# CONTAMINANTS IN WINTERING CANVASBACKS AND SCAUPS FROM SAN FRANCISCO BAY, CALIFORNIA

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**Abstract.** Organochlorines, metals, and trace elements were measured in liver, kidney, or wholebody tissues of canvasbacks (*Aythya valisineria*), lesser scaups (*A. affinis*), and greater scaups (*A. marila*) collected from San Francisco Bay and three coastal areas of California during the winter of 1986–1987. Potentially toxic concentrations of mercury (mean  $\leq 10.4 \ \mu g/g$ , dry weight) and selenium (mean  $\leq 32.7 \ \mu g/g$ , dry weight) were found in livers of scaups and canvasbacks from several San Francisco Bay sites. These elements varied spatially, temporally, and between species, with the highest concentrations found in late winter. Mean concentrations of mercury, selenium, and cadmium were generally higher in scaups than in canvasbacks. Of all the organochlorines included in the analyses, only p, p'-DDE and total PCBs were detected in all samples in this study. Mean whole-body concentrations of DDE and PCBs from San Francisco Bay ducks collected in late winter varied spatially and between species, but the concentrations were not considered toxic. Causes for inter-specific differences are unclear, but may be attributable to differences in diet, movement, or physiology.

Key words: canvasbacks, greater scaups, lesser scaups, metals, organochlorines, San Francisco Bay

# 1. Introduction

San Francisco Bay, the largest estuary on the west coast of the continental United States (Conomos *et al.*, 1985), has been greatly modified by human activity (Nichols *et al.*, 1986). Over the past century, more than 85% of the tidal wetlands that once surrounded the Bay have been lost to agricultural and industrial development (Nichols *et al.*, 1986). Loss of habitat has contributed substantially to declines in waterbirds and other wildlife species. For example, numbers of canvasbacks overwintering in San Francisco Bay have decreased about 50% over the past 25 years (USFWS, unpubl. data). Nevertheless, the Bay is a major wintering and feeding area for many species of waterfowl and shorebirds, including several

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endangered species. The open bay waters and salt evaporation ponds in and adjacent to San Pablo Bay (Figure 1) support more wintering canvasbacks than any other location in the western United States (USFWS, unpubl. data). As many as one million shorebirds have been observed on San Francisco Bay during spring migration (Stenzel and Page, 1988).

Besides lost habitat, wildlife has been exposed to a wide range of potentially hazardous pollutants discharged into the Bay (Phillips, 1987). Threats associated with the input of contaminants into southern San Francisco Bay (South Bay) from wastewater treatment plants and non-point sources are compounded by poor flushing due to low tidal exchange and low freshwater flows (Conomos, 1979). Concentrations greater than background levels of metals and trace elements have been measured in water (Cutter, 1989), sediments (Luoma and Cloern, 1982), and bivalves of south San Francisco Bay (Luoma *et al.*, 1985). At least one of these bivalves, *Macoma balthica*, is a primary food for canvasbacks in the Bay (White *et al.*, 1988).

Although flushing of contaminants by freshwater flows is greater in the North Bay, this region also receives large quantities of municipal, industrial, and agricultural discharges (Gunther *et al.*, 1987). In recent studies, concentrations of trace elements were elevated above background in bivalves from North San Francisco Bay and Suisun Bay (Luoma *et al.*, 1990).

A few studies have addressed the potential threats of contaminants to migratory waterfowl in San Francisco Bay. Elevated concentrations of mercury (Hg), cadmium (Cd), and selenium (Se) were found in greater scaups and surf scoters (*Melanitta perspicillata*) from San Francisco Bay in 1982 (Ohlendorf *et al.*, 1986c). In 1985, mean concentrations of Se, Hg, and Cd in scoters collected from the North Bay differed from scoters collected from the South Bay (Ohlendorf *et al.*, 1991). Se was found to accumulate in diving ducks wintering in the Bay to levels toxic to other species (White *et al.*, 1988). DDE and other organochlorines (OCs) were also found to accumulate in surf scoters during the winter (Ohlendorf *et al.*, 1991).

The present study was conducted to investigate waterfowl exposure to contaminants in San Francisco Bay. Specific objectives were to measure organic and inorganic contaminant residues in scaups and canvasbacks wintering in San Francisco Bay and at sites on the California coast, assess geographic differences in contaminant concentrations in these species from these sites, and document contaminant accumulation by ducks wintering in the Bay.

