Selenium Behavior in the Sacramento-San Joaquin Estuary, California

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Chapter 1. INTRODUCTION

Selenium is an element that can exist in several oxidation states and different chemical forms within an oxidation state (e.g., organic and inorganic). In aqueous solution, the dissolved selenium species (those that pass through a 0.45 μm filter) are selenite (SeIV), selenate (SeVI), and the selenides (Se-II, inorganic and organic forms). Any of selenium's oxidation states can be found in particulate material (material >0.45 μm). Rigorously, elemental selenium is insoluble and cannot be considered a dissolved species. However, as a colloid, Se(0) would pass through a 0.45 μm filter and thus be considered *dissolved*.

The chemical speciation of selenium is particularly important in the aquatic environment, because the biotic and abiotic reactivity of selenium is a function of its chemical form *(Wrench and Measures, 1982; Cutter and Bruland, 1984)*. Furthermore, the toxicity of selenium is also affected by its chemical form *(Shamberger, 1982)*.

With respect to selenium's bioreactivity, Wrench and Measures *(1982)* and Cutter and Bruland *(1984)* noticed that selenite seems to be preferentially taken up by primary producers in the marine system. In the absence of selenite, selenate is then removed from solution by phytoplankton. Subsequently, selenium is incorporated into protein material *(Wrench, 1978; Wrench and Campbell, 1981)*, a process that reduces selenite and selenate to selenide (as organic selenide).

These and other observations have led Cutter and Bruland *(1984)* to propose a marine biogeochemical cycle for selenium that includes:

- Reductive incorporation of selenite and selenate to organic selenides (seleno-amino acids) in phytoplankton,
- Formation of organic detritus through zooplankton grazing and phytoplankton mortality,
- Transport of detrital particles to deeper waters and sediments,
- Sequential regeneration of particulate organic selenide (dissolved organic selenide to selenite to selenate), and
- Kinetic stabilization of thermodynamically unstable organic selenide and selenite.

Selenium may also be affected by other processes in the aquatic system, including removal in anoxic waters via the formation of Se(0) and insoluble metal selenides *(Cutter, 1982)* and scavenging of selenite onto iron oxyhydroxides *(Howard, 1977)*.

While the oceanic cycling of selenium has received considerable attention, fewer studies have examined the estuarine behavior of selenium. Estuaries can affect the delivery of weathered continental material to the ocean (conservative and nonconservative mixing), are important to many fisheries, and can be significantly impacted by anthropogenic activities. The existing data on estuarine selenium are for several river systems that drain into the Atlantic Ocean.

Measures and Burton *(1978)* present findings on selenium in several small estuaries in England. Most of the systems they examined drain chalk strata, and thus have high alkalinity. Data are reported for two dissolved selenium fractions, selenite and UV-oxidized total selenium. Riverine total selenium averages 4.2 nanomoles per liter (0.33 ppb Se) in the chalk rivers, but in River Beaulieu – which is high in dissolved organic carbon, iron, and manganese – total selenium is 0.99 nmol/L (0.08 ppb Se).

Selenite comprises 3 to 8 percent of the total dissolved selenium in the rivers examined. In the chalk river estuaries, selenite and total selenium display apparent conservative mixing behavior, although analytical imprecision prohibits a careful evaluation. In the Beaulieu estuary, total selenium had a small maximum, at 13 ppt salinity, but a more careful examination was not performed.

Estuarine selenium has also been examined by Takayanagi and Wong *(1984)* in the James River estuary, Virginia, and the southern Chesapeake Bay. Total selenium is 1.9 nmol/L (0.15 ppb Se) in the riverine input, with selenite comprising 90 percent of the total. With the exception of the freshwater endpoint, total selenium concentrations fall on a conservative dilution line with increasing salinity. In the mid- and lower James River estuary, selenite also displays conservative dilution. However, at salinities below 4 ppt, nonconservative selenite removal is apparent. Takayanagi and Wong estimate that about 50 percent of the riverine selenite is removed in this region. In the region between 0 and 4 ppt salinity, selenate displays nonconservative input. This may be an analytical artifact, since selenate is calculated as the difference between total selenium (conservative) and selenite (nonconservative removal).

In the St. Lawrence River, Canada, Takayanagi and Cossa *(1985)* found a total selenium concentration of 2.12 nmol/L (0.17 ppb Se); selenite comprised 73 percent, selenate 17 percent, and organic selenium 10 percent. During estuarine mixing, total selenium, selenate, and organic selenium show conservative behavior, although scatter in the data may limit interpretation. Only selenite has nonconservative behavior, and this is restricted to the very low salinity region (<0.2 ppt). From these data, Takayanagi and Cossa calculate a 22 percent loss of riverine selenite.

Finally, selenium behavior has been briefly examined in the polluted Scheldt estuary in Belgium. Van der Sloot and coworkers *(1985)* found that selenite makes up 85 $\pm$ 6 percent of the total dissolved selenium. In comparison to the results cited above, concentrations of selenite are remarkably high, ranging from 1 to 30 nmol/L (0.08 to 2.37 ppb Se). Their results indicate a large selenite input to the estuary near Antwerp. Anthropogenic selenium inputs clearly affect estuarine behavior of the element in the Scheldt.

No clear pattern has emerged with respect to selenium speciation, concentration, and mixing behavior in estuaries. Until recently, selenium data for San Francisco Bay and the Sacramento-San Joaquin estuary have not been available. Agricultural drainage from California's southern Central Valley has elevated levels of dissolved selenium, primarily selenate *(Cutter, submitted)*. Since some of this drainage water flows into the San Joaquin River, an examination of selenium in the Sacramento and San Joaquin rivers and their estuary is imperative.

This report reviews current data on selenium in the estuary and quantitatively describes the behavior of selenium (estuarine fluxes) using estuarine geochemical models *(Boyle et al., 1974; Officer, 1979; Officer and Lynch, 1981; Kaul and Froelich, 1984)*.

Chapter 2. METHODS

In 1984 and 1985, U.S. Bureau of Reclamation personnel collected surface water samples from stations in the Sacramento-San Joaquin estuary. In July, September, and October 1984 and in January 1985, sampling was confined to the upper estuary (low salinity area). In June 1985, they sampled an 8-station transect covering most of the estuary.

Riverine selenium variability was monitored during 1986 with samples obtained at Freeport/Greene's Landing (Sacramento) and Vernalis (San Joaquin) by California Department of Water Resources and U.S. Geological Survey personnel. For these estuarine and riverine samples, water was vacuum filtered through 0.45 μm filters, placed in linear polyethylene bottles, and acidified to pH 1.5 with hydrochloric acid. The samples were shipped to Old Dominion University and refrigerated until analysis. Determinations of selenium species were made within one month after arrival in the laboratory.

More complete estuarine sampling was performed on April 22 and 23 and September 23 and 24, 1986. For this work, a crew from the Department of Water Resources and the Bureau of Reclamation used the Bureau's research vessel *Scrutiny*. In April 1986, 20 stations were sampled: 3 in South San Francisco Bay, 16 in the estuary, and one each in the Sacramento River (Rio Vista) and San Joaquin River (Antioch). The crews tried to select stations at 2 ppt salinity intervals. They took water from 1 meter below the surface and 2 meters above the bottom (except 1 meter depth only in the river stations). Station locations are shown in Figure 1

In September 1986, 26 stations were sampled: 5 in South Bay, 19 in the main estuary (northern reach), and one each in the Sacramento and San Joaquin rivers. Stations were spaced at about 1 ppt salinity intervals in the northern reach, and water was taken from 1 meter below the surface (also 2 meters above the bottom at Station 15). Station locations are shown in Figure 2.

For the April and September 1986 field work, 5-liter Go-Flo sampling bottles were used to obtain water from the estuary. By pressurizing the bottles with nitrogen (8 psi), water was directly filtered through 0.45 μm, pre-cleaned and weighed Nuclepore membrane filters (volume of water measured with a graduated cylinder). Water samples were placed in 1-liter linear polyethylene bottles and acidified to pH 1.5 with HCl. Filters were carefully folded, placed in polyethylene vials, and immediately frozen.

To isolate dissolved organic selenium, 30 mL of acidified sample (pH 1.6) was passed through a precleaned Sep-Pak cartridge, followed by 6 mL of pH 1.6 adjusted (HCl) water. This procedure was performed after each day of sampling, and the cartridges were refrigerated until laboratory processing.

Samples were analyzed at my laboratory at Old Dominion University, Norfolk, Virginia.

Dissolved Selenium Speciation

Determination of dissolved total selenium, selenite, selenate, and Se(-II + 0) has already been thoroughly described *(Cutter, 1978, 1982, 1983)*. The technique involves selective generation of hydrogen selenide, liquid nitrogen-cooled trapping, and atomic absorption detection.

Selenite is determined directly with samples acidified to 4 M HCl and subsequent sodium borohydride addition to produce hydrogen selenide. A sulfanilamide solution is added to remove potential interference from nitrite.

Selenite + selenate is determined by boiling a 4 M HCl acidified sample for 15 minutes and then following the selenite procedure.

Selenate is determined by difference.

Determination of total dissolved selenium entails boiling a 4 M HCl acidified sample, with potassium persulfate addition, for 1 hour; the resultant solution is analyzed as a selenite sample. The difference between total selenium and selenite + selenate is the concentration of dissolved Se(-II + 0).

All determinations are done in triplicate, and the *standard additions* method of calibration is used to ensure accuracy.

For determining selenium on Sep-Pak cartridges, 10 mL of methanol is used to elute organic material from the Sep-Pak. The eluant is rotary evaporated to dryness; the residue is taken up and transferred using 4 M HCl; and a determination of total selenium is performed. Past work has operationally called the Se(-II + 0) fraction "organic selenide" *(Cutter, 1982; Cutter and Bruland, 1984)*. Using Sep-Paks allows direct determination of organic selenium.

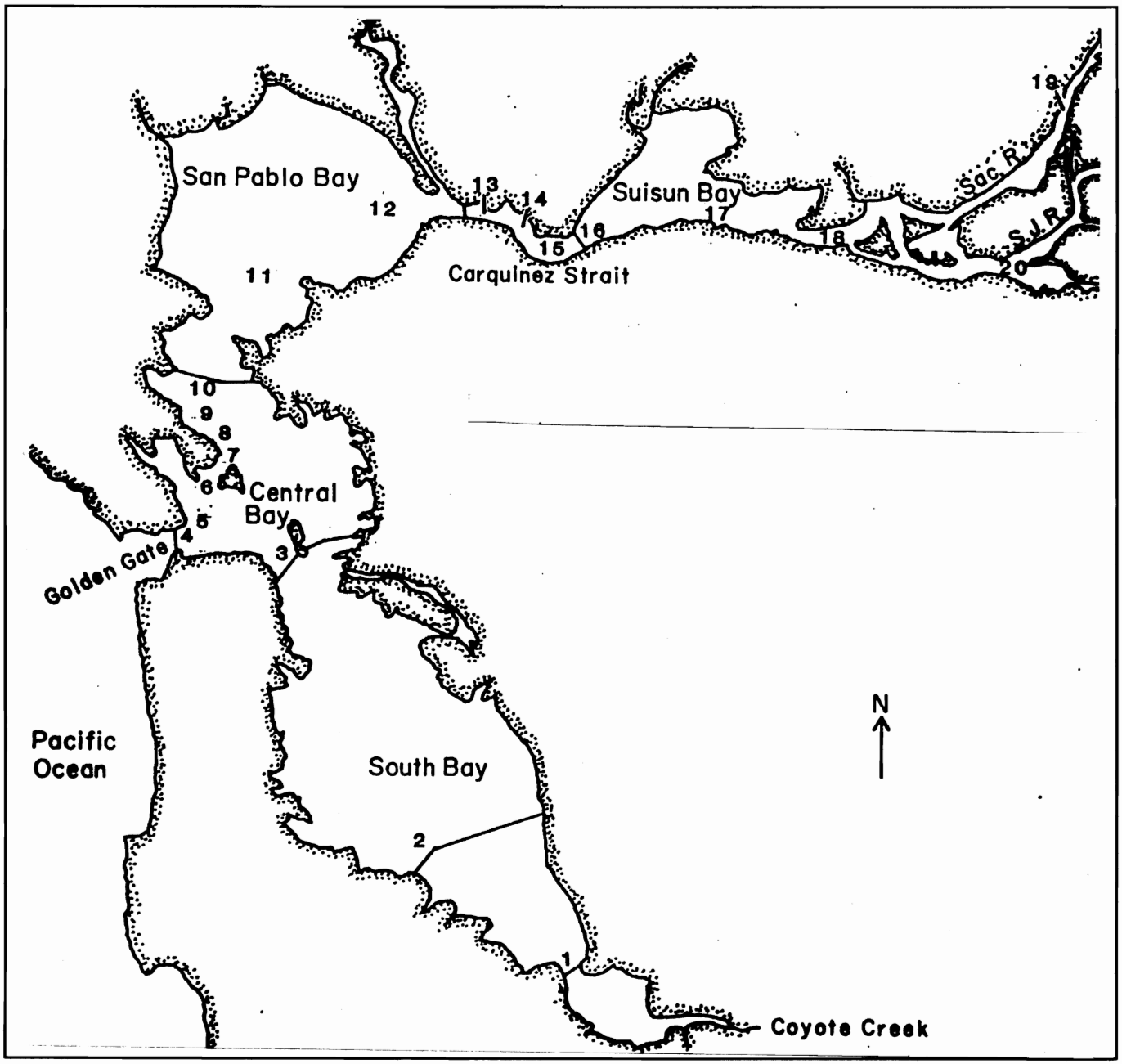

Figure 1
SAMPLING LOCATIONS, APRIL 1986

Particulate Selenium Determination

Total suspended particulate selenium is determined using the *digestion* procedure described by Cutter *(1985)*. The filters are dried at 40°C and weighed to determine the concentration of total suspended matter. A 3-step nitric-perchloric acid digestion follows, with the last step being evaporation of most of the acid.

The residue is then taken up in 4 M HCl, and the resultant solution is passed through a column filled with 5 mL of Bio-Rad AG1x8 anion exchange resin (chloride form, 100-200 mesh). After collecting the column flow-through solution, three 3 mL, 4 M HCl rinses are passed through the column, and these solutions are combined with the original. This column procedure removes the large amounts of iron found in suspended material without affecting speciation or concentration of selenium in the original solution.

Aliquots of the combined column flow-throughs are treated as total dissolved selenium samples.

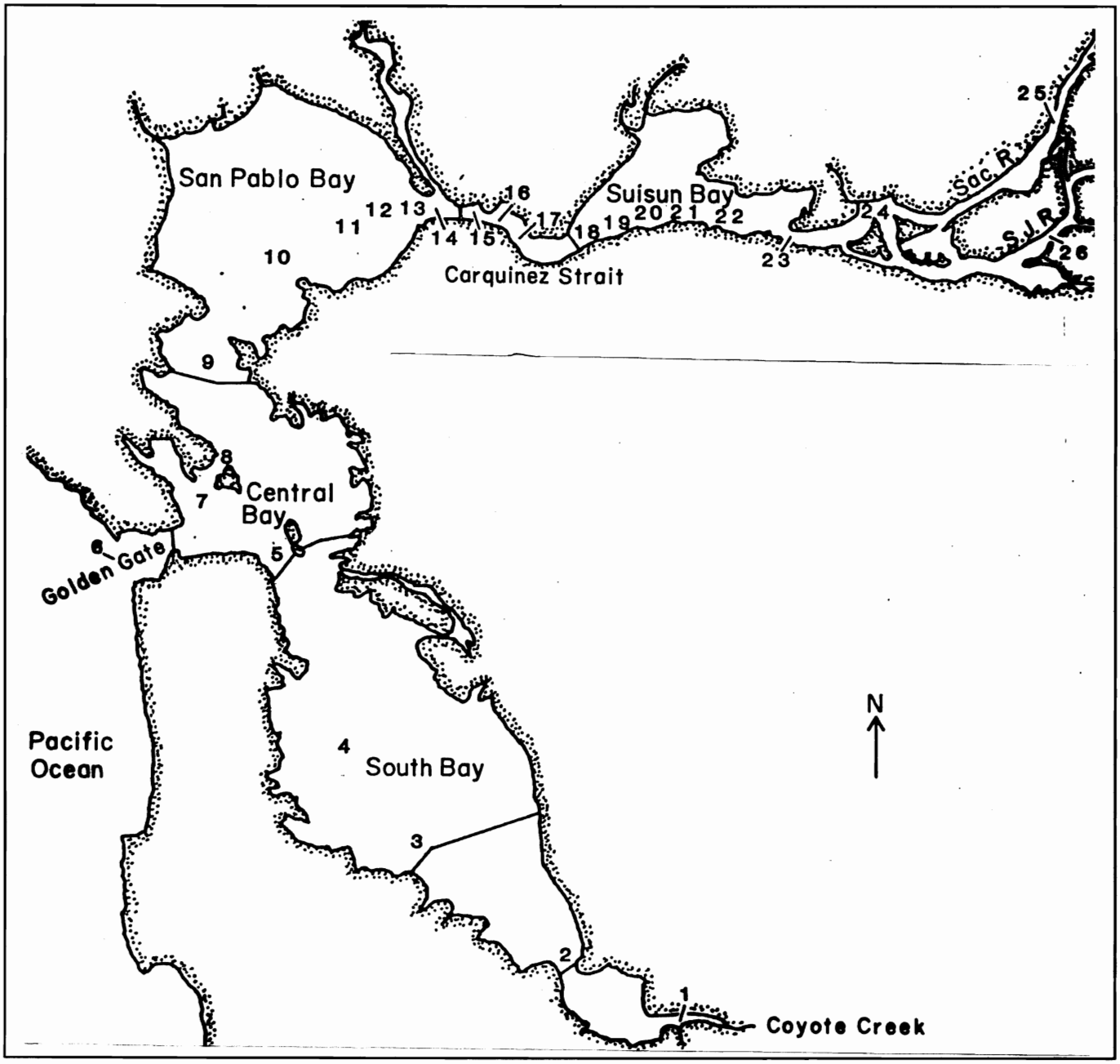

Figure 2
SAMPLING LOCATIONS, SEPTEMBER 1986

Chapter 3. RESULTS AND DISCUSSION

Selenium speciation results from 1984 and 1985 provide information on the low salinity behavior of the element and a basic picture of selenium's reactivity during estuarine mixing. Surface water distribution data are summarized in Table 1 and displayed in Figures 3, 4, and 5.

