$, $p = 0.004$); therefore, years could not be pooled and tested for spatial differences.

The absence of statistically significant spatial differences stands in contrast to other RMP findings that have documented higher selenium concentrations in Suisun Bay than in the South Bay. Mean selenium concentrations in breast muscle of surf scoters (*Melanitta perspicillata*) and greater scaup (*Aythya marila*) in 2002 were significantly higher in Suisun Bay compared with San Pablo Bay and South Bay (Hunt et al., 2006). Concentrations may have been higher in Suisun Bay scoters due to the proximity to sources of selenium (oil refinery discharges and San Joaquin Valley agricultural drainage) and were also correlated with high selenium concentrations in scoter prey items. One explanation for the differences between ducks and cormorants may be that different areas were sampled for the different studies.

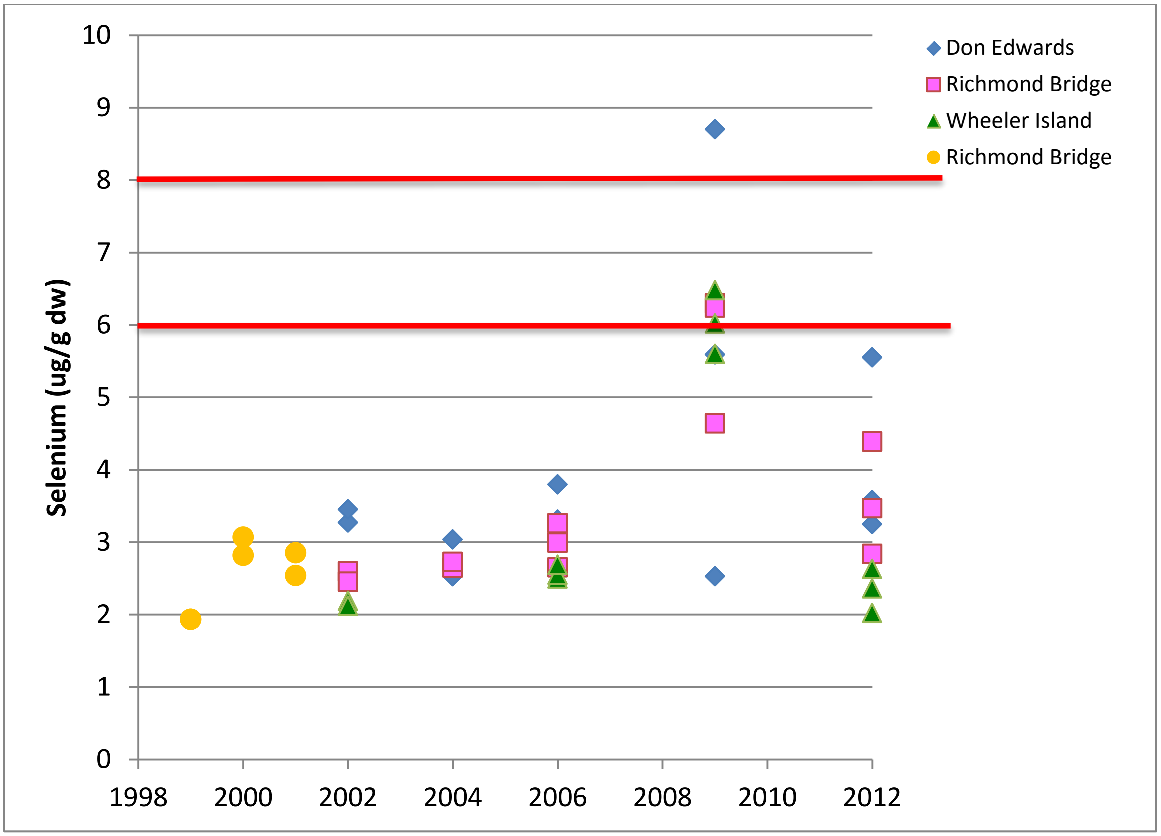
Temporal Trends

There was a statistically significant increase in selenium concentrations at the Richmond Bridge (Kendall's rank correlation: $z = 2.69$, $p = 0.007$, $tau = 0.595$). Wheeler Island (Kendall's rank correlation: $z = 0.73$, $p = 0.467$, $tau = 0.181$) and Don Edwards ($z = 1.13$, $p = 0.260$, $tau = 0.251$) had no significant trends - high variance among samples in 2009 and 2012 reduced the power to detect trends at Don Edwards and Wheeler Island.