#### 2. Materials and Methods

#### 2.1. Study areas

The California Department of Fish and Game (CDFG) collected canvasbacks, greater scaups, and lesser scaups during the winter of 1986–1987 from five sites



*Figure 1.* Collection sites for canvasbacks and scaups: Lake Earl (LKE), Humboldt Bay (HMB), Morro Bay (MRB), Grizzly Bay (GRB), San Pablo Bay (SPB), Central San Francisco Bay (CSFB), Alameda Flood Control Channel (AFCC), and Alviso (ALV). Shaded areas indicate Don Edwards San Francisco Bay NWR in the South Bay and San Pablo NWR in the North Bay.

within San Francisco Bay and from three sites on the California coast (Figure 1). Canvasbacks were collected in early winter (December 1986) from four sites: Lake Earl (LKE), near Crescent City on California's north coast, Alviso (ALV) in the South Bay, and from Grizzly Bay (GRB) and San Pablo Bay (SPB), two sites in the North Bay. Canvasbacks were collected in late winter (March 1987) from the Alameda Flood Control Channel (AFCC) in the South Bay and SPB in the North Bay.

Greater scaups were collected in early winter from SPB and Humboldt Bay (HMB), near Eureka on California's north coast; lesser scaups were collected at LKE. Greater scaups were collected in late winter from AFCC, SPB, and Central San Francisco Bay (CSFB). Lesser scaups were collected in late winter at Morro Bay (MRB), on California's central coast.

#### 2.2. FIELD METHODS

Personnel of the CDFG collected 50 canvasbacks and 50 scaups by shotgun using steel shot. The total number of ducks per species per site and time period ranged from 4 to 11 and included both sexes and both juvenile and adult birds. Greater and lesser scaups were collected, but they were treated separately for each collection site. Too few females and juveniles were collected to allow comparisons by sex and age. Therefore, only adult males were used for site and species comparisons.

After the ducks were collected, livers and kidneys were removed and placed in chemically cleaned jars. Livers, kidneys, and carcasses were stored on dry ice in the field and later frozen (-20 °C).

#### 2.3. CHEMICAL ANALYSES

Inorganic elements in livers, analyzed at the Environmental Trace Substances Research Center, Columbia, Missouri, included aluminum, arsenic, boron, barium, beryllium, Cd, chromium, copper (Cu), iron, lead, magnesium, manganese, Hg, molybdenum, nickel, Se, silver, strontium, tellurium, vanadium, and zinc (Zn). Cd residues were also determined from kidneys.

Hg, Se, and kidney Cd concentrations were determined by atomic absorption spectrophotometry (AA) using cold vapor reduction (Hg and Cd) and graphite furnace (Se) techniques (see Lonzarich *et al.*, 1992). The lower limit of detection (LOD) was 0.1  $\mu$ g/g, dry weight (dw). The other metals and trace elements were analyzed by Inductively Coupled Plasma Emission Spectroscopy (ICP).

Before carcasses were analyzed for OCs, the feet, bill, feathers, and gastrointestinal tract were removed. The remaining carcasses were then analyzed for OCs at the Mississippi State University Chemical Laboratory, Mississippi State, Mississippi (canvasbacks) and Weyerhaeuser Analytical and Testing Services, Tacoma, Washington (scaups). OCs included in the analyses were hexachlorobenzene (HCB),  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -benzene hexachloride (BHC), heptachlor, heptachlor epoxide,

70

oxychlordane,  $\alpha$ - and  $\gamma$ -chlordane, *trans*-nonachlor, *cis*-nonachlor, endrin, mirex, toxaphene, o, p'-DDE, p, p'-DDE, o, p'-DDD, p, p'-DDD, o, p'-DDT, p, p'-DDT, dieldrin, and total PCBs. Analyses were performed by gas liquid chromatography with 10% of the samples confirmed by gas chromatography/mass spectrometry (see Lonzarich *et al.*, 1992 for details). The LOD for toxaphene and PCBs was 0.05  $\mu$ g/g (wet weight (ww)), and for all other OCs it was 0.01  $\mu$ g/g (ww).

The mean percent moisture levels for livers, kidneys, and carcasses of canvasbacks were 71.2%, 75.3%, and 71.8%, respectively. In scaups, the respective means were 72.6%, 75.3%, and 72.4%. The mean percent lipid concentrations in carcasses were 14.4% for canvasbacks and 15.4% for scaups. Unless otherwise stated, all concentrations of inorganic elements are expressed on a dry-weight (dw) basis. To simplify comparisons of these data with literature values reported on a wet-weight (ww) basis, we estimated the dry-weight values using a value of 70% for moisture content. Organic concentrations were expressed on a wet-weight basis.

Recovery rates on spiked tissues and reference material ranged from 96% to 106% for the inorganics and from 67% to 110% for the organics, and accuracy was acceptable for all analytes. Precision, as estimated by duplicate sample analyses, was acceptable for all analytes, and residue data were not corrected for rates of recovery. For duplicate samples, we used the value from the initial analysis for all statistical tests.

# 2.4. STATISTICAL ANALYSES OF RESIDUE DATA

Geometric means were calculated after transforming concentrations to common logarithms to improve homogeneity of variances. Means were calculated when a contaminant was detected in  $\geq$ 50% of the samples. A value equal to 50% of the LOD was assigned to any not-detected values before logarithmic transformation.