Table 1
SUMMARY OF SURFACE WATER DISTRIBUTION DATA, 1984 AND 1985

ID	Date	Station	Total Se *(nM)*	Se(IV) *(nM)*	Se(VI) *(nM)*	Se(-II+0) *(nM)*	Salinity *(ppt)*
U500	07/24/84	RSAC139	0.65 ± 0.01	0.09 ± 0.01	0.29 ± 0.04	0.27 ± 0.04	0.09
U501	07/24/84	RSAN087	9.06 ± 0.23	0.94 ± 0.05	8.38 ± 0.47	ND	0.49
U507	07/25/84	LSBB22	1.09 ± 0.01	0.25 ± 0.01	0.53 ± 0.08	0.31 ± 0.08	1.53
U509	07/25/84	SLNYK2	0.96 ± 0.01	0.20 ± 0.01	0.19 ± 0.05	0.57 ± 0.05	0.55
U512	07/25/84	RSAC056	1.74 ± 0.09	0.40 ± 0.02	0.42 ± 0.04	0.92 ± 0.10	8.31
U513	07/25/84	RSAC063	1.21 ± 0.01	0.45 ± 0.01	0.52 ± 0.05	0.24 ± 0.05	5.12
U514	07/25/84	RSAC068	0.86 ± 0.03	0.20 ± 0.02	0.42 ± 0.05	0.24 ± 0.06	1.58
U515	07/25/84	RSAC075	0.72 ± 0.03	0.15 ± 0.01	0.17 ± 0.01	0.40 ± 0.03	0.87
U516	07/25/84	RSAC077	0.77 ± 0.02	0.22 ± 0.01	0.38 ± 0.04	0.17 ± 0.04	0.75
U517	07/25/84	RSAC081	0.91 ± 0.05	0.21 ± 0.01	0.38 ± 0.03	0.32 ± 0.06	0.44
U647	09/05/84	RSAN087	5.61 ± 0.34	1.22 ± 0.10	3.59 ± 0.13	0.80 ± 0.35	0.38
U653	09/05/84	RSAC056	1.65 ± 0.15	0.55 ± 0.05	0.51 ± 0.05	0.59 ± 0.15	9.72
U654	09/05/84	RSAC063	1.35 ± 0.13	0.34 ± 0.05	0.44 ± 0.09	0.57 ± 0.15	4.73
U655	09/05/84	RSAC068	0.88 ± 0.04	0.18 ± 0.01	0.20 ± 0.04	0.50 ± 0.05	1.55
U656	09/05/84	RSAC075	0.99 ± 0.05	0.20 ± 0.01	0.48 ± 0.04	0.31 ± 0.06	1.09
U657	09/06/84	RSAC077	0.77 ± 0.06	0.17 ± 0.02	0.53 ± 0.04	ND	0.83
U658	09/06/84	RSAC081	0.65 ± 0.09	0.15 ± 0.03	0.50 ± 0.05	ND	0.65
U661	09/06/84	LSBB11	1.25 ± 0.11	0.31 ± 0.01	0.16 ± 0.02	0.78 ± 0.11	4.09
U662	09/06/84	LSBB22	0.84 ± 0.03	0.24 ± 0.01	0.26 ± 0.003	0.34 ± 0.04	1.13
U663	09/06/84	SLYNK2	0.17 ± 0.02	0.15 ± 0.01	ND	ND	0.33
U664	09/06/84	RSAN007	0.71 ± 0.04	0.19 ± 0.03	0.17 ± 0.03	0.35 ± 0.04	0.27
U665	09/06/84	RSAC139	0.81 ± 0.05	ND	0.35 ± 0.05	0.46 ± 0.07	0.13
U1070	10/23/84	RSAC139	0.71 ± 0.05	0.11 ± 0.01	0.33 ± 0.01	0.27 ± 0.05	0.10
U1071	10/23/84	RSAN087	1.72 ± 0.05	0.27 ± 0.01	1.23 ± 0.01	0.22 ± 0.05	0.23
U1088	10/25/84	RSAC075	0.92 ± 0.08	0.17 ± 0.01	0.68 ± 0.05	ND	0.57
E001	01/08/85	RSAC139	1.04 ± 0.05	0.07 ± 0.02	0.92 ± 0.03	ND	0.11
E002	01/08/85	RSAN087	5.10 ± 0.36	0.19 ± 0.01	4.44 ± 0.08	0.47 ± 0.37	0.32
E008	01/08/85	RSAC056	2.07 ± 0.08	0.88 ± 0.04	1.09 ± 0.20	ND	6.02
E013	01/10/85	RSAC075	1.16 ± 0.08	0.23 ± 0.01	1.01 ± 0.10	ND	1.40
E017	01/10/85	RSAC081	0.96 ± 0.04	0.14 ± 0.01	0.71 ± 0.04	0.11 ± 0.06	0.18
E018	01/10/85	RSAN007	1.03 ± 0.01	0.11 ± 0.01	0.57 ± 0.06	0.35 ± 0.06	0.28
E19	06/20/85	BAY BRDG	1.28 ± 0.04	0.07 ± 0.01	0.71 ± 0.03	0.50 ± 0.05	29.48
E20	06/20/85	RICH BRDG	1.43 ± 0.00	0.10 ± 0.01	0.93 ± 0.10	0.40 ± 0.10	27.87
E21	06/20/85	CARQ BRDG	2.48 ± 0.15	1.36 ± 0.06	0.79 ± 0.12	0.33 ± 0.18	20.37
E22	06/20/85	RSAC056	2.84 ± 0.08	1.19 ± 0.05	0.98 ± 0.13	0.67 ± 0.14	14.41
E23	06/20/85	RSAC068	1.94 ± 0.06	0.64 ± 0.03	0.62 ± 0.03	0.68 ± 0.06	5.39
E24	06/20/85	RSAN007	0.89 ± 0.07	0.25 ± 0.02	0.39 ± 0.06	0.25 ± 0.09	0.99
E25	06/20/85	RSAC139	0.50 ± 0.03	0.13 ± 0.01	0.25 ± 0.01	0.12 ± 0.03	0.09
E26	06/20/85	RSAN087	28.6 ± 0.90	1.07 ± 0.04	16.9 ± 0.10	10.6 ± 0.90	0.50

ND = Non-detectable (0.01 nM)

