DFG Exhibit 52

Exhibit 52, entered by the California Department of Fish and Game for the State Water Resources Control Board 1987 Water Quality/ Water Rights Proceeding on the San Francisco Bay/Sacramento-San Joaquin Delta.

# Selenium in Fish and Wildlife of San Francisco Bay and the Sacramento-San Joaquin Estuary 1986-1987

# EXECUTIVE SUMMARY

This report covers findings by the Selenium Verification Study from October 1986 through May 1987. This program represents a continuation of a statewide investigation of selenium in fish and wildlife begun in January 1986. Efforts in 1986-1987 concentrated on San Francisco Bay, the Sacramento-San Joaquin Delta and the lower San Joaquin River.

Diving ducks wintering on San Francisco Bay had higher selenium concentrations than measured in counterparts at Humboldt Bay and Morro Bay. Selenium levels in diving duck tissues increased during the winter months when these migratory birds were using San Francisco area bays, particularly San Pablo Bay and South San Francisco Bay.

Selenium levels in surf scoters and scaup from Suisun Bay, where the highest levels were measured in diving ducks the previous winter (January 1986), increased between early-winter (December 1986) and mid-winter (January 1987) then appeared to decline by late-winter (March 1987). Selenium in diving duck food organisms did not decline in Suisun Bay; suggesting late-winter bird specimens perhaps were transients migrating north rather than winter-long visitors.

Selenium levels in surf scoters and scaup were 1.5 to 3 times higher in specimens collected from San Pablo and South San Francisco Bay in late-winter 1987 than in late-winter 1986. In Suisun Bay, selenium levels in diving duck tissues were similar in January 1986 and January 1987 specimens.

Humboldt Bay, Lake Earl, and Morro Bay were deemed acceptable control sites at which biota contained background levels of selenium.

Canvasbacks contained lower levels of selenium than surf scoters and scaup. Food habit differences probably account for the difference.

Histopathological examination of diving duck tissues revealed no abnormal conditions. Observations were comaptible with those expected from exposure to a normal environment.

Diving ducks in Suisun Bay accumulated selenium up 30,000 times the concentration of total selenium dissolved in Bay water. Filter-feeding clams, which are food for these ducks, contained 4000-5500 times the waterborne level and diving ducks had 2 to 42 times higher levels than clams, depending on duck species and tissue type. The importance of bioaccumulation of selenium from water by plankton is unknown but may account for much of the concentration difference between clams and water.

Bioaccumulation of selenium in mussels and oysters transplanted to sites in San Francisco Bay indicated selenium enrichment in areas near oil refineries in Suisun Bay and San Pablo Bay and near municipal/industrial discharges in South San Francisco Bay. Water and bird sampling done by other investigators indicate similar patterns of selenium distribution.

Coots collected in winter 1986-1987 near potential sources of selenium in Suisun Bay and southermost South San Francisco Bay contained slightly higher selenium levels than coots collected from marshes on Grizzly Island and Gray Lodge State Wildlife Areas in winter and spring, 1986.

Striped bass from the Sacramento-San Joaquin Estuary contained higher selenium levels in spring 1987 than in spring 1986. Levels in striped bass from the Estuary were higher than in those from an inland population in Success Lake. Selenium impacts on striped bass have not been documented.

White sturgeon collected from San Pablo Bay in spring 1987 contained higher selenium levels than those from Suisun Bay in 1987 and those from San Pablo Bay in spring 1986. The effect of these levels on sturgeon is unknown but they may be of concern from a public health standpoint.

White catfish and channel catfish from Mud Slough and Salt Slough had higher selenium levels than those from several sites in the San Joaquin River, the Sacramento River, and the western Delta. Selenium levels in catfish from the San Joaquin River downstream from the Merced River, Salt Slough and Mud Slough in January and April-May 1987 were similar to those in August 1986, suggesting stable levels of biologically available selenium in a dry year and with current drainwater management practices. Catfish in the western Delta apparently were not influenced by selenium from sources downstream in Suisun Bay.

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# INTRODUCTION

The Selenium Verification Study, begun in December 1985, is one element of the State Water Resources Control Board (State Board) study entitled "Selenium and Other Trace Elements in California". The purpose of the Verification Study is to measure selenium and trace elements in biota from suspected problem areas and determine if these potentially toxic elements occur at levels harmful to fish and wildlife.

The Selenium Verification Study was conducted by the California Department of Fish and Game under an interagency agreement with the State Board. Two laboratories within the Department of Fish and Game were involved in this study. Sample collection and data analysis and interpretation were performed by the Bay-Delta Project in Stockton. Sample preparation and analyses were performed by the analytical chemistry unit of the Fish and Wildlife Water Pollution Control Laboratory (WPCL) in Rancho Cordova.

Collection of bird, fish, aquatic invertebrate, and water samples was begun in January, 1986 from five suspected problem areas and, for comparison, from several areas where there was no evidence suggesting selenium or trace element contamination. The areas investigated in 1986 were: the San Francisco Bay-Estuary, including the Suisun Marsh; subsurface agricultural drainage evaporation ponds in Kern County; Salton Sea, including several surface water systems tributary to the Salton Sea and tributaries to the Colorado River in Imperial and Riverside counties; the Stony Creek drainage, including Black Butte Reservoir in Glenn and Tehama counties; and the San Joaquin River and selected tributaries in western Merced County. These areas were selected for investigation based on data from the Toxic Substances Monitoring Program (TSMP), State Mussel Watch (SMW), Regional Water Quality Control Boards (RWQCBs), the Department of Fish and Game (DFG), and the U.S. Fish and Wildlife Service (USFWS). During the planning process, coordination meetings were held providing opportunities for input to the program design. Findings from these areas were compared with results from samples collected at Humboldt Bay, Gray Lodge State Wildlife Area and the Sacramento National Wildlife Refuge where human activities have not altered selenium levels in the environment and therefore concentrations in animal tissues would reflect exposure to background levels of selenium.

The 1986-1987 Verification Study Program was developed based on results through August 1986 reported by White et al. (1987). The 1986-1987 Program emphasized investigations in the San Francisco Bay and Estuary, the Sacramento-San Joaquin Delta, and the San

Joaquin River and its tributaries in the Grasslands area. Specific aspects of the study were designed to identify potential point sources of selenium to the San Francisco Bay-Estuarine system, measure site-specific rates of bioconcentration in the food chain of diving ducks containing above-background tissue levels of selenium, obtain earlier collections of waterfowl wintering in the San Francisco Bay area to determine baseline selenium levels in their tissue upon arrival and whether or not selenium uptake occurs during the winter from sources in the Estuary, and add control sites for waterfowl for comparison with levels in San Francisco Bay area birds. The expression of biological effects of tissue selenium concentrations measured in waterfowl was assessed through histological examination of liver, heart, and spleen. Additional bird collections were made in the Suisun Marsh and in northeastern California to expand the food habit and geographic bases of selenium data for birds. Catfish were collected from the Delta and upstream sites to evalaute the relative effect of upriver agricultural sources of selenium and industrial sources downstream. Striped bass, an important sportfish and the focus of debate over Bay-Delta water quality/quantity issues, were collected again from the Sacramento and San Joaquin rivers as well as at three new sites (Clifton Court Forebay, Lake Havasu on the Colorado River and a control site, Success Lake) to put selenium levels in Bay-Delta striped bass population into perspective. White sturgeon were collected from San Pablo and Suisun bays to compare with 1986 findings which were inconclusive with respect to potential public health impacts of selenium in sturgeon.

The Stony Creek drainage was not included for further study in 1986-1987 since no significant selenium contamination of fish was identified in 1986. Evidence of fish and wildlife contamination by selenium was found in 1986 at the Salton Sea and at Kern County agricultural drainage evaporation ponds, however, neither of these locations was included in the 1986-1987 Selenium Verification Study because other on-going or proposed investigations were deemed adequate to address the information needs at these sites.

The presence of selenium in biota was determined by analyzing specific tissues. Selenium was measured in liver tissue of fish and birds to be consistent with previous studies and other on-going investigations of trace elements in biota and because it is a good indicator of an animal's exposure to selenium (Lemly 1982). Selenium was measured in the breast muscle of bird species known to be consumed by humans and in the skeletal muscle of most fish species because of potential public health concerns. Selenium was measured in the soft tissue of clams and mussels. Selenium was measured in the tissues of each individual bird, striped bass, and white sturgeon. Analysis of individual organisms yields more information than analysis of several organisms combined in a single sample. Nevertheless, catfish were analyzed in composite samples of six individuals to accommodate the constraint on total analyses and still include more fish in the samples. Channel catfish and white catfish were not mixed in composite samples.

This report covers results from biota collected from October 1986 through May 1987. Findings are interpreted in relation to the continuously growing body of knowledge of selenium and its effects on biological systems. Tissue burdens measured in organisms depend on the exposure history of organisms to selenium in terms of concentration and duration; on species-specific rates of uptake and depuration; and on the age, sex, and reproductive condition of individuals. Relating tissue burdens to local environmental conditions depends on an understanding of factors affecting the speciation and bioavailability of selenium in natural systems; trophic pathways through which uptake of selenium occurs; processes of biological accumulation in individuals and biomagnification through food chains which produce high tissue concentrations of selenium from low ambient levels; and, particularly for migratory species, knowledge of selenium exposure at different locations in other seasons. Determining the implications of tissue burdens for the health of individual organisms and populations requires documenting adverse effects associated with above-normal tissue burdens yet for most species normal levels are not well defined. Only a few studies have documented the toxic effects of selenium to fish and wildlife, most notably in wetlands contaminated with agricultural drain water (Ohlendorf et al. 1986 a, b) and in cooling water reservoirs receiving effluent from ash settling basins at coal-fired power plants (Lemly 1985). Selenium may impact individual organisms through impairment of various physiological functions and, even without mortality of individual adults, may eliminate populations by making individuals functionally sterile (Lemly, 1987).

Protection of fish and wildlife from the toxic effects of selenium will involve establishing criteria for concentrations in water, a difficult task given the small differences between essential levels and toxic levels of selenium in some animals and the tendency for biological accumulation in food chains from low levels in water. Recent laboratory experiments have begun to provide some data on "effect levels" of selenium in fish and wildlife diets and tissues. However, only a few species have been included in experimental investigations. Other trace elements may react synergistically or antagonistically with selenium. These interactions are poorly understood and complementary data for other elements are not always available. This study has measured tissue burdens in biota, with no intent to evaluate reproductive success or effects on target species at the population level. Measured levels of selenium in biota are compared with data from other sources; conclusions are drawn, appropriately qualified in the context of the uncertainties described above. In the absence of complete information, hypotheses are stated to stimulate thought and identify needs for additional information.

# FIELD AND LABORATORY OPERATIONS

## FIELD METHODS

### Sample Collections

Nine species of birds, four species of fish and one invertebrate were collected from October to May, 1987 (Tables 1, 2A, and 2B). Samples were collected from 25 locations statewide (Figure 1, Table 3). Specific sites are depicted in Figures 2 through 4 and described in Appendix A.

### Bird Collection and Processing

Birds were collected using 12 gauge shotguns and steel shot. To reduce intraspecific variation among individuals, we collected adult males when identification and availability permitted. Female and immature birds collected inadvertently were analyzed and included in our results.

Birds were weighed using spring scales. Age was determined based on plumage; sex was determined from plumage or examination of gonads. The liver was removed from all birds; a breast muscle sample was obtained in accordance with the study plan.

Disposable polyethylene gloves were worn during field dissections to prevent sample contamination through contact with human skin. After the skin was peeled from the breast muscle, the furcula and ribs were cut with stainless steel shears, the whole breast with sternum attached was removed and placed in a 4 mil plastic Ziploc bag. The liver was removed with Tefzel forceps and a scalpel and placed in a separate bag. The two sample bags were placed in a third bag with a sample label. Samples were put on dry ice immediately and frozen; they were subsequently stored in a chest freezer at -12°C, usually for a few weeks but at most two months, until they were delivered to the DFG Fish and Wildlife Water Pollution Control Laboratory (WPCL) in Rancho Cordova. Sample storage conditions at WPCL are described in the section on laboratory operations.

In order to investigate possible pathways of selenium into the avifauna, the food habits of collected birds were examined. The esophagus, proventriculus, and gizzard of each bird were removed and their contents emptied into a small jar. Ethyl alcohol was used to preserve the food items for later identification. Food items were quantified by frequency of occurrence. Volumetric measurements were not made because digestion of soft parts had already occurred in many samples.

TABLE 1
COMMON NAME, SCIENTIFIC NAME, FAMILY AND SPECIES NAME CODE
OF BIRDS, FISHES AND INVERTEBRATES COLLECTED IN 1986-87

BIRDS

| Common Name | Species | Family | Code |
|---|---|---|---|
| mallard | Anas platyrhynchos | Anatidae | MALLRD |
| pintail | Anas acuta | " | PNTAIL |
| northern shoveler | Anas clypeata | " | NOSHOV |
| lesser scaup | Aythya affinis | " | LSCAUP |
| greater scaup | Aythya marila | " | GSCAUP |
| canvasback | Aythya valisneria | " | CNVSBK |
| surf scoter | Melanitta perspicillata | " | SCOTER |
| American coot | Fulica americana | Rallidae | AMCOOT |
| American bittern | Botaurus lentiginosuss | Ardeidae | AMBITT |

FISHES

| | | | |
|---|---|---|---|
| white sturgeon | Acipenser transmontanus | Acipenseridae | WSTRGN |
| white catfish | Ictalurus catus | Ictaluridae | WHTCAT |
| channel catfish | Ictalurus punctatus | " | CHNCAT |
| striped bass | Morone saxatilis | Percichthyidae | STBASS |

INVERTEBRATES

| | | | |
|---|---|---|---|
| (Asiatic) freshwater clams | Corbicula fluminea | Corbiculidae | CRBCLA |

## TABLE 2A

## SELENIUM VERIFICATION COLLECTION PROGRAM, 1987

### BIRDS

| LOCATION[1/] | SPP. COLLECTED[2/] | DATE COLLECTED |
|---|---|---|
| CNSFB | SCOTER, GSCAUP, LSCAUP | 11/86 3/87 |
| GRYLG | AMBITT, NOSHOV | 10/86 3/87 |
| HMBLT | SCOTER, GSCAUP, LSCAUP | 12/86 3/87 |
| LEARL | CNVSBK, GSCAUP, LSCAUP | 12/86 3/87 |
| MORRO | SCOTER, GSCAUP, LSCAUP | 12/86 3/87 |
| SJWTR | AMCOOT | 12/86 2/87 |
| SNPBB | GSCAUP, LSCAUP, SCOTER, CNVSBK | 11,12/86 2,3/87 |
| SOSFB | GSCAUP, LSCAUP, SCOTER, CNVSBK | 11,12/86 1,2,3/87 |
| SUISB | AMCOOT, LSCAUP, SCOTER, GSCAUP, CNVSBK | 11,12/86 1,2,3/87 |
| SUISM | AMBITT, NOSHOV | 10,11/86 3,4,5/87 |
| TLNWR | NOSHOV, MALLARD, PNTAIL | 10/86 |

## TABLE 2B

## SELENIUM VERIFICATION COLLECTION PROGRAM, 1987

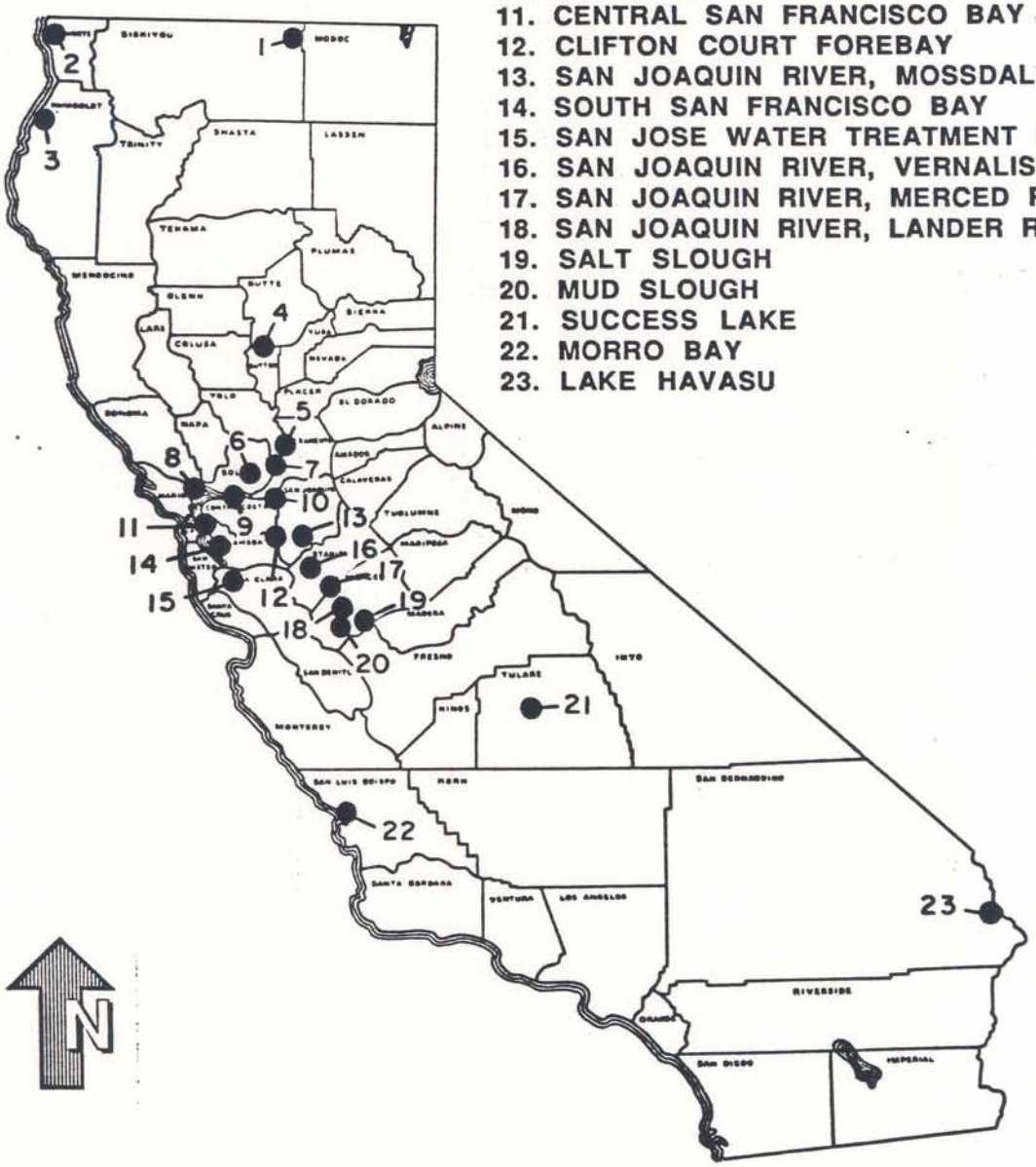
### FISH and INVERTEBRATES

| LOCATION[1/] | SPP. COLLECTED[2/] | DATE COLLECTED |
|---|---|---|
| ANTCH | STBASS | 4/87 |
| CLFCT | STBASS | 4/87 |
| CLKBG | STBASS | 4/87 |
| HAVSU | STBASS | 4,5/87 |
| MOSSD | WHTCAT | 1/87, 4/87 |
| MUDSL | CHNCAT | 4/87 |
| MYBYS | WHTCAT | 1/87, 5/87 |
| RIOVS | WHTCAT | 1/87, 5/87 |
| SALTS | CHNCAT, WHTCAT | 4/87 |
| SJRLN | WHTCAT, CHNCAT | 4/87 |
| SJRMR | CHNCAT, WHTCAT | 1/87, 4/87 |
| SNPBB | WSTRGN | 3,4/87 |
| SUCLK | STBASS | 5/87 |
| SUISB | WSTRGN, CRBCLA | 1,2,4,5/87 |
| VRNLS | WHTCAT | 1/87, 5/87 |

1/ See Table 3 for key to location codes.
2/ See Table 1 for key to species codes.

FIGURE 1

1. TULE LAKE NATIONAL WILDLIFE REFUGE
2. LAKE EARL STATE WILDLIFE AREA
3. HUMBOLDT BAY
4. GRAY LODGE STATE WILDLIFE AREA
5. SACRAMENTO RIVER,CLARKSBURG
6. SUISUN MARSH [GRIZZLY ISLAND SWA]
7. SACRAMENTO RIVER, RIO VISTA
8. SAN PABLO BAY
9. SUISUN BAY/GOODYEAR SLOUGH
10. ANTIOCH/MAYBERRY SLOUGH
11. CENTRAL SAN FRANCISCO BAY
12. CLIFTON COURT FOREBAY
13. SAN JOAQUIN RIVER, MOSSDALE
14. SOUTH SAN FRANCISCO BAY
15. SAN JOSE WATER TREATMENT PLANT
16. SAN JOAQUIN RIVER, VERNALIS
17. SAN JOAQUIN RIVER, MERCED RIVER
18. SAN JOAQUIN RIVER, LANDER ROAD
19. SALT SLOUGH
20. MUD SLOUGH
21. SUCCESS LAKE
22. MORRO BAY
23. LAKE HAVASU