Temporal and spatial comparisons were made using one-way analysis of variance (ANOVA) and Tukey's multiple comparison test. T-tests were used for interspecific comparisons where both canvasbacks and scaups were collected in the same location and during the same time period. However, in a few comparisons the data failed the normality test, and the Mann-Whitney Rank Sum Test was used. For PCBs, within species, canvasbacks and scaups failed tests of equal variance and normality, respectively; Kruskal-Wallis one-way ANOVA on ranks was used here. The significance level was P < 0.05 unless otherwise stated. The power of each test was determined using  $\alpha = 0.05$ . Power less than 0.80 generally indicated an inadequate sample size.

#### 3. Results and Discussion

#### 3.1. INORGANICS

Geometric mean concentrations and ranges of Cd, Cu, Hg, Se, and Zn ( $\mu$ g/g) are

	Early			Late		
	San Francisco Bay	Coast sites		San Francisco Ba	١y	Coast sites
Element	San Pablo Bay <sup>a</sup> (N=4)	Humboldt Bay $(N=3)$	Lake Earl $(N=3)$	Central Bay $(N = 11)$	Alameda FCC $(N=9)$	Morro Bay $(N=7)$
Cadmium	2.55 A <sup>bc</sup>	4.01 A <sup>c</sup>	$0.606  \mathrm{A}^{\mathrm{c}}$	13.4 B	33.9 A	4.96 C
	(0.80 - 21)	(3.6-4.6)	(0.49 - 0.84)	(6.6-26)	(19–85)	(2.4 - 15)
Copper	$101 \mathrm{A}^{\mathrm{c}}$	$88.6  \mathrm{A}^{\mathrm{c}}$	$114 \mathrm{A}^{\mathrm{c}}$	104 A	65.8 B	46.9 C
	(80-120)	(62 - 120)	(100-130)	(65-140)	(50 - 93)	(37–82)
Mercury	2.37 B	4.24 A	3.95 A	$10.4 \text{ A}^{c}$	$5.72 \ B^{c}$	$6.39 \text{ AB}^{\circ}$
	(1.8-2.8)	(3.5-5.2)	(3.5-4.9)	(3.7-20)	(1.8-10)	(3.6 - 9.9)
Selenium	20.7 A	7.01 B	3.55 C	32.7 A	27.4 A	10.7 B
	(15-24)	(5.8 - 7.8)	(2.8-4.2)	(7.2 - 140)	(14-50)	(7.1 - 19)
Zinc	$158  \mathrm{A}^{\mathrm{c}}$	$171 \ A^{c}$	$157 \mathrm{A}^{\mathrm{c}}$	174 A <sup>c</sup>	$162 \text{ AB}^{\circ}$	$153 \ B^{c}$
	(130 - 190)	(170 - 180)	(150 - 160)	(150-200)	(140 - 190)	(140 - 170)

Geometric mean concentrations (minimum-maximum) of inorganic contaminants (µg/g dw) in livers and kidneys (cadmium only) of male scaups collected early (November or December 1986) and late in the winter (February or March 1987). Scaups are Table I

( $\mu g/g$  dw) were: Cd = 24.7, Cu = 87.8, Hg = 8.31, Se = 35.5, and Zn = 178. <sup>b</sup> Means within element and time period not sharing the same letter are different from one another (One-way ANOVA and Tukey's multiple comparison, P < 0.05). <sup>c</sup> Power ( $\alpha = 0.05$ ) for this test was below the desired level (0.80).

	San Francisco	Bay				Coast site
	San Pablo Bay	,a	Grizzly Bay	Alviso Slough	Alameda FCC	Lake Earl
Element	Early <sup>b</sup>	Late <sup>c</sup>	Early	Early	Late	Early
	(N = 4)	(N=7)	(N = 10)	(N=5)	(N=7)	(N=7)
Cadmium	0.319 C	3.61	3.63 A	1.78 AB	2.27	0.513 BC
	(0.06 - 1.2)	(0.31 - 9.1)	(2.1 - 5.8)	(0.53 - 3.3)	(1.1 - 3.4)	(0.16 - 5.6)
Copper	110 A	121	192 A	224 A	121	88.2 A
	(69-140)	(77 - 180)	(67-460)	(110 - 760)	(76-270)	(9.0 - 830)
Mercury	0.825 AB 2)	2.66	0.287 B	2.47 A	5.44	0.091 C
	(0.49 - 1.2)	(1.2 - 4.3)	(0.87 - 1.3)	(0.66 - 4.2)	(3.3 - 9.4)	(0.03 - 0.18)
Selenium	9.02 AB	11.9	5.66 B	10.4 A	14.2	1.91 C
	(6.2 - 13)	(6.9-23)	(3.4 - 8.3)	(5.5 - 18)	(13-16)	(0.86 - 3.5)
Zinc	164 A	181	172 A	205 A	187	180 A
	(140 - 170)	(130 - 250)	(120 - 260)	(160-240)	(150 - 250)	(140 - 320)
<sup>a</sup> At San Pablc	Bay, mean conc	entrations of Cd	and Hg were high	er during the late-w	vinter period; Cu, Se	, and Zn were not
different. <sup>b</sup> Within eleme	ents and time per	iods, sites not sha	aring the same let	ter are different (O	ne-way ANOVA and	ł Tukey's multiple
comparison, P	$< 0.05$ ). Tests ( $\alpha$	= 0.05) had low I	power (< 0.80) foi	: Cu during the early	<i>i</i> period and for all e	lements during the
<sup>c</sup> For late sites,	Hg was higher a	t Alameda FCC tl	han at San Pablo E	3ay; other elements	were not different.	