Comparison to Effect Thresholds

The maximum selenium concentration in this study was 8.7 ug/g dw at Don Edwards in 2009, slightly above the 8 µg/g concentration of concern discussed previously. Two composites from Richmond Bridge and Wheeler Island in 2009 were in the 6 – 8 µg/g range of concern. This is in contrast to the observation of Schwarzbach and Adelsbach (2002) that selenium concentrations in cormorant eggs from the Bay region collected in 2000 and 2001, with a mean of 2.6 ug/g dw in 8 eggs, were not a cause for concern for San Francisco Bay cormorants. The maximum concentration observed in a composite sample of cormorant eggs in the CISNET study was 3.0 ug/g dw, below the 6 µg/g concentration of concern.

Figure 13. **Selenium concentrations (ug/g dw) in cormorant egg composites from San Francisco Bay, 1999-2012.** Data from sites monitored during the San Pablo Bay Coastal Intensive Site Network study (Davis et al., 2004) are shown in orange circles. The red lines indicate the range of concern (6-8ug/g dw).



FORSTER'S TERNS

Spatial Patterns

Across all sites, the mean (± standard error) selenium concentration in tern eggs in 2009 was 4.21 ± 0.26 ug/g dw, and concentrations in individual eggs ranged from 2.37 ug/g at Napa Marsh to 6.23 ug/g at Pond AB2 on Don Edwards (Figure 14). Selenium concentrations varied significantly among colonies (Kruskal-Wallis: $H = 11.90$, $df = 5$, $p = 0.036$). Post-hoc pairwise comparisons at a family error rate of 0.05 were not significant, but at a family error rate of 0.10 selenium concentrations at Napa Marsh were significantly lower than at Pond AB2 (Dunn's Test: $z = 2.91$, $p = 0.004$).

Across all sites, the mean selenium concentration in tern eggs in 2012 was 3.74 ± 0.09 ug/g, and concentrations in individual eggs ranged from 3.19 ug/g at Pond A2W on Don Edwards to 4.51 ug/g at Cargill Pond A7 (Figure 14). Selenium concentrations varied significantly among the six colonies (Kruskal-Wallis: $H = 11.70$, $df = 5$, $p= 0.039$), but no significant pairwise differences between colonies could be determined (adjusted for ties).

There were no significant differences among years (Kruskal-Wallis: $H = 1.12$, $df = 1$, $p = 0.289$), so data were combined and tested for spatial patterns. When the data for all years were combined there was a significant difference among sites (Kruskal-Wallis: $H = 19.93$, $df = 8$, $p = 0.011$). Post-hoc pairwise comparisons indicated selenium concentrations at Pond AB2 in Don Edwards were significantly greater than at Napa Marsh (Dunn's Test: $z = 3.31$, $p = 0.001$).