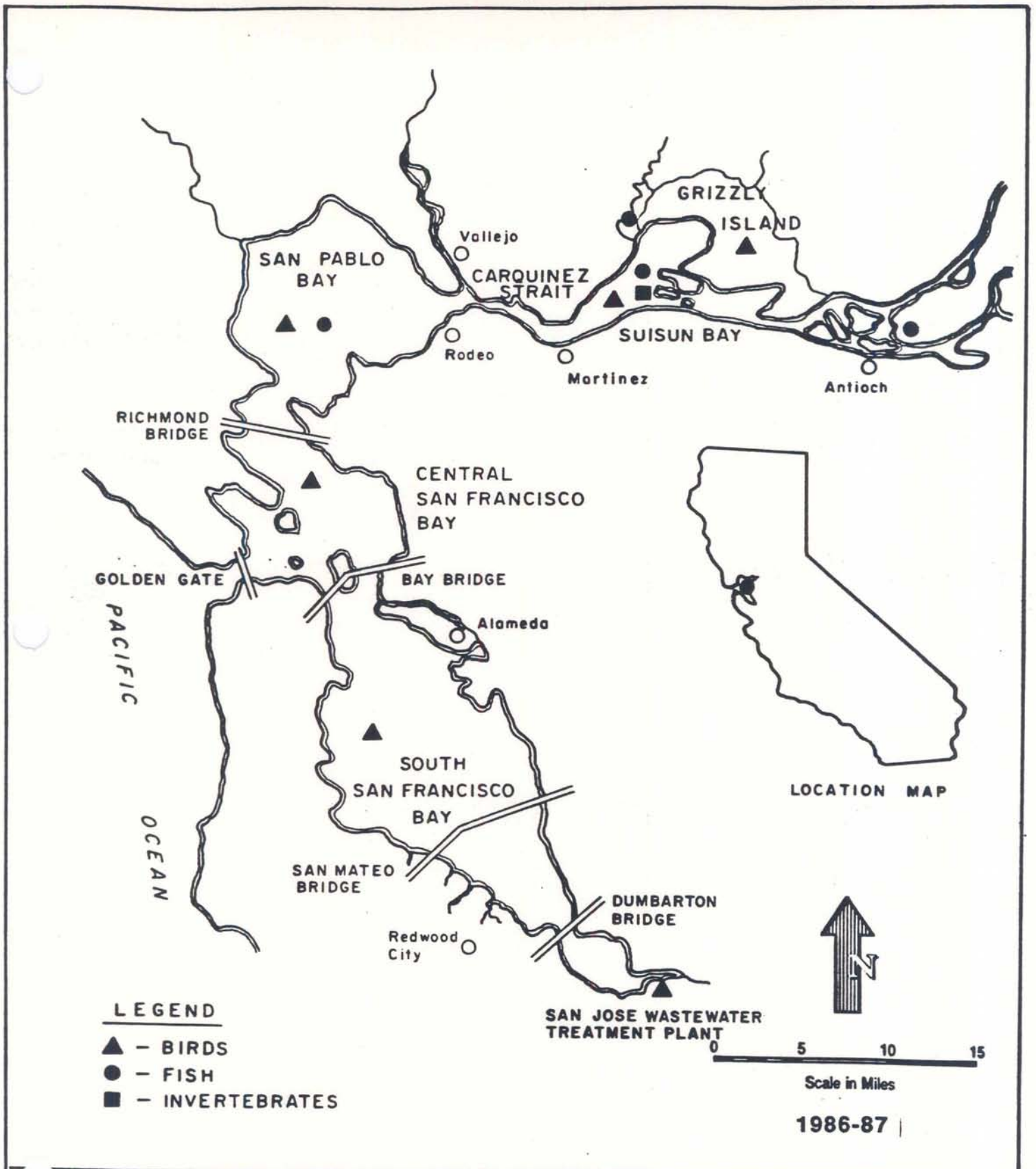

**SELENIUM VERIFICATION STUDY: STATEWIDE DISTRIBUTION OF SAMPLING SITES-1986-87**

TABLE 3
SELENIUM VERIFICATION STUDY
SAMPLING LOCATIONS AND LOCATION NAME CODES

| Location Code | Location[1/] |
|---|---|
| ANTCH | San Joaquin River near Antioch, Contra Costa County |
| CLFCT | Clifton Court near Byron, Contra Costa County |
| CLKBG | Sacramento River near Clarksburg, Yolo County |
| CNSFB | Central San Francisco Bay |
| GDYRS | Goodyear Slough near Benecia, Solano County |
| GRYLG | Gray Lodge Wildlife Area, near Gridley, Butte County |
| HAVSU | Lake Havasu on the Colorado River, San Bernardino County |
| HMBLT | Humboldt Bay, Humboldt County |
| LEARL | Lake Earl near Crescent City, Del Norte County |
| MORRO | Morro Bay, San Luis Obispo County |
| )SSD | San Joaquin River near I-5 bridge, San Joaquin County |
| MUDSL | Mud Slough, at Kesterson NWR, Merced County |
| MYBYS | Mayberry Slough near Antioch, Contra Costa County |
| RIOVS | Sacramento River north of Rio Vista, Solano County |
| SALTS | Salt Slough, near Stevinson, Merced County |
| SJRLN | San Joaquin River near Lander Avenue Bridge, Merced County |
| SJRMR | San Joaquin River downstream of Merced River confluence, Merced County |
| SJWTR | San Jose Wastewater Treatment Channel, near Alviso, Santa Clara Co. |
| SNPBB | San Pablo Bay |
| SOSFB | South San Francisco Bay |
| SUCLK | Success Lake east of Porterville, Tulare County |
| SUISB | Suisun Bay, including Grizzly Bay |
| SUISM | Suisun Marsh, near Fairfield, Solano County |
| TLNWR | Tulelake National Wildlife Refuge, near Tulelake, Siskiyou Co. |
| VRNLS | San Joaquin River near Vernalis, Stanislaus County |

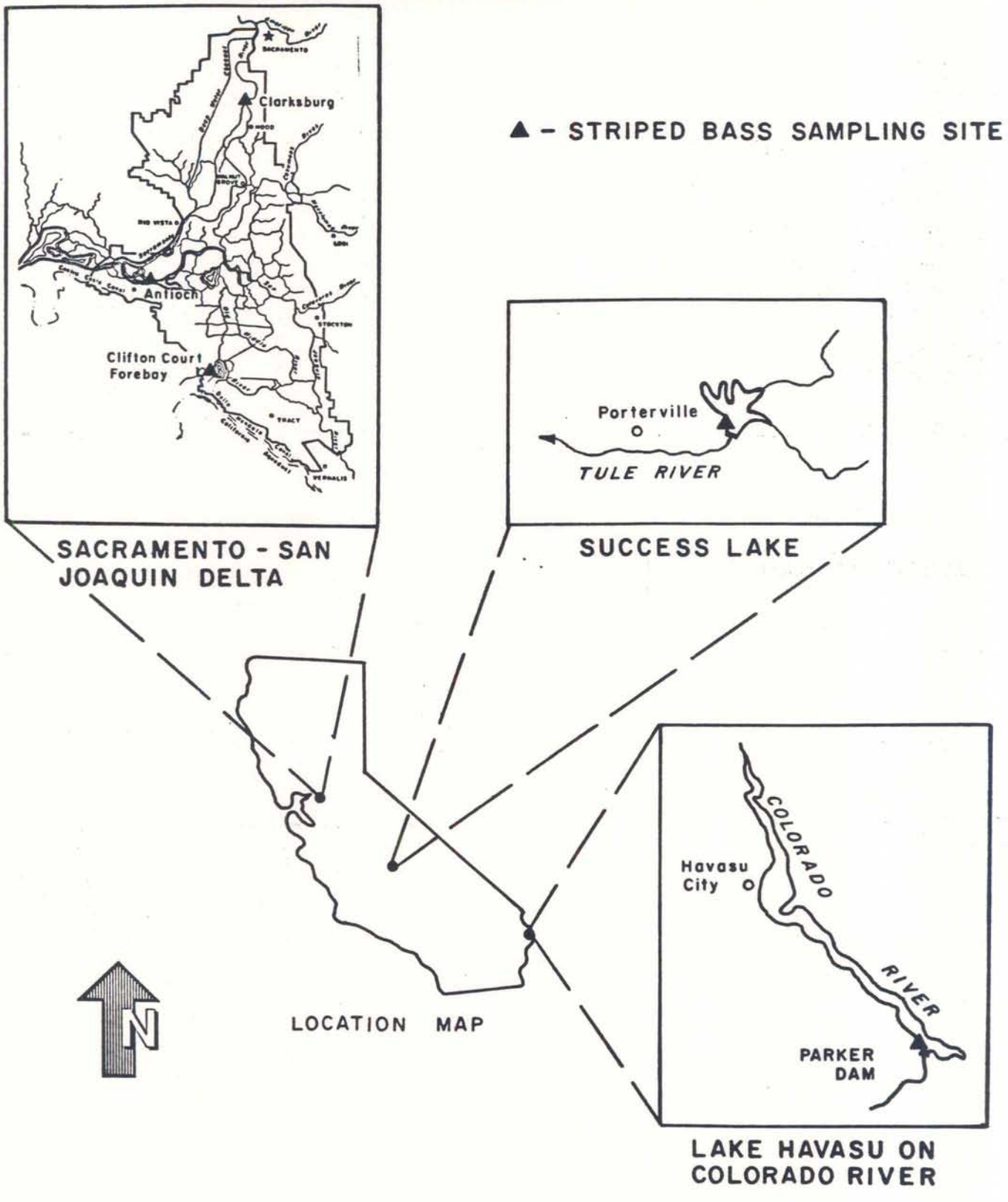
1/ See Appendix A for location description.

FIGURE 2



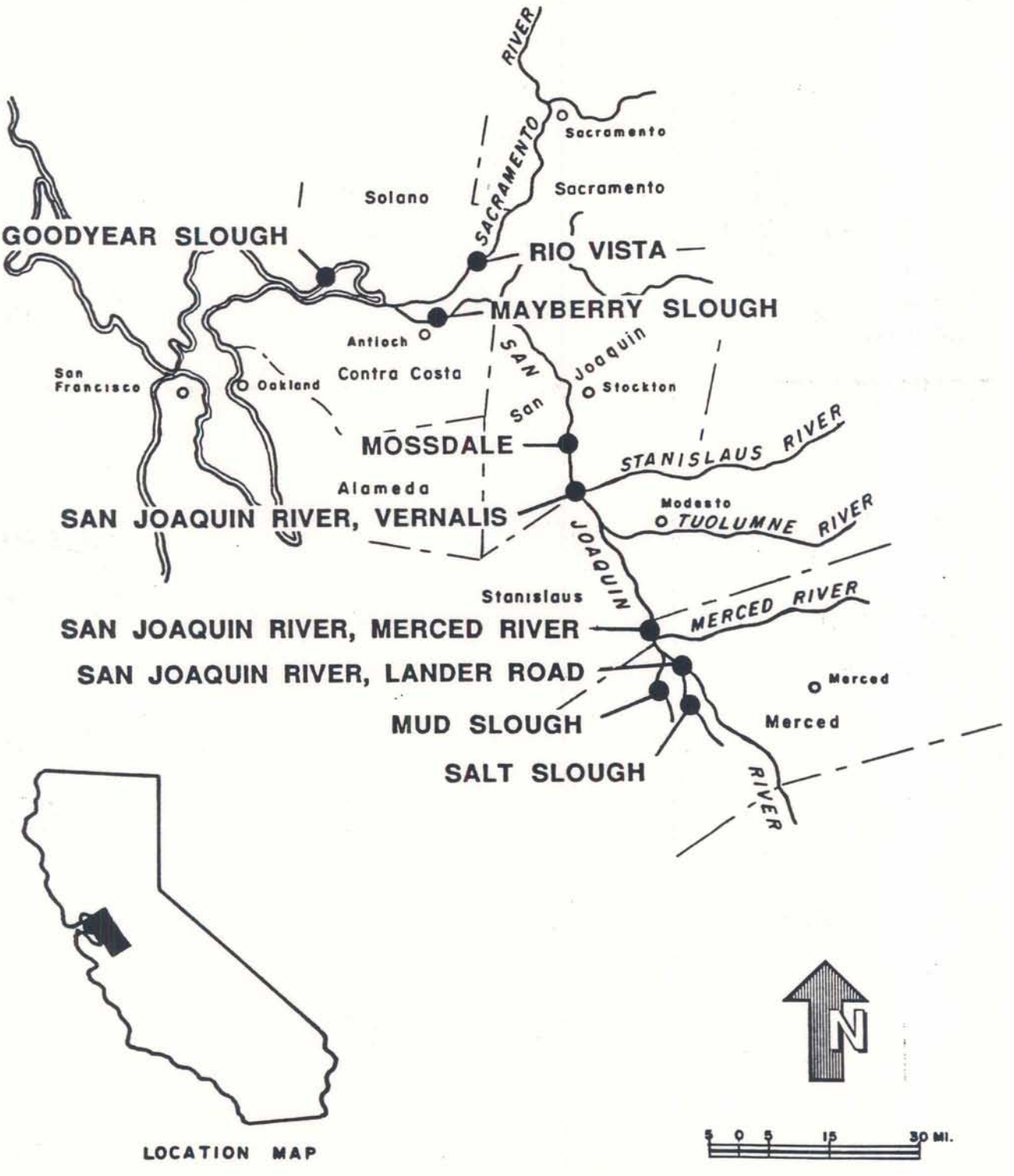

**SELENIUM VERIFICATION STUDY: SAN FRANCISCO BAY-ESTUARY SAMPLING SITES**

FIGURE 3




**SELENIUM VERIFICATION STUDY: STRIPED BASS SAMPLING SITES-1986-87**

FIGURE 4




**SELENIUM VERIFICATION STUDY: CATFISH SAMPLING SITES-1986-87**

Spleen, liver and heart tissue samples were collected from selected diving ducks and examined for histological abnormalities. The tissue samples were preserved in formalin and later examined by H.J. Olander, DVM, Ph.D, Veterinary Medical Teaching Hospital, University of California, Davis.

Fish and Aquatic Invertebrate Collection and Processing

Fish sampling gear included hoop nets, variable mesh monofilament gillnets, and hook and line. Clams were collected with a sled-mounted rake and a Petersen-type grab dredge. Four river otters (Lutra canadensis) accidently drowned in hoop nets set for catfish. Livers of these aquatic mammals were analyzed for selenium by WPCL.

As soon as possible after collection, fish and invertebrate samples were placed in Ziploc bags, frozen with dry ice and subsequently stored in a chest freezer at -12°C until delivered to WPCL for dissection, sample preparation, and analysis.

Water and Sediment Collection and Processing

Four water samples were collcted at selected catfish collection sites in acid-rinsed polyethylene bottles of approximately 2 liter capacity. The samples were preserved with nitric acid and refrigerated until analyzed by the WPCL.

Benthic sediment samples were collectd at selected sites with a Petersen-type grab sampler. The dredged samples were put into polyethylene Ziploc bags and frozen immediately on dry ice. Samples were subsequently stored in a chest freezer at -12°C until delivered to WPCL.

To assess bioconcentration processes in Suisun Bay, sample collections were made in late January and early April. During each 24 h collection period, samples of filtered water, filterable solids, and electro-conductivity data were obtained at two sites on Suisun Bay on each of four consecutive slack tides. Samples of birds, invertebrates and sediments were also collected at both sampling sites during the two periods.

Water samples were collected with Van Dorn bottles at a depth of 1 m, filtered through 0.45 um pre-cleaned Nuclepore filters and the filtrate acidified with HCL. The filters were carefully folded, placed in polyethylene vials and frozen on dry ice for later particulate selenium determinations. The acidified filtrate was analyzed for total selenium, selenite, selenate and organic selenide (Cutter 1982) by Dr. G.A. Cutter, Old Dominion University, Norfolk, Virginia.

## STATISTICAL METHODS

Selenium concentrations were transformed to common logarithms prior to statistical analysis because distributions were non-normal and variances tended to be proportional to sample means (coefficients of variation relatively similar). Two-way analysis of variance was used to test the effects of time period and collection location on selenium concentrations. Because sample sizes varied, a regression approach was used to partition sums of squares in testing hypotheses. This approach tested the significance of individual model components after adjusting for all other effects in the Anova model. When a main effect was significant, Tukey's studentized range test (HSD) was used to compare main-effect means and identify nonsignificant subsets. These analyses were performed on a micro-computer with SAS statistical package (SAS Institute Inc. 1985).

Between-year comparisons of selenium concentrations in striped bass and sturgeon were done with either t-tests or Mann-Whitney tests using SPSS/PC+ (Norusis 1986) or by hand (Zar 1984).

Means presented in the text or in tables are geometric means whereas figures present arithmetic means of untransformed data. Differences between geometric and arithmetic means were usually small.

Statistical significance was determined at P=0.05; references in the text to "significant" differences unaccompanaied by a probability value imply statistical significance at the 0.05 level or higher.

## LABORATORY OPERATIONS

### Tissue Sample Preparation

All whole body samples and field dissected birds were received frozen at the Fish and Wildlife Water Pollution Control Laboratory (WPCL) in Rancho Cordova. Samples remained frozen at -15°C until preparation was begun (within 3 months).

All samples were prepared for analysis in a "clean room" to minimize contamination. All glassware, tools, and work surfaces were cleaned as described in Appendix B (Hammond, 1986). Samples were then dissected and homogenized in the clean room as described in Appendix B.

After homogenization, the samples were refrozen until they were subsampled for analysis. Once the analysis was complete, a portion of each sample was transferred to a clean 30 mL linear polyethylene wide-mouth bottle (see Sample Container Preparation, Appendix B). These samples were then sent to cold storage and archived at -80°C.

### Analytical Techniques for Selenium in Tissues

All tissue samples were analyzed by hydride generation atomic absorption spectrophotometry (HGAA) at WPCL. Analytical procedures used for tissue samples at WPCL are described in detail in Appendix C (Hammond, 1986). In addition, approximately 130 of the tissue samples were analyzed in duplicate by neutron activation analysis (NAA) at the University of Missouri Research Reactor (UMRR) using the method described by McKown and Morris (1978). In addition to selenium, samples were also analyzed for moisture content at WPCL. These moisture values were used to convert NAA dry weight results to wet (fresh) weight values to facilitate comparison with WPCL results.

Approximately 10 percent of the samples analyzed by HGAA were done in duplicate to determine intra-laboratory precision. The relative standard deviation (RSD = {standard deviation / mean} x 100) also called the coefficient of variation (Zar 1984)) was calculated for each duplicate pair and reported with the corresponding data pair (Appendix D). The duplicate sample analyses for selenium by HGAA averaged 2.2 percent RSD (range 0 to 20), while moisture determinations completed by WPCL averaged 0.35 percent RSD (range 0 to 10). The reported RSD for duplicate samples of selenium by NAA averaged 3.0 percent (range 0 to 20). As indicated from duplicate sample analyses described above, HGAA provided slightly better precision than NAA for tissue analyses. Based on duplicate analyses we conclude that both methods provide acceptable levels of precision for analysis of selenium in tissue.

National Bureau of Standards (NBS) reference materials were analyzed with each set of samples to verify accuracy (Table 4). Analysis of NBS reference materials by HGAA indicated accuracy within two standard deviations of the certified selenium concentration in bovine liver and oyster tissue (NBS 1577a, 1566), and non-certified value of tuna (NBS 50). The analysis of both the bovine liver and oyster tissue reference materials demonstrated a small negative bias for selenium HGAA. Average results reported by WPCL for the analysis of selenium in tuna (NBS 50) and bovine liver (NBS 1577) were identical to values reported by the National Bureau of Standards. Results in Table 4 indicate that both HGAA and NAA provide acceptable accuracy for the analysis of selenium in tissue.

Analytical Techniques for Selenium in Water

Water samples were collected in polyethylene bottles which had been previously cleaned with 1.0 M concentrated nitric acid (analytical reagent grade) and rinsed with Type I water (ASTM 1986). The unfiltered water samples were preserved at the time of collection with nitric acid (ultra pure grade) to a final concentration of 0.08 Molar. The samples were frozen and then sent to WPCL where they remained refrigerated until the time of analysis.

A new method for the analysis of selenium in water was developed at WPCL and used for all the water samples (Appendix C). Nine water samples were analyzed in duplicate and the results are reported in Appendix E. A magnesium nitrate dry ashing digestion was used for water samples because the technique has a low detection limit (0.2 ug/L) with little background interference, produced consistent results, and performed well on U.S. Environmental Protection Agency round-robin samples.

Twenty of the water samples were sent to UMRR for NAA to verify the accuracy of the WPCL method. The NAA analyses were analyzed in duplicate as described in Appendix C and the average values are reported in Appendix E for comparison with WPCL results.

Analytical Techniques for Selenium in Sediment

All sediment samples were collected in plastic self-sealing bags and frozen at the time of collection. The samples remained frozen until the day of analysis. A new method of analysis for selenium in sediment was developed at WPCL and used for all sediment samples (Appendix C). The results of the sediment analyses performed by WPCL are reported as acid hydrolyzable selenium on a dry weight bases (Appendix E).

Five of the sediment samples were sent to California Analytical Laboratories (CAL) for acid hydrolyzable selenium analysis and moisture determination to verify the accuracy of the WPCL analyses. A brief description of the procedure used by CAL for

the analysis of selenium is provided in Appendix C. The CAL values are reported along with the WPCL results in Appendix E. The comparison of the five results show that both methods produced essentially the same values.

Table 4. WPCL and UMRR Analysis of NBS reference materials[1] in ug/g dry weight.

| Certified Se Value | NBS 50[2] (Tuna) 3.6±0.4 | | NBS 1566 (Oyster) 2.1±0.5 | NBS 1577a (Bovine Liver) 0.71±0.07 | | NBS 1577 (Bovine Liver) 1.1±0.1 | |
|---|---|---|---|---|---|---|---|
| HGAA Results: | 3.7 | 3.4 | 2.1 | 0.68 | 0.67 | | |
| | 3.7 | 3.7 | 2.0 | 0.70 | 0.70 | | |
| | 3.6 | 3.6 | 1.9 | 0.71 | 0.72 | | |
| | 3.5 | 3.5 | 2.0 | 0.71 | 0.71 | | |
| | 3.6 | 3.6 | | 0.67 | 0.70 | | |
| | 3.7 | 3.6 | | 0.70 | 0.73 | | |
| | 3.5 | 3.6 | | 0.65 | 0.75 | | |
| | 3.8 | 3.4 | | 0.67 | 0.72 | | |
| | 3.5 | 3.6 | | 0.66 | 0.70 | | |
| | 3.8 | | | 0.73 | 0.70 | | |
| | | | | 0.71 | 0.66 | | |
| | | | | 0.67 | 0.66 | | |
| | | | | 0.67 | 0.70 | | |
| | | | | 0.67 | | | |
| NAA Results: | | | | | | 1.2 | 1.1 |
| | | | | | | 1.2 | 1.1 |
| | | | | | | 1.2 | 1.1 |
| | | | | | | 1.1 | 1.1 |
| | | | | | | 1.1 | |
| Mean | 3.6 | | 2.0 | 0.69 | | 1.1 | |
| Std. Error[3] | .03 | | 0 | 0.005 | | 0.02 | |
| RSD (%)[4] | 3.2 | | 4.1 | 3.7 | | 4.5 | |
| Bias (%)[5] | 0 | | -4.8 | -2.8 | | 0 | |

1/ National Bureau of Standards, Washington D.C. 20234

2/ Noncertified value of constituent element.

3/ Standard error = standard deviation/ (number of values)$^{1/2}$.

4/ Relative standard deviation = (standard deviation/mean) X 100.

5/ Bias (% difference) = (experimental value - NBS value)/NBS value X 100.

## RESULTS AND DISCUSSION

### SURVEILLANCE OF SELENIUM LEVELS IN DIVING DUCKS

Diving ducks collected in winter 1986 from San Francisco Bay contained above-background levels of selenium (White et al. 1987). Further studies were conducted beginning in Fall 1986 to answer questions about spatial and temporal variability and the sources and significance of selenium concentrations in these birds.

#### Surf Scoter

The surf scoter (Melanitta perspicillata) is a sea duck common in winter along both coasts of North America. In California, Tomales Bay, Drake's Bay, and San Francisco Bay hold almost half the wintering population (Bellrose 1978). Scoters are found along the coast and in harbors, bays, and estuaries from October to May (Small 1974). Their breeding range is the closed and open boreal forests of Canada and Alaska. They feed by diving to the bottom to obtain food. Comprised mostly of animal matter, their diet includes bivalve molluscs (mussels, clams), crustaceans (barnacles), and small percentages of aquatic insects and plant material (eelgrass, wigeon grass). Surf scoters, although taken by hunters, are probably not sought after with the enthusiasm directed to other waterfowl species found together on California bays.

#### Scaup

Greater scaup (Aythya marila) and lesser scaup (A. affinis) are winter visitors to California saltwater bays, lagoons, and estuaries with lessers also using fresh-water lakes, ponds and rivers. Most greater scaup wintering in California concentrate in San Francisco Bay with small numbers in Morro Bay and San Diego Bay; most lesser scaup in California also are found in the San Francisco Bay area with smaller numbers along the north coast, south coast, Imperial Valley and Central Valley (Bellrose 1978). Greater scaup follow a coastal and offshore migration corridor to primary breeding grounds in the Yukon Delta where they mix with greaters that winter on the Atlantic and Gulf coasts. Lesser scaup in California may have migrated as far south as Guatemala along a coastal corridor. Banding data suggest half the lesser scaup in California originate in British Columbia with most of the balance coming from breeding grounds in Alberta and Alaska. Lesser scaup occur in California from September to May (Small 1974); greaters may arrive later and leave sooner (Bellrose 1978). Both species feed by diving and consume both animal (molluscs, crustaceans) and plant (eelgrass, wigeon grass) foods. Greater scaup consume more animal foods (90 percent molluscs in Humboldt Bay; Yocum and Keller 1961) whereas lesser scaup consume a higher percentage of plant material (35% plants in Humboldt Bay, 45%

clams, 9% unidentified molluscs, 5% unidentified crustaceans and 5% wheat (bait)). Along with the canvasback (Aythya valisineria), greater and lesser scaup are probably the favored diving ducks of waterfowl hunters.

Canvasback

The canvasback is a large diving duck that primarily nests in the interiors of Canada and Alaska. Approximately 27% of the entire population winters in the Pacific flyway and about 77% of these (or 20% of the continental population) winter on San Francisco and San Pablo bays. Due to low population levels and a precarious status, canvasbacks have received special considerations in the waterfowl hunting regulations, such as reduced bag limits and closed seasons. Canvasbacks consume both plant and animal foods. In this study, canvasbacks from Lake Earl were feeding exclusively on sago pondweed seeds and tubers and wigeongrass seeds, while those from San Francisco Bay fed wholly on invertebrates, chiefly Baltic clams (Macoma).