* To convert to ppb Se, multiply by 0.079

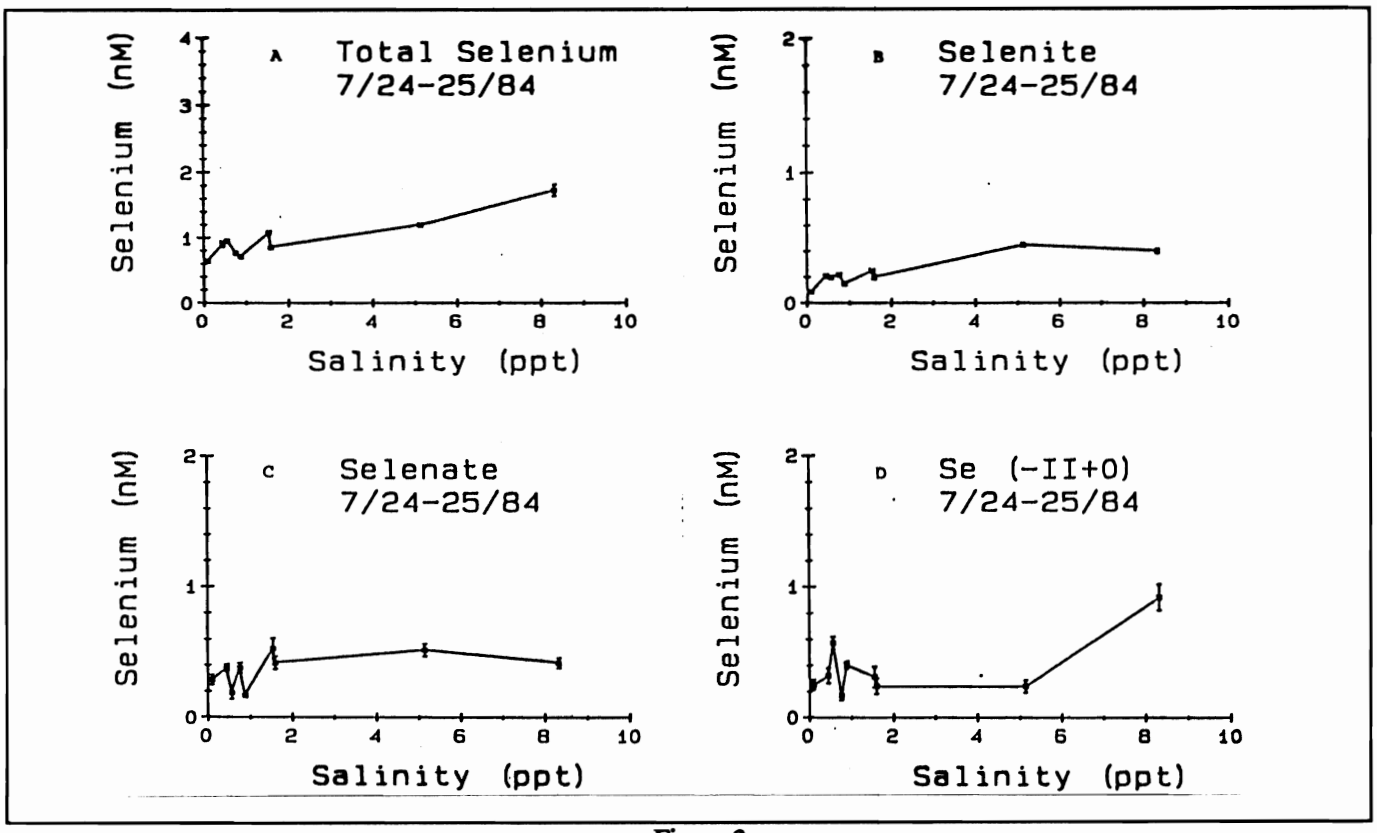

Figure 3
DISTRIBUTION OF SELENIUM SPECIES, JULY 1984

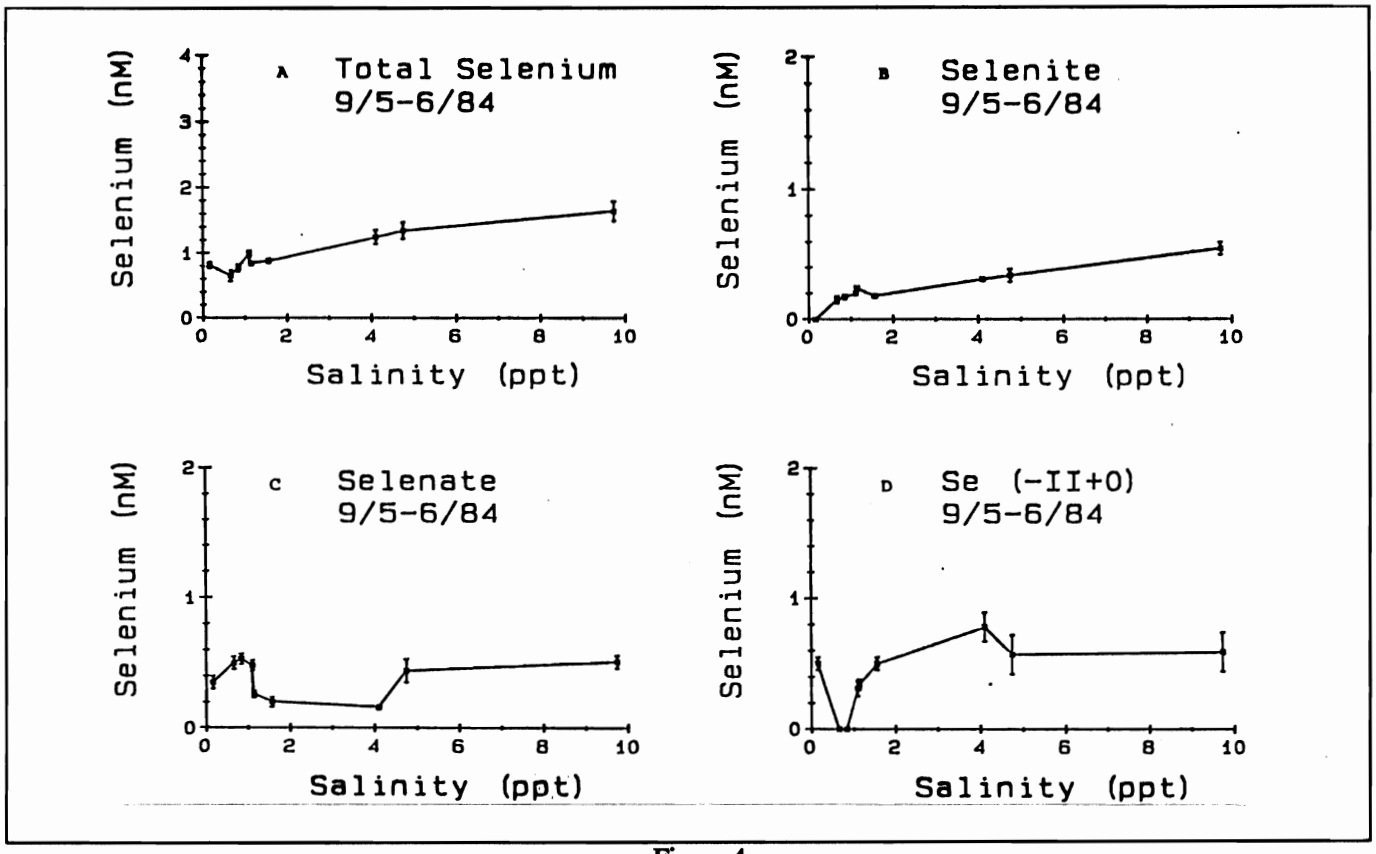

Figure 4
DISTRIBUTION OF SELENIUM SPECIES, SEPTEMBER 1984

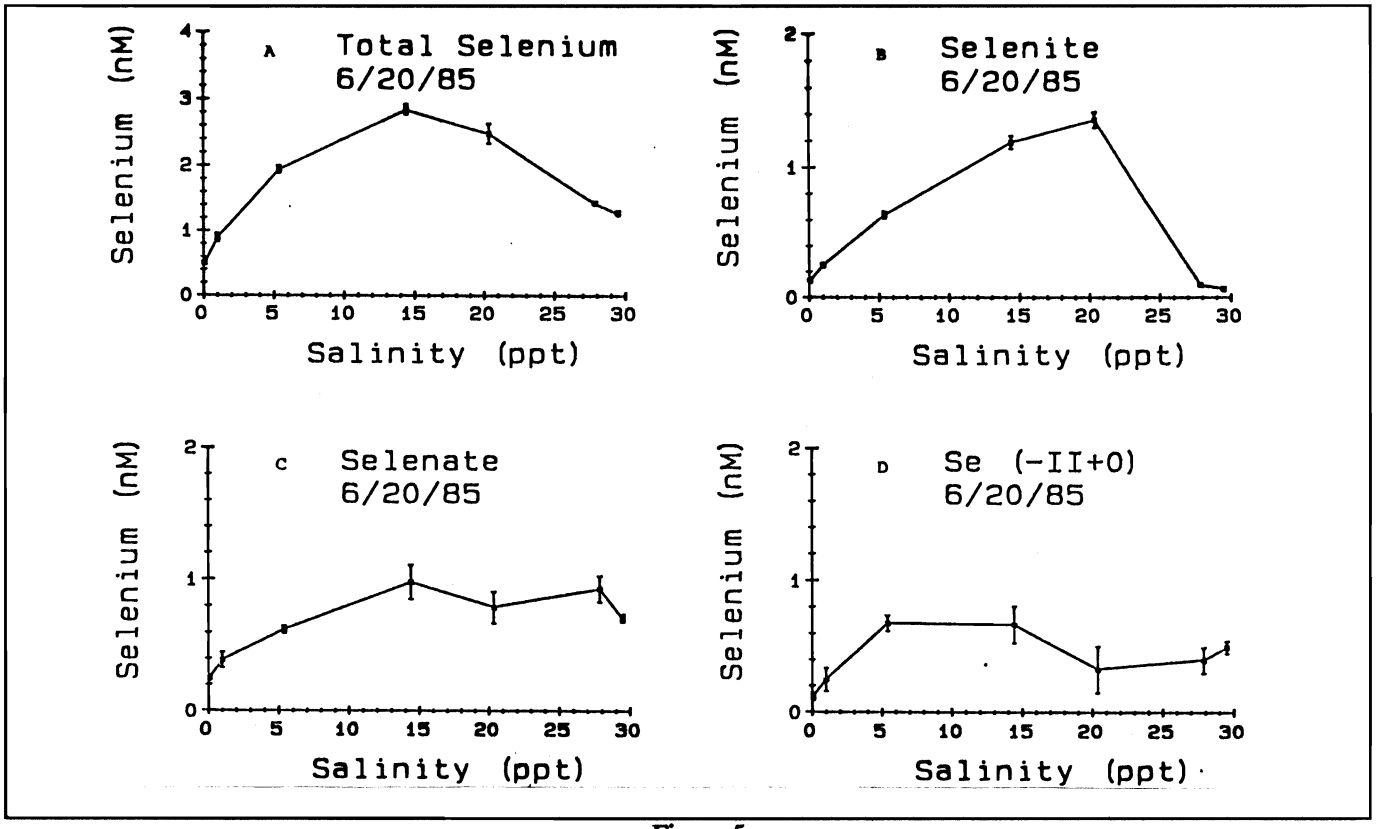

Figure 5
DISTRIBUTION OF SELENIUM SPECIES, JUNE 1985

Sampling stations in 1984 ran from the western end of Suisun Bay (RSAC 056) to well upstream in the Sacramento (RSAC 139) and San Joaquin (RSAN 087) Rivers. For the 1985 transect, samples were from the Central Bay, San Pablo Bay, Carquinez Strait, Suisun Bay, and the two rivers.

Estuarine Selenium

Data for selenium in the upper, low salinity region of the estuary are shown in Figures 3 and 4. The riverine, lowest salinity data come from the Sacramento River (RSAC 139), since little or no water from the San Joaquin River flowed into the Sacramento River system or downstream bays between July 1984 and January 1986. This aspect will be elaborated in the Riverine Selenium discussion to follow.

Although concentrations vary in the lowest salinity region, concentrations of all selenium species essentially increase with increasing salinity. The selenium variations below 2 ppt (Figures 3 and 4) are not surprising, considering the complex nature of the estuary (multiple tributaries; potential inputs from agricultural runoff).

In spite of the low salinity variations, both total selenium (Figures 3A and 4A) and selenite (Figures 3B and 4B) show conservative mixing behavior in the upper estuary. The correlation coefficient for a linear fit of total selenium versus salinity is 0.93 in July 1984 and 0.95 in September 1984; for selenite versus salinity it is 0.87 in July and 0.94 in September. In contrast, selenate and Se(-II + 0) show evidence of input and removal in the upper estuary (i.e., apparent nonconservative behavior). Correspondingly, the correlation coefficients for linear fits of these species versus salinity range from 0.15 to 0.58.

Data obtained in June 1985 allow a first look at the behavior of selenium in the entire San Francisco Bay estuarine system. Again, the riverine data are from the Sacramento River, since little or no San Joaquin River water flowed into the upper estuary at this time.

Total dissolved selenium (Figure 5A) again shows increasing concentration with increasing salinity in the upper estuary. However, the broad concentration maximum centered at 15 ppt salinity indicates input in the mid-estuary. Selenite (Figure 5B) also shows input, with a large mid-estuarine maximum. In comparison, selenate (Figure 5C) shows a slight increase in the mid-estuary, but otherwise mixes conservatively throughout the estuary ($r = 0.75$, $n = 7$). The profile of Se(-II + 0) (Figure 5D) shows minor input in the upper estuary and removal in the lower estuary.

Riverine Selenium

Selenium data for the San Joaquin and Sacramento rivers are compiled in Table 2. These results show that San Joaquin concentrations are much higher than those in the Sacramento. Total dissolved selenium in the San Joaquin River ranges from 1.72 to 28.6 nmol/L (0.14-2.26 ppb Se) over a 2-year period. The Sacramento River shows considerably less variation with time and lower total dissolved selenium concentrations (0.50-1.32 nmol/L, or 0.04-0.10 ppb Se).

The selenium speciation pattern also diverges for the two rivers. Using results in Table 2, selenite averages 12 percent of the total selenium in both rivers. In the Sacramento River, selenate is 51 percent and Se(-II + 0) is 34 percent of the total. In the San Joaquin, selenate averages 76 percent and Se(-II + 0) averages 13 percent of the total dissolved selenium. Thus, most San Joaquin River selenium is in the fully oxidized state.

During most of the year, when the San Joaquin discharge rate is low, little if any water from this river enters the upper estuary. This occurs when export pumping from the southern Delta exceeds the San Joaquin River flow. Under these conditions, Sacramento River water is drawn south across the Delta and into the lower San Joaquin. Thus, most of the fresh water in the estuary originates from the Sacramento, such as it did from July 1984 through January 1986. For the existing data set (Table 2), a portion of San Joaquin water entered the Delta only during April and May 1986

Since the Sacramento and San Joaquin rivers join near the head of the estuary, riverine selenium data for these two periods are combined via weighting the selenium concentration by the river discharge, adding the two together, and recomputing a *single* river end-member concentration. For April 16, 1986, the discharge-weighted selenium concentrations are:

4.06 nmol/L total selenium (0.32 ppb Se)
0.25 nmol/L selenite (0.02 ppb Se)
3.28 nmol/L selenate (0.26 ppb Se)
0.53 nmol/L (0.04 ppb) Se(–II + 0)

The discharge-weighted values for May 1, 1986, are:

1.95 nmol/L total selenium (0.15 ppb Se)
0.22 nmol/L selenite (0.02 ppb Se)
1.13 nmol/L selenate (0.09 ppb Se)
0.60 nmol/L (0.05 ppb) Se(-II + 0)

These computed values and those in Table 2 for the Sacramento can now be used to obtain an initial seasonal description of riverine selenium input. A quantitative estimate of this variability is needed for accurate estuarine modeling.

When examining the data in Table 2, several trends emerge. First, concentrations of total selenium and selenate appear to be related to river discharge. When the two discharge-weighted and eight Sacramento concentrations are plotted against the Delta Outflow Index at the time of sampling, a roughly linear relationship (increased DOI, increased selenium concentration) is obtained:

Total Selenium
$r = 0.9203$
$n = 10$
Mean Concentration =
1.32 ± 1.04 nmol/L, or
0.10 ± 0.08 ppb Se

Selenate
$r = 0.8888$
$n = 10$
Mean Concentration =
0.80 ± 0.80 nmol/L, or
0.06 ± 0.06 ppb Se

Table 2
SELENIUM IN THE SACRAMENTO AND SAN JOAQUIN RIVERS
(All Concentrations in Nanomoles/Kilogram)

		Sacramento (Greene's Landing/Freeport)				San Joaquin (Vernalis)			
Date	DOI*	Total Se	Se(IV)	Se(VI)	Se(-II + 0)	Total Se	Se(IV)	Se(VI)	Se(-II + 0)
07/24/84	2.70	0.65 ± 0.01	0.09 ± 0.01	0.29 ± 0.04	0.27 ± 0.04	9.06 ± 0.23	0.94 ± 0.05	8.38 ± 0.47	ND
09/06/84	2.50	0.81 ± 0.05	ND	0.35 ± 0.05	0.46 ± 0.07	5.61 ± 0.34	1.22 ± 0.10	3.59 ± 0.13	0.80 ± 0.35
10/23/84	2.20	0.71 ± 0.05	0.11 ± 0.01	0.33 ± 0.01	0.27 ± 0.05	1.72 ± 0.05	0.27 ± 0.01	1.23 ± 0.01	0.22 ± 0.05
01/08/85	3.46	1.04 ± 0.05	0.07 ± 0.02	0.92 ± 0.03	ND	5.10 ± 0.36	0.19 ± 0.01	4.44 ± 0.08	0.47 ± 0.37
06/20/85	0.92	0.50 ± 0.03	0.13 ± 0.01	0.25 ± 0.01	0.12 ± 0.03	28.6 ± 0.09	1.07 ± 0.04	16.9 ± 0.10	10.6 ± 0.90
04/16/86	10.0	1.40 ± 0.02	0.14 ± 0.006	0.94 ± 0.04	0.32 ± 0.04	7.69 ± 0.52	0.40 ± 0.03	6.48 ± 0.14	0.81 ± 0.54
05/01/86	3.39	1.32 ± 0.05	0.21 ± 0.007	0.60 ± 0.02	0.51 ± 0.05	4.76 ± 0.16	0.28 ± 0.02	3.46 ± 0.06	1.02 ± 0.17
08/29/86	1.20	1.18 ± 0.09	0.09 ± 0.03	0.68 ± 0.04	0.41 ± 0.09	18.7 ± 0.49	1.75 ± 0.13	15.3 ± 0.58	1.67 ± 0.75
09/17/86	2.05	1.12 ± 0.06	0.17 ± 0.01	0.57 ± 0.04	0.38 ± 0.07	6.59 ± 0.30	0.77 ± 0.06	5.84 ± 0.27	ND
09/29/86	4.23	1.21 ± 0.08	0.44 ± 0.02	0.15 ± 0.08	0.62 ± 0.11	8.05 ± 0.02	0.43 ± 0.03	4.88 ± 0.21	2.74 ± 0.21

ND = Nondetectable (0.01 nM)
* Delta Outflow Index (x 10^{10} liters/day)
To convert to ppb Se, multiply by 0.079

Historical data *(Conomos et al., 1979)* show that the maximum DOI occurs in January and February and that the minimum is during July and August. Therefore, maximum riverine concentrations of total selenium and selenate would be expected in the winter months. Selenite and Se(–II +0) do not display this strong correlation with river discharge (selenite versus DOI, r = 0.4486; Se(–II + 0) versus DOI, r = 0.3957). Se(–II + 0) concentrations are actually highest in spring and summer; in comparison to concentrations farther downstream, variations in selenite are minimal.

Estuarine Selenium Modeling

While limited in extent, the June 1985 data can be used to make preliminary estimates of selenium fluxes in San Francisco Bay. For this exercise it will be assumed that riverine variability does not affect the profiles and that only two water types are mixing, river water and sea water. In this manner, a straight line between the riverine concentration end-member and the seaward end-member defines conservative dilution.

For the limited June 1985 results, these assumptions are acceptable. However, the assumptions will be tested later with more complete data sets. For this modeling effort, concentrations of selenium species in the Sacramento River will be used as the riverine end-members, since low flows in June 1985 exclude San Joaquin River input. The river end-member concentrations (C_o's) are given in Table 3. In June 1985, the average Delta Outflow Index (i.e., river discharge into the estuary) was 1.35×10^{10} liters/day.

Table 3
SELENIUM FLUX DATA, JUNE 1985

Species	C_o *(nmoles/L)*	C**	F_{riv}	F_{int} *(moles/d)*	F_{est}
Total Se	0.50	5.21	6.7	63.4	70.1
Selenite	0.13	4.39	1.8	57.3	59.1
Selenate	0.25	0.82	3.4	7.6	11.0
Se(-II + 0)	0.12	0.0	1.6	-1.6	0.0

Negative F_{int} indicates removal within the estuary; positive F_{int} indicates production within the estuary.

To convert fluxes (F_{riv}, F_{int}, F_{est}) from moles Se/d to kg Se/d, multiply by 0.079.

Boyle et al. *(1974)* and Officer *(1979)* describe the estuarine mixing behavior of nonconservative constituents. For 1-dimensional, tidally averaged conditions, the flux of a dissolved constituent out of the estuary is:

$$F_{est} = R(C_s - S_s(dC/dS)_s) = RC^*$$

where

F = flux, in nmoles/day

R = river discharge, in liters/day

S = salinity
(S_s, salinity at seawater end-member; S_0, salinity at river end-member)

C = concentration, in nmoles/liter
(C_s, concentration of seawater end-member; C_o, concentration of river end-member)

The terms within parentheses are referred to as C*, the concentration of a river end-member that would explain the observed seawater concentration if only conservative mixing were present. Graphically, C* is where the tangent (dC/dS) to the concentration/salinity curve at the seawater end-member intersects the concentration axis at $S = S_0$. The flux from the river is simply $F_{riv} = RC_0$, and the net internal removal and production flux within the estuary is:

$$F_{int} = R\,(C^* - C_o)$$

For the June 1985 data, the tangent was constructed using a linear regression of the three data points nearest the seawater end-member. The estimated C*'s and corresponding fluxes are listed in Table 3. Compared to the riverine flux, the flux of total selenium out of the estuary is over 10 times greater, the estuarine flux of selenite is 33 times higher, the flux of selenate is a factor of 3 larger, and Se(-II + 0) is completely lost.

As an internal check of these values (i.e., mass balance), the individually determined F_{int}'s for each species can be compared to that for total dissolved selenium. The sum of the internal estuarine fluxes for selenite, selenate, and Se(-II + 0) is equivalent to that for total selenium (which is composed of these three fractions).

Compared to the previous estuarine studies, these preliminary results indicate that selenium in the Sacramento-San Joaquin estuary behaves quite differently. In particular, selenium shows a combination of removal and production depending on the species. These results provide a comparison for the more complete data set to be presented later.

April 1986 Transect

Since the previous data are scattered in time and did not provide a rigorous survey of the estuary, further sampling was performed in April 1986 (sampling locations are shown in Figure 1). This work included examination of not only dissolved selenium speciation, but also suspended particulate selenium. The latter analyses were made to provide insight into the sources and sinks of dissolved selenium in the estuary. Additionally, the April sampling was designed to compare the behavior of selenium during high river discharge with behavior during low streamflow (September 1986 sampling).

Freshwater residence time changes dramatically with discharge, and consequently effects of estuarine reactions (removal, production) on selenium can also vary. If, for example, removal rates are slow, then during periods of high flow and short residence time, the effect on selenium is minimized; slow removal rates assert more effect during periods of low flow and long residence time.

In the northern reach of San Francisco Bay (from the Golden Gate to the Sacramento and San Joaquin rivers) freshwater residence times can range from 1.2 to 60 days *(Walters et al, 1985)*. Therefore, it is imperative to obtain data for high flow and low flow conditions. Although results from April 1986 represent high flow conditions, they may be slightly atypical due to severe flooding in Northern California in February that year. From 1969 to 1977, the April Delta Outflow Index averaged 1000 m^3/sec *(Conomos et al, 1979)*; in 1986 it averaged 1,184 m^3/sec. While this flow is not unusual, it follows extremely high discharges in February and March (Figure 6). The net effect of this flood on estuarine behavior of selenium is difficult to estimate, but it must be kept in mind when examining the data.