• Table II

presented for scaups (Table I) and canvasbacks (Table II). The other metals and trace elements were below the LOD for more than 50% of the samples and are not reported.

#### 3.1.1. *Copper*

The only significant spatial difference for Cu was for late-winter scaups (Table I). Greater scaups from CSFB had more Cu (104  $\mu$ g/g) than those from the South Bay (AFCC) (65.8  $\mu$ g/g). Cu was higher in greater scaups from both San Francisco Bay sites than in the lesser scaups from MRB (46.9  $\mu$ g/g) (Table I). The mean Cu concentration in scaups collected from the South Bay in March and April 1982 (96.8  $\mu$ g/g) (Ohlendorf *et al.*, 1986c) was higher than that found in scaups from AFCC (65.8  $\mu$ g/g) in this study. Overall mean Cu concentrations in surf scoters from north (29.3  $\mu$ g/g) and south (53.8  $\mu$ g/g) San Francisco Bay in 1985 (Ohlendorf *et al.*, 1991) were more similar to scaups from MRB (46.9  $\mu$ g/g) than to scaups from San Francisco Bay from this study.

In 1988, mean Cu concentrations were higher in canvasbacks collected from the South Bay (129  $\mu$ g/g) than from the North Bay (80  $\mu$ g/g) (Miles and Ohlendorf, 1993). In the present study, however, Cu concentrations in canvasbacks did not differ spatially or temporally within San Francisco Bay or when compared with Lake Earl canvasbacks (Table II). The only site where the mean Cu concentration in canvasbacks was higher than in scaups was AFCC in late winter (Figure 2). The ranges of means in San Francisco Bay canvasbacks (110–224  $\mu$ g/g) and scaups (65.8–104  $\mu$ g/g) were similar or slightly higher than the means for these species (115  $\mu$ g/g and 55.0  $\mu$ g/g, respectively) from Chesapeake Bay (Di Giulio and Scanlon, 1984) and canvasbacks from Louisiana (85–187  $\mu$ g/g) (Custer and Hohman, 1994).

Cu is an essential element and generally well regulated metabolically (Furness and Rainbow, 1990). Therefore, differences are probably natural variation, taking into account differences in diet and potential interactions with other elements.

# 3.1.2. Zinc

The mean Zn concentration in scaups collected late from CSFB was higher than that found in scaups from MRB, but, within San Francisco Bay, Zn did not differ either spatially or temporally for either species (Tables I and II). Mean Zn concentrations in canvasbacks (range: 164–205  $\mu$ g/g) and scaups (range: 157–174  $\mu$ g/g) in this study were not different at any site. They were higher than the means for the same species from Chesapeake Bay (103  $\mu$ g/g and 75  $\mu$ g/g, respectively) (Di Giulio and Scanlon, 1984).

Mean Zn concentrations in canvasbacks from this study were similar to the means from both North (165  $\mu$ g/g) and South bays (154  $\mu$ g/g) in 1988 (Miles and Ohlendorf, 1993). Mean Zn concentrations in scaups were similar to the South Bay mean for scaups in 1982 (151  $\mu$ g/g) (Ohlendorf *et al.*, 1986c). Means from this study were higher than the range in scaups from British Columbia (134–139  $\mu$ g/g)



*Figure 2.* Geometric means of contaminants ( $\mu$ g/g, dw) in livers (Cd in kidneys) of canvasbacks and scaups collected in early winter from San Pablo Bay (SPB)and Lake Earl (LKE) and from the Alameda Flood Control Channel (AFCC) in late winter. Means within element and site not sharing the same letter are different from one another (P < 0.05). The Mann-Whitney Rank Sum Test was used for comparisons of SPB copper and AFCC selenium because they failed the normality test; *t*-tests were used for all other comparisons. The power of tests marked with \* had power < 0.80.

(Vermeer and Peakall, 1979) but lower than that for scaups from New Jersey (198–202  $\mu$ g/g) (Gochfeld and Burger, 1987).

The means cited above were similar to the mean in control mallards (*Anas platyrhynchos*) in a study of Zn toxicity (180  $\mu$ g/g) (Gasaway and Buss, 1972). Treated mallards in the study were fed 3000–12 000  $\mu$ g/g Zn in their diets, and all groups exhibited zinc toxicosis. Mean Zn concentrations in livers of the treated ducks were six to nine times that of the controls. It appears that the Zn concentrations observed in this study were well within the normal range. Like Cu, Zn is usually well regulated metabolically (Furness and Rainbow, 1990), and differences probably reflect natural variation.