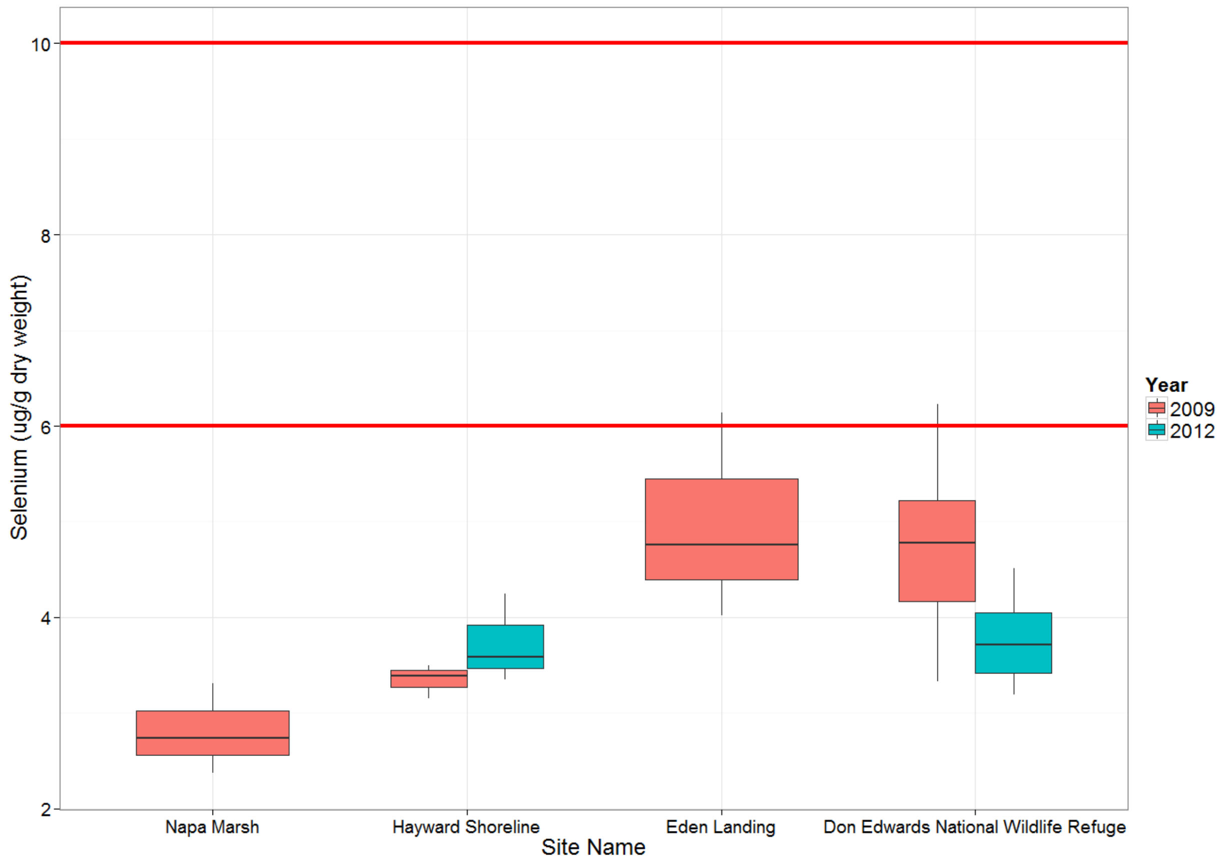
Temporal Trends

Insufficient data were collected to assess inter-annual trends based on RMP data, as sites have been monitored for less than three years (Figure 14).

Comparison to Effect Thresholds

The maximum selenium concentration for Forster's Tern eggs in 2009 was 6.23 ug/g dw at Pond AB2, within the 6 – 8 ug/g range of concern to sensitive species. One composite from Eden Landing (6.14 ug/g) was also in the 6 – 8 ug/g range. In 2012, the maximum selenium concentration was 4.51 ug/g dw at Cargill Pond A7. These data suggest that selenium contamination is generally of low concern.

Figure 14. Selenium concentrations (ug/g dw) in tern egg composites from San Francisco Bay, 2009 and 2012. The bottom, middle, and top lines of each box are the 25th, 50th, and 75th percentiles of the data. Whiskers extend from the top and bottom of the boxes to the highest and lowest values that are within 1.5 times the interquartile range (distance between the 25th and 75th percentiles) of the upper or lower hinge (25th or 75th percentile).



G. DIOXINS, DIBENZOFURANS, AND COPLANAR PCBS

Chlorinated dibenzodioxins and dibenzofurans are ubiquitous contaminants that are potent toxicants. Calculating toxic equivalents (TEQs) is standard practice for reporting dioxin and dibenzofuran data. TEQs convey the relative toxicity of a dioxin-like compound in comparison to 2,3,7,8-tetrachlorodibenzo-p-dioxin, the most toxic dioxin congener. TEQs are presented separately for dioxins+dibenzofurans (DD TEQs) and for the dioxin-like coplanar PCBs and were calculated using World Health Organization toxic equivalency factors (TEFs) (WHO, 2005).