Ancillary Data

The ancillary data for the April 1986 sampling includes nutrients, chlorophyll *a*, salinity, and total suspended matter. These data are contained in Table 4, and the surface water values are displayed in Figures 7 through 11.

The nitrate-salinity distribution (Figure 7) indicates generally conservative behavior during the sampling period, with some removal evident at 17 ppt salinity. Within the scatter of the data, phosphate (Figure 8) also appears conservative. In contrast, ammonium (Figure 9) shows strong removal of the

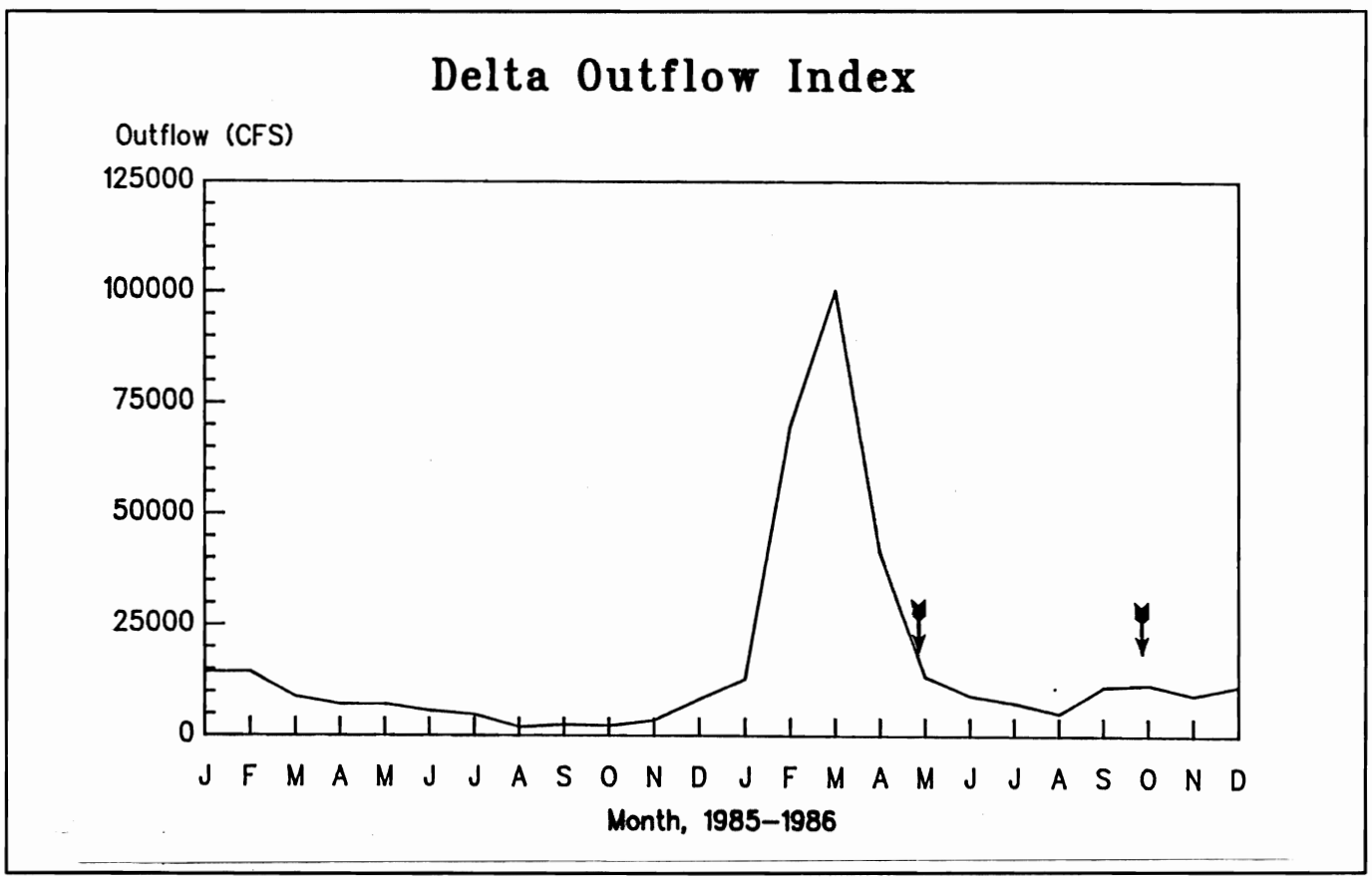

Figure 6
RECORD OF RIVER DISCHARGE (DELTA OUTFLOW INDEX) INTO SAN FRANCISCO BAY, 1985 AND 1986
(Arrows Indicate Sampling Times)

riverine input at 17-18 ppt salinity and an increase toward the seaward end-member. The one point, ammonium maximum at 5 ppt salinity may be due to contamination. In general, nitrate and phosphate concentrations and the shapes of their profiles are similar to those presented by Peterson et al. *(1985)* for typical "wet" May-June periods (closest to our sampling time). However, the riverine ammonium

Table 4
DATA SUMMARY, ANCILLARY MEASUREMENTS, APRIL 22 AND 23, 1986

Stn. No.	Depth *(m)*	Salinity *(ppt)*	Chl a *(ug/L)*	TSM *(mg/L)*	PO_4 *(uM)*	NO_2 *(uM)*	NO_3 *(uM)*	NH_3 *(uM)*
1	1	17.54	49.23	64.60	5.81	0.64	7.14	0.50
	12	18.37	-.-	145.44	4.84	0.64	7.14	1.50
2	1	20.40	10.74	35.72	2.90	0.57	3.50	1.07
	13	20.86	-.-	53.30	2.81	0.57	5.21	1.86
3	1	24.06	5.89	16.60	2.10	0.71	12.14	2.07
	27	27.45	-.-	24.75	2.10	0.86	18.57	1.93
4	1	26.82	4.72	24.64	1.94	0.79	7.14	1.64
5	1	25.72	4.08	24.64	2.06	0.70	14.29	1.71
	16	26.24	-.-	20.10	1.97	0.70	15.00	1.60
6	1	25.74	3.32	17.52	1.90	0.71	15.00	1.36
	16	27.05	-.-	30.37	1.90	0.70	15.71	1.60
7	1	23.73	4.00	29.91	1.90	0.79	15.71	1.93
	40	27.39	-.-	68.44	1.94	0.70	14.29	1.60
8	1	20.96	3.20	27.49	1.81	0.70	13.57	1.60
	13	24.16	-	41.74	2.00	0.71	14.29	2.00
9	1	20.19	3.12	26.57	1.74	0.71	12.86	0.71
	9	23.29	-.-	45.35	1.90	0.64	15.71	1.71
10	1	17.67	4.31	25.35	1.65	0.64	11.43	0.64
	12	22.13	-.-	54.98	1.87	0.86	14.29	1.21
11	1	16.49	12.23	31.64	1.90	0.71	15.00	1.57
	9	19.46	-.-	121.73	1.84	0.79	14.29	1.14
12	1	14.62	12.28	17.92	2.29	0.71	15.71	2.29
	7	18.55	-.-	294.76	1.90	0.64	15.00	1.79
13	1	12.30	9.71	13.88	2.00	0.71	17.14	2.79
	9	16.81	-.-	258.76	1.94	0.64	15.00	1.79
14	1	9.15	13.78	23.90	1.97	0.71	17.86	3.36
	22	13.10	-.-	267.36	2.03	0.64	17.14	3.36
15	1	7.67	14.37	27.65	2.06	0.79	18.57	4.07
	10	9.98	-.-	71.46	2.10	0.60	18.57	4.20
16	1	6.06	12.16	58.86	2.23	0.60	20.71	6.80
	13	8.46	-.-	71.86	2.19	0.60	19.29	5.10
17	1	2.11	9.21	63.69	2.06	0.64	20.71	5.00
	10	5.75	-.-	60.34	2.20	0.60	20.00	5.60
18	1	0.53	3.92	41.86	2.06	0.60	21.42	5.90
	7	1.20	-.-	49.02	2.10	0.60	21.43	5.90
19	1	0.09	2.50	20.13	1.58	0.40	17.86	7.00
20	2	0.09	2.24	27.90	2.03	0.60	20.71	4.90

-.- = No Sample

concentrations are higher than those they reported, and removal is more prominent during our sampling. Reasons for this discrepancy are unclear.

Data for chlorophyll *a* (Figure 10) show a pronounced maximum in the 2-12 ppt salinity range, corresponding to San Pablo Bay and Carquinez Strait. These data are consistent with those presented by Ball and Arthur *(1979)* for high flow conditions. Finally, total suspended matter (Figure 11) has a maximum of 63.7 mg/L, which occurs in Suisun Bay, and an average of 24.3 mg/L in the rest of the northern reach. The location of maximum total suspended matter is similar to that found by Arthur and Ball *(1979)* for periods of high river discharge.

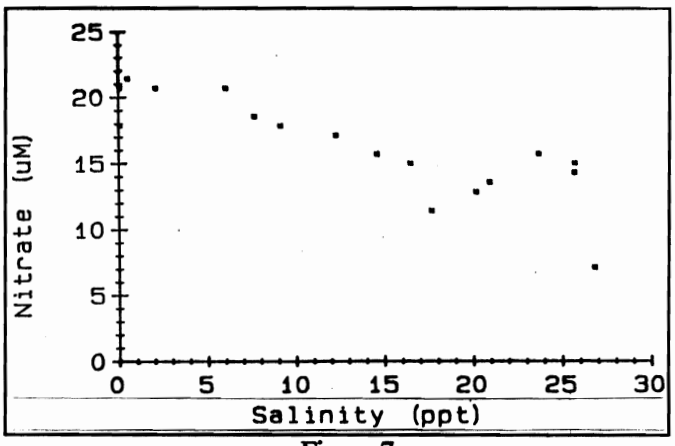

Figure 7
SURFACE WATER DISTRIBUTION OF NITRATE IN THE NORTHERN REACH OF SAN FRANCISCO BAY, APRIL 1986

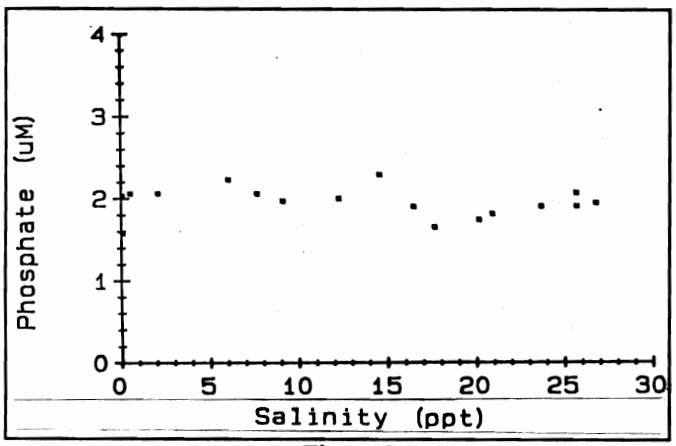

Figure 8
SURFACE WATER DISTRIBUTION OF PHOSPHATE IN THE NORTHERN REACH OF SAN FRANCISCO BAY, APRIL 1986

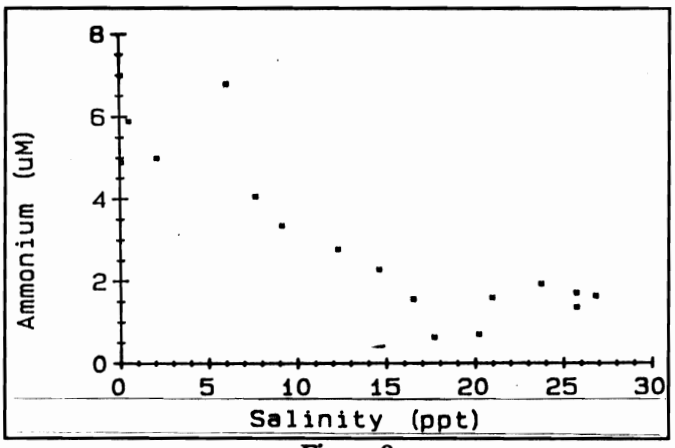

Figure 9
SURFACE WATER DISTRIBUTION OF AMMONIUM IN THE NORTHERN REACH OF SAN FRANCISCO BAY, APRIL 1986

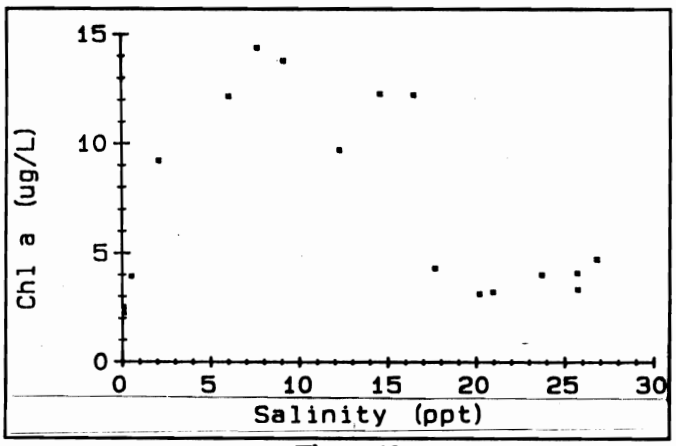

Figure 10
SURFACE WATER DISTRIBUTION OF CHLOROPHYLL *a* IN THE NORTHERN REACH OF SAN FRANCISCO BAY, APRIL 1986

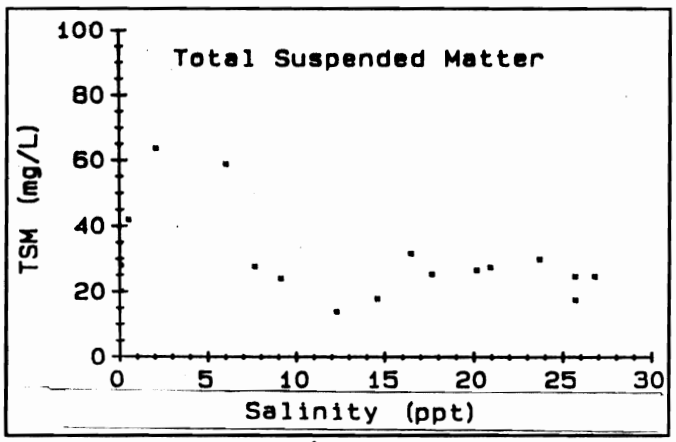

Figure 11
SURFACE WATER DISTRIBUTION OF TOTAL SUSPENDED MATTER IN THE NORTHERN REACH OF SAN FRANCISCO BAY, APRIL 1986

Selenium Data

Selenium speciation data for all stations are listed in Table 5, and the surface water results are shown in Figures 12 through 19. Total selenium concentrations in the two rivers differ by more than a factor of 2 (Table 5), with the highest concentration in the San Joaquin. This is consistent with the previous riverine data (Table 2). As described above, if the concentrations are discharge-weighted and conservatively mixed, then the riverine end-member total selenium (C_0) is 2.02 nmol/L (0.16 ppb Se).

Throughout the estuary, total dissolved selenium (Figure 12) is nearly conservative, but shows some production in the upper estuary (Suisun Bay) and removal near 14 ppt salinity (eastern San Pablo Bay). At the two stations nearest the Golden Gate, total selenium concentrations appear to be elevated. These removal and input features are not found in the June 1985 results (Figure 5A) and will be discussed in more detail shortly.

The selenite-salinity distribution for the main estuary (Figure 13) is qualitatively similar to that in June 1985 (Figure 5B). However, the broad selenite maximum is centered at about 9 ppt salinity (Carquinez Strait), rather than at 20 ppt. Maximum selenite concentration in April 1986 is also about half that in June 1985. Selenite concentrations in the rivers (Table 5) are nearly identical, and the discharge-weighted selenite concentration (C_0) is 0.21 nmol/L (0.02 ppb Se). Riverine selenite concentrations do not vary appreciably in samples taken before and after the cruise. Selenite is 10 percent of total selenium in the river end-member, but at its estuarine maximum (Stations 14-16), selenite rises to 23 percent of total dissolved selenium.