# 3.1.3. Cadmium

Cd accumulated in canvasbacks from SPB, with the late-winter mean more than eleven times greater than that in the early-winter birds (Table II). A similar accumulation seemed to occur in scaups from SPB, with means increasing from 2.55  $\mu$ g/g to 24.7  $\mu$ g/g, but the late-winter sample size (n = 2) was inadequate for statistical comparisons. Mean Cd concentrations were from 8 to 15 times higher in greater scaups than canvasbacks (Figure 2) at comparable sites in San Francisco Bay (AFCC-late and SPB-early). However, canvasbacks and lesser scaups did not differ at Lake Earl (P = 0.828).

The highest mean Cd concentrations were recorded for late-winter greater scaups collected from AFCC (33.9  $\mu$ g/g), whereas the lowest were in early-winter lesser scaups and canvasbacks from LKE and canvasbacks from SPB. Within San Francisco Bay, spatial differences were found in late-winter scaups and early winter canvasbacks (Tables I and II). The mean for late-winter scaups from AFCC in the South Bay was more than twice that for CSFB birds (13.4  $\mu$ g/g). Similarly, mean Cd concentrations were higher in surf scoters from the South Bay than from the North Bay in 1982 and 1985 (Ohlendorf *et al.*, 1991; Ohlendorf and Fleming, 1988).

Mean Cd concentrations in San Francisco Bay canvasbacks collected late in this study (2.27–3.61  $\mu$ g/g) were similar to the means in canvasbacks collected from San Francisco Bay in late winter (2.22–2.40  $\mu$ g/g) in 1988 (Miles and Ohlendorf, 1993). They were also similar to those from the upper Mississippi River in 1976–1977 (3.1  $\mu$ g/g) (Fleming, 1981). They were lower, however, than canvasbacks from Chesapeake Bay in 1973–1976 (7.67  $\mu$ g/g) (White *et al.*, 1979) and 1976–1980 (6.0  $\mu$ g/g) (Di Giulio and Scanlon, 1984).

Mean concentrations in late-winter scaups from San Francisco Bay (AFCC) (Table I) were higher than scaups from San Francisco Bay in March and April 1982 (15.5  $\mu$ g/g) (Ohlendorf *et al.*, 1986c). However, mean Cd concentrations for both species in this study were well below the range (260–450  $\mu$ g/g) associated with kidney and gonadal toxicity in mallards fed a diet supplemented with Cd (White *et al.*, 1978).

# 3.1.4. Mercury

Spatial and temporal differences were more common for Hg than for the other elements. For early-winter scaups, the mean at SPB was lower than either coastal site (Table I). In late winter, the mean in greater scaups from CSFB (10.4  $\mu$ g/g) was higher than the mean from AFCC (5.72  $\mu$ g/g), but the mean in lesser scaups from MRB was intermediate (6.39  $\mu$ g/g) (Table I). Means for scaups (10.6  $\mu$ g/g) and surf scoters (12.5  $\mu$ g/g) collected from the South Bay in late winter of 1982 (Ohlendorf *et al.*, 1986c) were higher than the mean in scaups from the South Bay (AFCC) in this study. However, they were similar to the mean in scaups from CSFB.

The mean in early-winter canvasbacks from ALV (2.47  $\mu$ g/g), a South Bay site, was from three to eight times higher than those of the two North Bay sites. It was also 27 times higher than that in canvasbacks from Lake Earl (Table II). The concentration in late-winter canvasbacks from the South Bay was twice as high as the North Bay. Miles and Ohlendorf (1993) also found Hg to be higher in late-winter canvasbacks from the South Bay. Mercury also was higher in the South Bay than the North Bay for both early- and late-collected surf scoters in 1985 (Ohlendorf and Fleming, 1988), and it appeared to accumulate from January to March.

In this study, Hg accumulated in canvasbacks over the winter at SPB, increasing by more than threefold. Insufficient data were available to compare temporal changes in scaups at any of the sites. However, two greater scaups collected late from SPB had a mean Hg concentration of 8.31  $\mu$ g/g, 3.5 times greater than the four collected early in the winter.

Mean Hg was higher in scaups than canvasbacks at both sites sampled in early winter (SPB and LKE). However, scaups and canvasbacks were not different in late winter at AFCC (Figure 2).

Mean Hg concentrations from all San Francisco Bay sites sampled in this study were higher than those in Chesapeake Bay canvasbacks (0.8  $\mu$ g/g) (White *et al.*, 1979). Mean Hg concentrations in scaups from both late collection sites and in canvasbacks from AFCC, were greater than means from an uncontaminated site in England (0.5–3.0  $\mu$ g/g) (Parslow *et al.*, 1982). Most also were higher than the range of means in livers (2.97–5.40  $\mu$ g/g) from a laboratory study in which mallards fed 0.5  $\mu$ g/g Hg exhibited reproductive impairment (Heinz, 1979).