Spatial Patterns

No statistically significant spatial differences were found among cormorant egg sampling sites within each year (2002, 2004, 2006, and 2012) for the DD and coplanar PCB TEQs. There was a statistically significant difference among the years (all sites combined) for the DD (Kruskal-Wallis: $H = 12.33$, $df = 3$, $p = 0.006$) and coplanar PCB TEQs (Kruskal-Wallis: $H = 19.80$, $df = 3$, $p = <0.0005$), so the data could not be pooled and tested for spatial differences.

Although not statistically significant, the data suggest a consistent pattern of lower concentrations of DD TEQs at Don Edwards than at Wheeler Island and Richmond Bridge (Figure 15).

In contrast, coplanar PCB TEQs tended to be higher at Don Edwards than at Wheeler Island and Richmond Bridge (Figure 16).

These patterns suggest relatively greater dioxin inputs and contamination in the North Bay, and relatively greater PCB inputs and contamination in the Lower South Bay.

Temporal Trends

There was a statistically significant decrease in DD TEQs at the Don Edwards (Kendall's rank correlation: $z = -2.70$, p-value = 0.007, tau -0.711), Richmond Bridge ($z = -2.14$, p-value = 0.032, tau -0.564), and Wheeler Island ($z = -1.99$, p-value = 0.047, tau -0.619) sites (Figures 15). No significant trends in coplanar PCB TEQs were documented for any of the sites (Don Edwards: $z = 1.77$, p-value = 0.077, tau = 0.466, Richmond Bridge: $z = 0.46$, p-value = 0.642, tau = 0.123, and Wheeler Island: $z = 0.93$, p-value = 0.354, tau = 0.289; Figure 16). The coplanar PCB TEQs measured in 2012 were the highest observed in the four rounds of sampling.

Figure 15. **Total dioxin and dibenzofuran TEQ concentrations (ng/g lw) in cormorant egg composites from San Francisco Bay, 2002-2012.**