In contrast to selenite, selenate concentrations are very different in the two rivers (Table 5), with the San Joaquin value more than twice that in the Sacramento. The discharge-weighted riverine selenate concentration (C_0) is 1.51 nmol/L (0.12 ppb Se), and large concentration variations are seen with time (Table 5). Selenate displays nonconservative behavior in the estuary, with apparent removal in the upper to mid-salinity range dominating the profile (Figure 14). Near the Golden Gate, where large increases in total selenium are observed, only a slight selenate increase is discernible. In the river

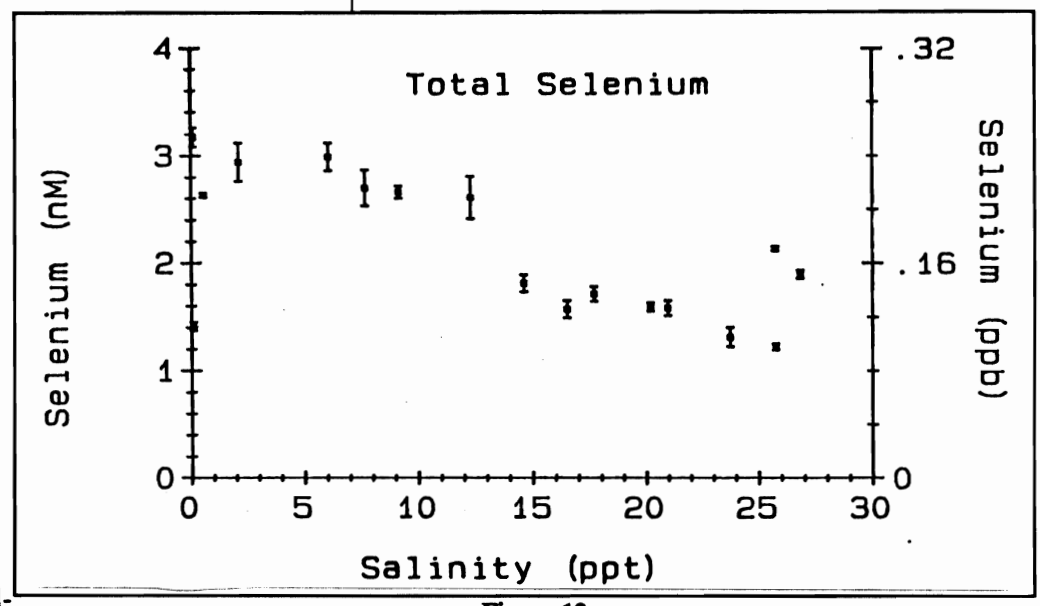

Figure 12
TOTAL SELENIUM DISTRIBUTION IN SURFACE WATERS FROM THE NORTHERN REACH OF SAN FRANCISCO BAY, APRIL 1986

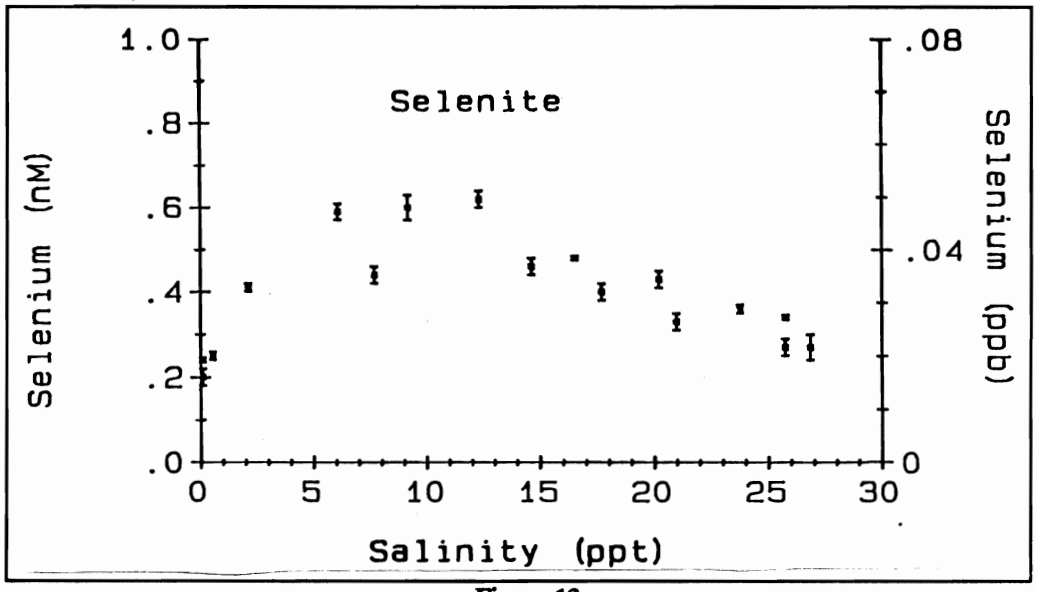

Figure 13
SELENITE DISTRIBUTION IN SURFACE WATERS FROM THE NORTHERN REACH OF SAN FRANCISCO BAY, APRIL 1986

Table 5
DATA SUMMARY, SELENIUM MEASUREMENTS, APRIL 22 AND 23, 1986

Stn. No.	Depth (m)	Total Se (nM)	Se(IV) (nM)	Se(VI) (nM)	Se(-II + 0) (nM)	Sep-Pak (nM)	Particulates (nM)	Salinity (ppt)
1	1	4.09±0.05	0.33±0.02	1.28±0.11	2.48±0.12	0.40	0.31±0.02	17.54
	12	3.51±0.04	0.24±0.02	1.14±0.03	2.13±0.04	0	0.70±0.02	18.37
2	1	3.26±0.02	0.21±0.02	0.68±0.03	2.37±0.03	0.16	0.03±0.02	20.40
	13	2.62±0.15	0.21±0.006	0.71±0.06	1.70±0.16	0	0.28±0.02	20.86
3	1	2.07±0.01	0.28±0.01	0.61±0.05	1.18±0.05	0.39	0.10±0.004	24.06
	27	1.93±0.08	0.31±0.02	0.64±0.07	0.98±0.11	0	0.11±0.001	27.45
4	1	1.89±0.04	0.27±0.02	1.00±0.06	0.62±0.07	0.03	0.11±0.003	26.82
5	1	2.13±0.02	0.27±0.02	0.69±0.03	1.17±0.03	0.08	0.10±0.001	25.72
	16	1.20±0.005	0.25±0.02	0.60±0.06	0.35±0.06	0	0.08±0.01	26.24
6	1	1.22±0.03	0.34±0.006	0.88±0.02	0	0.42	0.09±0.005	25.74
	16	1.11±0.05	0.25±0.02	0.58±0.03	0.28±0.05	0	0.11±0.008	27.05
7	1	1.31±0.09	0.36±0.01	0.57±0.02	0.38±0.09	0	0.09±0.01	23.73
	40	1.15±0.05	0.21±0.006	0.97±0.06	0	0	0.27±0.03	27.39
8	1	1.58±0.07	0.33±0.02	0.92±0.02	0.33±0.07	0.18	0.11±0.007	20.96
	13	1.26±0.04	0.26±0.02	1.04±0.02	0	0.04	0.18±0.01	24.16
9	1	1.59±0.04	0.43±0.02	0.72±0.04	0.44±0.05	0.009	-.-	20.19
	9	1.37±0.05	0.32±0.02	0.74±0.07	0.31±0.09	0	0.18±0.01	23.29
10	1	1.71±0.07	0.40±0.02	0.81±0.03	0.50±0.07	0	0.10±0.006	17.67
	12	1.15±0.02	0.39±0.01	0.72±0.01	0.04±0.02	0.27	0.20±0.01	22.13
11	1	1.57±0.08	0.48±0.005	0.83±0.02	0.26±0.08	0	0.16±0.004	16.49
	9	1.56±0.02	0.42±0.01	0.87±0.07	0.27±0.07	0	0.37±0.03	19.46
12	1	1.81±0.08	0.46±0.02	0.96±0.02	0.39±0.08	0.09	0.16±0.01	14.62
	7	1.69±0.13	0.43±0.01	0.14±0.02	1.12±0.13	0	0.78±0.04	18.55
13	1	2.61±0.20	0.62±0.02	0.86±0.04	1.13±0.20	0	0.14±0.001	12.30
	9	1.74±0.13	0.54±0.02	0.93±0.07	0.27±0.15	0.24	0.29±0.02	16.81
14	1	2.66±0.06	0.60±0.03	1.10±0.14	0.96±0.15	0.28	0.15±0.01	9.15
	22	1.96±0.02	0.80±0.005	0.82±0.07	0.34±0.07	0.005	0.68±0.003	13.10
15	1	2.70±0.17	0.44±0.02	1.53±0.02	0.73±0.17	0.03	0.19±0.02	7.67
	10	2.35±0.005	0.44±0.01	1.87±0.01	0.04±0.01	0.21	0.40±0.004	9.98
16	1	2.99±0.13	0.59±0.02	2.31±0.09	0	-.-	0.26±0.002	6.06
	13	2.76±0.14	0.56±0.02	2.09±0.16	0	0.23	0.31±0.001	8.46
17	1	2.94±0.18	0.41±0.01	2.38±0.02	0	0.49	0.27±0.02	2.11
	10	2.31±0.08	0.52±0.04	1.53±0.10	0.26±0.12	0.29	0.25±0.005	5.75
18	1	2.63±0.02	0.25±0.01	2.26±0.14	0	0.14	0.19±0.004	0.53
	7	3.21±0.19	0.29±0.02	1.74±0.04	1.18±0.19	0.19	-.-	1.20
19	1	1.41±0.04	0.20±0.02	1.01±0.02	0.20±0.04	-.-	0.04±0.002	0.09
20	2	3.17±0.09	0.24±0.006	2.47±0.02	0.46±0.09	0.29	0.13±0.007	0.09
RV/4-16		1.66 (n = 1)	0.28±0.02	1.30±0.12	0.08±0.12			
A/4-16		3.04±0.07	0.27±0.01	2.58±0.25	0.19±0.26			
RV/5-1		2.40±0.10	0.23±0.01	1.02±0.05	1.15±0.11			
A/5-1		3.36±0.02	0.28±0.02	2.40±0.03	0.68±0.03			

0 = Non-detectable.
-.- = No sample
RV = Rio Vista, Sacramento River
A = Antioch, San Joaquin River
To convert to ppb Se, multiply by 0.079.

output (discharge-weighted), selenate is 75 percent of the total dissolved selenium, an average of 82 percent of the total in its low salinity maximum (Stations 16-18), and then averages 49 percent of the total dissolved selenium in the rest of the estuary.

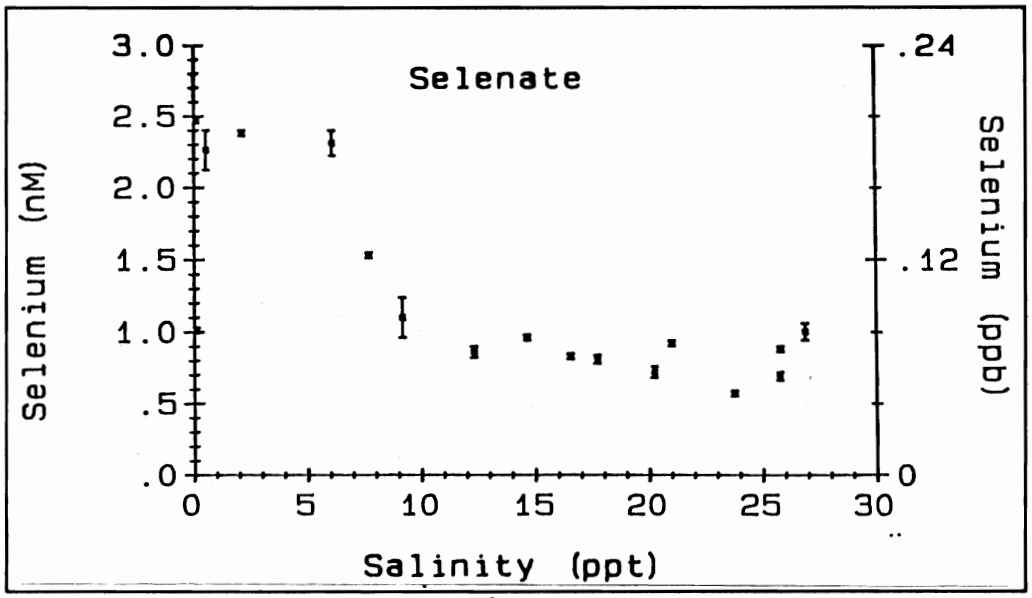

Figure 14
SELENATE DISTRIBUTION IN SURFACE WATERS FROM THE NORTHERN REACH OF SAN FRANCISCO BAY, APRIL 1986

The Se(-II + 0) fraction is determined as the difference between total selenium and selenite + selenate. As a consequence, precision is poorer (larger error bars), especially if Se(-II + 0) is calculated from the difference between two large values. When the error is larger than the calculated concentration, Se(-II + 0) is considered nondetectable (e.g., Table 5, Station 16, 1 m). The Se(-II + 0)-salinity distribution (Figure 15) displays two maxima, one centered at 10 ppt salinity and the other near the Golden Gate. The discharge-weighted riverine Se(-II + 0) concentration (C_0) is 0.29 nmol/L (0.02 ppb Se), and amounts to 14 percent of the total dissolved selenium. In its low salinity maximum, Se(-II + 0) reaches 35 percent of the total, while the high salinity maximum is 44 percent of the total selenium.

Cutter and Bruland *(1984)* operationally defined the Se(-II + 0) fraction as organic selenide, but did not examine estuarine waters in their work. In this study, Sep-Pak cartridges were used to provide an independent estimate of the organic selenium fraction. Sep-Pak organic selenium averages 33 percent of Se(-II + 0) throughout the estuary, indicating that the remainder of Se(-II + 0) is inorganic or small organic molecules that are not retained on the C_{18} resin (e.g., free amino acids, dimethyl selenide).

As noted above, anomalously high concentrations of total selenium and Se(-II + 0) are found near the Golden Gate (Stations 4 and 5), especially in comparison to typical Pacific Ocean concentrations (e.g., *Cutter and Bruland, 1984)*. These values can be explained by examining selenium speciation data from the South Bay transect (Stations 1-4, Figure 1).

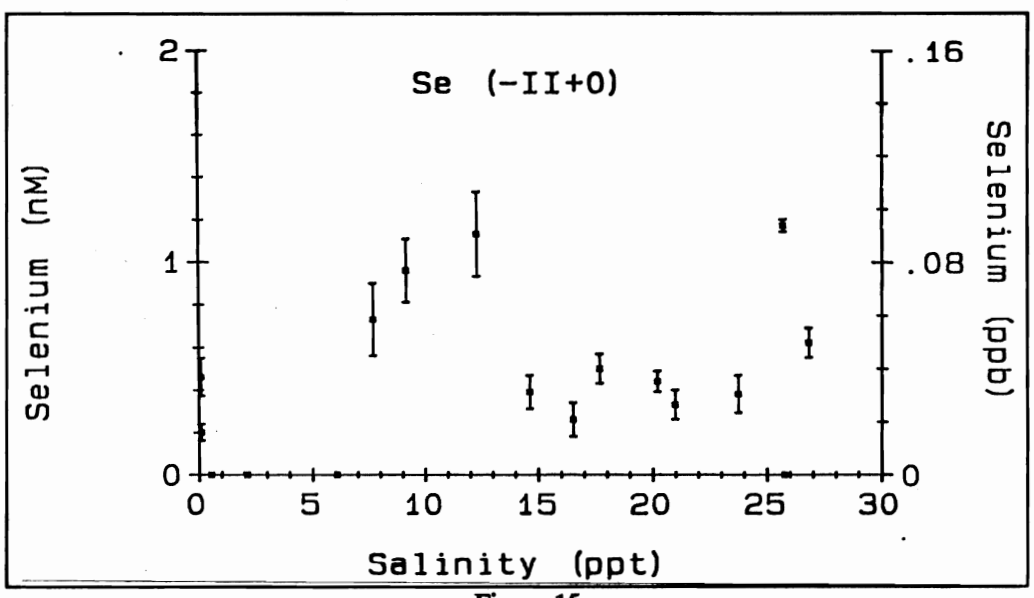

Figure 15
Se(-II + 0) DISTRIBUTION IN SURFACE WATERS FROM THE NORTHERN REACH OF SAN FRANCISCO BAY, APRIL 1986

When the South Bay data are plotted against salinity (Figures 16-19), linear mixing lines are obtained for Se(-II + 0) and total selenium (total Se, r = 0.9771, n = 5; Se(-II + 0), r = 0.9631, n = 5); the behaviors of selenite and selenate (Figures 17 and 18) are more complex. These results strongly indicate that the elevated total selenium and Se(-II + 0) concentrations at the Golden Gate originate in the South Bay. If the linear mixing lines are extrapolated to zero salinity, the South Bay riverine end-member would have a total selenium concentration of 8.2 nmol/L (0.65 ppb Se) and a Se(-II + 0) concentration of 6.2 nmol/L (0.49 ppb Se). Thus, the South Bay is noteworthy for its elevated total selenium concentration.