#### 3.1.5. Selenium

Although Se did not accumulate significantly in canvasbacks from SPB, accumulation seemed to occur in scaups from SPB (Table II). Mean Se concentrations increased from 20.7  $\mu$ g/g in early winter to 35.5  $\mu$ g/g in late winter. However, the late-winter sample size (n = 2) was inadequate for statistical comparisons.

Mean Se concentrations were always higher in ducks from San Francisco Bay than those in birds from the coastal sites (Tables I and II). Within San Francisco Bay, concentrations in late-winter scaups from CSFB and AFCC were not different. The mean Se concentration was higher in early-winter canvasbacks from the South Bay (10.4  $\mu$ g/g at AlV) than from one North Bay site (5.66  $\mu$ g/g at GRB); Se from the other North Bay site (SPB) was intermediate (Table II). Mean Se in latewinter canvasbacks from the North (SPB) and South bays (AFCC) did not differ. All mean Se concentrations from San Francisco Bay were higher than those in Louisiana canvasbacks (3.3–4.4  $\mu$ g/g) (Custer and Hohman, 1994).

Mean Se concentrations were higher in scaups than canvasbacks in both the North (early) and South (late) bays, but there was no interspecific difference at Lake Earl. Scaups from the South Bay had a higher mean Se concentration  $(27.4 \ \mu g/g)$  than was found in the late winter of  $1982 (19.3 \ \mu g/g)$ . However, the mean was lower than in surf scoters from the South Bay the same year  $(34.4 \ \mu g/g)$  (Ohlendorf *et al.*, 1986c). Scaups from both studies had lower Se concentrations than surf scoters from the South Bay in 1985 (overall mean =  $52.4 \ \mu g/g$ ) (Ohlendorf and Fleming, 1988).

The mean Se concentrations in livers of both canvasbacks and scaups were higher than the estimated threshold concentration for impaired reproduction (8.0– 12 µg/g) in female mallards (Heinz *et al.*, 1989). Concentrations in eggs from these mallards ranged from 11.3 µg/g to 37 µg/g. There also was a high incidence of embryotoxicosis in dabbling ducks nesting at Kesterson National Wildlife Refuge (Ohlendorf *et al.*, 1986a, 1986b, 1990; Ohlendorf and Hothem, 1995), and the concentrations of Se in scaups from San Francisco Bay were within the range of means found at Kesterson (20.0–36.1 µg/g). However, as shown by Henny *et al.* (1995), the use of liver Se to predict egg Se may not be valid in sea ducks. White-winged scoters (*Melanitta fusca*) with a mean of 54 µg/g Se in their livers were found to have < 5 µg/g Se in their eggs, nearly 10-fold less than would be predicted in freshwater species (Henny *et al.*, 1995).

#### 3.2. Organochlorines

Of all the OCs included in the analyses, only p, p'-DDE and total PCBs were found in every sample. DDE varied spatially in San Francisco Bay, with scaups having a higher mean DDE concentration at the central Bay site (CSFB: 0.698  $\mu$ g/g) than at the South Bay site(AFCC: 0.419  $\mu$ g/g) (Figure 3). For canvasbacks, the mean DDE concentration in birds from the South Bay (AFCC: 0.941  $\mu$ g/g) was not different from that in birds from the North Bay (SPB: 0.574  $\mu$ g/g) (P = 0.07). At AFCC, the mean DDE concentration was higher in canvasbacks than scaups (P < 0.001).

Surf scoters collected in the Central Bay (Richmond Harbor) in March 1985 (Ohlendorf *et al.*, 1991) had a higher mean DDE concentration (2.39  $\mu$ g/g) than scaups collected from that area in this study (0.698  $\mu$ g/g). The mean DDE concentration in scoters (1.12  $\mu$ g/g) collected from the South Bay (Coyote Creek-Guadalupe Slough) in March 1985 (Ohlendorf *et al.*, 1991) was similar to that in canvasbacks from AFCC in the present study. The mean DDE concentrations in canvasbacks collected by Miles and Ohlendorf (1993) from both the North (0.289  $\mu$ g/g) and South bays (0.584  $\mu$ g/g) in 1988 were lower than in canvasbacks



*Figure 3.* Geometric mean concentrations and ranges of p, p'-DDE and total PCBs ( $\mu$ g/g, ww) in male canvasbacks and greater scaups from San Francisco Bay, California in winter 1987. Within contaminant and species, sites not sharing the same letter are different from one another. DDE comparisons were made using One-way ANOVA and Tukey's multiple comparison, P < 0.05 (Power < 0.80 for scaups, > 0.80 for canvasbacks); PCB comparisons were made using Kruskal-Wallis one-way ANOVA on ranks (Power = < 0.80). At AFCC, PCBs were not different between species (Mann-Whitney Rank Sum Test, P = 0.21; Power < 0.80); DDE was higher in canvasbacks (*t*-test, P < 0.001; Power > 0.80).

from this study. Mean concentrations of DDE in both species were similar to that in wintering northern pintails (*Anas acuta*) from the Salton Sea, California in 1982 (0.602  $\mu$ g/g) (Mora *et al.*, 1987). However, they were higher than the canvasbacks from Chesapeake Bay (0.36–0.56  $\mu$ g/g) (White *et al.*, 1979). The concentrations of DDE found in birds from this study were lower than those assumed to impair reproduction or survival.