## Dynamics of Tissue Selenium Concentrations in Wintering Diving Ducks

Analysis of tissue samples collected from February to April, 1986 indicated diving ducks wintering in the San Francisco Bay system contained selenium at above-background levels (White et al. 1987). Furthermore, diving ducks taken from Suisun Bay in late winter had higher levels than those from the other bays in the system. Neither those data nor other available information were adequate to determine if diving ducks were accumulating selenium from sources in San Francisco Bay-Estuary and, if so, were there differences in accumulation among ducks using individual bays. Thus an effort was made to collect specimens as soon a possible after these species were observed on San Francisco area bays in fall 1986 to determine baseline levels in wintering populations, and to repeat collections several months later to determine if selenium levels changed during winter and if changes were related to geographic areas where ducks were found. Early collections were in November-December, 1986 and late collections in February-March 1987.

Overall, there was a significant effect of time period and location on selenium concentrations in muscle tissue of surf scoters, scaup, and canvasbacks and in liver of canvasbacks but not scoters or scaup (Table 5). Selenium levels in canvasbacks did not differ among sites in San Francisco Bay but were higher in San Francisco area bays than at Lake Earl. Selenium concentrations in canvasbacks increased in all areas where they were collected both early and late in the wintering period (Figure 5). Unexpectedly no canvasbacks were found in mid-March at north coast control sites (Humboldt Bay, Lake Earl) thus preventing a

Table 5. Geometric mean selenium concentration ppm (wet wt.) and range of concentrations in muscle and liver of diving ducks collected from Fall 1986 through late-winter 1987.

| | | | | Selenium Concentration, ppm (wet wt.) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Muscle | | Liver | |
| Species | Date | Location | N | Mean | Range | Mean | Range |
| Canvas-back | 12/86 | Lake Earl | 7 | 0.22 | 0.13 -0.30 | 0.63 | 0.29 - 1.2 |
| | 12/86 | Suisun Bay | 10 | 0.53 | 0.34 -0.93 | 1.9 | 1.0 - 2.7 |
| | 12/86 | San Pablo Bay | 6 | 0.76 | 0.20 -1.3 | 2.8 | 1.4 - 4.7 |
| | 12/86 | So. SF Bay | 9 | 0.79 | 0.18 -1.8 | 3.1 | 0.60 - 6.5 |
| | 3/87 | Suisun Bay | 2 | 2.8 | 2.8 -2.8 | 6.7 | 5.8 - 7.8 |
| | 3/87 | San Pablo Bay | 7 | 1.5 | 0.78 -2.8 | 4.0 | 2.1 - 8.1 |
| | 2/87 | So. SF Bay | 8 | 1.7 | 1.4 -2.6 | 4.7 | 3.9 - 6.1 |
| Surf Scoter | 12/86 | Humboldt Bay | 7 | 0.61 | 0.48 -0.90 | 2.9 | 1.4 - 6.1 |
| | 12/86 | Morro Bay | 7 | 1.0 | 0.58 -1.8 | 5.3 | 3.2 - 9.5 |
| | 12/86 | Suisun Bay | 7 | 2.9 | 1.8 -3.8 | 22. | 11. -28. |
| | 11/86 | San Pablo Bay | 7 | 2.3 | 1.5 -4.1 | 26. | 12. -43. |
| | 11/86 | Cent. SF Bay | 10 | 1.4 | 0.73 -4.6 | 9.3 | 5.1 -24. |
| | 11/86 | So. SF Bay | 7 | 1.7 | 0.67 -4.0 | 11. | 4.2 -23. |
| | 1/87 | Suisun Bay | 8 | 3.7 | 1.8 -6.1 | 24. | 12. -41. |
| | 3/87 | Humboldt Bay | 8 | 0.97 | 0.45 -1.8 | 4.2 | 2.1 - 8.4 |
| | 3/87 | Morro Bay | 7 | 1.3 | 0.91 -1.8 | 5.1 | 4.7 -10. |
| | 3/87 | Suisun Bay | 7 | 2.0 | 1.0 -3.2 | 11. | 3.8 -22. |
| | 3/87 | San Pablo Bay | 7 | 5.7 | 4.0 -9.2 | 38. | 27. -55. |
| Scaup | 12/86 | Humb/Earl | 8 | 0.68 | 0.29 -1.5 | 1.7 | 1.0 - 3.4 |
| | 12/86 | Morro Bay | 7 | 1.6 | 0.94 -2.4 | 2.6 | 2.1 - 3.9 |
| | 12/86 | Suisun Bay | 3 | 2.4 | 1.6 -4.3 | 12. | 7.6 -25. |
| | 11/86 | San Pablo Bay | 7 | 1.9 | 0.68 -3.6 | 5.8 | 3.8 - 9.6 |
| | 11/86 | Cent. SF Bay | 12 | 1.8 | 0.33 -4.0 | 4.7 | 1.2 -12. |
| | 11/86 | So. SF Bay | 6 | 1.8 | 0.78 -3.0 | 4.7 | 2.4 - 8.5 |
| | 1/87 | Suisun Bay | 8 | 2.4 | 0.98 -8.4 | 5.6 | 4.3 -25. |
| | 3/87 | Humb/Earl | 7 | 2.1 | 1.0 -3.9 | 4.1 | 2.2 - 8.9 |
| | 3/87 | Morro Bay | 7 | 2.1 | 0.95 -4.5 | 3.4 | 2.4 - 5.9 |
| | 3/87 | Suisun Bay | 7 | 1.6 | 0.75 -4.0 | 4.1 | 2.1 - 8.9 |
| | 3/87 | San Pablo Bay | 9 | 4.0 | 1.3 -7.9 | 9.4 | 3.2 -14. |
| | 3/87 | Cent. SF Bay | 7 | 3.1 | 1.4 -6.7 | 7.5 | 2.2 -29. |
| | 2/87 | So. SF Bay | 12 | 3.7 | 1.6 -7.8 | 8.5 | 4.1 -16. |

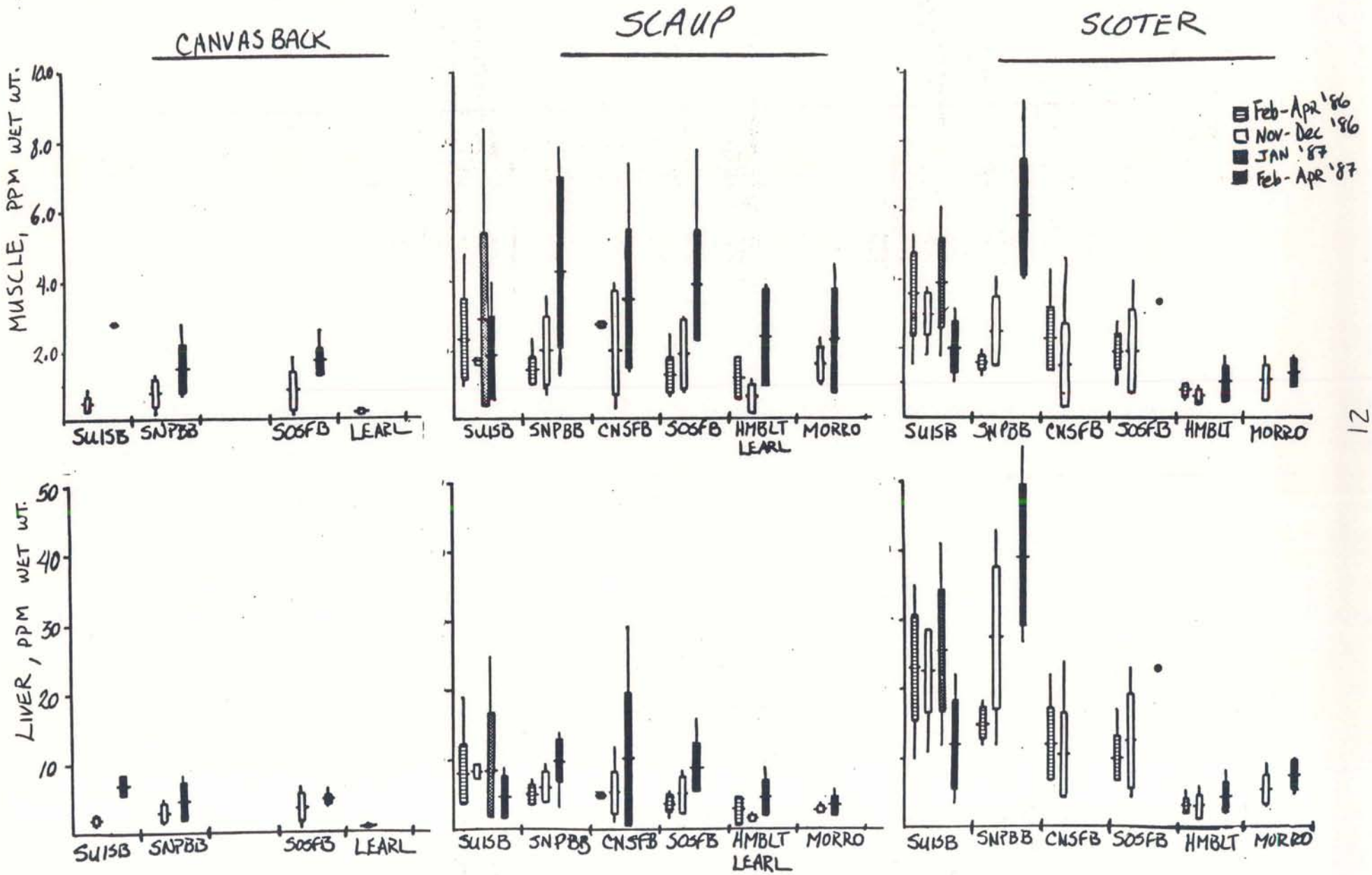



Figure 5. Selenium concentrations ($\bar{x}\pm s$, range; ppm wet weight) in muscle and liver tissues of diving ducks, 1986-1987. Location codes defined in Table 3.

seasonal comparison there. Canvasbacks do not winter in significant numbers south of San Francisco Bay, hence none were collected at our second control site, Morro Bay.

Selenium levels in scoter muscle were higher in San Pablo and Suisun bays than at coastal control sites (Humboldt Bay, Morro Bay) (Figure 5). Scoter muscle selenium levels increased between early and late winter collection periods in San Pablo Bay, decreased between sampling periods in Suisun Bay and changed very little in birds wintering at Humboldt and Morro bays (Figure 5). Patterns of variation in liver selenium levels were similar to muscle but the time period difference was not significant. The interaction effect of time period and location on selenium concentrations was significant because the magnitude and direction of seasonal changes in selenium concentrations were not the same in all areas.

Selenium data for scaup were the most difficult to interpret. Although scaup collections included the most comprehensive coverage of locations and time period, they consisted of a combination of greater scaup and lesser scaup. Results of three-way analyses of variance for scaup data were inconclusive in assessing the effects of species, time period, and location on selenium concentrations in scaup. Muscle tissue data indicated the effects of species, season, and location all were significant (probability levels slightly less than $p=0.05$) whereas only location significantly affected selenium levels in scaup liver ($p<0.005$). The mix of greater and lesser scaup resulted in a significant species-location interaction but a non-significant species-time period effect.

Selenium levels in scaup were generally higher in San Francisco-area bays than at control sites, tended to be higher in greater scaup than lesser scaup, and increased from early winter to late winter (Figure 5). However, late season levels in scaup from Suisun Bay were not higher than early winter levels and were closer to levels in scaup at control sites than to levels in scaup from San Pablo, Central and South San Francisco bays.

Two thirds of the scaup were greater scaup and when analyzed separately from lesser scaup selenium levels were found to differ among locations but not time periods. The overall impressions with respect to location and season effects from this single species analysis were not different from the analysis of greater and lesser scaup combined.

Overall, these findings suggest diving ducks accumulate selenium while wintering in San Francisco Bay. Ohlendorf et al. (1987) found no difference between January and March selenium levels in surf scoters collected from San Francisco Bay in 1985. They hypothesized selenium uptake to equilibrium levels in tissue had already occurred prior to January collections. Our data indicates their hypothesis probably was correct.

We detected a significant seasonal effect on selenium levels in muscle of all three diving duck species, however, in liver tissue samples, the effect was significant only for canvasbacks. A possible explanation is related to more with timely collection of first-arriving canvasbacks than of surf scoters or scaup. Canvasback arrival was clearly documented and the logistics of collecting them were favorable. In contrast, surf scoters and scaup first appeared at each collection site over a period of several weeks, hence the progressive movement of birds to individual bays in the San Francisco area may have confounded the early-winter picture with respect to selenium levels in these species. If accumulation of selenium from a newly-encountered source (e.g., food organisms in San Francisco Bay) occurs more rapidly in bird liver than in muscle, delayed collection of early winter specimens would more likely obscure a seasonal change of selenium levelin liver because accumulation of selenium above baseline levels would have progressed farther in liver than muscle.

Some scaup and scoters were present before they became abundant enough to make sample collection feasible, creating an additional source of variability in early-winter levels if the earliest arrivals were included in our samples with other birds which arrived closer to our collection date.

The seasonal decline in selenium levels in scaup from Suisun Bay was unexpected since levels in scaup and scoters collected in winter 1986 were higher in Suisun Bay than other bays (White el al. 1987). Our data indicated selenium levels also declined in surf scoters wintering in Suisun Bay during 1987. Levels in canvasbacks apparently increased, however only two canvasbacks were collected in late season sampling, thus greater uncertainty is attached to these data than to scaup and scoter results. The impact on tissue selenium levels of diving ducks using Suisun Bay in winter 1987 is unclear from data we collected. The flux of selenium in diving duck tissues should correspond to levels occurring in food organisms. Other data (presented in a discussion of bioconcentration) provide no evidence of a seasonal decline in selenium in scaup and scoter dietary items collected from Suisun Bay. Migration to Suisun Bay by birds from other bays in the San Francisco area or elsewhere may be confounding our impression of changing selenium levels in these ducks. We have no direct evidence to evaluate this hypothesis, however, the earlier (January 1987) samples with higher tissue levels were lesser scaup whereas the March sample with lower levels were all greater scaup. This contrast with the overall tendency for higher selenium levels in greaters than in lessers. Nineth-five percent of scaup collected from Suisun Bay prior to March 1987 were lesser scaup, suggesting the seven greaters collected there in March were transients.

## Annual Comparison of Selenium Levels in Diving Ducks

Surf scoters and scaup were collectd in February-April, 1986 (White et al. 1987) and February-March, 1987 at three locations for each species, thus permitting a between-year comparison in selenium levels near the end of the wintering period. Overall there was a significant difference between 1986 and 1987 in selenium levels in scaup muscle (P=0.0001) and liver (P=0.0038), but no overall difference in levels among scaup from Suisun, San Pablo, and South San Francisco Bays (P=0.188 muscle, P=0.180 liver) (Figure 5). In San Pablo Bay and South San Francisco Bay selenium concentrations in scaup tissue were two to three times higher in 1987 than in 1986 whereas in scaup from Susiun Bay selenium levels were lower (-24% muscle, -45% liver) in 1987 than in 1986. A difference of approximately 25 to 45 percent observed in Suisun Bay could result from sample variability, however selenium concentration differences of nearly 200 percent more likely indicate actual differences between years in populations of wintering scaup sampled on San Pablo and South San Francisco bays.

The effect of record outflows through the estuary in winter 1986 on the bioavailability of selenium in the system is unknown. The winter 1986 collections of scaup in Suisun Bay preceded a ten day storm which produced record high outflow to the bay, whereas scaup were collected from San Pablo and South San Francisco Bays after the storm period and had lower selenium levels in their tissue. Diving ducks collected after January 1986, may have experienced a recent decline in tissue selenium levels. Diving ducks accumulate selenium from the environment through their food. It is possible that selenium levels in benthic biota important as food for diving ducks declined under post-storm conditions which provided significant flushing and greatly reduced salinities throughout the estuary and may have reduced selenium bioavailability. If selenium is eliminated rapidly by birds when their food no longer contains elevated levels, ducks collected after the storm period might have lower levels than those collected a few weeks earlier. Heinz et al. (1987) observed a reduction in selenium tissue levels within two weeks when mallards were switched from experimental diets containing selenium to a control diet with no selenium added. The rate at which selenium may have depurated from clam or bird tissues under the circumstances is unknown.

Selenium levels in surf scoters had the same relationships between years as the scaup in Suisun and San Pablo Bays, with a 40 to 50 percent decline in levels in Suisun Bay birds and a 150 to 250 percent increase between years in scoters from San Pablo Bay. At Humboldt Bay, the third site where scoters were collected during late-winter in both years, selenium levels increased an average 25% in muscle and 35% in liver between 1986 and 1987. Overall for surf scoters, the difference between years was significant for muscle tissue selenium levels (P=0.001) but not for liver

concentrations (P=0.077). Because one of the sites was a control site, the effect of location on selenium levels was highly significant (P=0.0001) for scoters whereas it was not significant for scaup from three San Francisco-area bays.

## Control Site Evaluation

Surf scoters and scaup were collectd from Morro Bay, a small coastal embayment about 250 km south of San Francisco Bay to compare with birds from San Francisco Bay, and particularly from Humboldt Bay which some had suggested was deficient in selenium and thus not an appropriate site for establishing background levels in biota. Selenium levels in surf scoters collected from Morro Bay in early (December 1986) and late (March 1987) winter were slightly higher but not significantly different from levels in scoters collected during comparable periods from Humboldt Bay, which, in turn, were very similar to levels in scoters collected from Humboldt Bay in February 1986 (Figure 5).

Selenium levels in scaup from Morro Bay, Humboldt Bay, and Lake Earl, a coastal lagoon about 150 km north of Humboldt Bay were not significantly different. Muscle tissue levels in control site birds were significantly lower than selenium levels in scaup from San Pablo and South San Francisco Bay but only Humboldt Bay birds had significantly lower levels than scaup from Central San Francisco Bay and Suisun Bay as well. The evidence indicates Morro Bay, Lake Earl, and Humboldt Bay are acceptable control sites and levels in biota there approximate background levels.

Even at control sites where selenium in the aquatic environment has not been altered by human activity, there were small increases in selenium levels between birds collected during early and late wintering periods. This suggests the winter diet of diving ducks along the California coast, made up mostly of bivalve molluscs, may contain more selenium than the food they consume during the summer at nesting grounds in boreal forests and river delta areas in Canada and Alaska.

## Comparison of Selenium Levels in Canvasbacks, Surf Scoters and Scaup

Canvasbacks were included for study in 1986-1987 because they historically have been an important species in the hunters' bag and because their population levels have declined in recent years. Canvasbacks had the lowest selenium levels of the three diving duck species we studied. Selenium concentrations in canvasback muscle averaged less than one ppm in early collections, and although levels increased during the winter, late-period levels were above 2 ppm in only a few individual birds. In comparison, selenium levels in scaup collected in late winter averaged 2 ppm or higher and late-season surf scoters from San Pablo Bay average about 6 ppm in muscle with a maximum of over 9 ppm. Canvasback

apparently present less of a problem than scaup and scoters from the standpoint of public health concerns related to selenium. Based on available evidence, selenium levels in canvasbacks are probably not contributing to the decline in their abundance.

Food habit differences among the diving duck species may account for lower selenium levels in canvasbacks than in scaup and surf scoters. Siegfried (1976) found that although canvasbacks and scaup fed in the same area, their diets were different. Our food habit investigations indicated canvasbacks in San Francisco Bay have more specialized food habits than scaup and scoters; two marine bivalves, Macoma balthica and Mya arenaria were the primary identifiable food organisms found in canvasbacks. Macoma was not found in scaup or surf scoters, which contained some Mya as well as several other clams and mussels. Canvasbacks with their specialized bill tend to feed deeper in the substrate than the broader billed scaup, which may explain the canvasbacks preference for the deeper burrowing Macoma. Diving ducks at control sites also had somewhat different food habits, probably indicative of food organism availability at those sites (Table 6, Appendices F, G). Greater scaup and lesser scaup have similar feeding behavior, thus their winter diets are comparable except when the two species are spatially segregated and food organism availability differs between areas. Differences in selenium concentration between greater and lesser scaup collected from our study sites may be caused by differential dietary exposure in turn resulting from either the composition of the diet or disparate selenium concentrations in common food items at several sites. The two scaup species breed in different areas of Canada and Alaska, hence summer dietary intake of selenium may also contribute to interspecific tissue level differences.

Canvasbacks may have lower selenium levels due to physiological or biochemical differences between them and surf-scoters and scaup.

## BIOEFFECTS OF SELENIUM IN WATERFOWL

Several studies have revealed high levels of selenium in diving ducks from San Francisco area bays and particularly from Suisun Bay, compared to those from Humboldt Bay (Ohlendorf et al. 1986a, 1987; White et al. 1987). Some of these birds had liver concentrations equaling those in different bird species taken from Kesterson Reservoir (Ohlendorf et al. 1986b). High selenium concentrations in dabbling ducks, coots, and shorebirds at Kesterson caused severe reproductive impacts and toxicosis in adult birds (Ohlendorf et al. 1986a, 1986b). Histopathology of internal organs including liver, spleen and heart as well as breast muscle atrophy also were observed in birds at Kesterson.

TABLE 6. Food items found in at least 20% of surf scoters, scaup, and canvasbacks at each collection location.

| FOOD ITEMS | Species and Location[1/] | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Surf Scoter | | | | | | Scaup | | | | | | | Canvasback | | | | |
| | SUISB | SNPBB | CNSFB | SOSFB | HMBLT | MORRO | SUISB | SNPBB | CNSFB | SOSFB | HMBLT | LEARL | MORRO | SUISB | SNPBB | CNSFB | SOSFB | LEARL |
| Annelida, | | | | | | | | | | | | | | | | | | |
| Polychaete tube worms | | | | | X | | | | | | | | | | | | | |
| Crustacea, | | | | | | | | | | | | | | | | | | |
| Malacostracans | | | | | | X | | | | X | | | | | | | | |
| Mollusca, | | | | | | | | | | | | | | | | | | |
| Gastropoda, Mitrella spp. | | | | | X | X | | | | | X | | X | | | | | |
| " Barleeia haliotiphila | | | | | | | | X | | | | | | | | | | |
| " unidentified | | | | | | X | | X | | X | X | | X | | | | | |
| Bivalvia, Corbicula fluminea | X | | | | | | X | | | | | | | | | | | |
| Mya arenaria | X | X | | | | | X | X | | X | | | | | | X | | |
| Tapes/Protothaca | | X | X | X | X | | | X | X | X | | | | | | X | | |
| Musculus senhousia | | X | X | X | | | | | X | X | | | | | | | | |
| Macoma nasuta | | | | | X | | | | | | | | | | | | | |
| Macoma balthica | | | | | | | | | | | | | | | X | X | | |
| Transenella spp. | | | | | | | | | | | X | | X | | | | | |
| Unidentified fragments | | | | | X | X | | | | | | | | X | | | | |
| Plants, | | | | | | | | | | | | | | | | | | |
| Potamogeton pectinatus, seeds | | | | | | | | | | | | X | | | | | | X |
| " " corms | | | | | | | | | | | | | | | | | | X |
| Ruppia maritima, seeds | | | | | | | | | | | | X | | | | | | X |
| Scirpus, seeds | | | | | | | | | | | | X | | | | | | |
| Miscellaneous, | | | | | | | | | | | | | | | | | | |
| Herring (Clupea harengus) eggs | | | | | | | | X | | | | | | | | | | |

1/ SUISB - Suisun Bay
SNPBB - San Pablo Bay
CNSFB - Central San Francisco Bay
SOSFB - South San Francisco Bay
HMBLT - Humboldt Bay
LEARL - Lake Earl
MORRO - Morro Bay

The impact of selenium accumulated in tissues of diving ducks wintering in San Francisco Bay is unknown. Direct evaluation of reproductive impacts are not feasible because these diving duck species do not breed locally. The impacts of selenium on mallard reproduction have been measured in controlled experiments (Heinz et al. 1987), however, those results may not be relevant to other species. Similar studies probably could be done with scaup or surf scoters but none are proposed and results would not be obtainable soon.