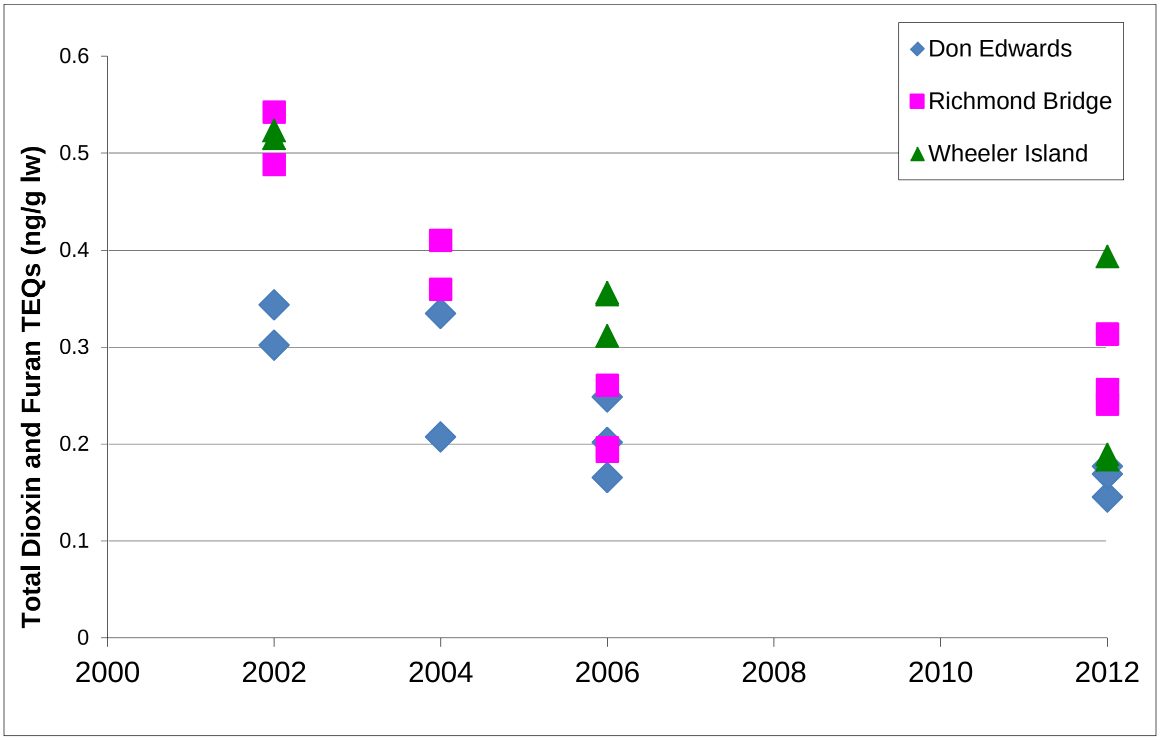
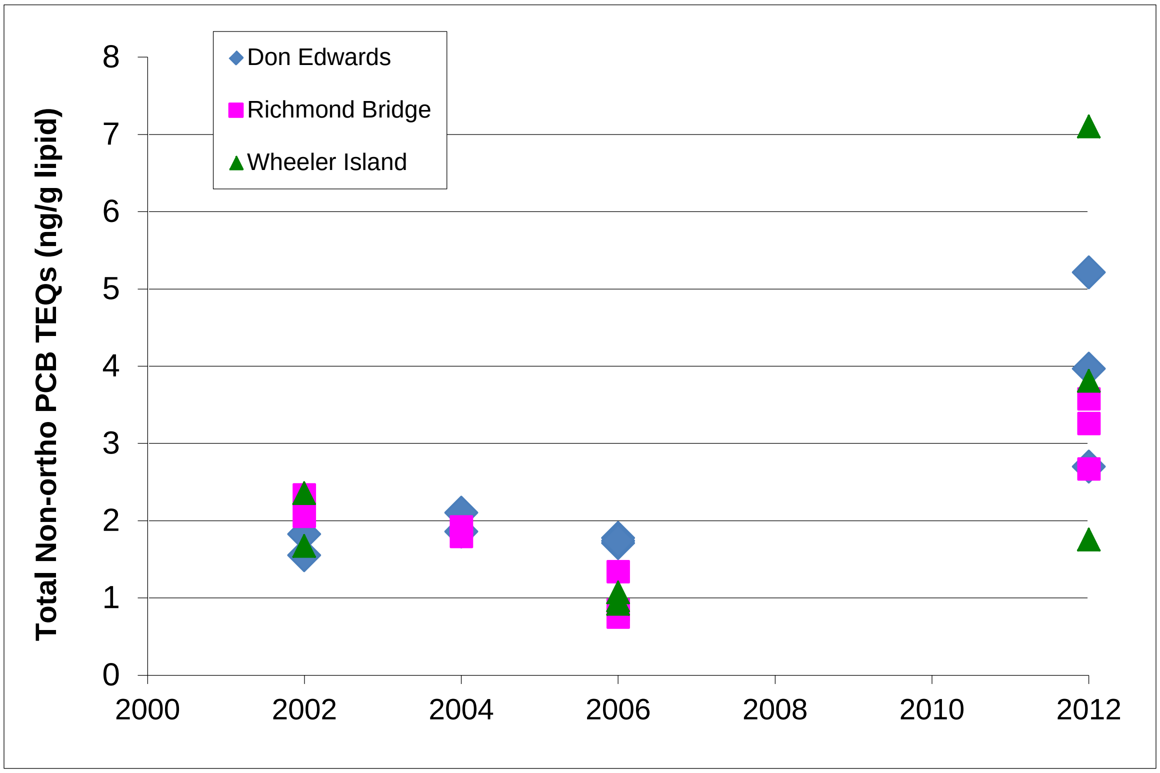


Figure 16. **Total coplanar PCB TEQ concentrations (ng/g lw) in cormorant egg composites from San Francisco Bay, 2002-2012.**



Comparison to Effect Thresholds

Adelsbach and Maurer (2007) reviewed literature on effect thresholds for dioxin TEQs in birds as part of their assessment of contaminant concentrations in San Francisco Bay terns from 2000-2003. They applied a threshold range beginning at 0.2 ng/g ww for terns, which is consistent with thresholds applied in other studies (Frank et al., 2001; Seston et al., 2010).