Furthermore, the selenium speciation in the South Bay is significantly different than that from the northern reach. In the South Bay, Se(-II + 0) averages 64 percent of the total dissolved selenium (Table 5, Stations 1-3). The input of this reduced selenium to the South Bay may be the weathering of sulfide deposits in the Almaden Hills or the outflow from sewage treatment plants such as the large San Jose/Santa Clara facility. During high flows when residence times are short, this input may not have time to oxidize to selenite and selenate.

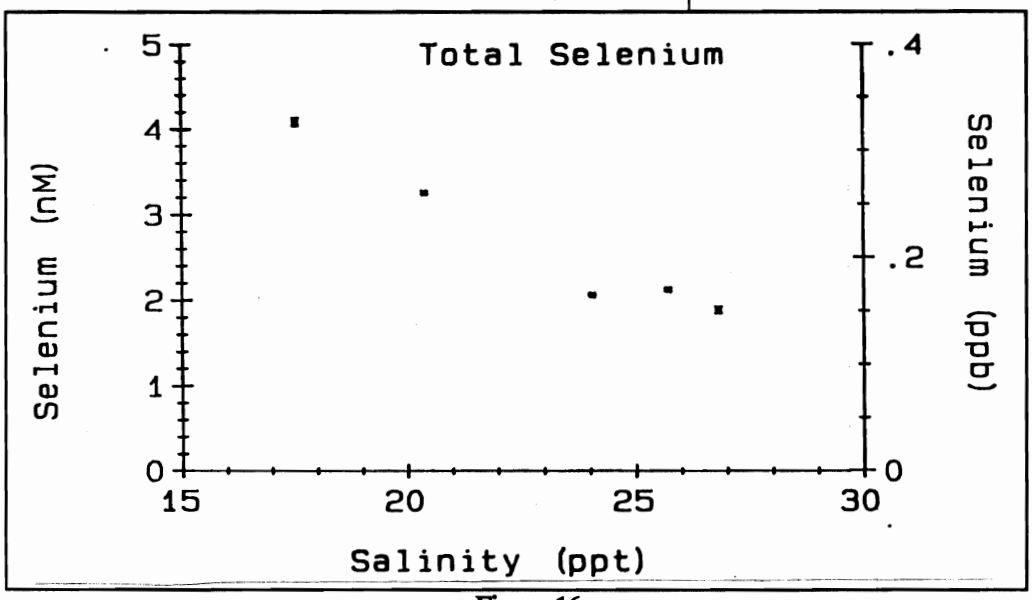

Figure 16
TOTAL SELENIUM DISTRIBUTION IN SURFACE WATERS FROM SOUTH AND CENTRAL SAN FRANCISCO BAY, APRIL 1986

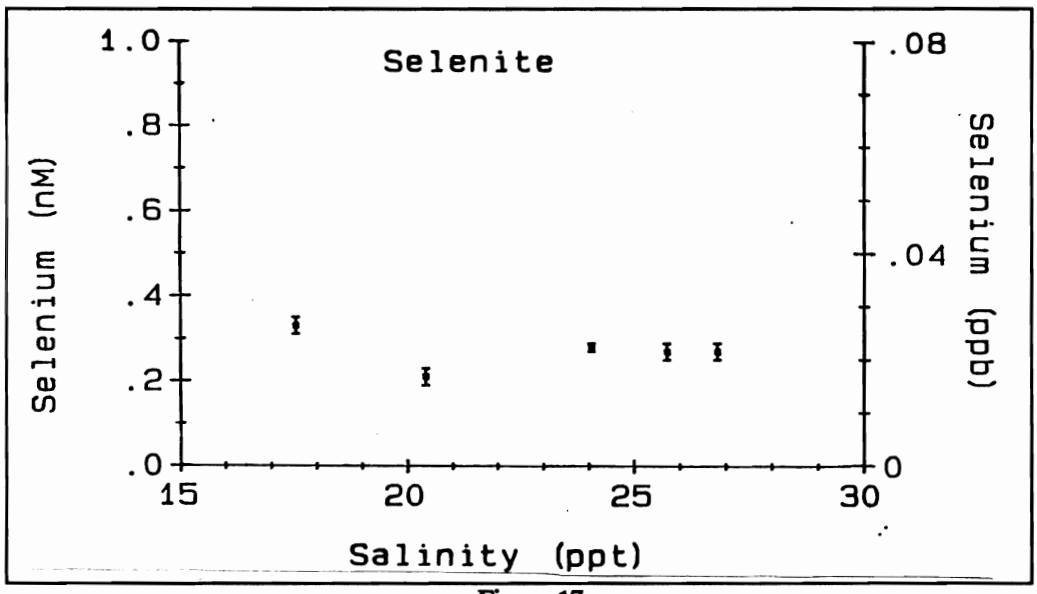

Figure 17
SELENITE DISTRIBUTION IN SURFACE WATERS FROM SOUTH AND CENTRAL SAN FRANCISCO BAY, APRIL 1986

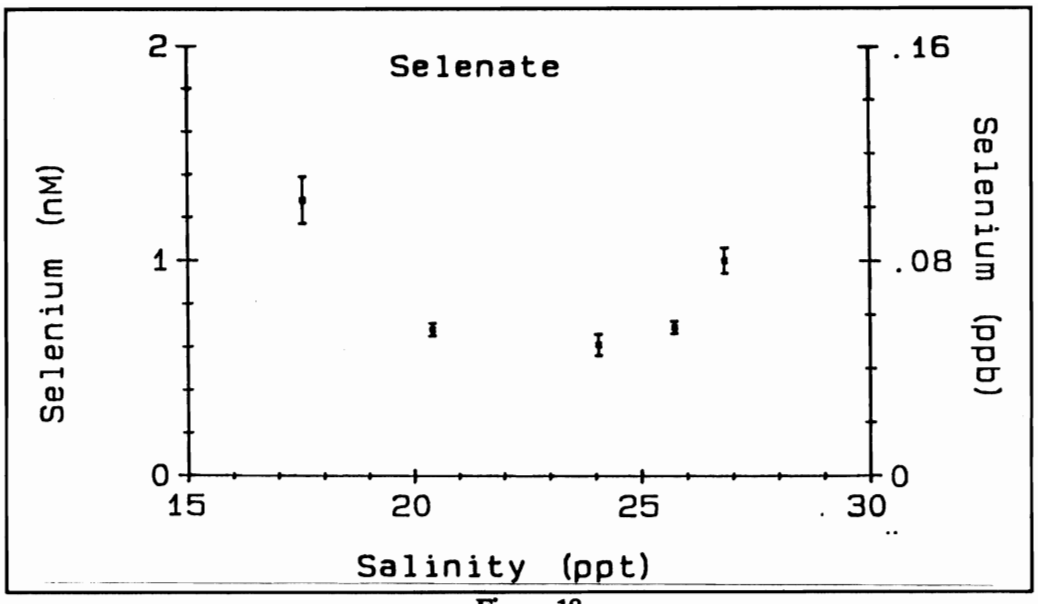

Figure 18
SELENATE DISTRIBUTION IN SURFACE WATERS FROM SOUTH AND CENTRAL SAN FRANCISCO BAY, APRIL 1986

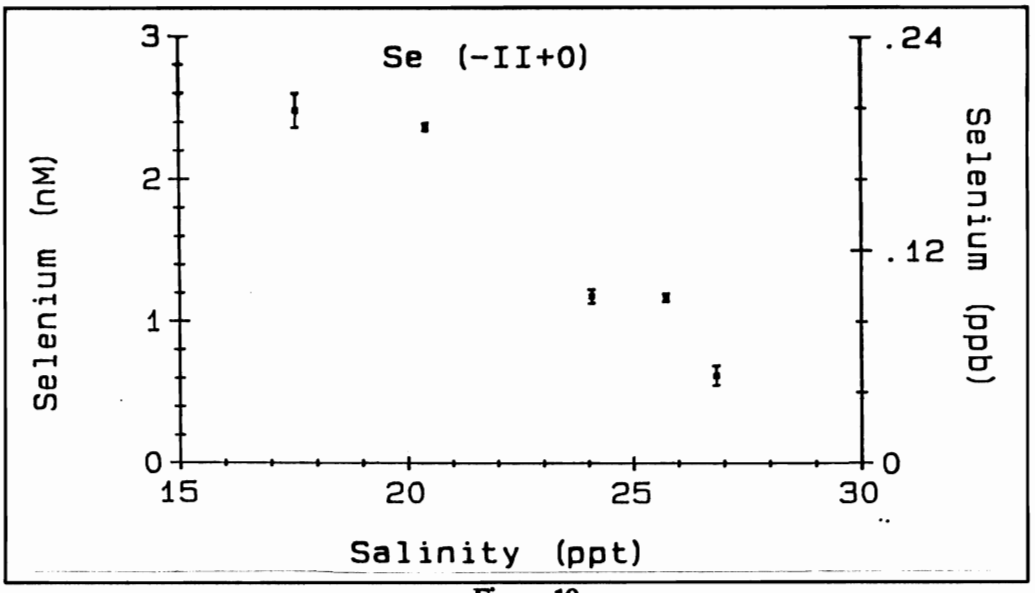

Figure 19
Se(-II + 0) DISTRIBUTION IN SURFACE WATERS FROM SOUTH AND CENTRAL SAN FRANCISCO BAY, APRIL 1986

Thus far, only data from surface water samples have been discussed, but deeper samples were obtained to assess vertical homogeneity with respect to selenium. The data are summarized in Table 5 and shown in Figure 20. Figure 20A, a plot of total selenium at surface and bottom depths versus salinity, shows a generally well mixed system (i.e., most points fall in the same line). Selenite (Figure 20B) is also well mixed, except for a 0.2 nmol/L (0.02 ppb Se) divergence at 7-15 ppt salinity (bottom water concentrations lower). Selenate (Figure 20C) is also well mixed with depth, except from 2-8 ppt salinity. Here bottom water selenate concentrations are about 0.5 nmol/L (0.04 ppb Se) lower.

The greatest difference between bottom water and surface concentrations occurs with Se(-II + 0), with bottom water having the lower concentration (Figure 20D). Overall, it appears that sampling surface waters adequately represents the range of selenium concentrations and speciation in San Francisco Bay.

The description of estuarine selenium cannot be restricted to dissolved species. The concentration/salinity profile for suspended particulate selenium in the northern reach (Figure 21) shows a prominent maximum, like total suspended matter (Figure 11), in the low salinity region. Throughout the

northern reach surface waters, suspended particulate selenium averages 7.1 ± 1.7% (n = 13) of the total dissolved selenium. While suspended selenium is a relatively small and constant proportion of the total estuarine selenium, this does not preclude its importance to specific selenium forms (e.g., source/sink relationship).

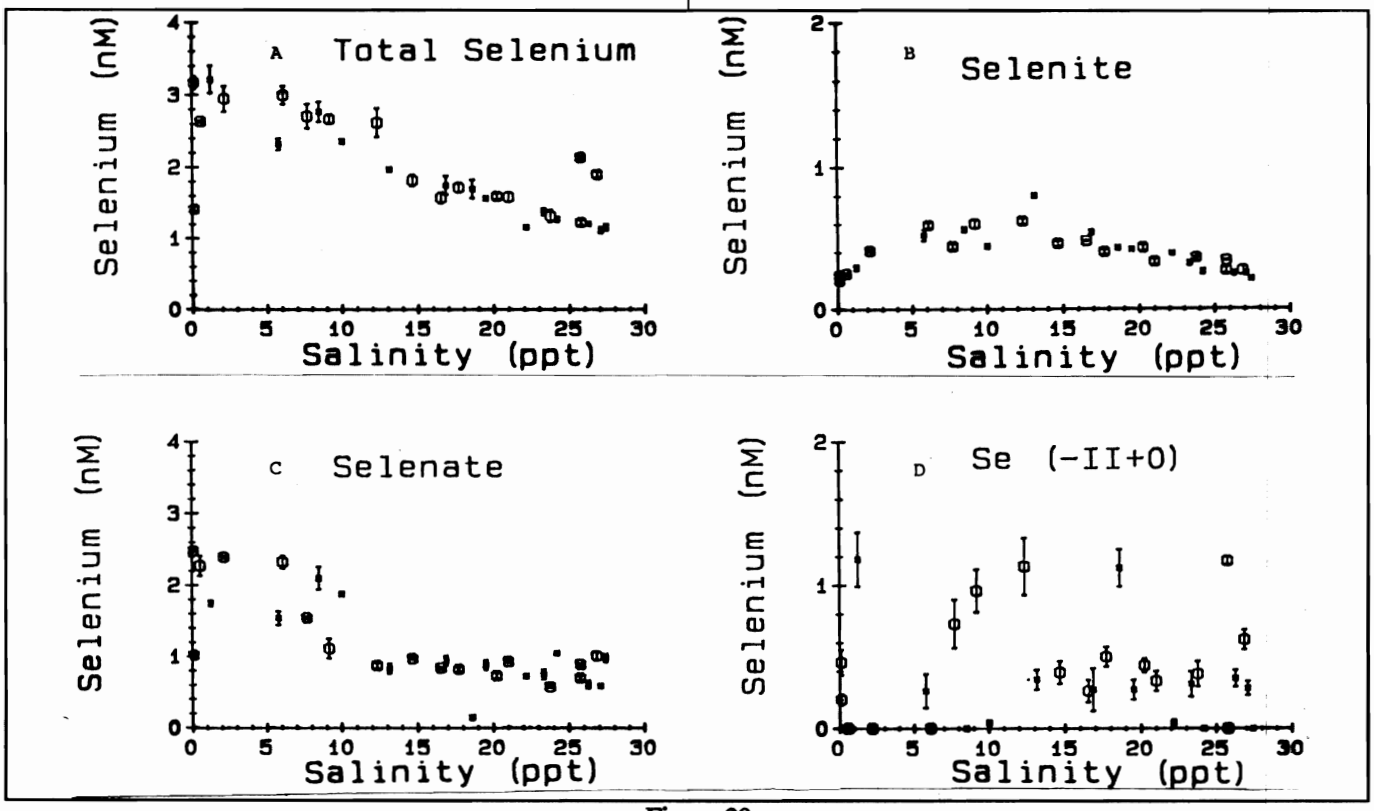

Figure 20
DISTRIBUTION OF SELENIUM SPECIES IN
SURFACE AND BOTTOM WATERS OF THE NORTHERN REACH OF SAN FRANCISCO BAY,
APRIL 1986
(Large symbols represent surface values.)

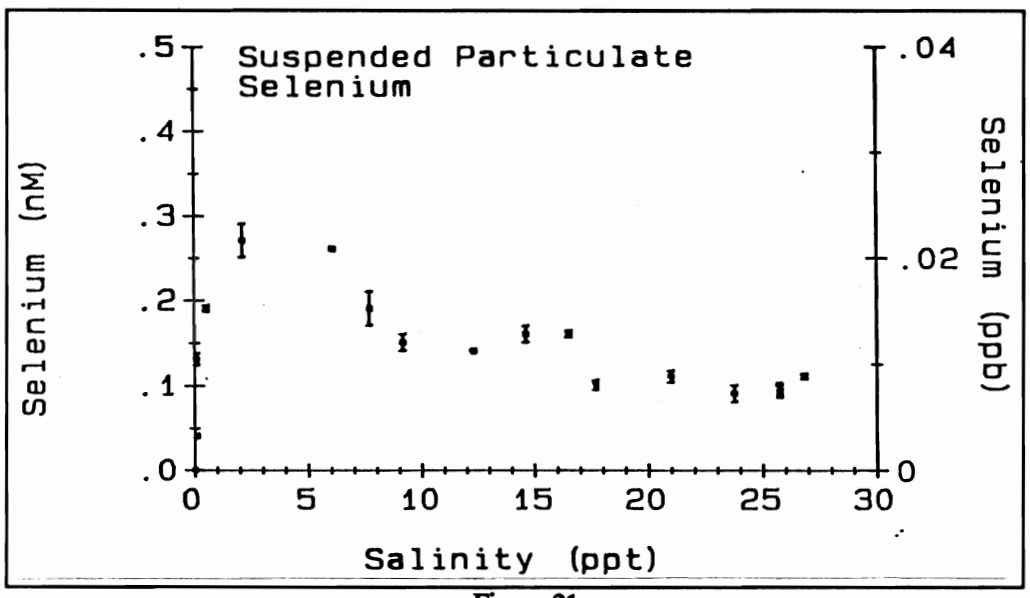

Figure 21
DISTRIBUTION OF SUSPENDED PARTICULATE SELENIUM IN THE
NORTHERN REACH OF SAN FRANCISCO BAY,
APRIL 1986

September 1986 Transect

The primary emphasis in the September 1986 field work was to obtain selenium data for low streamflow/long residence time period, to perform more detailed surface water sampling (closer salinity spacing) and to make a more thorough survey of selenium in the South Bay. The stations sampled are shown in Figure 2; timing of the sampling run relative to river discharge can be seen in Figure 6.