Histopathological examination of internal organs of scaup, surf scoters and canvasbacks from an area with elevated selenium levels was adopted as the only viable approach to assessing potential selenium impacts on these birds. Tissue samples were obtained from 24 early-season and 14 late-season birds. In addition, collected bird specimens were examined for breast muscle atrophy.

In general, conditions observed in sections of liver, spleen and heart tissue were compatible with those expected from exposure to a normal environment and there were no identifiable differences between the diagnoses of early- and late-season birds. Livers had evidence of "mild to moderate pericholangitis in which cellular infiltrates consisted of lymphocytes, plasma cells, granulocytes and macrophages". Observed in livers of most of the birds, these conditions "are compatible with a common antigenic stimulation, probably of parasitic origin". Varying amounts of iron were present in bile canaliculi. "Minimal to moderate hyperplastic changes" in spleens from both sets of samples are probably of similar origin. Myocardial sections were normal except for a few sarcosporidial cysts, lesions (probably of septic origin), and several small foci of lymphocytic myocarditis.

These observations do not indicate unusually extensive tissue pathology associated with exposure to toxicants or from any other cause. Histological examination was conducted on individual specimens from Suisun Bay, chosen without knowledge of their tissue levels but based on data from winter 1986. Unlike winter 1986, in 1987 selenium levels were highest in ducks from San Pablo Bay and not Suisun Bay. This approach to assessing selenium impacts could be improved if internal organs from all birds were preserved and selection of individuals for histopathology was deferred until tissue selenium concentrations were determined to enhance the representativeness of the sample.

Seven birds, including 3 canvasbacks, 2 surf scoters, one scaup and one mallard were characterized as having abnormal breast muscle development. These birds were from San Francisco bays and control sites and did not contain higher selenium tissue levels than levels representative of each site, indicating muscle atrophy probably was not caused by selenium but by other factors not necessarily related to toxicants.

Another significant unknown with potential implications to the interpretation of these data is the interaction between trace elements which may afford protection in some cases from the deleterious effects of contaminants. For example there is some evidence (Hill 1975) suggesting mercury, arsenic, cadmium, and copper may react antagonistically with selenium, suppressing symptoms of selenium toxicosis known to occur with similar tissue levels under other circumstances. This study has measured only selenium in tissues of the diving ducks, however archieved samples could be analyzed for other trace elements either by our laboratory or by the U.S. Fish and Wildlife Service in a complementary investigation of contaminants in San Francisco Bay. USFWS laboratory studies are addressing the question of interaction among contaminants.

## POINT SOURCE MONITORING

Cutter (1987) studied selenium behavior in the Sacramento-San Joaquin Estuary and indicated selenium inputs in lower Suisun Bay and the Carquinez Strait and in the southern end of South San Francisco Bay. Oil refineries were identified as probable point sources of selenium in the Carquinez Strait-Suisun Bay vicinity whereas South Bay sources were tentatively identified as municipal/industrial wastewater treatment plants. Riverine inputs and regeneration of selenium from sediments were also discussed by Cutter. We took several approaches to assessing the distribution of biologically available selenium in the estuary.

### Bioaccumulation of Selenium in Transplanted Mussels and Oysters

California mussels (Mytilus californianus) were deployed in eight general locations near industrial (oil refinery) or municipal discharges and at several other sites in the estuary to measure the effect of localized selenium input on the accumulation of selenium by biota in the vicinity (Figure 6). The field work for this investigation was conducted by Department of Fish and Game staff assigned to the State Mussel Watch Program following established protocol (Hayes and Phillips, 1986). Mussels were obtained from Bodega Head and deployed at test sites for approximately two months in fall, 1986. Control samples of mussels contained an average of 0.53 ppm (wet weight).

Poor survival of the coastal California mussel at sites upstream of Carquinez Strait indicted the marine mussels were severely stressed (G. Ichikawa, pers. comm.), probably by low salinity. Disruption of normal physiology likely influences processes of bioaccumulation, hence mussel data from these sites were deemed unreliable and the effort was repeated in January using oysters (Crassostrea gigas) transplanted from Humboldt Bay. The average selenium concentration in control oyster samples was 0.66 ppm.

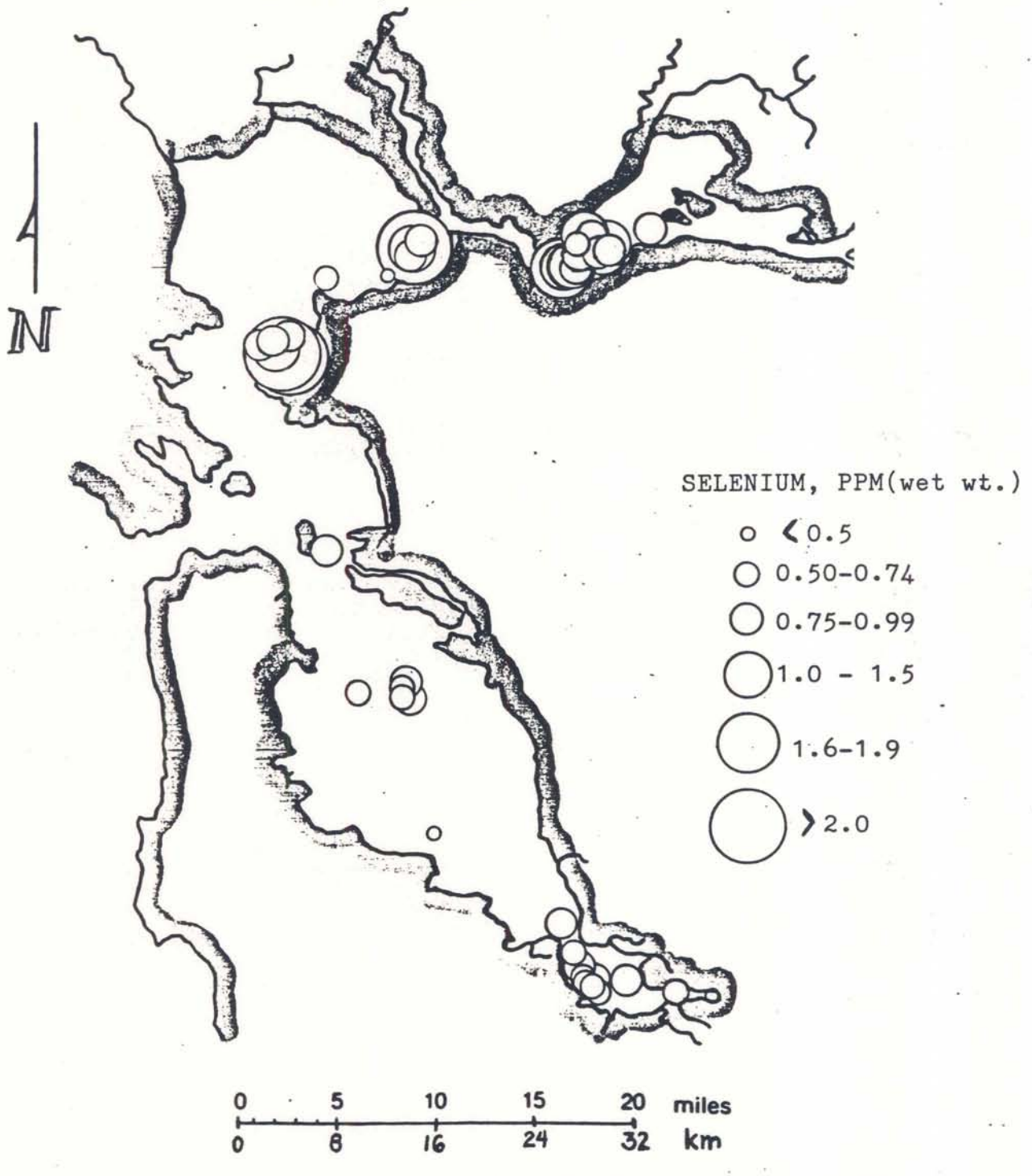



Figure 6. Selenium concentrations in transplanted bivalve molluscs at sites in the San Francisco Bay system, 1986-1987. Coastal mussels (Mytilus californianus) were deployed for approximately 2 months at all sites but survived poorly upstream of San Pablo Bay. Concentrations at sites in western Suisun Bay and Carquinez Strait are in oysters (Crassostrea gigas) deployed where mussels did not survive. Mussels transplanted from Bodega Head initially averaged 0.53 ppm Se and oysters from Humboldt Bay contained 0.66 ppm Se.

The highest concentrations of selenium in mussels were accumulated at sites near the discharges of oil refineries in eastern and southern San Pablo Bay (Figure 6). Selenium levels averaged 2.28 ppm in mussels at one site near Rodeo (UNOCAL outfall) and 3.03 ppm in mussels at a Castro Creek site (Chevron Oil refinery) near Richmond. Less selenium was accumulated at nearby sites (e.g. Point San Pablo, 0.84 ppm; Point Pinole, 0.57 ppm) and only a few miles from discharge points (Wilson Point near Hercules, 0.46 pm) levels were below those in control samples.

In South San Francisco Bay levels increased to slightly above control levels in mussels at some sites, however, concentrations did not exceed 1 ppm at any site and no pattern or trend was indicated. Highest selenium levels in the southern area were in mussels near Treasure Island, north of Dumbarton Bridge, and near Palo Alto. These sites represent municipal discharges in South Bay. Results are generally consistent with waterborne concentrations measured in April and September, 1986 (Cutter 1987) although these data do not indicate proportionately elevated selenium levels in mussels in southern South Bay as were found in water by Cutter (1987).

Upstream of San Pablo Bay, oysters at some sites in lower Suisun Bay and the upper Carquinez Strait near oil refineries in Martinez and Benicia, accumulated selenium to concentrations over two times control levels. The relationship of these oyster selenium levels to their controls suggests a source of selenium in this vicinity. Cutter's (1987) data for water samples indicated selenium input in the Carquinez Strait and lower Suisun Bay. Preliminary data from Johns and Luoma (1987) also included elevated selenium levels in Corbicula from the western Delta and Suisun Bay relative to areas upstream, indicating regional enrichment of selenium.

## Bioaccumulation of Selenium From Receiving Waters

Selenium concentrations in receiving waters at mussel/oyster placements ranged from less than 0.2 ppb at sites in Suisun Bay to 7.2 ppb at the UNOCAL refinery outfall in San Pablo Bay (Table 7). High concentrations (2.2 ppb) also were found in Castro Cove/Creek near the Chevron refinery. Ratios of selenium concentrations in bivalves to concentrations in receiving water (bioiaccumulation factors) ranged from about 300 at the UNOCAL outfall (2280:7.2) to about 6500 (1290:0.2) at another site only a few hundred meters away. Bioaccumulation factors for mussels at most sites in San Pablo Bay and South San Francisco Bay were between 2000 and 5000. For surviving mussels in Suisun Bay (most mussels were dead) bioaccumulation factors ranged from about 500 to 1350. In some cases this represented a loss of selenium from initial (control) levels even though waterborne levels were similar to downstream areas where selenium was acumulated by 3000-5000 times, indicating stress-related inhibition of metabolism and the accumulation process in mussels at upstream sites. Bioaccumulation factors in

TABLE 7. Selenium concentrations in water (ppb) at mussel and/or oyster deployment sites, and in these transplanted bivalves (ppm), and the ratio of tissue:water selenium concentrations (bioaccumulation factor) at sites in San Pablo Bay, Carquinez Strait, and Suisun Bay near oil refineries in winter 1986-1987.

| Site | Mussel Oyster[1/] | Se(ppm) Tissue | Se(ppb) Water | Selenium Bioaccumulation Factor Tissue:Water |
|---|---|---|---|---|
| Suisun Bay/Carquinez Strait | | | | |
| Suisun Bay Chan. Mark. 11 | O | 0.71 | <0.2 | >3550 |
| Inner E Avon Pier | O | 0.99 | 0.2 | 4950 |
| W. End Avon Pier (Tosco) | O | 0.97 | 0.3 | 3230 |
| High Volt. Platform-Suisun | O | 0.75 | <0.2 | >3750 |
| Exxon Outfall East | O | 0.77 | 0.2 | 3850 |
| Exxon Railroad Bridge | O | 0.84 | 0.3 | 2800 |
| SE Benicia/Martinez Br. | M | 0.26 | 0.5 | 520 |
| E. End West Shell Pier | O | 1.58 | 0.3 | 5270 |
| San Pablo Bay | | | | |
| Unocal Pier Base | M | 0.94 | 0.4 | 2350 |
| Unocal Outfall | M | 2.28 | 7.2 | 320 |
| North Unocal Outfall | M | 1.29 | 0.2 | 6450 |
| Bennett's Marina | M | 0.75 | 0.5 | 1500 |
| Point Pinole | M | 0.58 | 0.3 | 1930 |
| Castro Cone Entrance | M | 0.94 | 0.3 | 3130 |
| Castro Cove Mid-Channel | M | 1.37 | 1.0 | 1370 |
| Castro Cover Upper Channel | M | 2.89 | 2.2 | 1310 |
| Castro Cove Br. (Chevron) | M | 3.03 | 2.2 | 1380 |
| Pt. San Pablo Yacht Harbor | M | 0.90 | 0.3 | 3000 |
| Point San Pablo | M | 0.84 | 0.2 | 4200 |
| South San Francisco Bay | | | | |
| Hayward Outfall 1 | M | 0.76 | 0.2 | 3800 |
| Hayward Outfall 5 | M | 0.86 | <0.2 | >4300 |
| Palo Alto | M | 0.81 | 0.3 | 2700 |
| San Francisquito Ck. | M | 0.64 | 0.2 | 3200 |
| Coyote Creek Br. | M | 0.38 | 0.3 | 760 |
| Alviso Slough Tower | M | 0.64 | 0.3 | 2130 |
| Channel 18 | M | 0.75 | 0.3 | 2500 |

1/ Coastal Mussel, Mytilus californianus, transplanted from Bodega Head with 0.53 ppm Se (wet weight).
Oyster, Crassostrea gigas, transplanted from Humboldt Bay with 0.66 ppm Se (wet weight).

oysters in lower Suisun Bay ranged from about 3000 to 5000, similar to healthy mussels downstream. However, accumulation of selenium by oysters may not be comparable to that of mussels, hence the bioavailability of selenium in Suisun Bay relative to that in San Pablo Bay or South Bay cannot be determined. Additional bivalve transplant studies are needed to better define the relative significance of discharges throughout the bay. Other species of bivalves including the Bay mussel (Mytilus edulis) and freshwater clam (Corbicula) may be better adapted to conditions in the upper estuary (Corbicula occur in Suisun Bay) and provide a more realistic measure of bioaccumulation by organisms with normal physiological function unaffected by extreme environmental conditions, as the coastal mussel species was apparently stressed by low salinity in Suisun Bay.

The availability to sedentary organisms of selenium from point sources in the bay is partly determined by circulation patterns (combined influence of outflow and tides) which provide varying amounts of flushing action and dilution depending on the location. The significance of dilution is evident from the comparison of selenium concentrations in refinery discharges (6.5 ppb to 156 ppb; Cutter 1987) with concentrations in receiving waters measured at mussel deployment sites (<.2 to 7.2 ppb). Selenium loading to the Bay by refineries depends on both the concentration of selenium in the effluent and the volume discharged, the latter varying considerably among refineries and probably over time. Sampling to date is not adequate to fully characterize the impact of selenium from direct dischargers to the Bay on the levels in the Bay and its resident and seasonally-occurring biota. However, diving ducks (particularly surf scoters) collected from San Pablo Bay, where selenium input from refineries has been documented, had tissue selenium concentrations at least as high or higher than ducks from other bays in the system. Ohlendorf et al. (1987) also reported higher selenium levels in surf scoters from the Point San Pablo-Point Pinole (Castro Cove) and Hercules-Rodeo areas than in the Redwood Creek and Dumbarton Bridge area in South San Francisco Bay. The mussel data demonstrates that bivalve molluscs bioaccumulate selenium. Scaup, scoters, and canvasbacks wintering in San Francisco Bay eat bivalves. Available data suggest that selenium from sources in the Bay, in addition to other sources, enters the aquatic food chain and contributes to accumulation of selenium in the tissues of diving ducks spending the winter in the estuary. Industrial sources in San Pablo Bay (and probably the Carquinez Strait and lower Suisun Bay) appear to have a greater potential impact on biota than municipal sources contributing selenium in South Bay based on bioaccumulation of selenium by mussels.

## American Coots as Indicators of Local Sources of Selenium

The American coot (Fulica americana) is a common breeding bird in freshwater marshes and at lakes and ponds with suitable shoreline habitat. Small (1974) describes a southward and coastward shift in coot distribution in fall to wintering areas in both freshwater and saltwater habitats. Coots are omnivorous, consuming the leaves, fronds, and roots of submerged aquatic plants and marsh plant seeds. Fifteen percent of the diet may be animal food (aquatic insects, univalve and bivalve molluscs, and crustaceans), increasing to over 40 percent during summer (Martin et al. 1951). Coots also graze on upland grasses or feed on algae in tidal habitats (Small 1974). Coots are occasionally taken by waterfowl hunters.

Coots were collected from Grizzly Bay, Suisun Bay along the Contra Costa County shoreline near Port Chicago, and Mallard Slough near Alviso, a tributary to Coyote Creek and South San Francisco Bay, to evaluate the bioavailability of selenium at these sites. The sites were chosen because existing water quality data indicated potential sources of selenium in these areas (Cutter 1987). Probable sources of selenium were oil refineries near Suisun Bay and municipal/industrial wastewater treatement plants in South Bay. Coots were selected because they are relatively sedentary, on-site feeders likely to indicate the presence of biologically available selenium. Birds were collected twice at each site, once in late-November to mid-December and again in late February.

Among the three sites, no significant difference was found in selenium concentrations in either coot muscle or coot liver (Figure 7). Selenium levels in coot tissue also did not differ between time periods. These data indicate similar levels of biologically available selenium at all three sites and also suggest no seasonal change in selenium availability. This interpretation assumes selenium is entering the coot food chain and tissue levels equilibrate rapidly to changes in selenium intake. The two collection periods may have been too close in time to show a temporal difference.

Selenium levels in coots using these three estuarine sites were considerably lower than in coots at Kesterson National Wildlife Refuge in 1983 (DFG unpublished, $\bar{x}$=9.95 ppm, wet weight in liver; Ohlendorf et al. 1986a, $\bar{x}$=9.3 ppm wet weight in liver, converted from dry weight using 75 percent moisture) where selenium was apparently responsible for severe abnormalities in coot embryos and chicks, reduced hatching success, and poor survival of young (Ohlendorf et al. 1986a, b). Average levels also were less than half the average concentration found in coots at some evaporation ponds containing selenium enriched agricultural drainage water in the southern San Joaquin Valley ($\bar{x}$'s=2.0 to 2.5 ppm, wet weight, in muscle, White et al. 1987). Reproductive effects were not studied at the Kern County site, however the Department of Health Services has issued an advisory concerning human consumption of coots from those and other drainage evaporation ponds in the area.

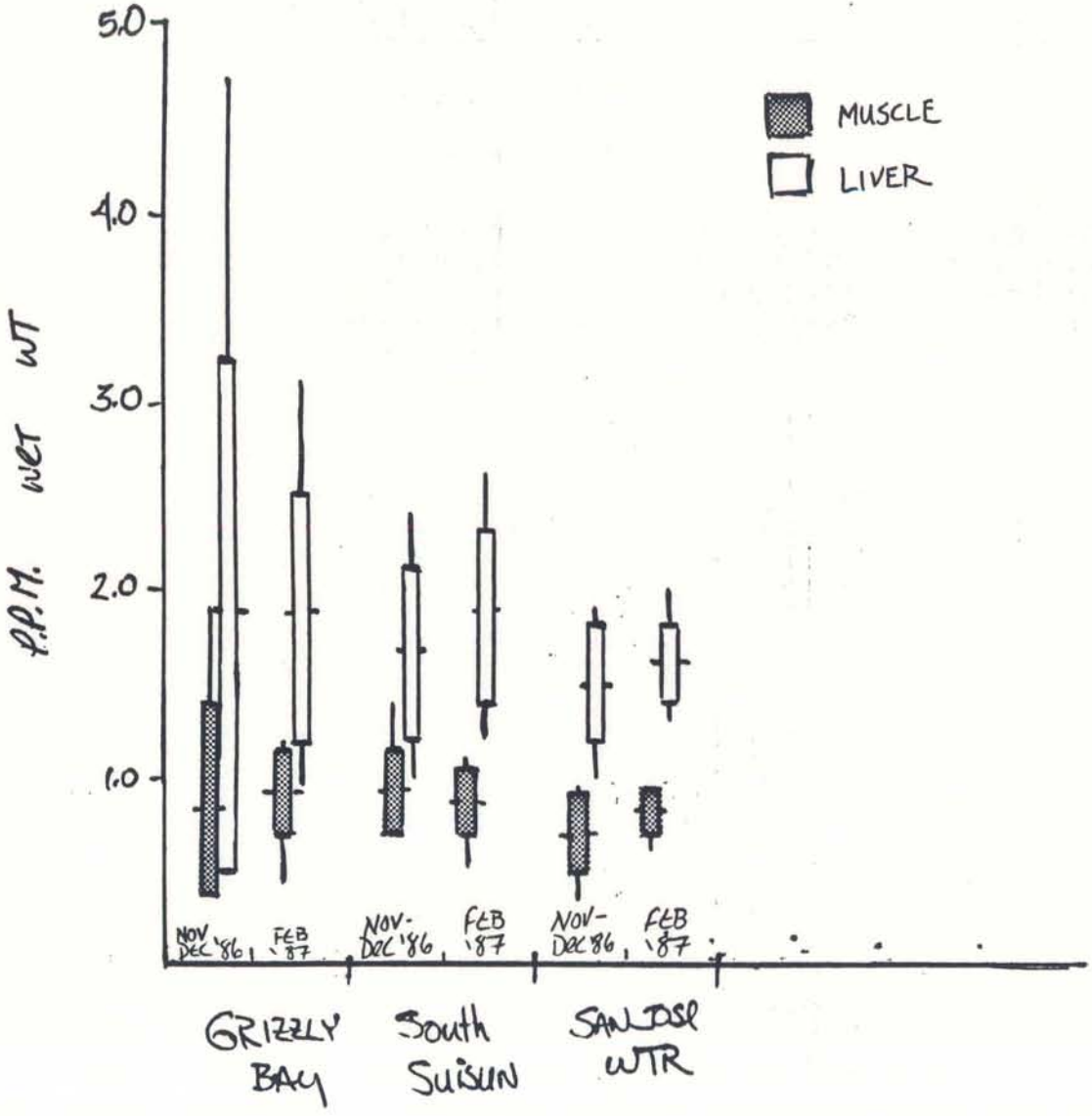



Figure 7. Selenium concentrations ( $\bar{x}\pm s$, range; ppm wet weight ) in muscle and liver tissues of American coots collected from Grizzly Bay, southern Suisun Bay,and in South San Francisco Bay near the discharge of the San Jose Wastewater Treatment Plant. 1986-1987.

The coots from Grizzly Bay, Suisun Bay and South San Francisco Bay contained slightly higher selenium levels than those measured in coots at Grizzly Island and Gray Lodge State Wildlife Areas in the winter and spring, 1986 (White et al. 1987). Coots in the sloughs and open-water estuarine habitats may accumulate higher selenium levels if their diet contains more selenium than the diet of coots inhabiting marshes. Dietary selenium intake is determined by food item selection and the amount of selenium entering the Estuary from point sources (municipal or industrial discharges), non-point sources upstream (agricultural drainage) or natural deposits (sediments) and accumulating in food chain components.