The maximum DD TEQs measured in cormorant eggs by the RMP was 0.03 ng/g ww at Wheeler Island in 2006 (Figure 17), well below the 0.2 ng/g threshold for effects. Dioxins and dibenzofurans were not present at concentrations that pose a significant risk to cormorants.

On the other hand, the maximum coplanar PCB TEQ (0.3 ng/g ww in a composite sample from Wheeler Island in 2012) and a sample from Don Edwards in 2012 (0.25 ng/g) exceeded the threshold (Figure 18). In general, concentrations of coplanar PCBs appear to be approaching the threshold for toxic effects. This conclusion is similar to that presented in the discussion in Section 3.A. based on total PCB concentrations. While the DD TEQs do not in themselves pose a significant risk, they do marginally add to and increase the TEQs and risk posed by coplanar PCBs.

Figure 17. **Total dioxin and dibenzofuran TEQ concentrations (ng/g ww) in cormorant egg composites from San Francisco Bay, 2002-2012.** The effects threshold for DD TEQs in terns is 0.2 ng/g ww (Adelsbach and Mauer, 2007).

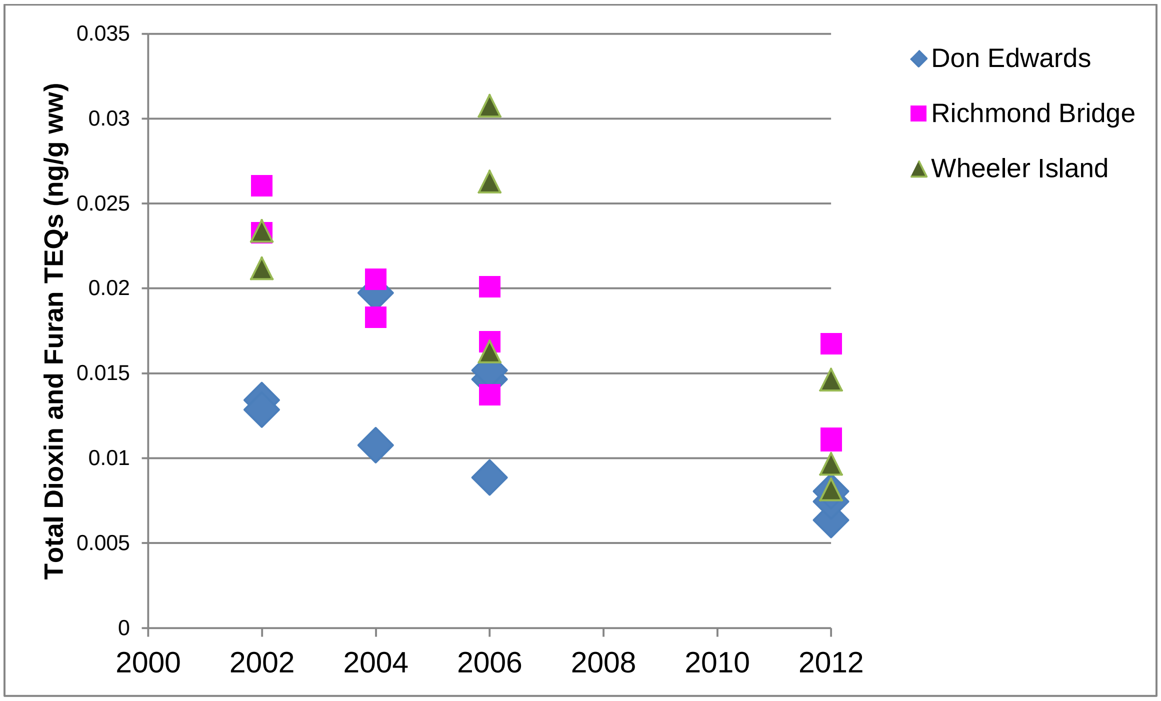


Figure 18. **Total coplanar PCB TEQ concentrations (ng/g ww) in cormorant egg composites from San Francisco Bay, 2002-2012.** The red line shows the effects threshold in terns is 0.2 ng/g ww (Adelsbach and Mauer, 2007)