Ancillary Data

As in April, ancillary data for the September 1986 sampling includes nutrients, chlorophyll *a*, and total suspended matter. Data for the northern reach are summarized in Table 6 and displayed in Figures 22 through 27.

In the two river stations, silicate (Figure 22) averages 245 umol/L, decreases rapidly in the upper estuary, and then shows a more gradual decrease to the seaward end-member (with the exception of two aberrant data). The nitrate-salinity profile (Figure 23) indicates slight removal in the upper estuary (2-8 ppt salinity), and input in the San Pablo Bay (18-27 ppt). Compared to the river stations, phosphate concentrations (Figure 24) show little decrease until mid-San Pablo Bay (ca. 25 ppt).

Whereas ammonium concentrations decreased from the upper to lower estuary in April 1986 (Figure 9), the opposite trend was found in September (Figure 25). Concentrations and estuarine distributions of these nutrients are essentially the same as those described by Peterson et al. *(1985)* for a September with an intermediate river discharge.

The distribution of chlorophyll *a* in September (Figure 26) displays a maximum concentration in western Suisun Bay (average of 7.1 ug/L), with a second, smaller maximum in San Pablo Bay. Compared to a September with similar river discharge *(Ball and Arthur, 1979)*, the observed chlorophyll maximum is a factor of 4 lower in concentration and shifted slightly downstream.

Table 6
DATA SUMMARY FOR THE NORTHERN REACH OF SAN FRANCISCO BAY, SEPTEMBER 23 AND 24, 1986

Stn. No.	Depth (m)	Salinity (ppt)	Chl a (µg/L)	TSM (mg/L)	PO_4^{-3} (µM)	NO_3^- (µM)	NH_4^+ (µM)	Si (µM)
1	1	24.58	3.86	42.05	33.7	149	16.4	173
2	1	27.85	2.95	32.42	22.8	67.9	10.3	128
3	1	29.78	1.39	21.41	11.9	31.4	12.4	98.0
4	1	30.36	1.63	22.67	7.0	23.6	10.3	61.6
5	1	30.40	1.61	18.24	3.1	12.1	7.6	20.0
6	1	31.58	3.45	10.72	2.1	8.6	5.5	15.0
7	1	31.95	2.42	11.96	1.8	7.9	5.2	6.7
8	1	31.30	2.44	13.47	2.2	10.0	6.6	15.0
9	1	27.77	4.73	25.60	2.8	12.1	4.1	28.3
10	1	27.33	3.69	14.36	3.0	10.0	4.4	28.3
11	1	24.01	3.59	31.78	3.2	14.3	3.8	33.3
12	1	20.97	4.89	63.75	3.2	14.3	3.6	46.7
13	1	19.46	4.50	44.16	3.1	15.0	4.6	49.9
14	1	17.45	3.13	23.60	3.2	15.7	4.6	63.5
15	1	13.89	2.75	16.76	3.1	15.7	4.4	78.4
15	21	19.76	2.44	22.89	3.1	15.0	4.6	46.7
16	1	13.22	4.29	16.20	3.3	16.4	4.5	83.5
17	1	11.56	3.06	22.70	3.1	16.4	4.3	88.2
18	1	11.06	5.46	15.12	3.1	17.1	5.1	177
19	1	9.65	7.52	18.04	3.2	17.1	4.1	107
20	1	7.57	6.84	30.71	3.0	17.1	2.9	119
21	1	5.10	6.87	33.46	3.0	18.6	3.4	155
22	1	3.61	3.57	42.84	3.0	20.7	2.6	228
23	1	1.51	2.78	49.24	3.2	22.1	3.7	93.3
24	1	0.39	2.20	59.53	3.0	20.7	0.9	248
25	1	0.07	0.65	28.42	2.3	9.3	7.4	247
26	1	0.19	-.-	28.87	2.9	21.4	0.4	24.3

-.- = No Sample

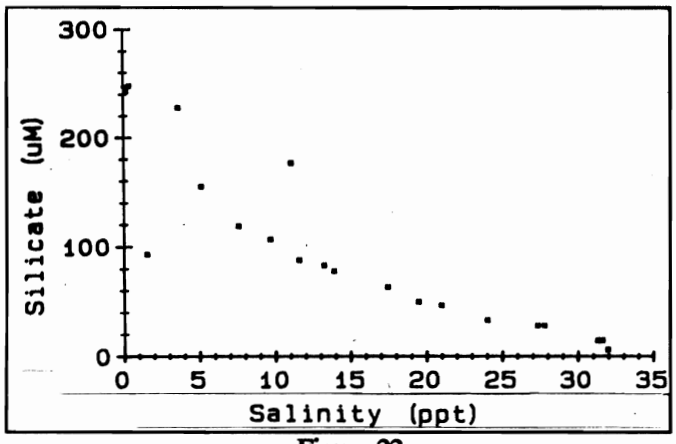

Figure 22
SURFACE WATER DISTRIBUTION OF SILICATE IN THE NORTHERN REACH OF SAN FRANCISCO BAY, SEPTEMBER 1986

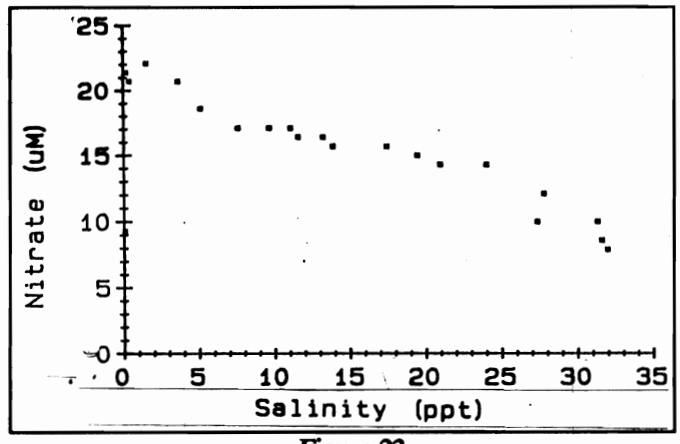

Figure 23
SURFACE WATER DISTRIBUTION OF NITRATE IN THE NORTHERN REACH OF SAN FRANCISCO BAY, SEPTEMBER 1986

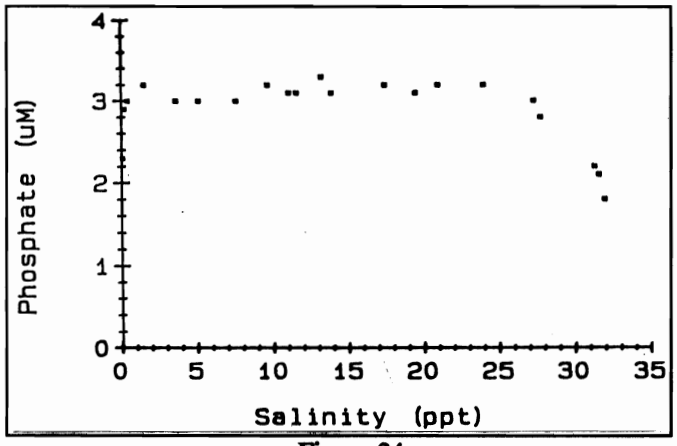

Figure 24
SURFACE WATER DISTRIBUTION OF PHOSPHATE IN THE NORTHERN REACH OF SAN FRANCISCO BAY, SEPTEMBER 1986

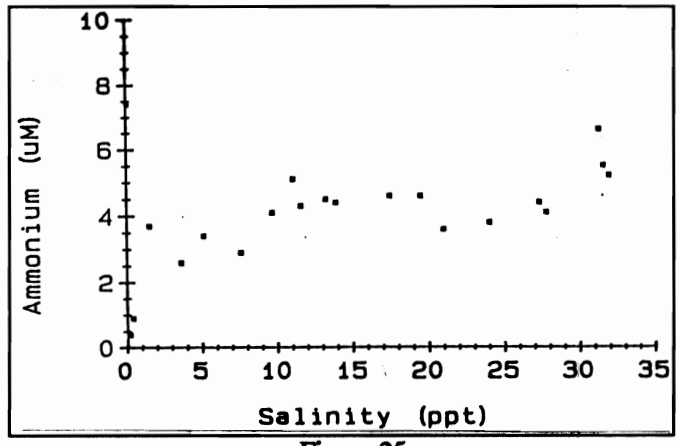

Figure 25
SURFACE WATER DISTRIBUTION OF AMMONIUM IN THE NORTHERN REACH OF SAN FRANCISCO BAY, SEPTEMBER 1986

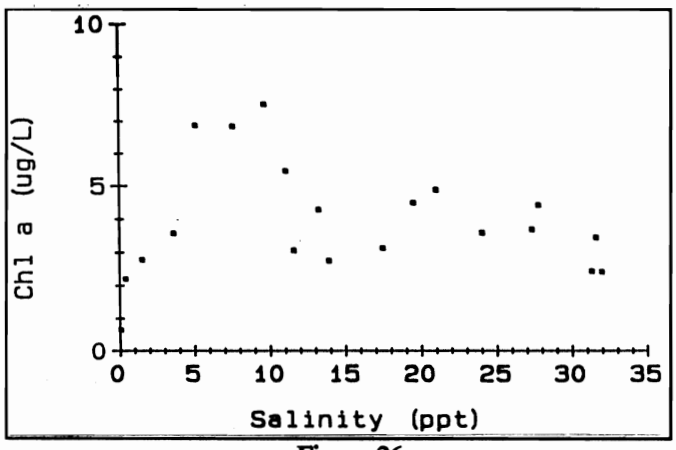

Figure 26
SURFACE WATER DISTRIBUTION OF CHLOROPHYLL *a* IN THE NORTHERN REACH OF SAN FRANCISCO BAY, SEPTEMBER 1986

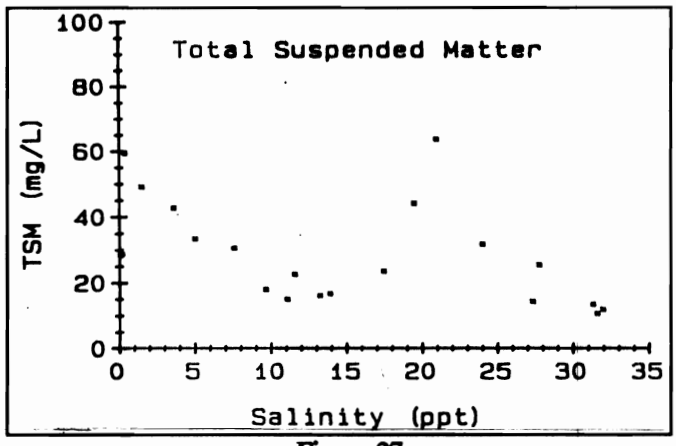

Figure 27
SURFACE WATER DISTRIBUTION OF TOTAL SUSPENDED MATTER IN THE NORTHERN REACH OF SAN FRANCISCO BAY, SEPTEMBER 1986

The highest concentrations of total suspended matter (Figure 27) are also found in the upper portion of the estuary (Station 24, 59.53 mg/L) and in San Pablo Bay (63.75 mg/L). Excluding data from the two stations above and below these maxima, total suspended matter averages 19.8 mg/L in the northern reach. It should be noted that upper San Pablo Bay (Stations 11-13) was sampled on a high slack tide in high winds. Under these conditions, Arthur and Ball *(1979)* reported that resuspended material may be transported from the productive northern shoals to the center channel (where the stations were located). Thus, the magnitude and location of the TSM and chlorophyll peaks in San Pablo Bay may reflect this short-term process.

Nutrient data for the South Bay transect are listed in Table 6 and shown in Figures 28 through 31.

Unlike the northern reach nutrient profiles, those of South Bay show nearly conservative behavior (nutrient versus salinity):

Si	r = -0.9419
Nitrate	r = -0.9816
Phosphate	r = -0.9791
Ammonium	r = -0.8930

The extremely high concentrations of nitrate, ammonium, and phosphate at Station 1 are consistent with input via sewage effluent. Conomos et al. *(1979)* reported similar concentrations and distributions of these nutrients in South Bay. Furthermore, they suggested that all of the phosphate and most of the nitrogenous compounds are supplied by sewage effluent. Station 1 in September 1986 was within one mile of the San Jose/Santa Clara sewage treatment plant outfall.

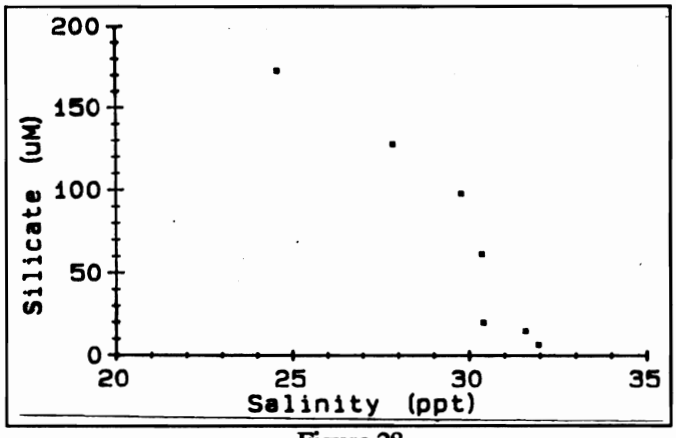

Figure 28
SURFACE WATER DISTRIBUTION OF SILICATE IN SOUTH AND CENTRAL SAN FRANCISCO BAY, SEPTEMBER 1986

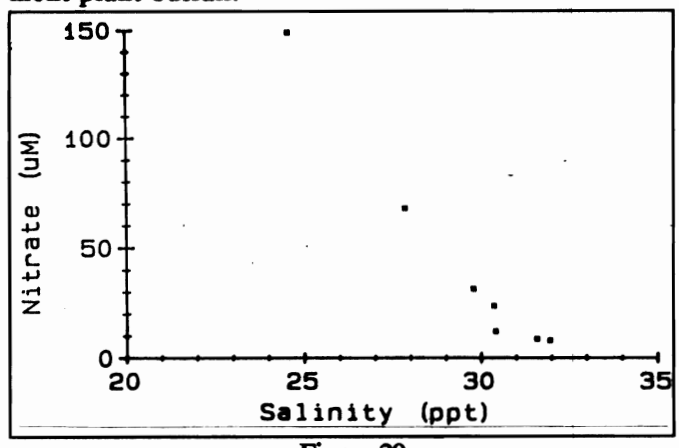

Figure 29
SURFACE WATER DISTRIBUTION OF NITRATE IN SOUTH AND CENTRAL SAN FRANCISCO BAY, SEPTEMBER 1986

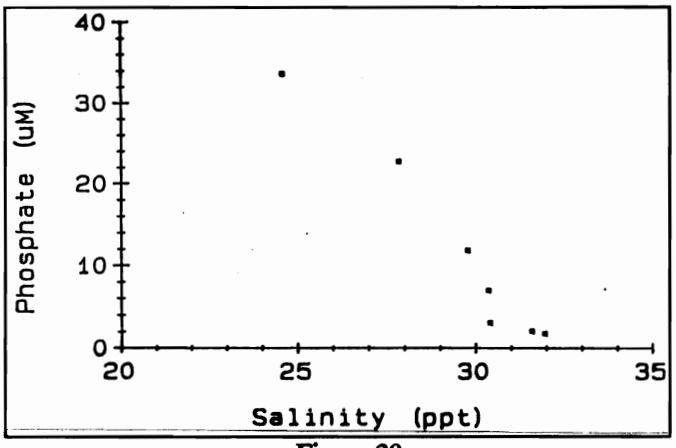

Figure 30
SURFACE WATER DISTRIBUTION OF PHOSPHATE IN SOUTH AND CENTRAL SAN FRANCISCO BAY, SEPTEMBER 1986

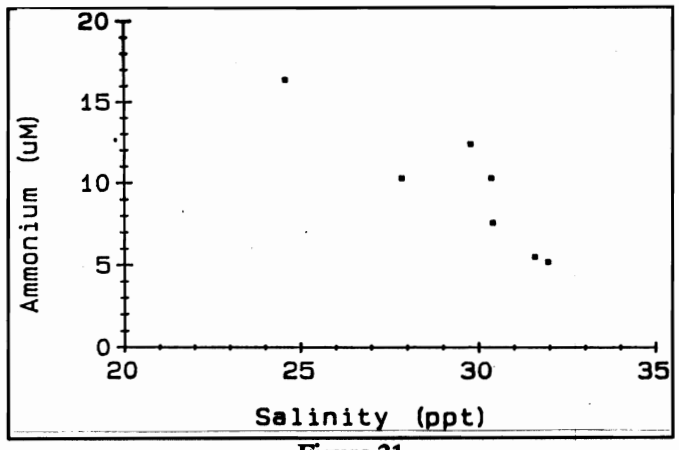

Figure 31
SURFACE WATER DISTRIBUTION OF AMMONIUM IN SOUTH AND CENTRAL SAN FRANCISCO BAY, SEPTEMBER 1986

Selenium Data

Data for selenium species at September 1986 stations can be found in Table 7; Figures 32 through 40 show these data versus salinity. September results are significantly different than those from April.