## SELENIUM MONITORING IN STRIPED BASS AND WHITE STURGEON

### Striped Bass

Striped bass (Morone saxatilis) spawn at age 3 (males) or 4 (females) in the Sacramento and San Joaquin rivers and Delta. Young bass remain in the upper estuary, moving downstream to the lower bays and the ocean as adults. Young bass are dependent on the opposum shrimp (Neomysis mercedis) for food; juvenile bass feed primarily on invertebrates but gradually shift to a diet dominated by fish as adults in the lower bays and ocean (Stevens 1966).

Muscle tissue samples were obtained in April 1987 from adult striped bass collected from the Sacramento River near Clarksburg and the San Joaquin River near Antioch by the Striped Bass Health Index Monitoring Program. Striped bass from this estuarine population also were collected in April at Clifton Court Forebay off Old River in the Southern Delta, and from inland, freshwater populations at Lake Havasu on the Colorado River and a control site at Success Lake, a Sierra Nevada foothill impoundment on the Tule River in Tulare County.

Analysis of variance indicted statistically significant differences in striped bass muscle tissue selenium concentrations among the five sites (Figure 8). Highest concentrations were in bass from Lake Havasu ($\bar{x}$=1.6 ppm). Selenium levels in muscle of bass from the San Joaquin River ($\bar{x}$=0.44 ppm), the Sacramento River ($\bar{x}$=0.41 ppm), and Clifton Court Forebay ($\bar{x}$=0.40 ppm) were all significantly lower than in bass from Lake Havasu; levels did not differ significantly among fish from the three Delta sites. Striped bass from both the Colorado River and the Sacramento-San Joaquin Estuary contained significantly higher selenium levels than bass from Success Lake, a control site ($\bar{x}$=0.14 ppm). Bass from Success Lake average 0.81 ppm selenium in liver.

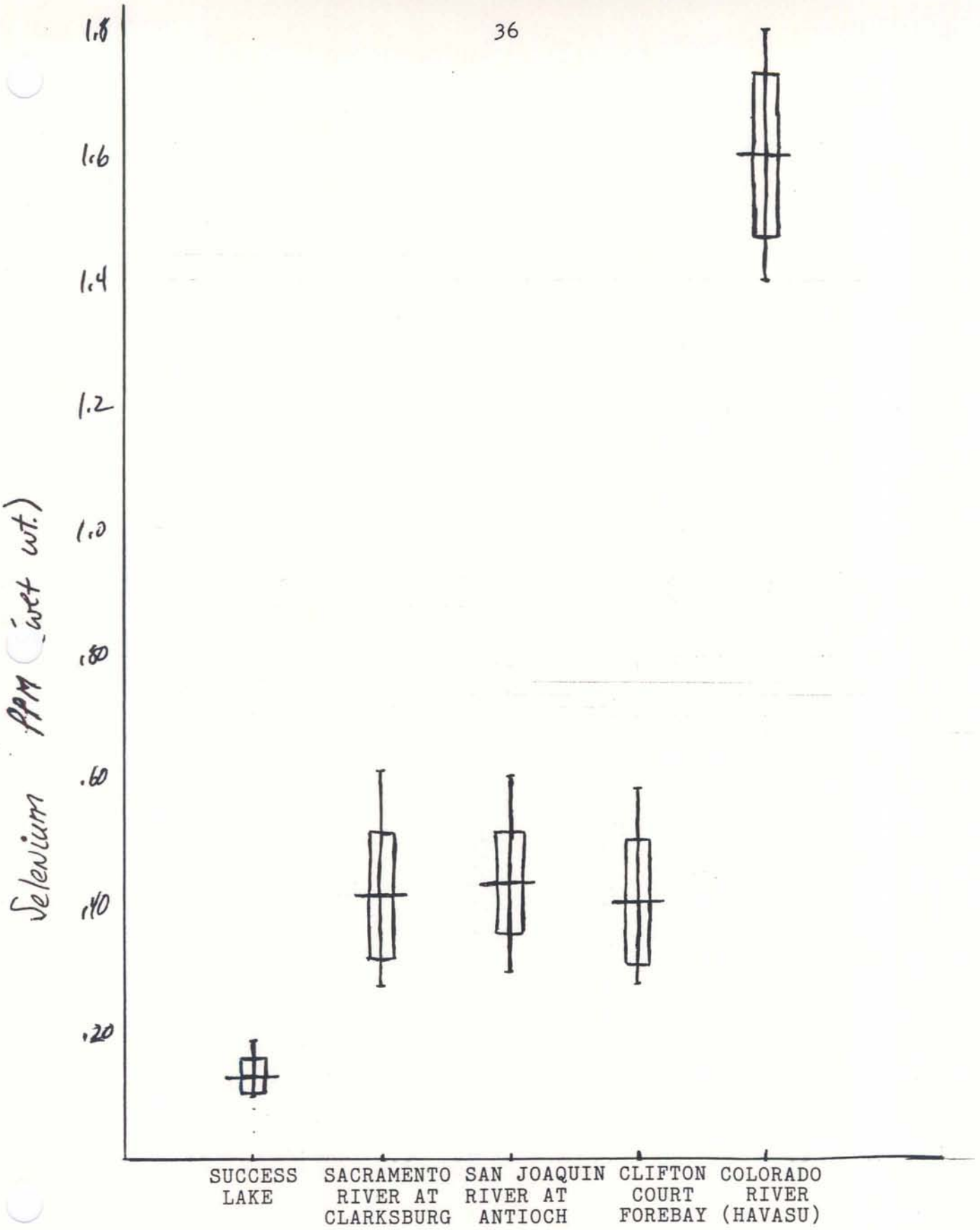



Figure 8. Selenium concentrations ($\bar{x}\pm s$, range; ppm wet weight) in muscle tissue of striped bass from the Sacramento-San Joaquin Estuary, Lake Havasu (Colorado R.), and Success Lake (Tule R.).

Lake Havasu striped bass contained the highest selenium levels we have measured in this species, suggesting exposure to selenium derived from either naturally occurring or anthropogenic sources in the Colorado River drainage upstream of Havasu. Major sources of agricultural drainwater possibly containing selenium flow into the Colorado River downstream from Havasu. Largemouth bass and common carp from the Palo Verde Outfall Drain contained selenium at slightly above background levels in 1986 (White et al. 1987). Selenium in the Colorado River upstream from Lake Havasu is being investigated by the U.S. Geological Survey.

It is unclear whether Lake Havasu striped bass contain selenium levels high enough to be harmful since "effect levels" have not been established for adult striped bass.

Selenium concentrations in bass did not differ between the Sacramento and San Joaquin rivers in either 1986 or 1987. This result was not unexpected since these bass were collected during the spring migration from the lower estuary and ocean (where they mix together from summer through winter) to the Delta and upriver spawning grounds. Some bass migrating past Antioch in the San Joaquin River eventually end up in the Sacramento River (via Three Mile Slough or the Mokelumne River) and are subject to capture at Clarksburg, thus increasing homogenity between sample groups. Striped Bass Health Index Monitoring has identified differences between these sites only in bass size, age, and striping pattern (Knudsen and Kohlhorst 1987).

Striped bass were collected from Clifton Court Forebay to detemine if that "population" might reflect a water quality influence from the San Joaquin River. Two possible explanations for a lack of difference between selenium levels in bass from the Forebay and those from other sites in the Delta are: 1) a distinct Forebay population does not exist; bass can and do move freely between the Forebay and the Delta (Robert Kano, pers. comm), and 2) under dry year (low outflow) conditions in winter-spring, 1986-1987, Sacramento River water comprised a high percentage of water drawn into Clifton Court Forebay by State Water Project pumps, thus reducing the San Joaquin River influence on water quality in the Forebay and south Delta.

Selenium analyses of striped bass liver from fish obtained by the Health Index Monitoring Program were not completed when this was written. Selenium in livers of striped bass caught in the Sacramento and San Joaquin rivers in 1986 were about twice those in Success Lake striped bass in 1987.

Striped bass collected from the Delta in spring 1987 contained significantly higher concentrations of selenium in muscle than bass collected there in spring 1986. Minimum concentrations were unchanged between years whereas the sample mean increased from 0.34 ppm to 0.43 ppm and the maximum values increased from 0.41

ppm to 0.63 ppm. Selenium concentrations in liver have been measured over a longer time period but data from 1987 samples which may help clarify the significance of this apparent increase are not available yet.

Higher selenium concentrations in tissues of bass from the Delta compared to a control site, Success Lake, suggest selenium occurs in the estuarine environment at levels above background. Selenium from agricultural and industrial activities in the Bay area and the Central Valley drainage probably contributes to observed levels in Bay biota. Bass in the anadromous population may have comparatively high selenium levels partly because a large portion of their diet is marine fishes (e.g., northern anchovies) which tend to contain more selenium than freshwater forage species (e.g., threadfin shad) eaten by bass at inland reservoirs. Northern anchovies in San Francisco Bay contained 0.45 to 0.62 ppm selenium (White et al. 1987); levels in freshwater forage fish species have not been measured. Selenium in striped bass from other coastal populations are not adequately documented.

Although selenium has been suggested as a possible contributing factor to the decline of striped bass in the Sacramento-San Joaquin Estuary (Greenberg and Kopec 1986), direct evidence of specific biological effects at tissue concentrations measured in these fish has not been presented and the significance of documented levels remains unknown.

## White Sturgeon

White sturgeon (Acipenser transmontanus) spawn primarily during March and April in the Sacramento River and probably in the San Joaquin River and use the rivers, Delta, and estuary as a nursery. Most white sturgeon remain in the estuary, although coastal migrations have been documented (Chadwick 1959). Sturgeon are long-lived; based on their size, those in our sample were 8 to 15 years old (Kohlhorst et al. 1980). Benthic invertebrates dominate the diet of white sturgeon with clams, barnacles, crabs, shrimp and herring eggs being seasonally important (McKechnie and Fenner 1971). Some small fish also are consumed.

Eight white sturgeon caught in San Pablo Bay between March 14 and April 25, 1987 averaged 2.6 ppm selenium in muscle, significantly higher than the 1.8 ppm average in five white sturgeon caught in Suisun Bay between April 24 and May 9, 1987 (Table 8). Selenium concentrations ranged from 1.1 ppm to 4.3 ppm in sturgeon from San Pablo Bay and from 1.0 ppm to 2.3 ppm in those from Suisun Bay. Sturgeon from Suisun Bay averaged about 90 mm longer than those from San Pablo Bay (1260 mm vs. 1170 mm, total length) but there was no relationship between size and selenium levels within the size range in the sample (1016 mm to 1397 mm, TL).

TABLE 8. Selenium concentrations in muscle tissue of adult white sturgeon (Acipenser transmontanus) from the Sacramento-San Joaquin Estuary, 1987. Concentrations in ppm, wet weight.

| Location | Date | Selenium Concentrations (PPM) |
|---|---|---|
| San Pablo Bay | 3/14/87 | 3.1 |
| " | 4/16/87 | 2.5 |
| " | 4/16/87 | 1.1 |
| " | 4/16/87 | 4.3 |
| " | 4/24/87 | 3.0 |
| " | 4/24/87 | 2.2 |
| " | 4/25/87 | 2.3 |
| " | 4/25/87 | 2.5 |
| Suisun Bay | 4/24/87 | 2.3 |
| " | 5/3/87 | 2.0 |
| " | 5/3/87 | 1.0 |
| " | 5/9/87 | 1.8 |
| " | 5/9/87 | 2.0 |
| | | $\bar{x} \pm s$: 2.3 $\pm$ 0.86 |

The 2.6 ppm average selenium concentration in white sturgeon caught in San Pablo Bay in spring 1987 was significantly higher than the 1.9 ppm average level measured in ten white sturgeon caught there in spring 1986 (White et al. 1987).

Not much is known about sturgeon distribution and movements within the Estuary; there is neither evidence to indicate sturgeon migrate frequently between San Pablo and Suisun bays nor any barrier to prevent them from it. Unless they move around extensively, tissue selenium levels in white sturgeon probably indicates differences in the biological availability of selenium in the area where the fish were caught. Data from white sturgeon suggest selenium levels were higher in at least some components of the ecosystem in San Pablo Bay than in Suisun Bay, including benthic organisms such as clams and shrimp, important foods for white sturgeon. Data from diving ducks which like sturgeon feed on benthic organisms, also indicated selenium enrichment in San Pablo Bay.

The interannual difference in selenium levels in white sturgeon suggest an increase in selenium in the aquatic environment of San Pablo Bay between 1986 and 1987. This interpretation assumes we sampled the same group of sturgeon in both years or that tissue levels in sturgeon indicate exposure to and uptake of selenium in recent weeks or months rather than the cumulative effect of exposure over years. Neither of these assumptions can be tested with available data. The mean and range of fish size were nearly equal in 1986 and 1987 samples, hence size did not contribute to the annual difference.

The significance to white sturgeon of the selenium levels measured in their tissues is unknown. White sturgeon abundance in the Estuary has increased steadily in the last ten to fifteen years, suggesting no problems with sturgeon reproduction. However, population levels are relative, are influenced by many factors, and hence are probably an insensitive indicator of potential effects of recent environmental changes, especially since sturgeon do not reproduce until they are relatively old (8-10 years). Nevertheless, this increase in the white sturgeon population has occurred while other prominent fish species in the Estuary have declined.

These data may have an impact on the recreational sturgeon fishery since seven of eight fish from San Pablo Bay contained selenium concentrations exceeding the level in edible tissue at which advisories limiting consumption by humans have been issued by the State Department of Health Services for other species of fish and wildlife.

## RECONNAISSANCE OF SELENIUM IN WATERFOWL AND WADING BIRDS

Reconnaisance level monitoring was undertaken to extend our data base to a new area (northeastern California) and to species with food habits different from those already studied (northern shoveler, an omnivorous dabbling duck and American bittern, an opportunistic, carnivorous wading bird).

### Mallards

The mallard (Anas platyrhynchos), a dabbling duck, is the most abundant and widely distributed duck in the northern hemisphere, a common resident throughout much of the United States and a winter visitor to the southern half. In California, mallards are found all year in freshwater lakes, ponds, rivers and marshes as resident breeding birds. Large numbes of mallards migrate from breeding areas in U.S. and Canadian prairies and other northern areas to winter in California, primarily in the marshes of the Central Valley and San Francisco Bay (Bellrose 1978). Mallards are primarily vegetarians, feeding on the seeds (some stems and leaves) of marsh plants. They have also adapted to the availability of agricultural grains (corn, rice, barley). Rice is the most important domestic food source for mallards in the Central Valley. The mallard is an important game species, usually ranking first or second in annual harvest statistics.

Mallards collected at Tulelake NWR in October 1986 had slightly lower ($\bar{x}$=0.24 ppm) muscle selenium levels (Figure 9) than those of mallards collected in February and June 1986 from Gray Lodge WA ($\bar{x}$'s=0.33 ppm and 0.43 ppm) and in March and June 1986 from Grizzly Island WA ($\bar{x}$=0.30 ppm and 0.40 ppm) (White et al. 1987). Liver selenium levels of the Tulelake mallards ($\bar{x}$=1.0 ppm) were approximately equal to those of the Gray Lodge ($\bar{x}$=1.1 ppm and 1.1 ppm) and Grizzly Island ($\bar{x}$=1.2 ppm and 0.91 ppm) mallards. Selenium concentrations in Tulelake mallards were well below any recognized harmful levels.

### Pintail

Pintail (Anas acuta) are usually the most common wintering waterfowl species found in California and are of the earliest arriving migrants in the fall (Cogswell 1977). California receives about half of the continentl population. They are the most common dabbling duck breeding in the Arctic although their most important breeding areas are in the mixed prairies and parklands of Central North America (Bellrose 1978). They are one of the most popular waterfowl species hunted in California and rank in the top three in numbers harvested annually. Pintail feed largely on seeds of grasses and aquatic plants. In the Central Valley of California they feed primarily on rice left after harvest. Birds that were collected from Tulelake NWR contained foliage of pondweeds and seeds of bulrush, pondweeds, and smartweeds.

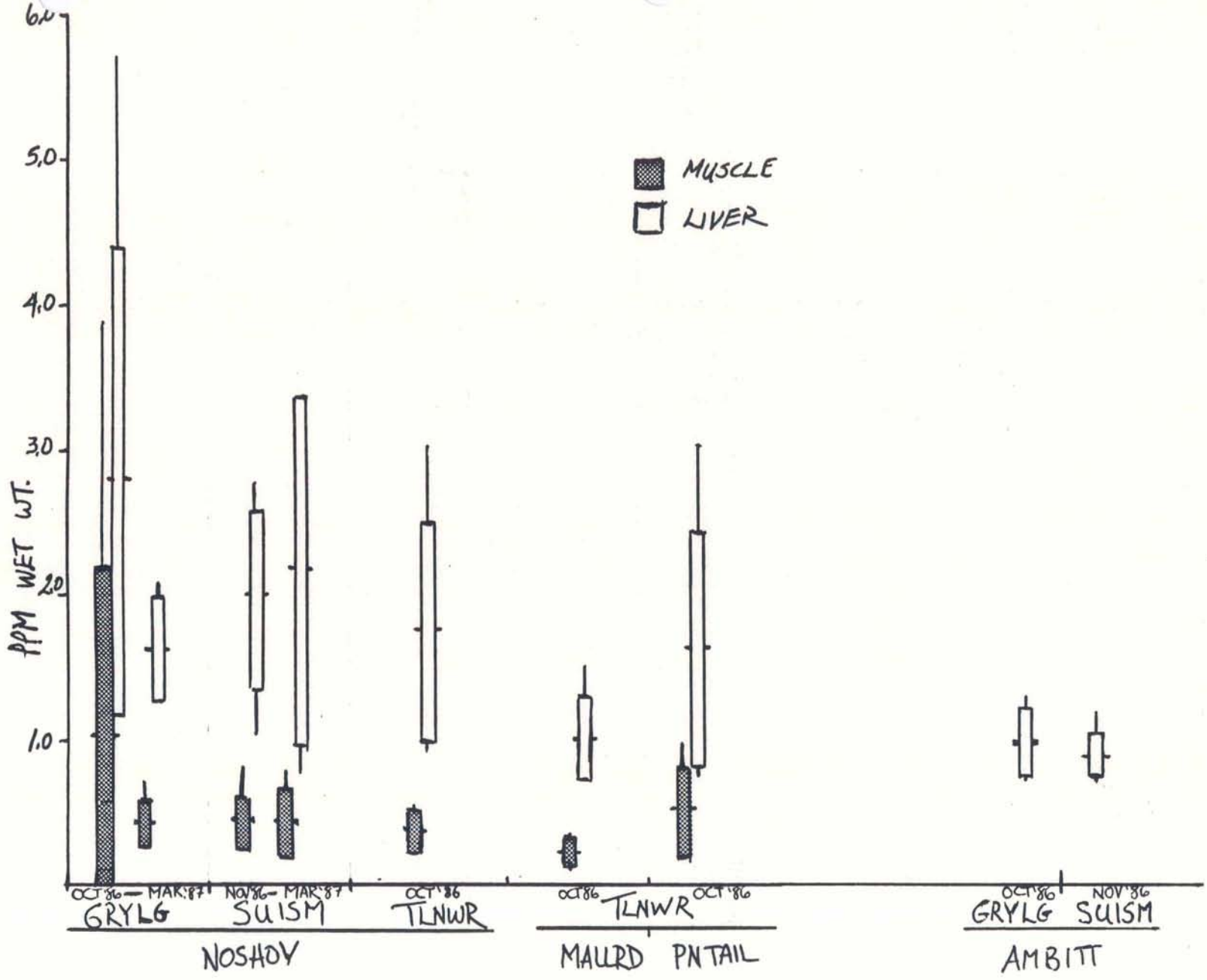



Figure 9. Selenium concentrations ($\bar{x}\pm s$,range; ppm wet weight) in muscle and liver tissues of northern shovelers, mallards, pintails, and American bitterns collected from Gray Lodge SWA, the Suisun Marsh, and Tulelake National Wildlife Refuge, 1986-1987.

Pintail collected at Tulelake NWR in October 1986 had liver selenium levels ($\bar{x}$=1.6 ppm) that were not significantly different from those of mallards ($\bar{x}$=1.0 ppm) collected at the same location (Figure 9). Pintail muscle selenium levels ($\bar{x}$=0.54 ppm) were significantly higher than those of the mallards ($\bar{x}$=0.24 ppm), however, all muscle selenium levels were less than 1.0 ppm, well below concentrations known to impact waterfowl or consumers of waterfowl.

## Northern Shoveler

The northern shoveler (Anas clypeata) is a migrant dabbling duck that is commonly found in California from October through March. Although a few shovelers nest in California, the majority nest in the prairie potholes area of the great plains. Shovelers are largely planktonic feeders and strain small plants and animals from the water with their large flattened bills. Because of this unique mode of feeding, shovelers consume both plant and animal matter and are therefore less highly esteemed on the table than grain or seed-eating ducks. Although shovelers are not highly regarded, they are commonly shot and eaten by waterfowl hunters and comprise a large share of the annual California waterfowl harvest.

Shovelers were collected in October 1986 from Tulelake National Wildlife Refuge, Gray Lodge State Wildlife Area and Grizzly Island SWA. Shovelers were collected again in March 1987 at Gray Lodge and from March to May at Grizzly Island.

There were no significant differences in muscle or liver selenium concentrations among shovelers collected in October 1986 from Gray Lodge (muscle, $\bar{x}$=0.47 ppm; liver, $\bar{x}$=2.0 ppm), or Tulelake NWR (muscle, $\bar{x}$=0.39 ppm; liver, $\bar{x}$=1.7ppm) (Figure 9). There were no differences in either muscle or liver selenium concentrations between spring collected shovelers from Gray Lodge (muscle, $\bar{x}$=0.43 ppm; liver, $\bar{x}$=1.6 ppm) and Grizzly Island (muscle, $\bar{x}$=0.47 ppm; liver, $\bar{x}$=2.0 ppm). Finally, there was no significant difference in selenium levels between shovelers collected in fall and spring.

Although selenium levels in shovelers collected at Gray Lodge in the fall were not significantly different than those collected elsewhere, they had a greater range than those from other sites and seasons. The four highest shoveler muscle selenium levels and three highest liver concentrations came from the fall Gray Lodge birds. Two of the shovelers collected in October from Gray Lodge had muscle selenium levels over 2.0 ppm, wet wt., the current State Department of Health Services "level of concern" for edible tissues.

One possible explanation, supported by circumstantial evidence, for the elevated selenium levels seen in some shovelers collected at Gray Lodge in October 1986 is that they were recent migrants from a location with elevated selenium levels. One portion of the shoveler population stages in the Carson Sink at Stillwater National Wildlife Refuge in Nevada before migrating into the Sacramento Valley (Bellrose 1978). Record numbers of shovelers were observed at Stillwater NWR in fall 1986 (Steve Thompson, USFWS, pers. comm). Preliminary studies indicated elevated levels of boron, mercury and selenium at Stillwater (Robert Hallock, USFWS, pers. comm.).

Furthermore, it is unlikely shovelers were accumulating selenium at Gray Lodge. Selenium levels in shovelers at Gray Lodge in March were low, suggesting selenium occurs at background levels in the wildlife area marshes and other wetlands in the region. Mallards, coots, and black-necked stilts taken from Gray Lodge in February through April, 1986 also had low levels of selenium in their tissues (White et al. 1987).

## American Bitterns

American bitterns (Botaurus lentiginosus) are wading birds closely related to herons and egrets. They are residents of suitable habitat throughout the State (Small 1974) and are commonly found in the heavy vegetation of shallow marshes. In addition to the resident bittern population, some bitterns migrate into California in winter from other areas. Bitterns occupy the end of marsh food chains and are one of the few piscivorous/carnivorous birds found in shallow marshes. Their diet consists of fish, snails, insects, crustaceans, amphibians, reptiles and small mammals (Cogswell 1977).

American bitterns were collected in October 1986 on the Gray Lodge Wildlife Area and in November 1986 on the Grizzly Island Wildlife Area in the Suisun Marsh. Average selenium level in the livers of Grizzly Island bitterns ($\bar{x}$=0.89 ppm) was not significantly different from that of bitterns collected at Gray Lodge ($\bar{x}$=0.96 ppm) (Figure 9). The Grizzly Island bitterns were feeding almost entirely on meadow mice (Microtues sp.) while those at Gray Lodge were feeding on crayfish. While no data on selenium concentrations and toxic effects specific to American bitterns was found, levels in this range have not impacted other species.