H. PERFLUORINATED CHEMICALS

PFCs are used in numerous commercial products like fire protection agents, textile protection agents, floor polishers, detergents, paints, paper treatment agents and electronic equipment (SFEI, 2013). As a result of their chemical stability and widespread use, PFCs such as PFOS have been detected widely in the environment. PFOS and related PFCs have been associated with a variety of toxic effects including mortality, carcinogenicity, and abnormal development.

Spatial Patterns

The RMP began analyzing cormorant eggs for PFCs in 2006. Consistent with other published studies, PFOS was the dominant PFC detected in cormorant eggs. PFOS concentrations over the sampling period 2006-2012 have shown a consistent gradient, increasing from north to south. In 2006, the lowest concentrations in individual composites was 0.063 ug/g ww at Richmond Bridge and the highest was 1.63 ug/g ww at Pond A9/10 on Don Edwards (Figure 19). In 2009, the lowest composite concentration was at Wheeler Island and the highest was at Don Edwards (1.76 ug/g). In 2012, the same pattern was observed but the PFOS concentration at the Don Edwards had declined to 0.466 ug/g.

Spatial differences within each year (2006, 2009, and 2012) were investigated and a statistically significant difference was found among sites for 2009 (Kruskal-Wallis: $H = 6.49$, $df = 2$, $p = 0.039$) with concentrations significantly greater in the South Bay (Don Edwards) than at Wheeler Island (Dunn's Test: $z = 2.53$, $p = 0.011$).

There was no statistically significant difference among years (2006-2012, all sites combined; Kruskal-Wallis: $H = 1.52$, $df = 2$, $p = 0.467$); therefore, data were pooled and significant differences among sites were found (Kruskal-Wallis: $H = 16.27$, $df = 2$, $p = <0.0005$) with post-hoc pairwise comparisons indicating PFOS concentrations at Don Edwards were significantly greater than at Richmond Bridge (Dunn's Test: $z = 3.27$, $p=0.001$) and Wheeler Island ($z = 3.68$, $p = <0.0005$).