The spatial variation of total PCBs within San Francisco Bay was similar to DDE (Figure 3). Canvasbacks from AFCC in the South Bay had a higher mean PCB concentration  $(1.40 \ \mu g/g)$  than those from SPB in the North Bay  $(0.682 \ \mu g/g)$ . The mean PCB concentration in scaups was higher in birds from CSFB  $(2.26 \ \mu g/g)$  than in those from AFCC  $(1.75 \ \mu g/g)$ . PCBs did not differ between species at AFCC. Mean PCB concentrations in canvasbacks from the North and South Bays were similar to those in this species collected from those areas in 1988  $(0.694 \ \mu g/g)$  and  $1.84 \ \mu g/g$ , respectively) (Miles and Ohlendorf, 1993). The mean concentration of PCBs  $(2.40 \ \mu g/g)$  in surf scoters from Richmond Harbor in the Central Bay in 1985 (Ohlendorf *et al.*, 1991) was similar to the mean found in scaups from the same area in this study. The mean for South Bay scoters  $(2.67 \ \mu g/g)$  was higher

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cisco Bay, Californ	ia, February–Ma	arch 1987 <sup>a</sup>			
	Canvasbacks		Scaups		
Contaminant <sup>a</sup>	AFCC	SPB	AFCC	CSFB	
	(N = 7)	(N = 7)	(N = 9)	(N = 7)	
Oxychlordane	0.0135 A <sup>b</sup>	0.0074 B	0.0141 B	0.0245 A	
	(7) <sup>c</sup>	(4)	(8)	(7)	
trans-nonachlor	0.0200 A (7)	0.0107 A	$NC^d$	0.0129	
	(7)	(4)	(3)	(6)	
$o, p' extsf{-}DDT$	ND <sup>e</sup>	ND	NC	0.0117	
			(2)	(6)	

Geometric mean concentrations of organochlorines ( $\mu g/g$ , ww) detected in > 50% of carcasses of male canvasbacks and greater scaups from San Francisco Bay, California, February–March 1987<sup>a</sup>

<sup>a</sup> *Cis*-chlordane, heptachlor epoxide, o, p'-DDE, p, p'-DDT,  $\beta$ -BHC, and Mirex were detected in < 50% of the samples.

(6)

ND

0.0129 A

ND

NC

(3)

ND

(6)

0.0141

<sup>b</sup> Within contaminant and species, sites not sharing the same letter are different from one another. For all comparisons ( $\alpha = 0.05$ ), the power of the test was low (< 0.80).

<sup>c</sup> Number of samples with detected contaminant.

0.0288 A (7)

(7)

ND

<sup>d</sup> NC = not calculated; the contaminant was  $\geq$  LOD in < 50% of the samples.

<sup>e</sup> ND = < LOD in all samples.

Dieldrin

HCB

than either species in this study. The mean PCB concentrations in canvasbacks from Chesapeake Bay (1.5–2.7  $\mu$ g/g) (White *et al.*, 1979) were higher than San Francisco Bay.

In a laboratory study, mallards fed 25  $\mu$ g/g PCBs (Arochlor 1254) had more than 13 times higher PCB concentrations (> 55  $\mu$ g/g) than the highest concentration found in the present study, and reproduction was not affected (Custer and Heinz, 1980). Therefore, PCB concentrations found in this study were not expected to be toxic.

 $\beta$ -BHC, *cis*-chlordane, heptachlor epoxide, o, p'-DDE, p, p'-DDT, and mirex were detected in one or more samples. However, means or comparisons were not made because these OCs were found in < 50% of the samples per species and site. HCB and o, p'-DDT were not found in canvasbacks, but they were found at low levels in 56% and 50%, respectively, of the scaup samples (Table III).

Dieldrin was not detected in scaups, but it was detected at low levels in 13 of the 14 canvasbacks at concentrations (Table III) similar to those from the same areas in 1988 (Miles and Ohlendorf, 1993). These means were lower, however, than those in canvasbacks from Chesapeake Bay in 1973 and 1975 (0.19  $\mu$ g/g) (White *et al.*, 1979). The highest mean in mallard ducklings exposed to dieldrin in food (Nebeker

*et al.*, 1994) was 62 times higher in muscle and 2800 times higher in lipid than the highest mean (0.0288  $\mu$ g/g) in canvasbacks from the current study. Dieldrin had no impact on growth or survival of mallard ducklings in the feeding study, and ducks were not likely to have been affected in this study.