Four river otters, drowned accidentally in hoop nets set for catfish in Goodyear Slough in January 1987, contained 1.0, 1.1, 1.2 and 1.6 ppm selenium in liver. Wren (in Eisler, 1985) reported 2.1 ppm selenium in livers of river otters from Ontario, Canada. No other data on selenium in otters was found.

## VALLEY-DELTA CATFISH STUDY

Fish in the Suisun Bay-Western Delta area might be exposed to selenium from local industrial sources as well as input from the Central Valley, whereas those in upstream areas would be influenced only by selenium from sources in Valley drainages. Catfish occur throughout the Valley and the Delta and in some waters connected to Suisun Bay. Tagging studies indicate catfish are non-migratory, sedentary fishes, hence, careful selection of sampling locations may help determine if selenium accumulation is different in segments of the Valley, Delta and upper Estuary with different water quality influences.
White catfish (Ictalurus catus) and/or channel catfish (Ictalurus punctatus) were collected from six sites on the San Joaquin River system, one site on the Sacramento River, one site near the confluence of the Sacramento and San Joaquin rivers, and one site adjacent to Suisun Bay (Figure 4). Catfish were obtained from Goodyear Slough near Suisun Bay only in January 1987, from the three southernmost sites in the San Joaquin River system (SJRLN, MUDSL, SALTS) only in April 1987, and from the five remaining sites in both January and April/May 1987 (Table 2B).

Selenium concentrations in catfish muscle and liver collected in January were not significantly different from those collected in April/May (Figures 10 and 11). Muscle selenium concentrations were significantly higher in catfish from Salt Slough ($\bar{x}$=0.31 ppm) and Mud Slough ($\bar{x}$=0.52 ppm) than from all other sites (range of $\bar{x}$'s=0.13 ppm to 0.23 ppm) (Figure 10). Highest liver selenium levels also occurred in Salt Slough ($\bar{x}$=2.5 ppm) and Mud Slough $\bar{x}$=2.4 ppm) although their separation from the other sites (range of $\bar{x}$'s=1.3 ppm to 2.1 ppm) was less clearly defined (Figure 11).

Selenium levels in catfish from Mud Slough, Salt Slough and the San Joaquin River downstream of the Merced River confluence were similar to levels found in catfish from the same sites in August 1986 (White et al. 1987), suggesting an equilibrium condition exists with respect to selenium in these fish under the environmental conditions produced during a dry year with current drainwater management practices.

Selenium levels in catfish from the San Joaquin River were low and not significantly different from those of catfish collected in the Sacramento River (Rio Vista) in which waterborne selenium is typically <0.1 ppb (Cutter 1987).

Selenium levels in catfish suggest a depletion in biologicaly available selenium moving downstream in the San Joaquin River from Salt and Mud Sloughs, sources of selenium enriched drainwate from some Valley farms. Possible mechanisms contributing to reduced selenium availability for catfish include dilution by low-selenium waters from east-side tributaries (Merced, Tuolumne and Stanislaus rivers) and uptake by organisms not in the catfish food chain (e.g., other fishes or aquatic macrophytes).

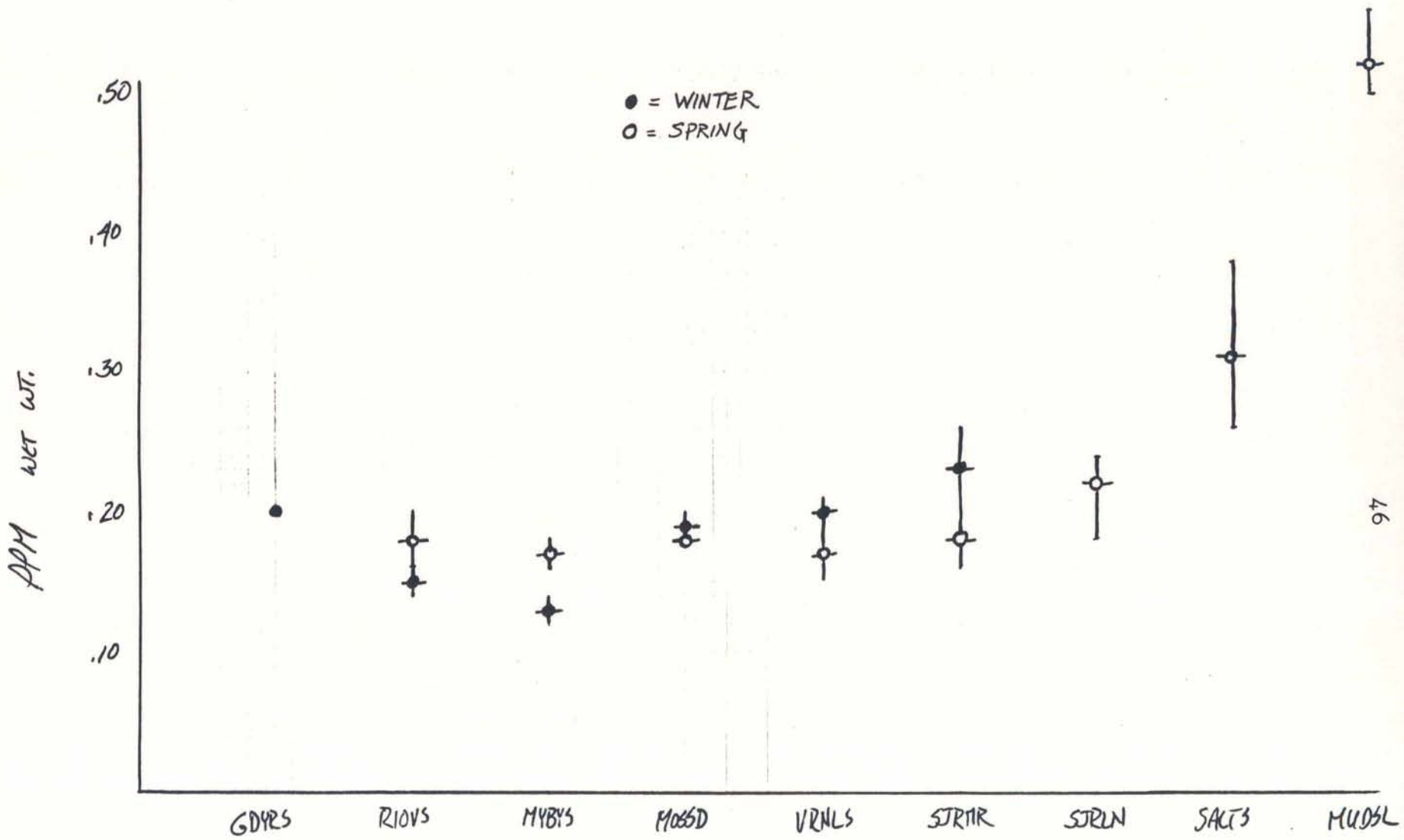



Figure 10. Selenium concentrations ($\bar{x}\pm s$, range; ppm wet weight) in muscle tissues of white catfish and channel catfish collected from sites in the San Joaquin Valley and the Sacramento-San Joaquin Delta, 1987.

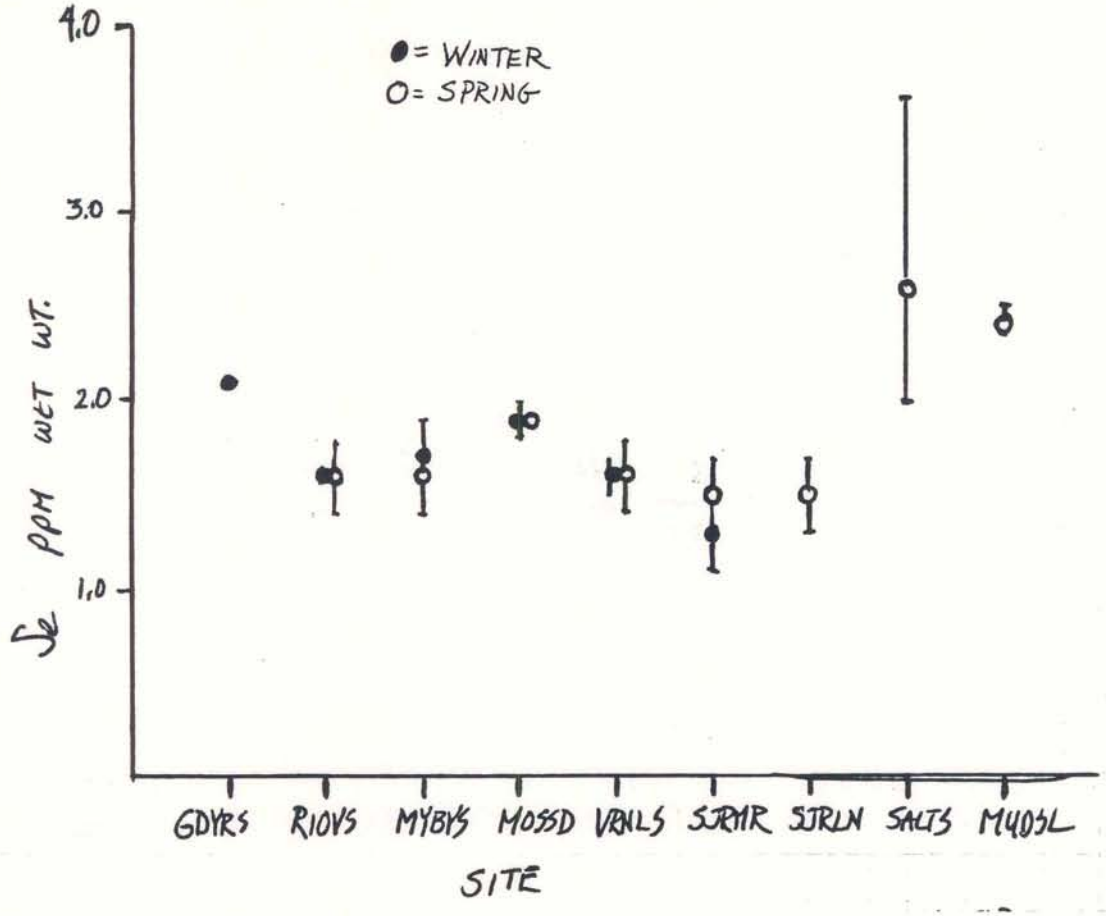



Figure 11. Selenium concentrations ($\bar{x}\pm s$, range; ppm wet weight) in liver tissues of white catfish and channel catfish collected from sites in the San Joaquin Valley and the Sacramento-San Joaquin Delta, 1987.

Selenium levels in catfish from Mayberry Slough in the western Delta, the site closest to potential industrial sources of selenium downstream at which complete samples were obtained, were not different than levels in catfish from the Sacramento or San Joaquin rivers. This indicates that selenium sources downstream in Suisun Bay do not affect resident biota in the western Delta, even under the low outflow conditions of winter 1987 which would be the most conducive to an upstream impact. San Joaquin River influence on selenium levels in the western Delta probably was minimal also since most of the San Joaquin flow was being withdrawn by South Delta pumping plants, and water in the western Delta was Sacramento River water drawn across the Delta.

Sediment samples were collected at all spring catfish collecting locations and at two winter catfish collecting site.s Compared to other sites, Mud Slough sediments collected in January and Salt Slough sediments in both time periods had higher selenium levels (Figure 12). However, Mud Slough sediments collected in April were not elevated in comparison to other sites. One possible explanation for the discrepancy in selenium levels from Mud Slough is variability in sediment characteristics which may affect their affinity for selenium. Mud Slough has a serpentine course and the bottom has areas of sand, hard clay and soft mud. Another possible explanation is that selenium in the sediments is mobile and the levels fluctuate with fluctuating selenium levels in the water or in response to other water quality characteristics. USGS water sampling data for this area is not yet available for the time period of our fish and sediment collections.

## BIOCONCENTRATION OF SELENIUM IN WATERFOWL FOOD CHAIN

Elevated concentrations of selenium were measured in diving ducks in winter 1986, particularly in Suisun Bay. Waterborne selenium concentrations in the Bay were thought to be relatively low, suggesting selenium accumulated by diving ducks had been concentrated in the food chain.

To assess the significance of selenium bioconcentration in the food chain we collected samples of water, suspended (filterable) matter, sediment, and clams (Corbicula) at two locations within Suisun Bay in January and April, 1987. Surf scoters and scaup also were collected from Suisun Bay at the same time. Collections were made at Middle Ground in both months, in northwestern Suisun Bay near the Suisun Slough Channel entrance marker in January and near Roe Island in southern Suisun Bay in April.

Water samples were collected on four consecutive slack water periods to measure the influence of tidal excursion on waterborne selenium. Electrical conductivity generally followed the expected

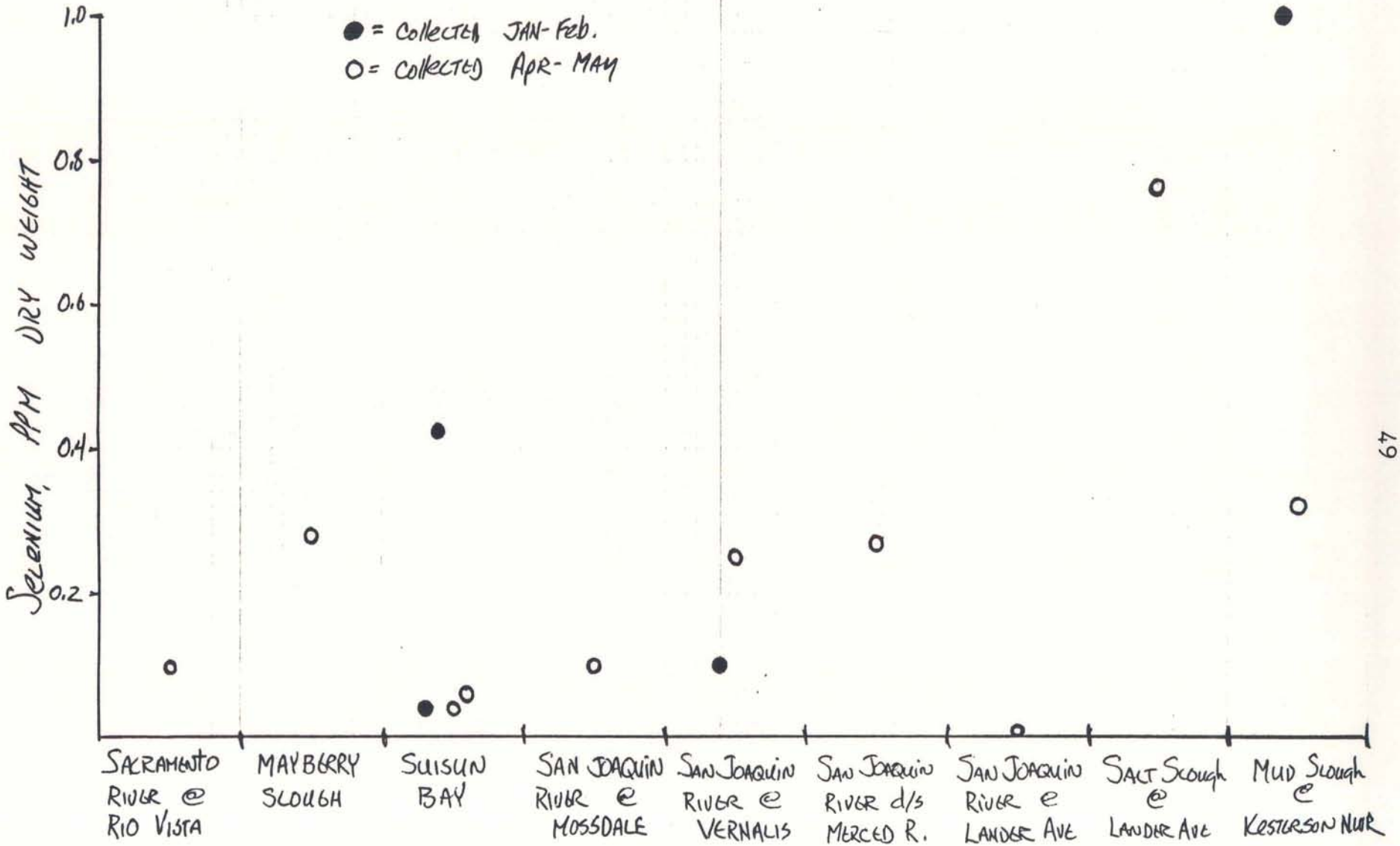



Figure 12. Selenium concentrations ( ppm, dry weight) of sediment samples collected at sites in the San Joaquin Valley and the Sacramento-San Joaquin Delta.

pattern in relation to the tides. Dissolved total selenium also varied during each 24 h sampling period, however total selenium bore no apparent relationship to salinity (Table 9). Selenium concentrations in water ranged from 0.124 ppb to 0.193 ppb in January and from 0.127 ppb to 0.189 ppb in April.

Selenium in sediments was very low at the Middle Ground site in January (0.06 ppm, dry weight) and April (0.04 ppm) and at Roe Island in April (0.06 ppm). These sediments were relatively coarse, sandy sediments compared to the finer, silt-clay type sediments at the Suisun Slough channel entrance which had 0.42 ppm selenium.

The filter feeding clam, Corbicula, was very abundant in the sandy substrate at Middle Ground and Roe Island and sparsely distributed in the muddy bottom at the Suisun Slough site. The former two sites probably represent important feeding areas for diving ducks in Suisun Bay. Ninety-five percent of scaup and 83 percent of surf scoters collected from Suisun Bay had been eating Corbicula (Appendix F). Corbicula contained between 0.61 ppm and 0.86 ppm (wet weight) selenium with a slightly higher concentration at Middle Ground in April than in January. The clams had concentrated selenium to about 4250-5500 times the concentration of total selenium dissolved in water (Figure 13). In comparison, selenium levels in diving ducks were approximately 2 to 7 times higher in muscle tissue and 5 to 42 times higher in liver tissue than selenium levels in the clams, the principal item in their diet.

Uptake by plankton is an important component in the bio-geochemical cycling of selenium in aquatic systems (Cutter 1987). Selenium has not yet been measured in the suspended material filtered from samples of water. Since suspended matter is the primary source of nutrition for filter feeding clams, concentration of selenium from water by phytoplankton may account for a significant percentage of the apparent bioconcentration of selenium by clams. Data on selenium in filterable matter (analyses pending) may facilitate evaluation of this hypothesis.

Currently available data suggest bioconcentration of selenium from low levels in water occurs at all trophic levels but that most bioconcentration takes place at the low and intermediate links in the food chain (phytoplankton and benthic bivalves). The data are not adequate to evalute the significance of sediments as a source/sink of selenium.

TABLE 9. Selenium concentrations in water (filtered), sediment, benthic bivalves (Corbicula), and diving ducks from Suisun Bay in January and April 1987.

| Location | Tide/ E.C. Surface umho/cm$^2$ | Water ppb[1/] | Sediment ppm (dry wt.) | Benthic Bivalve (Corbicula) ppm (wet) | Surf Scoter ppm (wet) | Scaup ppm (wet) |
|---|---|---|---|---|---|---|
| Date: January, 1987 | | | | | | |
| Middle Ground | | | | | | |
| | HL/912 | 0.124 | | | | |
| | HH/1730 | 0.145 | | | | |
| | LL/880 | 0.160 | | | | |
| | LH/1530 | 0.147 | | | 3.9(M) | 2.9 |
| | Mean | 0.144 | 0.06 | 0.61 | 25.5(L) | 9.4 |
| Suisun Slough Channel Entrance Marker | | | | | | |
| | HL/1450 | 0.167 | | | | |
| | HH/1950 | 0.160 | | | | |
| | LL/1520 | 0.188 | | | | |
| | LH/1760 | 0.193 | | | | |
| | Mean | 0.177 | 0.42[2/] | 0.78 | | |
| Date: April, 1987 | | | | | | |
| Middle Ground | | | | | | |
| | LL/490 | 0.127 | | | | |
| | LH/306 | 0.148 | | | | |
| | HL/247 | 0.189 | | | | |
| | HH/421 | 0.165 | | | 2.0(M) | 1.8 |
| | Mean | 0.157 | 0.04 | 0.86 | 12.0(L) | 4.6 |
| Roe Island | | | | | | |
| | LL/223 | 0.142 | | | | |
| | LH/480 | 0.165 | | | | |
| | HL/384 | 0.168 | | | | |
| | HH/608 | 0.168 | | | | |
| | Mean | 0.161 | 0.06 | 0.82 | | |

1/ Dissolved total selenium. (analyses by G. Cutter)

2/ February 1987 silty clay sediment compared to sand substrate at other sites.

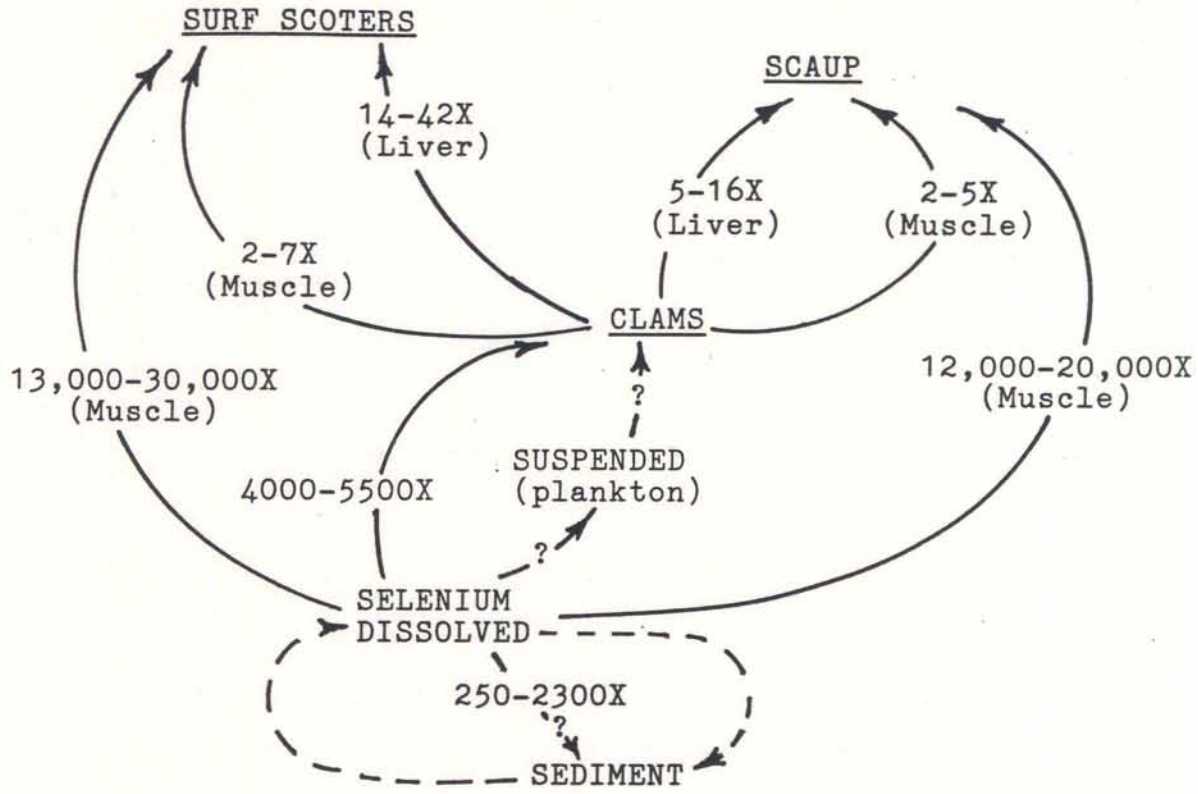



Figure 13. Bioaccumulation factors between trophic levels in the food chain of diving ducks, Suisun Bay,1987. Factors were derived from mean concentrations in samples expressed as described in Table 9.