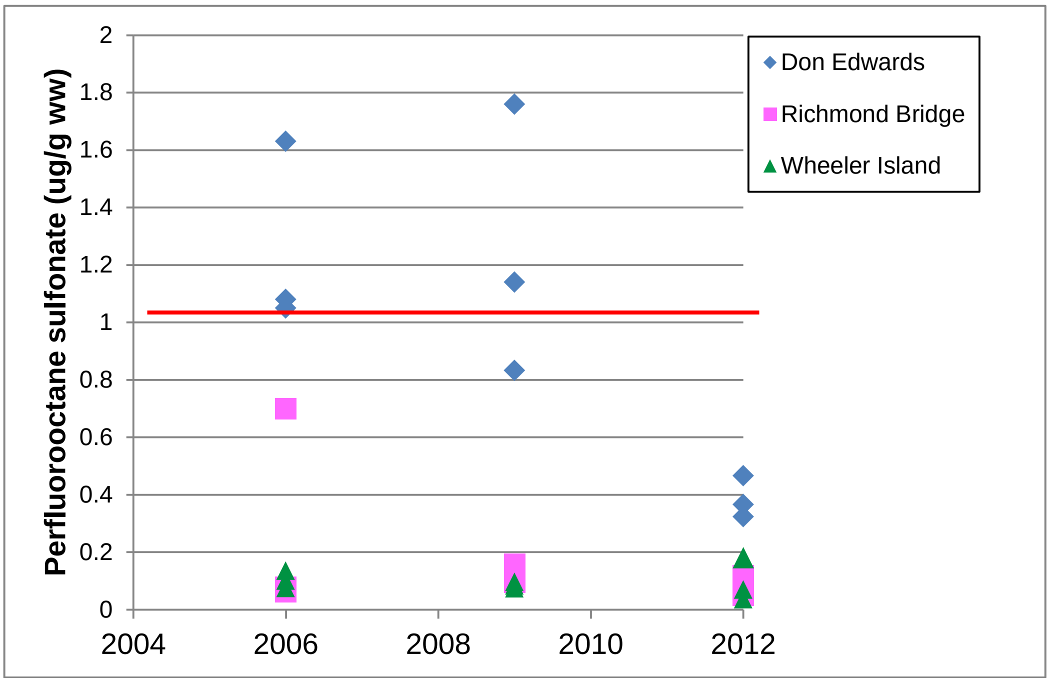
Temporal Trends

No significant trends were found in PFOS concentrations (Don Edwards: $z = -1.89$, p-value = 0.059, tau = -0.545, Richmond Bridge: $z = -0.56$, p-value = 0.579, tau = -0.160, and Wheeler Island: $z = -1.22$, p-value = 0.222, tau = -0.353). The concentrations measured in 2012, however, were the lowest observed in the three rounds of sampling.

Comparison to Effect Thresholds

Newsted et al. (2005) developed a predicted no effect concentration (PNEC) of 1 ug/g ww for eggs, based on effects on northern bobwhite quail offspring survival. Norden et al. (2013) showed reduced embryo survival at 8.5 ug/g PFOS and 2.5 ug/g PFOA in chicken eggs, while cormorant eggs were shown to be less sensitive (difference in sensitivity of 2.6 for PFOS and 3.5 for PFOA). The cormorant data suggest that PFCs appear to be reaching concentrations of potential concern in the San Francisco Bay with five of nine (56%) composite concentrations from the Don Edwards sampling site in the South Bay exceeding this PNEC. However, none of the most recent samples (2012) exceeded the PNEC.

Figure 19. Perfluorooctane sulfonate (PFOS) concentrations (ug/g ww) in cormorant egg composites from San Francisco Bay, 2006-2012. The red line shows the predicted no effect concentration of 1 ug/g ww.



IV. SUMMARY OF FINDINGS

The purpose of this report is to present the avian egg data collected by the RMP in 2006, 2009, and 2012 and the results of analyses of spatial patterns and temporal trends using all available data collected by the RMP and CISNET since 1999. Statistically significant findings include:

Spatial Patterns (see Tables 2 and 3)

- For cormorant eggs, there were several significant relationships indicating higher concentrations for PCBs and PFOS in the South Bay relative to the North Bay. This also was true for mercury, but spatial differences were significant only in 2009, when Don Edwards was significantly higher than Wheeler Island. For PCBs, Richmond Bridge concentrations were higher than those at Wheeler Island when data for all years were pooled.
- For tern eggs, selenium concentrations were higher in a South Bay site (AB2) compared to the Napa Marsh site. There were some statistically significant differences in mercury concentrations indicating higher concentrations in lower South Bay than in South Bay sites, but no significant differences between North Bay and South Bay sites.

Temporal Trends (see Tables 2 and 3)

- For cormorant eggs, there were decreasing trends for PBDEs (all sites), dioxin TEQs (all sites), the DDT (at North Bay sites), and dieldrin (at the Richmond Bridge only). There were mixed trends for mercury with concentrations decreasing at the Don Edwards site in South Bay and increasing at the Richmond Bridge site in North Bay. Finally, selenium concentrations increased at the Richmond Bridge.
- For terns, there were too few years of data to assess trends. At nearly all of the sites, there were data for only one or two years.

In addition, the recent results were compared to ecotoxicological effects thresholds to assess risk. In the most recent dataset (2012), the measured concentrations for PCBs and mercury were higher than effects thresholds at one or more sites, indicating a continued risk to avian species.

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