Oxychlordane and *trans*-nonachlor were detected in both species from all sites (Table III). In canvasbacks, means for both contaminants closely mimicked the means from the 1988 study (Miles and Ohlendorf, 1993), with the South Bay having slightly higher concentrations of both contaminants. Overall, mean concentrations in this study were low, with the highest mean being < 5% of the mean of nonachlor and oxychlordane in non-affected starlings (*Sturnus vulgaris*) fed nonachlor (Stickel *et al.*, 1983). At least 10 times more oxychlordane and 7–13 times more *trans*-nonachlor was found in canvasbacks from Chesapeake Bay in 1975 (White *et al.*, 1979). The carcasses of two red-shouldered hawks (*Buteo lineatus*) found dead from chlordane poisoning had 60–90 times more oxychlordane and 150–225 times more *trans*-nonachlor (Blus *et al.*, 1983) than the San Francisco Bay ducks with the highest means.

#### 4. Conclusions

The mean concentration of an inorganic contaminant was higher at a coastal reference site in only mercury for early-winter scaups. In all other cases, San Francisco Bay concentrations of inorganic contaminants were higher or were not different from the coastal sites. Selenium was the only element that was always higher in the Bay samples. The most consistent differences were found for scaup in late winter when concentrations of all but mercury were higher in San Francisco Bay. During the early collection period, most birds had just recently arrived in the Bay and were likely carrying contaminant burdens acquired elsewhere. Birds collected in the late winter were more likely to have burdens acquired locally. Other studies have found that, although contaminants are widespread in biota and sediments throughout the ecosystem, all areas of San Francisco Bay have had concentrations elevated above those from coastal reference sites (Long *et al.*, 1988).

Few temporal comparisons were possible with these data, but canvasbacks were observed to accumulate Cd and Hg during the winter in San Francisco Bay. Limited data suggested that scaups may have also accumulated Cd and Hg and perhaps Se during the winter. This is further evidence that San Francisco Bay contaminant concentrations exceed background levels.

By late winter, Hg and Se had accumulated to concentrations in scaups and, to a lesser degree, in canvasbacks, that have impaired reproduction in game-farm mallards (Heinz, 1979; Heinz *et al.*, 1989) and in dabbling ducks in the wild (Ohlendorf *et al.*, 1986a, 1990). Further study is needed to examine the chronic toxicity of Se and Hg to adult diving ducks and to learn if reproduction by scaups and canvasbacks is similarly affected by these contaminants (Henny *et al.*, 1995).

Several major sources of Se discharges exist in San Francisco Bay. The northern end of the estuary receives Se from the San Joaquin River drainage and from several petroleum refineries (Cutter, 1989). In the South Bay, the primary source of Se is sewage treatment plants. Sources of Hg are less well defined. Sediment data suggest that Hg sources are either ubiquitous or Hg from historical sources has become well mixed over time. Higher concentrations in small creeks suggest the importance of urban runoff as a source.

Both PCBs and DDE were detected in all samples analyzed in this study, but none of the means or maximum values were considered toxic to these species. Many sources of PCBs exist in the estuary, without a major gradient in contamination of the Bay. A large reservoir of DDT and metabolites that presumably still exists in the Central Valley will likely continue to release residues to the estuary slowly, preserving this 'background' degree of contamination (Phillips and Spies, 1988). In addition, San Francisco Bay has certain 'hot spots' that are heavily polluted. For example, sites in Richmond Harbor (CSFB) are contaminated with DDT and other OCs from a former nearby pesticide formulation and packaging plant. The cleanup of contamination at this and many other identified sites in San Francisco Bay is under way.

The reasons for the interspecific differences found for both inorganic and organic contaminants are likely related to differences in diet, movements, physiology, or a combination of these factors. Diets of canvasbacks and scaups differed, as determined from a small sample of ducks collected from San Francisco Bay in conjunction with this study (White *et al.*, 1988). Although the overall pattern of spatial variation for both inorganic and organic contaminants suggests that both canvasbacks and scaups exhibit some degree of site fidelity in the Bay, further study is needed to confirm this.

In other studies, geographic patterns in contaminant concentrations have been found to vary from chemical to chemical, with considerable variation and patchiness in the Bay. This has made it difficult to piece together an overall picture of trends. Previous studies have shown that the highest concentrations of many contaminants occur in the peripheral areas, such as harbors and boat basins. Many are more concentrated in and near the southern end of the south Bay (ALV and AFCC), in the Sacramento-San Joaquin Delta (GRB), off the Richmond/Berkeley shore (CSFB), or near point source discharges. For some contaminants, however, geographic trends are not apparent; they are scattered relatively uniformly throughout the system (Long *et al.*, 1988). Although such a distribution makes the cleanup a difficult task, monitoring and regulation are needed to insure that contaminants do not exceed levels considered safe for the health of canvasbacks, scaups, and other waterfowl.

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