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APPENDIX A.
Locations of Sampling Sites, October 1986 - May 1987

Antioch - 38°03'N, 121°42'W. The San Joaquin River near Schad Landing, approximately 7 km upstream of the Antioch Bridge, Contra Costa County.

Central San Francisco Bay - 37°54'N, 122°25'W. The portion of San Francisco Bay bordered by the Richmond-San Rafael Bridge to the north, the Golden Gate Bridge to the west and the Oakland-Bay Bridge to the south.

Clarksburg - 38°26'N, 121°31'W. Sacramento River adjacent to Clarksburg, Yolo County.

Clifton Court - 37°51'N, 121°35'W. Clifton Court Forebay, Approximately 7 km southeast of Byron, Contra Costa County.

Goodyear Slough - 38°07'N, 122°06'W. Goodyear Slough, east of Highway 680, approximately 10 km northeast of Benecia, Solano County.

Gray Lodge Wildlife Area - 39°29'N, 121°48'W. Off Pennington Road approximately 16 km southwest of Gridley, Butte County.

Humboldt Bay - 40°43'N, 124°14'W. Humboldt Bay, Humboldt County.

Lake Earl - 41°49'N, 124°12'W. Lake Earl, north of Crescent City, Del Norte County.

Lake Havasu - 34°25'N, 114°14'W. Lake Havasu on the Colorado River, San Bernardino County.

Mayberry Slough - 38°02'N, 121°49'W. Mayberry Slough, approximately 4 km northeast of Antioch, Contra Costa County.

Morro Bay - 35°23'N, 120°53'W. Morro Bay, San Luis Obispo County.

Mossdale - 37°48'N, 121°18'W. San Joaquin River near Interstate 5 Bridge, 8 km west of Manteca, San Joaquin County.

Mud Slough - 37°16'N, 12°55'W. Mud Slough on Kesterson National Wildlife Refuge, approximately 200 m. north of the end of the San Luis Drain, Merced County.

Rio Vista - 38°10'N, 121°39'W. Sacramento River at mouth of Steamboat Slough, upstream from Rio Vista, Solano County.

Salt Slough - 37°15'N, 120°51'W. Salt Slough upstream from the Lander Avenue (Highway 165) crossing, Merced County.

San Joaquin River at Lander Road - 37°18'N, 120°50'W. San Joaquin River downstream from the Lander Avenue (Highway 165) crossing, Merced County.

San Joaquin River at Merced River - 37°21'N, 120°58'W. San Joaquin River just downstream from its confluence with the Merced River, Merced County.

San Jose Water Treatment Plant - 37°27'N, 121°58'W. The slough channel extending south from Coyote Creek to the San Jose Sewage Disposal Plant, 3 km north of Alviso, Santa Clara County.

San Pablo Bay - 38°03'N, 122°23'W. San Pablo Bay north of the Richmond-San Rafael Bridge and west of the Carquinez Bridge.

South San Francisco Bay - 37°38'N, 122°15'W. San Francisco Bay south of the Oakland-Bay Bridge.

Success Lake - 36°06'N, 118°55'W. Success Lake, approximately 12 km east of Porterville, Tulare County.

Suisun Bay - 38°04'N, 122°03'W. Suisun Bay between the Carquinez Bridge and Antioch, including Grizzly Bay.

Suisun Marsh - 38°08'N, 121°57'W. That protion of the Suisun Marsh on Grizzly Island Wildlife Area, south of Fairfield, Solano County.

Tulelake NWR - 41°55'N, 121°32'W. Tulelake and Lower Klamath National Wildlife Refuges, West of Tulelake, Siskiyou County.

Vernalis - 37°36'N, 121°10'W. San Joaquin River south of the Highway 132 crossing, 10 km east of Vernalis, Stanislaus County.

# APPENDIX B. Sample Preparation.

## Sample Container Preparation

Glass milk dilution bottles (160 mL) with Teflon-lined screw lids serve as sample containers. Bottles and lids are washed with warm water and soap (Haemo-sol) manually or by dishwasher. Care must be taken using the dishwasher because soap residue may adhere to the inner surface of the bottles and/or lids. Usually a second rinse will correct this problem. After thoroughly rinsing both bottle and lid with tap water, rinse the inner surfaces as follows:

1) 25 mL of 1.0 M nitric acid (analytical reagent grade);
2) 25 mL of Type I reagent grade water (ASTM 1986);
3) 25 mL of 2-propanol (analytical reagent grade).

To ensure all surfaces are exposed to solvents, rotate bottles when pouring out solvents. Allow 15 minutes for bottles to air-dry before using.

If linear polyethylene (LPE) bottles are to be used, fill with 1.0 M nitric acid and allow to soak for at least 24 hours and rinse with Type I water.

## Clean Room Preparation for Dissection and Homogenization

Before entering the clean room, set the fan to the highest speed. This will create a positive pressure of filtered air to prevent contaminants from entering the room. Hands must be washed thoroughly before handling any samples or equipment used in dissection. Allow deionized water to run 5 to 10 minutes to purge the pipes. All counter tops and glass surfaces must be wiped with Kimwipes and Type III general laboratory water (ASTM 1986). Finally, the glass surfaces used for dissection must be covered with aluminum foil with the dull face of the foil exposed. Use the following list for equipment check:

aluminum foil
chromium coated nickel-silver scalpel handles
carbon steel scalpel
Teflon forceps
large and small "v" tissue forceps
pliers, cutting
glass milk dilution bottles (160 mL) with Teflon lined lids
1.0 M nitric acid (analytical reagent grade)
2-propanol (analytical reagent grade)
vernier caliper
deionized water (Type I and Type III)

APPENDIX B (Continued)

## Dissection Tool Preparation

All dissecting tools must be chemically cleaned before touching the sample(s). All tools must be recleaned and blades changed after each composite or individual sample.

Wash tools (except blades) using warm soapy water and toothbrush. Attach clean blades to scalpels, then briefly rinse all tools in 1.0 M nitric acid, Type I water, and 2-propanol. Place tool handles on a foil covered box so blades are suspended over the edge on the box.

Periodic washing of the solvent bottles and changing of the solvents will be necessary to reduce the possibility of contaminating subsequent samples. Solvent bottles must be washed at least once a week and solvents changed about every tenth sample or after each day.

Sample portions to be used for analysis may only be touched by dissecting tools and the inside of the bottle. Contaminated equipment must be recleaned. Minimize solvent contact with skin. Wash skin after contact with solvents.

## Dissection Procedures

### General

Remove frozen samples from freezer and thaw just enough to allow dissection. Packages may be thawed overnight in the refrigerator, or to accelerate thawing the package is opened and the exposed samples are placed under running Type III deionized water. If whole body samples are to be used, Type I water is used to thaw samples (see Whole Body Samples). Record length (to nearest mm) and weight (to nearest 0.1 g) for each individual. For example, fork length is used for fish and the length of beak to tail is used for birds. Samples to be dissected are then placed on aluminum foil to air dry. If there is excess mucous, a toothbrush and Type I water may be used to scrub the fish (for non-whole body samples only). Whole body samples can be cleaned by holding the individual(s) with chemically cleaned Teflon forceps under a stream of Type I water.

All dissected portions of the sample are placed in a chemically cleaned milk dilution bottle and labeled with the sample number. The bottle weight and the weight of the bottle plus the dissected material must be recorded on a dissection data sheet. The sample is then ready for homogenization.

### Fish Flesh

Dissect the smallest fish of a composite first. The weight of this tissue sample will determine the weight of the tissue core

APPENDIX B (Continued)

to be taken from other fish in the composite; these weights should be equal. The weight contribution of each fish in the composite is recorded. Ideally, a total of 50 g of flesh is needed for analysis. Blade changes or instrument washing is not necessary when cutting fish from same composite unless instruments become contaminated.

Make a U-shaped incision in the skin using a clean scalpel (Figure 1). The curved portion of the incision is just posterior of the operculum. The legs of the U-shaped incision run the length of the body just ventral to the dorsal fin and just ventral of the lateral line and should be just deep enough to cut only the skin. Grasp the skin near the operculum with the tissue forceps and pull the skin caudally, exposing the flesh. If the fish is unusually large or the skin unusually hard to peel back, the pliers used to remove the scalpel blades can be used to remove the skin. Naturally, the pliers must be chemically cleaned before this use.

Make an oval incision with a second scalpel in the flesh inside the "U" formed by the previous incision. This new incision should be well inside the area touched by either the incision scalpel or the forceps as described in previous steps. Ideally, take the inner core 1 cm inside the anterior end of the incision scalpel cut and 5 mm inside the remaining portion of the "U". Small fish do not allow the luxury of these buffering zones and may require that flesh from both sides of fish be taken.

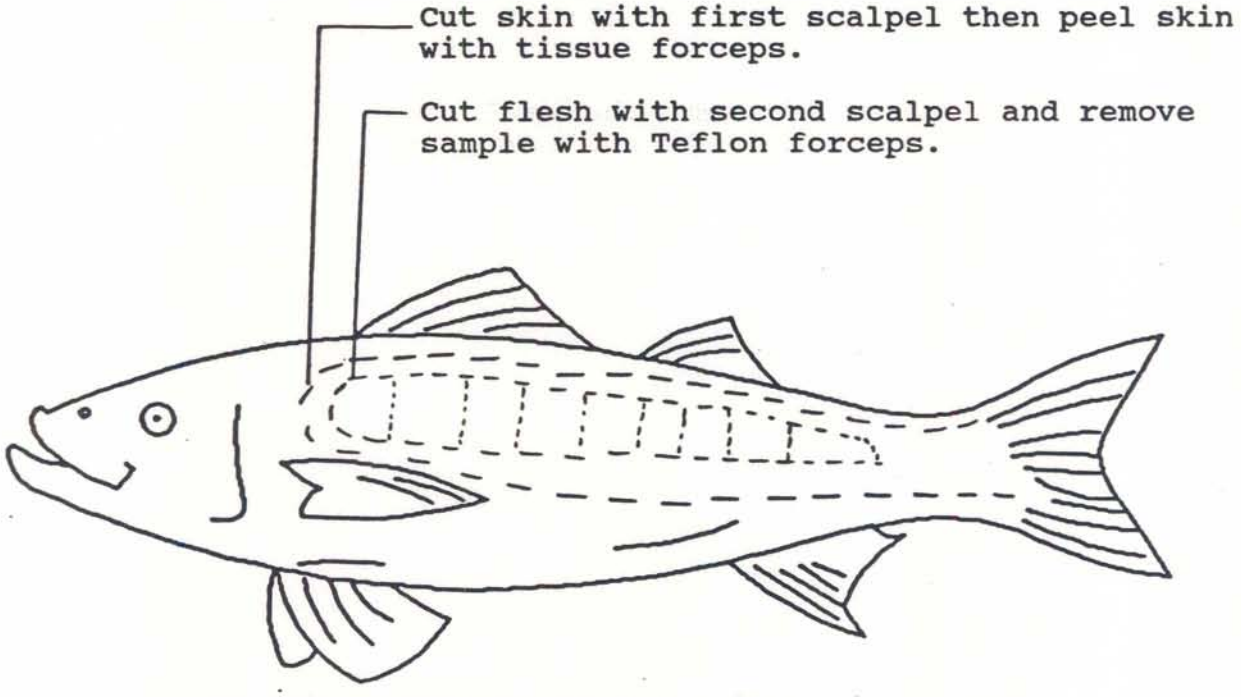


FIGURE 1. Diagram of fish dissection.

APPENDIX B (Continued)

Care must be taken to minimize the contact of flesh samples from small fish with the incision cut. Use clean Teflon forceps to hold the core while the coring scalpel is used to free it from the skeleton. Subsamples from the core should represent the entire length of the fish; these should be cut in small pieces (5 to 10 g) and rinsed with Type I water before being placed in the bottle. Weigh the empty bottle and the flesh from each individual for composite samples. Any sample pieces dropped must be thrown away. Any irregularities like tumors, parasites, or wounds should be noted on the data sheet.

Bird Flesh

After the flesh has been fluoroscoped to locate lead or steel shot, the portions not contaminated by pellets are ready for dissection. Use only the portions of breast that have not been exposed to the air (inner core) to make up the sample. Using a scalpel, dissect strips of flesh from the length of the breast for a total weight of approximately 50 g. These strips are then placed in a sample bottle. Use chemically cleaned instruments for dissection of each new sample to avoid cross contamination.

Liver

Livers of birds and some species of fish are removed for analysis. This is achieved by opening the thoracic and abdominal area using the incision scalpel and removing the liver using another scalpel and Teflon forceps. The liver is then rinsed with Type I water, and placed in the sample bottle. When preparing composite liver samples, each individual liver is weighed and values are recorded on the dissection sheet.

Whole Body Samples

If whole body samples are to be prepared, a slightly different technique is required. Only chemically clean Teflon instruments can touch whole body samples. Samples are removed from the freezer and allowed to thaw. Only Type I water is used to clean or thaw samples. Two Teflon forceps are used to handle and rinse (clean) samples. To accelerate thawing the sample(s) are rinsed under a stream of Type I water. Record the length of each individual using a vernier caliper and place in sample bottle. The weight of each individual of the composite is recorded.

Shellfish

The soft portions excluding the shell (carapace) are used for shellfish samples. The individual is weighed and the length is

APPENDIX B (Continued)

measured at its longest point before it is rinsed with Type I water. The outer shell may be touched by hand but the inner parts may not. The shell is then broken open by hand and tissue inside the shell is removed with the use of Teflon forceps and a scalpel. Dissected portions of the shellfish are placed in a sample bottle and measurements are recorded on the sample dissection sheet.

## Homogenization Procedures

Samples are first thawed. A measured amount of Type I water may be added to flesh and whole body samples to help facilitate homogenization. Water is not added to liver samples. Equipment needed in the homogenization procedure include:

Polytron with titanium shaft and Teflon bearing
Safety goggles and ear protectors
3 1000 mL beakers
2 400 mL beakers
1 160 mL milk dilution bottle
Teflon wash bottle
Teflon policemen
stainless steel forceps

The two 400 mL beakers and the 160 mL milk dilution bottle are chemically cleaned (see Sample Container Preparation, pg. B-1). The Polytron titanium shaft must be cleaned before and after each sample to eliminate possibility of cross contamination. Cleaning of the titanium shaft is accomplished as follows:

1) operate polytron for 3 minutes in a 1000 mL beaker filled with Type III water 6 to 20 changes or until water remains clear (use a toothbrush, stainless steel forceps and wash bottle to remove macro-sized particles only after turning main switch off);
2) rinse shaft with 1.0 M nitric acid (analytical reagent grade) by pouring acid in a 160 mL milk dilution bottle and placing the shaft in the bottle (note: replace acid after about 5 rinses);
3) operate unit in a 400 mL beaker filled with Type I water;
4) rinse shaft with 2-propanol (analytical reagent grade) by squirting solvent from a Teflon wash bottle;
5) allow unit to air dry for a minimum of 5 minutes before use.

APPENDIX B (Continued)

Caution

Homogenization of flesh and liver samples with a Polytron can be dangerous. Ear protection and safety goggles must be used at all times when operating the polytron. Place sample bottles in a LPE protective sleeve to protect operator from glass if the bottle shatters. Keep a firm grip on the beaker or bottle. High speeds should not be used because friction will cause the samples to burn; use only the minimal amount of power needed to homogenize the sample. Inspect the machine before and after each day's work for any loose play in the generator. The bushing in the shaft will have to be changed when the play becomes excessive and the generator sounds noticeably louder during operation.

# APPENDIX C. Analysis

## General

All tissue, sediment, and water samples are analyzed for selenium at WPCL by hydride generation atomic absorption spectrophotometry (HGAA). For the purpose of quality control for WPCL many selenium values for tissue and water are double checked using an alternate method of neutron activation analysis, which is done by the University of Missouri, Research Reactor Facility (UMRR). In addition, sediment samples are analyzed for acid hydrolyzable selenium by California Analytical Laboratories CAL as part of quality control.

## WPCL HGAA Selenium Analysis Procedure for Tissue

### Dry Ashing Procedure[1/]

1. In a 100 mL Pyrex beaker with watch glass cover, place approximately 0.25 g to 0.50 g of wet tissue or 0.20 g of lyophilized tissue wetted with methanol.
2. Add 10 mL of reagent grade 40% $Mg(NO_3)_2 \cdot 6H_2O$, 60% $H_2O$ (w/w).
3. Add 100 to 300 uL Dow Corning DB150A antifoam emulsion.
4. Place samples in Thermolyne programmable ashing furnace Model #F30430C. Program furnace to dry samples at 115°C for 800 minutes and ash at 500°C for 90 minutes with a 3°C/min ramp for both dwell temperatures.

### Reduction Procedure

1. Add 10 mL Type I water to ashed samples.
2. Add 15 mL concentrated hydrochloric acid (analytical reagent grade).
3. Dissolve residue by heating (do not boil) for 10 minutes on a hot plate set at a temperature of 200°C.
4. Quantitatively transfer samples to 100 mL volumetric flasks. Samples must be analyzed within 24 hours.

### Instrumental Conditions

Selenium samples are analyzed on a Varian Spectra 30 Atomic Absorption Spectrophotometer with a Vapor Generation Accessory (VGA) Model 76. The light source is provided by a Westinghouse electrodeless discharge lamp (EDL). Instrument parameters and selenite standard concentrations are described below (Table C-1).

1/ (May, T. 1982)

APPENDIX C (Continued)

Table C-1. Analytical Parameters for Hydride Generation Atomic Absorption Spectrophotometry

Varian Spectra 30 AA System parameters:

Instrument Parameters

| | |
|---|---|
| Element | Se |
| Lamp Position | 1 |
| Lamp Current (mA) | 5 |
| Slit Width (nm) | 1.0 |
| Slit Height | Normal |
| Wavelength (nm) | 196.0 |
| Flame | Air-Acetylene |
| Sample Introduction | Auto Normal |
| Replicates | 3 |
| Measurement Time (sec) | 8 |
| Delay Time (sec) | 40 |
| Background Correction | Optional |

Sample Changer

| | |
|---|---|
| Rinse Rate | 1 |
| Rinse Time (sec) | 30.0 |
| Recalibration | 8 |
| Reslope Rate | 0 |

Standards

| | |
|---|---|
| Standard 1 | 0.0050 |
| Standard 2 | 0.0100 |
| Standard 3 | 0.0150 |
| Standard 4 | 0.0200 |
| Concentration units | ug/mL (PPM) |

Selenite standards used must be of the same acid concentration as the samples. Reagents used with the VGA include concentrated hydrochloric acid (analytical reagent grade) and 0.33% sodium borohydride (w/w) stabilized with 0.5 percent sodium hydroxide (w/w) in Type I water.

For every batch of samples, the blank, sensitivity check, control materials, and duplicates are completed as described below. In addition, one or more samples of each kind of matrix in a batch are analyzed by standard addition to determine the matrix effect and the necessity to "spike" remaining samples.

APPENDIX C (Continued)

Blank

An analytical or procedural blank is carried through with each group of samples to determine Se contamination by reagents. Appropriate corrections are made to analytical results for samples based on the blank response.

Instrument Sensitivity Check

The sensitivity of the spectrophotometer is checked at the beginning of each group of samples. For an adequate sensitivity check, the resulting sensitivity response must be within 2 times of the manufacturer's specifications. If not, the instrument is again optimized and recalibrated using appropriate standards to achieve maximum sensitivity.

Control Materials

Two or more different types of control materials are analyzed with each sample group. Control materials include (i) National Bureau of Standards (NBS) 50 tuna, (ii) NBS 1566 oyster, and (iii) NBS 1577a bovine liver. Reference material results are acceptable only when they are within the 95% confidence level.

Duplicates

A total of 10% of the samples are selected at random and analyzed in duplicate as a check of analytical precision.

WPCL HGAA Selenium Analysis Procedure for Water[2/]

Digestion Procedure

1. Pour approximately 25 g of the water sample into a 100 mL Pyrex beaker.
2. Add 8 mL of reagent grade 50% $Mg(NO_3)_2 \cdot 6H_2O$, 50% $H_2O$ (w/w).
3. Place watch glass covers on beakers and dry samples in an oven or furnace at 115°C until most of the water has evaporated. This step may take as long as 20 hours to complete. The samples are dried until only a thin layer of a light yellow viscous solution remains.
4. Place the samples in a Thermolyne furnace Model # F30430C and program the furnace to reach a temperature of 500°C for 90 minutes. If the samples have been dry ashed properly the residue will appear to be fluffy white at

2/ (Hammond, 1987)

APPENDIX C (Continued)

the bottom of the beaker with no residue splattered on the upper sides.

5. Cool the samples.
6. Add 10.0 mL Type I water to ashed samples.
7. Add 15.0 mL concentrated hydrochloric acid (analytical reagent grade).
8. Dissolve residue by heating (do not boil) for 10 minutes on a hot plate set at a temperature of 200°C.
9. Quantitatively transfer samples to 100 mL volumetric flasks if samples are suspected to contain more than 20 ug/L of selenium. Samples with low levels of selenium (< 20 ug/L) should not be diluted to 100 mL but poured directly into a clean autosampler test tube or can be analyzed directly from the beaker.

Instrumental Conditions

Analyze samples using instrumental conditions described above (WPCL Selenium Analysis Procedure for Tissue). All selenite standards and blank solutions must be made up with the same acid concentration as the samples.

## WPCL HGAA Selenium Analysis Procedure for Sediment[2/]

Digestion Procedure

1. Place 0.2 to 0.7 g of the well mixed sediment sample into a 100 mL Pyrex beaker and cover with a watch glass.
2. Add 10 mL of reagent grade 50% $Mg(NO_3)_2 \cdot 6H_2O$, 50% $H_2O$ (w/w).
3. Add 5 mL of concentrated nitric acid (ultra pure grade). To minimize foaming the nitric acid must be added slowly.
4. Place samples in Thermolyne programmable furnace Model #F30430C. Program furnace to dry samples at 115°C for 800 minutes and ash at 500° for 90 minutes with a 3°C/min ramp for both dwell temperatures.
5. Add 10 mL Type I water to ashed samples.
6. Add 15 mL concentrated hydrochloric acid (analytical reagent grade).
7. Dissolve residue by heating (do not boil) for 10 minutes on a hot plate set at a temperature of 200°C.
8. Quantitatively transfer samples to 100 mL volumetric flasks if samples are suspected to contain more than 0.5 ug/g of selenium. Samples with low levels of selenium (< 0.5 ug/g) should not be diluted to 100 mL but poured directly into a clean auto sampler test tube or can be analyzed directly from the beaker. Improved selenium recovery has been reported when samples are filtered.

APPENDIX C (Continued)

Instrumental Conditions

Analyze samples using instrumental conditions described above (WPCL Selenium Analysis Procedure for Tissue). All selenite standards and blank solutions must be made up with the same acid concentration as the samples. In addition, all samples are run twice, once unspiked and the second time with a selenite standard spike. The percent recovery of the added selenium is determined and the selenium concentration for each individual sample is calculated based on spike recovery.

WPCL Sample Moisture Determination

Samples are sub-sampled into a pre-weighed aluminum weighing dish. The dish with the wet sample is weighed and placed in an oven for 48 hours at 80°C. After drying, the weight of the dry dish with the sample is taken and recorded for moisture calculations.

UMRR Neutron Activation Analysis Procedure for Selenium in Water

The analysis consists of pipetting 10 mL of water sample (in duplicate) into an Erlenmeyer flask and adding 6 mL of concentrated hydrochloric acid, arsenic carrier and a Se-75 tracer. The samples and blanks are heated on a hot plate until they reached 80°C. The arsenic and selenium are co-precipitated with hypophosphorous acid. After precipitation the samples are then filtered on a Nucleopore filter and packaged into polyethylene vials. All samples are counted for Se-75 tracer to determine the percent yield. The samples are then irradiated and analyzed as described by McKown and Morris, (1978). Finally, calculations are made to correct for the contributions due to blank and percent yield.

CAL HGAA selenium Analysis Procedure for Sediment[2/]

Procedure

1. A weight portion of the sample is refluxed in a solution of potassium persulfate and nitric acid.
2. Hydrochloric acid is added to the solution and it is again refluxed.
3. The solution is filtered and adjusted to volume.
4. Samples are analyzed with a Varian hydride generation system coupled to a Varian atomic absorption spectrophotometer.

3/ (Fisher, Bradford, 1982)

## References for Appendix C

Fisher, Bradford. USGS, a supplement to the determination of inorganic substance in water and fluvial sediment. Technical Resources Investigation Book 5, Laboratory Analysis Chapter A, Open File Report 82-272, 1982.

Hammond, D. Procedures for analysis of selenium in water and sediment. California Department of Fish and Game Fish and Wildlife Water Pollution Control Laboratory, 1987. (Manuscript in preparation).

May, T.W. 1982. Recovery of endogenous selenium from fish tissues by open system dry ashing. J. Assoc. Anal. Chem 65:1140-44.

APPENDIX D. Results of (WPCL) selenium duplicate analyses in ug/g wet weight.

| Sample # | HGAA Duplicates | | Mean | % RSD[1/] |
|---|---|---|---|---|
| B1008F | 0.29 | 0.29 | 0.29 | 0 |
| B1009F | 0.46 | 0.46 | 0.46 | 0 |
| B1010F | 1.0 | 1.1 | 1.0 | 7.1 |
| B1011F | 0.37 | 0.37 | 0.37 | 0 |
| B1048F[2/] | 4.1 | 4.1 | | |
| | 4.0 | 4.0 | 4.0 | 1.4 |
| B1049F[2/] | 0.69 | 0.64 | 0.66 | |
| | 0.66 | 0.68 | | 3.3 |
| B1050F[2/] | 0.80 | 0.75 | | |
| | 0.75 | 0.77 | 0.77 | 3.1 |
| B1051F[2/] | 3.3 | 3.1 | | |
| | 3.2 | 3.1 | 3.2 | 3.0 |
| B1052F | 1.6 | 1.5 | 1.6 | 4.4 |
| B1053F | 1.4 | 1.3 | 1.4 | 5.0 |
| B1054F | 0.83 | 0.74 | 0.78 | 8.2 |
| B1062F | 2.8 | 2.6 | 2.7 | 5.2 |
| B1063F | 2.9 | 3.0 | 3.0 | 2.4 |
| B1064F | 1.1 | 1.1 | 1.1 | 0 |
| B1066F | 0.73 | 0.73 | 0.73 | 0 |
| B1067F | 2.1 | 2.1 | 2.1 | 0 |
| B1068F | 0.95 | 0.94 | 0.94 | 0.75 |
| B1069F | 0.89 | 0.88 | 0.88 | 0.80 |
| B1070F | 0.88 | 0.89 | 0.88 | 0.80 |
| B1071F | 1.9 | 1.9 | 1.9 | 0 |
| B1072F | 0.96 | 0.97 | 0.96 | 0.74 |
| B1073F | 1.2 | 1.2 | 1.2 | 0 |
| B1074F | 4.0 | 4.0 | 4.0 | 0 |
| B1075F | 0.88 | 0.85 | 0.86 | 2.5 |
| B1076F | 3.2 | 3.2 | 3.2 | 0 |
| B1077F | 1.8 | 1.8 | 1.8 | 0 |
| B1078F | 1.1 | 1.1 | 1.1 | 0 |
| B1079F | 2.1 | 2.1 | 2.1 | 0 |
| B1080F | 2.7 | 2.6 | 2.6 | 2.7 |
| B1081F | 0.78 | 0.79 | 0.78 | 0.91 |
| B1082F | 3.6 | 3.6 | 3.6 | 0 |
| B1083F | 1.5 | 1.5 | 1.5 | 0 |
| B1084F | 2.0 | 2.0 | 2.0 | 0 |
| B1085F | 2.5 | 2.4 | 2.4 | 3.0 |
| B1086F | 3.0 | 3.0 | 3.0 | 0 |
| B1087F | 0.99 | 0.97 | 0.98 | 1.4 |
| B1088F | 0.68 | 0.67 | 0.68 | 1.0 |
| B1089F | 3.6 | 3.6 | 3.6 | 0 |

1/ Relative Standard Deviation (RSD) = (standard deviation/mean) x 100.
2/ More than one duplicate analyses performed on this sample.

APPENDIX D (continued)

| Sample # | HGAA Duplicates | | Mean | % RSD[1/] |
|---|---|---|---|---|
| B1090F | 1.9 | 1.9 | 1.9 | 0 |
| B1091F | 1.5 | 1.5 | 1.5 | 0 |
| B1092F | 2.2 | 2.2 | 2.2 | 0 |
| B1093F | 2.1 | 2.1 | 2.1 | 0 |
| B1095F | 1.8 | 1.8 | 1.8 | 0 |
| B1097F | 0.99 | 1.0 | 1.0 | 0.71 |
| B1098F | 0.50 | 0.54 | 0.52 | 5.4 |
| B1104F | 3.9 | 4.0 | 4.0 | 1.8 |
| B1127F | 0.20 | 0.22 | 0.21 | 6.7 |
| B1135F | 0.61 | 0.58 | 0.60 | 3.5 |
| B1136F | 0.34 | 0.32 | 0.33 | 4.3 |
| B1156F | 0.31 | 0.32 | 0.32 | 2.2 |
| B1158F | 0.46 | 0.46 | 0.46 | 0 |
| B1159F | 0.30 | 0.28 | 0.29 | 4.9 |
| B1160F | 0.26 | 0.25 | 0.26 | 2.7 |
| B1161F | 0.28 | 0.26 | 0.27 | 5.2 |
| B1192F | 8.9 | 9.0 | 9.0 | 0.79 |
| B1197F | 0.98 | 0.91 | 0.94 | 5.3 |
| B1198F | 1.1 | 1.1 | 1.1 | 0 |
| B1199F | 1.8 | 1.8 | 1.8 | 0 |
| B1200F | 4.0 | 4.0 | 4.0 | 0 |
| B1201F | 3.9 | 3.9 | 3.9 | 0 |
| B1216F | 3.3 | 3.3 | 3.3 | 0 |
| B1257F | 2.7 | 2.8 | 2.8 | 2.5 |
| B1279F | 0.92 | 0.97 | 0.94 | 3.8 |
| B1289F | 0.96 | 0.96 | 0.96 | 0 |
| B1303F | 1.4 | 1.4 | 1.4 | 0 |
| B1304F | 6.6 | 6.8 | 6.7 | 2.1 |
| B1317F | 5.9 | 5.9 | 5.9 | 0 |
| B1318F | 9.0 | 9.1 | 9.0 | 0.79 |
| B1319F | 3.9 | 3.9 | 3.9 | 0 |
| B1320F | 6.4 | 6.1 | 6.2 | 3.4 |
| B1001L | 0.92 | 0.84 | 0.88 | 6.4 |
| B1002L | 0.86 | 0.93 | 0.90 | 5.5 |
| B1003L | 0.73 | 0.76 | 0.74 | 2.9 |
| B1004L | 0.98 | 1.1 | 1.0 | 8.5 |
| B1041L | 1.6 | 1.6 | 1.6 | 0 |
| B1042L | 4.2 | 4.3 | 4.2 | 1.7 |
| B1043L | 3.2 | 3.2 | 3.2 | 0 |
| B1044L | 1.6 | 1.6 | 1.6 | 0 |
| B1081L | 2.0 | 2.0 | 2.0 | 0 |
| B1082L | 9.6 | 9.7 | 9.6 | 0.74 |
| B1084L | 6.5 | 6.5 | 6.5 | 0 |
| B1091L | 42 | 44 | 43 | 3.3 |
| B1094L | 39 | 38 | 38 | 1.9 |
| B1095L | 11 | 12 | 12 | 5.9 |

APPENDIX D (continued)

| Sample # | HGAA Duplicates | | Mean | % RSD[1/] |
|---|---|---|---|---|
| B1121L | 1.3 | 1.3 | 1.3 | 0 |
| B1122L | 3.1 | 3.1 | 3.1 | 0 |
| B1123L | 6.5 | 6.5 | 6.5 | 0 |
| B1124L | 6.1 | 6.0 | 6.0 | 1.2 |
| B1161L | 0.36 | 0.48 | 0.42 | 20. |
| B1162L | 0.62 | 0.79 | 0.70 | 17. |
| B1163L | 1.2 | 1.3 | 1.2 | 5.9 |
| B1164L | 0.64 | 0.62 | 0.63 | 2.2 |
| B1192L | 17 | 17 | 17 | 0 |
| B1200L | 26 | 25 | 26 | 2.7 |
| B1216L[2/] | 23 | 23 | 23 | |
| | 22 | 24 | | 3.5 |
| B1217L[2/] | 6.0 | 5.9 | | |
| | 6.1 | 6.1 | 6.0 | 1.5 |
| B1218L[2/] | 4.3 | 4.2 | | |
| | 4.2 | 4.2 | 4.2 | 1.2 |
| B1219L | 4.4 | 4.2 | | |
| | 4.3 | | 4.3 | 2.3 |
| B1220L | 5.2 | 5.1 | 5.2 | 1.4 |
| B1221L | 4.0 | 3.8 | 3.9 | 3.6 |
| B1222L | 4.6 | 4.4 | 4.5 | 3.1 |
| B1223L | 4.8 | 4.5 | 4.6 | 4.6 |
| B1224L | 4.9 | 4.8 | 4.8 | 1.5 |
| B1225L | 5.7 | 6.2 | 6.0 | 5.9 |
| B1226L | 7.2 | 6.8 | 7.0 | 4.0 |
| B1227L | 13 | 13 | 13 | 0 |
| B1228L | 7.5 | 7.5 | 7.5 | 0 |
| B1229L | 9.1 | 8.9 | 9.0 | 1.6 |
| B1230L | 11 | 10 | 10 | 7.1 |
| B1231L | 7.2 | 7.1 | 7.2 | 0.98 |
| B1232L | 16 | 16 | 16 | 0 |
| B1233L | 12 | 12 | 12 | 0 |
| B1234L | 6.6 | 6.5 | 6.6 | 1.1 |
| B1235L | 4.2 | 4.0 | 4.1 | 3.4 |
| B1236L | 9.6 | 9.3 | 9.4 | 2.3 |
| B1237L | 28 | 26 | 27 | 5.2 |
| B1238L | 40 | 40 | 40 | 0 |
| B1239L | 7.8 | 7.5 | 7.6 | 2.8 |
| B1240L | 8.1 | 8.1 | 8.1 | 0 |
| B1241L | 5.6 | 5.6 | 5.6 | 0 |
| B1242L | 5.3 | 5.3 | 5.3 | 0 |
| B1243L | 3.2 | 3.2 | 3.2 | 0 |
| B1244L | 11 | 11 | 11 | 0 |
| B1249L | 1.6 | 1.8 | 1.7 | 8.3 |
| B1257L | 7.8 | 7.7 | 7.8 | 0.91 |
| B1279L | 2.6 | 2.7 | 2.6 | 2.7 |
| B1280L | 2.7 | 2.7 | 2.7 | 0 |
| B1281L | 2.8 | 2.8 | 2.8 | 0 |

APPENDIX D (continued)

| Sample # | HGAA Duplicates | | Mean | % RSD[1/] |
|---|---|---|---|---|
| B1314L | 11 | 11 | 11 | 0 |
| B1321L | 34 | 33 | 34 | 2.1 |
| B1331L | 5.3 | 5.2 | 5.2 | 1.4 |
| B1335L | 4.7 | 4.8 | 4.8 | 1.5 |
| B1354L | 11 | 11 | 11 | 0 |
| B1356L | 3.8 | 3.7 | 3.8 | 1.9 |
| M1000L | 1.0 | 1.0 | 1.0 | 0 |
| M1003L | 1.2 | 1.1 | 1.2 | 5.9 |
| F1000F1 | 0.19 | 0.20 | 0.20 | 3.5 |
| F1027F1 | 0.23 | 0.23 | 0.23 | 0 |
| F1027F2 | 0.25 | 0.23 | 0.24 | 5.9 |
| F1028F1 | 0.20 | 0.16 | 0.18 | 16 |
| F1030F1 | 0.28 | 0.25 | 0.26 | 8.2 |
| F1059F1 | 1.8 | 1.9 | 1.8 | 3.9 |
| F1066F1 | 1.9 | 1.8 | 1.8 | 3.9 |
| F1070F1 | 4.4 | 4.2 | 4.3 | 3.3 |
| F1072F1 | 2.2 | 2.2 | 2.2 | 0 |
| F1036L1 | 1.8 | 1.8 | 1.8 | 0 |
| F1039L1 | 1.5 | 1.4 | 1.4 | 5.0 |

Mean RSD for HGAA duplicates = 2.2 percent

APPENDIX D. Results of (WPCL) duplicate Moisture determination

| Sample # | % Moisture Duplicate | | Mean | % RSD[1/] |
|---|---|---|---|---|
| B1008F | 73 | 73 | 73 | 0 |
| B1009F | 71 | 71 | 71 | 0 |
| B1010F | 72 | 72 | 72 | 0 |
| B1011F | 71 | 72 | 72 | 0.99 |
| B1048F | 73 | 73 | 73 | 0 |
| B1049F | 73 | 73 | 73 | 0 |
| B1050F | 71 | 70 | 70 | 1.0 |
| B1051F | 73 | 73 | 73 | 0 |
| B1095F | 73 | 73 | 73 | 0 |
| B1098F | 75 | 75 | 75 | 0 |
| B1104F | 72 | 77 | 74 | 4.7 |
| B1135F | 71 | 72 | 72 | 0.99 |
| B1136F | 72 | 72 | 72 | 0 |
| B1158F | 73 | 72 | 72 | 0.97 |
| B1159F | 73 | 73 | 73 | 0 |
| B1160F | 73 | 73 | 73 | 0 |
| B1161F | 74 | 74 | 74 | 0 |
| B1197F | 72 | 72 | 72 | 0 |
| B1198F | 73 | 72 | 72 | 0.97 |
| B1199F | 72 | 72 | 72 | 0 |
| B1200F | 72 | 73 | 72 | 0.97 |
| B1201F | 73 | 73 | 73 | 0 |
| B1216F | 73 | 73 | 73 | 0 |
| B1257F | 71 | 71 | 71 | 0 |
| B1279F | 72 | 72 | 72 | 0 |
| B1289F | 71 | 71 | 71 | 0 |
| B1303F | 70 | 71 | 70 | 0 |
| B1317F | 71 | 72 | 72 | 0.98 |
| B1318F | 72 | 72 | 72 | 0 |
| B1320F | 72 | 72 | 72 | 0 |
| B1001L | 76 | 76 | 76 | 0 |
| B1002L | 73 | 74 | 74 | 0.96 |
| B1003L | 74 | 74 | 74 | 0 |
| B1004L | 72 | 72 | 72 | 0 |
| B1041L | 73 | 74 | 74 | 0.96 |
| B1042L | 69 | 69 | 69 | 0 |
| B1043L | 70 | 69 | 70 | 1.0 |
| B1044L | 69 | 69 | 69 | 0 |
| B1081L | 72 | 72 | 72 | 0 |
| B1082L | 72 | 72 | 72 | 0 |
| B1083L | 72 | 72 | 72 | 0 |
| B1084L | 73 | 73 | 73 | 0 |
| B1094L | 72 | 71 | 72 | 0.99 |
| B1121L | 74 | 74 | 74 | 0 |
| B1122L | 71 | 71 | 71 | 0 |
| B1123L | 69 | 69 | 69 | 0 |
| B1124L | 70 | 70 | 70 | 0 |

APPENDIX D (continued)

| Sample # | % Moisture Duplicate | | Mean | % RSD[1/] |
|---|---|---|---|---|
| B1161L | 74 | 74 | 74 | 0 |
| B1162L | 72 | 72 | 72 | 0 |
| B1163L | 71 | 71 | 71 | 0 |
| B1164L | 73 | 73 | 73 | 0 |
| B1200L | 72 | 72 | 72 | 0 |
| B1216L | 71 | 71 | 71 | 0 |
| B1217L | 73 | 73 | 73 | 0 |
| B1218L | 73 | 73 | 73 | 0 |
| B1219L | 72 | 83 | 78 | 10 |
| B1257L | 72 | 72 | 72 | 0 |
| B1279L | 71 | 71 | 71 | 0 |
| B1280L | 71 | 71 | 71 | 0 |
| B1281L | 71 | 71 | 71 | 0 |
| B1314L | 76 | 76 | 76 | 0 |
| B1321L | 72 | 72 | 72 | 0 |
| B1331L | 70 | 70 | 70 | 0 |
| B1335L | 72 | 72 | 72 | 0 |
| B1354L | 72 | 72 | 72 | 0 |
| F1001F1 | 76 | 76 | 76 | 0 |
| F1027F1 | 82 | 82 | 82 | 0 |
| F1027F2 | 82 | 81 | 82 | 0.87 |
| F1030F1 | 80 | 80 | 80 | 0 |
| F1059F | 81 | 81 | 81 | 0 |
| F1066F1 | 76 | 77 | 76 | 0.92 |
| F1072F | 79 | 79 | 79 | 0 |
| F1036L1 | 80 | 80 | 80 | 0 |
| F1039L1 | 78 | 78 | 78 | 0 |
| M1000L | 73 | 73 | 73 | 0 |
| M1003L | 73 | 73 | 73 | 0 |

Mean RSD for moisture content = 0.35 percent

Appendix E. Selenium concentrations in water samples analyzed in duplicate at WPCL for quality control, and in water and sediment samples analyzed at WPCL and by Neutron Activation Analysis at UMRR or California Analytical Laboratory for quality assurance.

| WATER | | | | SEDIMENT | | | |
|---|---|---|---|---|---|---|---|
| Sample No. | WPCL-1 ppb Se | WPCL-2 ppb Se | NAA ppb Se | Sample No. | WPCL-1 ppm Se | WPCL-2 ppm Se | CAL ppm Se |
| 2 | 0.4 | | <0.5 | 03 | 1.0 | 0.92 | 1.1 |
| 2a | 0.2 | | <0.5 | 04 | 0.11 | 0.09 | |
| 3 | 7.2 | | 5.7 | 06 | 0.07 | 0.06 | |
| 4 | 0.2 | | <0.5 | 08 | 0.06 | 0.07 | |
| 5 | 2.2 | | 1.6 | 09 | 0.04 | 0.04 | 0.12 |
| 6 | 2.2 | | 1.4 | 10 | 0.44 | 0.41 | 0.48 |
| 6a | <0.2 | | <0.5 | 11 | 0.32 | 0.31 | |
| 7 | 1.0 | | " | 12 | 0.01 | 0.01 | |
| 7a | <0.2 | | <0.5 | 13 | 0.80 | 0.72 | 0.80 |
| 8 | 0.3 | | " | 14 | 0.26 | 0.28 | |
| 9 | 0.3 | | " | 15 | 0.24 | 0.26 | 0.29 |
| 10 | 0.2 | | " | 16 | 0.28 | 0.29 | |
| 10a | 0.3 | | " | 17 | 0.11 | 0.10 | |
| 11 | 0.3 | | " | 18 | 0.10 | 0.10 | |
| 12 | 0.6 | | " | | | | |
| 13 | 0.5 | | " | | | | |
| 13a | 0.3 | | " | | | | |
| 14a | 0.5 | | <0.5 | | | | |
| 15 | 0.2 | <0.2 | | | | | |
| 16 | <0.2 | <0.2 | | | | | |
| 17 | 0.3 | 0.3 | | | | | |
| 17a | 0.3 | | <0.5 | | | | |
| 18 | 0.2 | 0.2 | | | | | |
| 19 | 0.5 | 0.5 | | | | | |
| 20 | 0.3 | 0.3 | | | | | |
| 21 | 0.3 | 0.3 | | | | | |
| 102 | 0.4 | 0.4 | <0.5 | | | | |
| 106 | 0.7 | | " | | | | |
| 107 | 0.4 | | " | | | | |
| 108 | 0.1 | 0.2 | " | | | | |

Appendix F. Percent occurrence of food items in diving ducks from the San Francisco Bay-Estuary, Morro Bay, Humboldt Bay and Lake Earl.

| | Species and Location | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Scaup | | | | Scoter | | | | Canvasback | | | |
| FOOD ITEM | SUISB | SNPBB | CNSFB | SOSFB | SUISB | SNPBB | CNSFB | SOSFB | SUISB | SNPBB | SOSFB | |
| Crustacea, | | | | | | | | | | | | |
| Cirripedia (Balanus spp.) | 4 | | | | | | | | | | | |
| Decapoda, Cancer antennarius | | | | | | | 11 | | | | | |
| Rhithropanopeus harrisii | | | | | 13 | | | | | | | |
| Unidentified Crustacean fragments | | | 5 | 20 | 7 | 4 | | | | | | |
| Mollusca, | | | | | | | | | | | | |
| Gastropoda, Fusinus luteopictus | | | | 13 | | | | | | | | |
| Nassarius obsoletus | | | | 7 | | | | | | | | |
| Urosalpinx cinerea | | | | 7 | | | | | | | | |
| Barleeia haliotiphila | | 29 | | | | | | | | | | |
| Unidentified gastropods | | 23 | 16 | 20 | | | | | | | | |
| Bivalvia, Corbicula fluminea | 95 | 6 | | | 83 | | | | 8 | | | |
| Mya arenaria | 27 | 23 | 10 | 67 | 33 | 32 | | | 8 | 8 | 27 | |
| Tapes japonica/ Protothaca staminea | | 23 | 68 | 40 | | 59 | 89 | 100 | 15 | | | |
| Macoma balthica | | | | | | | | | | 69 | 67 | |
| Musculus senhousia | | 12 | 63 | 20 | | 45 | 89 | 86 | | | | |
| Unidentified bivalve fragments | 9 | | | | | | | | 85 | | | |
| Miscellaneous, | | | | | | | | | | | | |
| Herring (Clupea harengus) eggs | | 23 | | 7 | | 9 | | | | | | |
| Bulrush (Scirpus spp.) achenes | 9 | 18 | | 7 | | | | | | | | |
| Unidentified algae fragments | | 12 | | | | | | | | | | |
| Number of birds | 22 | 17 | 19 | 15 | 30 | 22 | 9 | 7 | 13 | 13 | 15 | |

| FOOD ITEM | Species and Location: Scoter MORRO | Scoter HMBLT | Scaup MORRO | Scaup HMBLT | Canvasback LEARL | Canvasback LEARL |
|---|---|---|---|---|---|---|
| Annelida, | | | | | | |
| Polycheate tube worms | | 27 | | | | |
| Crustacea, | | | | | | |
| Isopoda, Idoteidae | | 7 | | 17 | | |
| Amphipoda, Gammaridae | | | | | 10 | |
| Decapoda, Crangon nigracauda | 7 | | | 17 | | |
| Unidentified crustacean fragments | 36 | | 7 | | | |
| Mollusca, | | | | | | |
| Gastropoda, Mitrella spp. | 29 | 27 | 29 | 83 | | |
| Phyllaplysia taylori | | 7 | | | | |
| Unidentified gastropods | 64 | 7 | 21 | 33 | | |
| Bivalvia, Macoma nasuta | | 27 | | | | |
| Macoma spp. | | 20 | | | | |
| Mya arenaria | | 7 | | | | |
| Protothaca spp. | 7 | 20 | | | | |
| Transenella spp. | 7 | | 43 | 67 | | |
| Solen sicarius | | 13 | | | | |
| Unidentified bivalve fragments | 29 | 20 | | 17 | | |
| Plant material, | | | | | | |
| Potamogeton pectinatus, corms | | | | | | 57 |
| " " achenes | | | | | 100 | 100 |
| Ruppia maritima, achenes | | | | | 100 | 100 |
| Scirpus achenes | | | | | 60 | 14 |
| Unidentified seeds | | | 7 | | | |
| Eel grass (Zostera marina) | 7 | | | | | |
| Miscellaneous, | | | | | | |
| Herring (Clupea harengus) eggs | | | | 17 | | |
| Number of birds | 14 | 15 | 14 | 6 | 10 | 7 |