Total selenium in the two river stations (Stations 25 and 26) differ by a factor of two. However, since the major riverine input is the Sacramento, the riverine end-member (C_0) for total dissolved selenium in September is 0.61 nmol/L (0.05 ppb Se). Proceeding down the estuary, the concentration of total dissolved selenium (Figure 32) increases to a maximum between 10-20 ppt (average concentration, 2.79 nmol/L, or 0.22 ppb Se, n = 9), with a decrease thereafter to the seawater end-member. Geographically, the maximum total selenium is found in the Carquinez Strait region. Unlike April 1986, no significant total selenium anomaly is seen near the Golden Gate. Overall, the September 1986 distribution of total dissolved selenium in the estuary is very similar to that in June 1985 (Figure 5A).

Table 7
SELENIUM SPECIES DATA SUMMARY
SEPTEMBER 23 AND 24, 1986

Stn. No.	Depth *(m)*	Total Se *(nM)*	Se(IV) *(nM)*	Se(VI) *(nM)*	Se(-II + 0) *(nM)*	Sep-Pak *(nM)*	Particulates *(nM)*	Salinity *(ppt)*
1	1	4.54±0.10	0.98±0.05	2.41±0.11	1.15±0.14	0.20	0.28*	24.58
2	1	3.52±0.10	0.87±0.02	1.66±0.07	0.99±0.12	0.58	0.33±0.01	27.85
3	1	1.78±0.05	0.50±0.01	1.01±0.07	0.27±0.08	0.49	0.15±0.01	29.78
4	1	1.74±0.08	0.36±0.01	1.02±0.04	0.36±0.08	0.25	0.10±0.01	30.36
5	1	1.55±0.05	0.30±0.01	0.65±0.04	0.60±0.06	0.25	0.11±0.01	30.40
6	1	0.90±0.01	0.34±0.01	0.36±0.01	0.20±0.01	0.16	0.16±0.01	31.58
7	1	1.24±0.03	0.46±0.01	0.51±0.03	0.27±0.04	0.08	0.08±0.01	31.95
8	1	1.16±.003	0.39±0.01	0.21±0.01	0.56±0.01	0.29	0.12±0.01	31.30
9	1	1.39±0.04	0.42±0.01	0.96±0.05	N.D.	0.40	-.-	27.77
10	1	1.94±0.05	0.66±0.02	0.76±0.04	0.52±0.06	0.26	0.13±0.01	27.33
11	1	2.11±0.04	0.65±0.02	0.85±0.04	0.61±0.05	0.20	0.28±0.01	24.01
12	1	2.75±0.12	1.12±0.01	1.03±0.07	0.60±0.14	0.47	-.-	20.97
13	1	2.35±0.07	1.00±0.05	0.76±0.07	0.59±0.12	0.42	0.28±0.02	19.46
14	1	2.88±0.07	1.20±0.04	0.90±0.07	0.78±0.09	0.08	0.19±0.02	17.45
15	1	2.66±0.04	1.05±0.02	1.14±0.08	0.47±0.08	0.48	0.22±0.01	13.87
15	21	2.41±0.13	1.04±0.03	1.01±0.04	0.36±0.13	0.76	0.16*	19.76
16	1	2.79±0.02	1.01±0.03	0.95±0.11	0.83±0.11	0.44	0.16±0.01	13.22
17	1	2.49±0.09	1.13±0.03	0.70±0.05	0.66±0.10	0.56	0.30±0.01	11.56
18	1	3.16±0.09	1.32±0.04	1.06±0.06	0.78±0.09	0.33	-.-	11.06
19	1	3.64±0.16	1.30±0.04	1.26±0.06	1.08±0.16	0.49	0.26±0.03	9.65
20	1	2.74±0.07	0.83±0.04	0.59±0.05	1.32±0.08	0.32	0.29±0.01	7.57
21	1	2.52±0.07	0.73±0.02	0.91±0.04	0.88±0.07	0.47	0.32±0.01	5.10
22	1	1.85±0.16	0.60±0.03	0.88±0.06	0.37±0.17	0.49	0.39±0.02	3.61
23	1	1.62±0.07	0.35±0.01	0.73±0.01	0.54±0.07	0.14	0.34±0.02	1.51
24	1	1.40±0.05	0.35±0.01	0.49±0.01	0.56±0.05	0.33	0.32±0.01	0.39
25	1	0.61±0.02	0.24±0.01	0.29±0.02	0.08±0.03	0.06	0.14±0.01	0.07
26	1	1.34±0.12	0.33±0.01	0.30±0.02	0.71±0.12	0.05	0.35*	0.19

N.D. = Not Detectable

-.- = No Sample

*Some difficulties were encountered with these sample analyses, and no replicates were run.

To convert to ppb Se, multiply by 0.079.

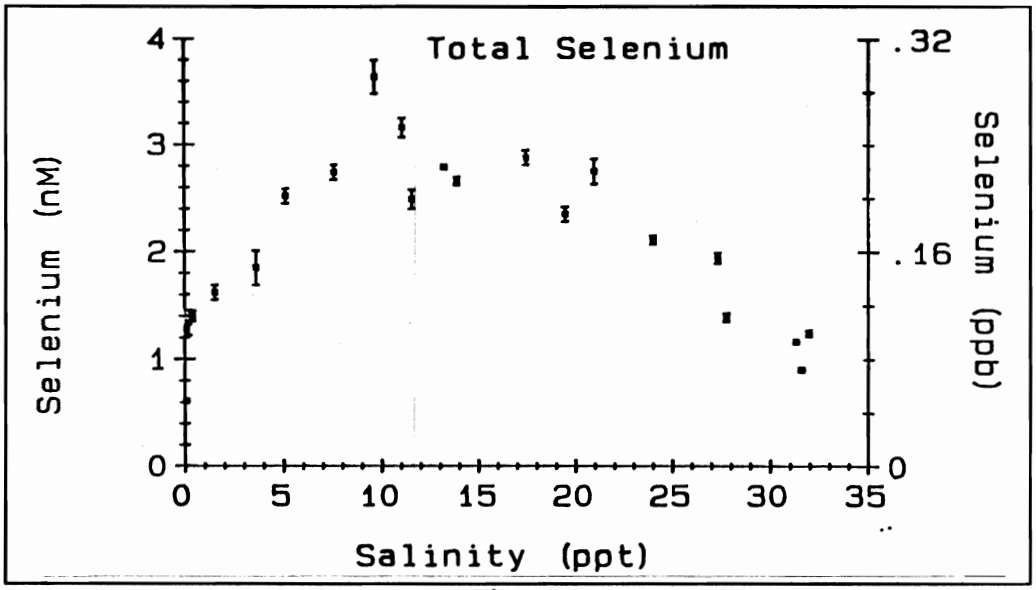

Figure 32
TOTAL SELENIUM DISTRIBUTION IN SURFACE WATERS FROM THE NORTHERN REACH OF SAN FRANCISCO BAY, SEPTEMBER 1986

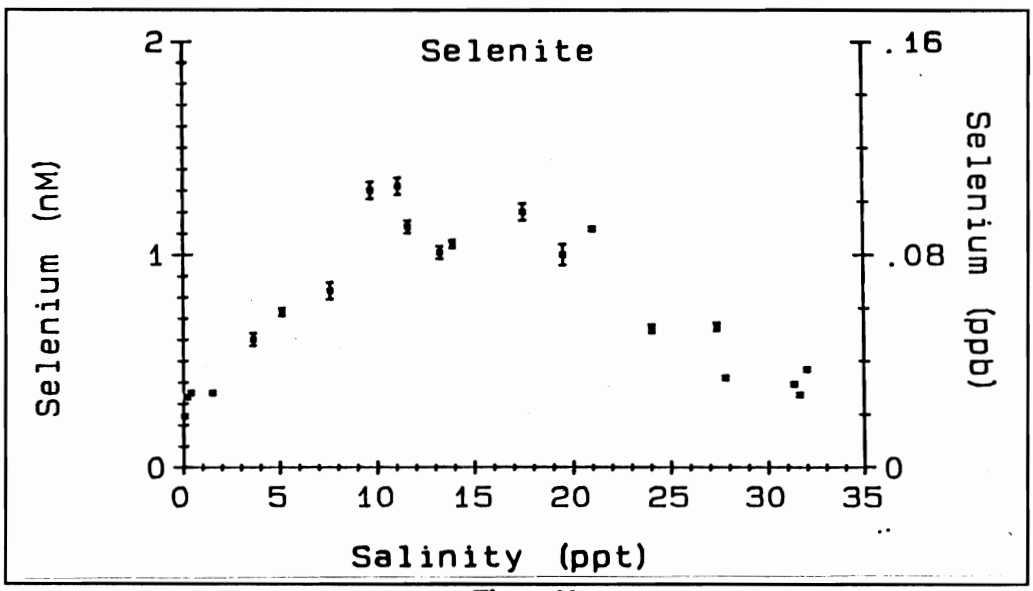

Figure 33
SELENITE DISTRIBUTION IN SURFACE WATERS FROM THE NORTHERN REACH OF SAN FRANCISCO BAY, SEPTEMBER 1986

The distribution of selenite versus salinity in the northern reach (Figure 33) is very similar to the estuarine distribution of total selenium. Selenite differs by 27 percent in the two river stations, and the riverine concentrations are higher than in April by about 40 percent. The single riverine end-member (C_o) is 0.24 nmol/L (0.02 ppb Se) and is 39 percent of the total selenium. The large selenite maximum between 9 ppt and 20 ppt has an average concentration of 1.13 nmol/L (0.09 ppb Se; n = 9), and is 41 percent of the total selenium in this region.

In the lower estuary, selenite decreases in concentration, making up 38 percent of the total dissolved selenium in the seawater end-member. Overall, selenite is a larger and more constant proportion of total selenium in September when compared to April 1986 (10 to 24 percent of the total).

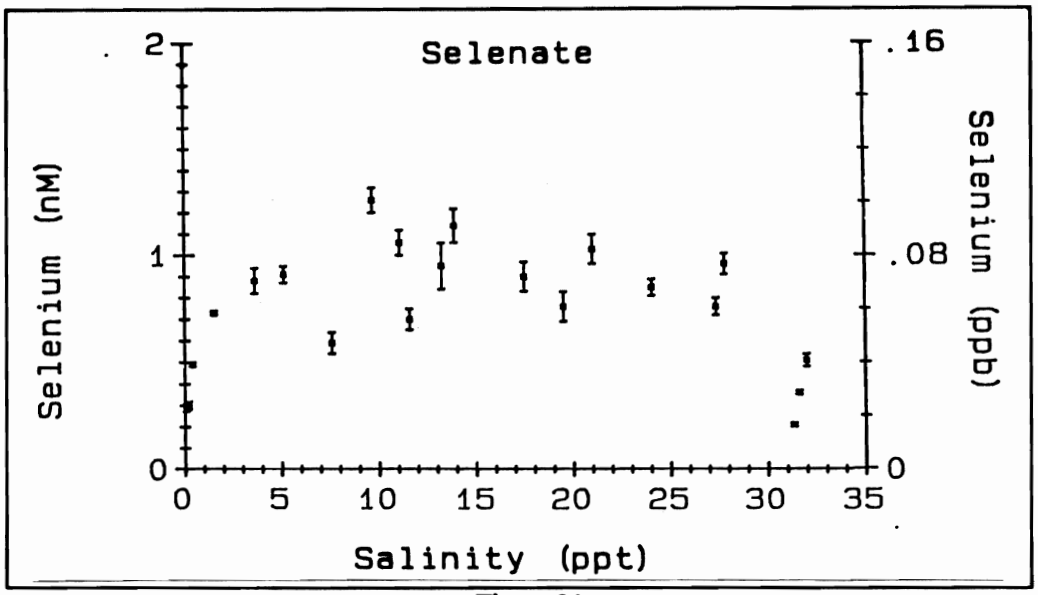

Figure 34
SELENATE DISTRIBUTION IN SURFACE WATERS FROM THE NORTHERN REACH OF SAN FRANCISCO BAY, SEPTEMBER 1986

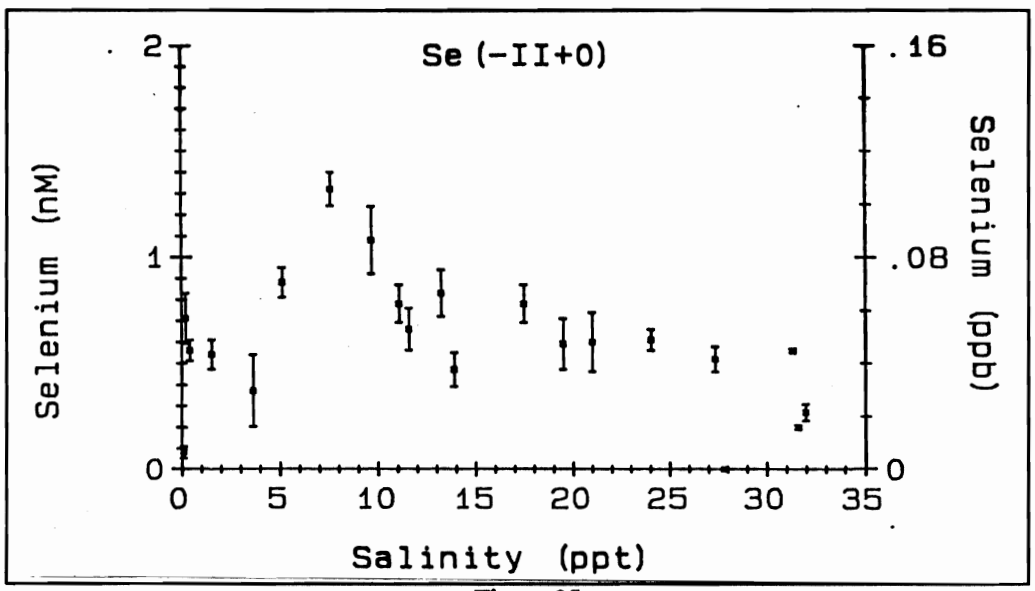

Figure 35
Se(-II + 0) DISTRIBUTION IN SURFACE WATERS FROM THE NORTHERN REACH OF SAN FRANCISCO BAY, SEPTEMBER 1986

The profile of selenate versus salinity in the northern reach (Figure 34) for September is more complex than that for April. Unlike the earlier data, selenate concentrations in the two river stations are identical (Table 7). The riverine end-member (C_o) is thus 0.29 nmol/L (0.02 ppb Se) for the September transect, comprising 48 percent of total selenium. Except for one data point, a selenate maximum centered at 11 ppt is seen (average selenate of 1.02 nmol/L, or 0.08 ppb Se, n = 6).

Selenate concentrations change rapidly near the Golden Gate, a feature reminiscent of the April total selenium and Se(-II + 0) data (Figures 12 and 15). In the three highest salinity stations (Sites 6-8), selenate averages 0.36 nmol/L (0.03 ppb Se), or 33 percent of total dissolved selenium. This calculation was made using the last three stations, since the seawater end-member is not well defined.

As for April 1986, error bars for Se(-II + 0) are larger than those for the other species because it is calculated as the difference between two typically large numbers. For the northern reach, the Se(-II + 0)/salinity distribution (Figure 35) shows one prominent maximum (1.32 nmol/L, or 0.10 ppb

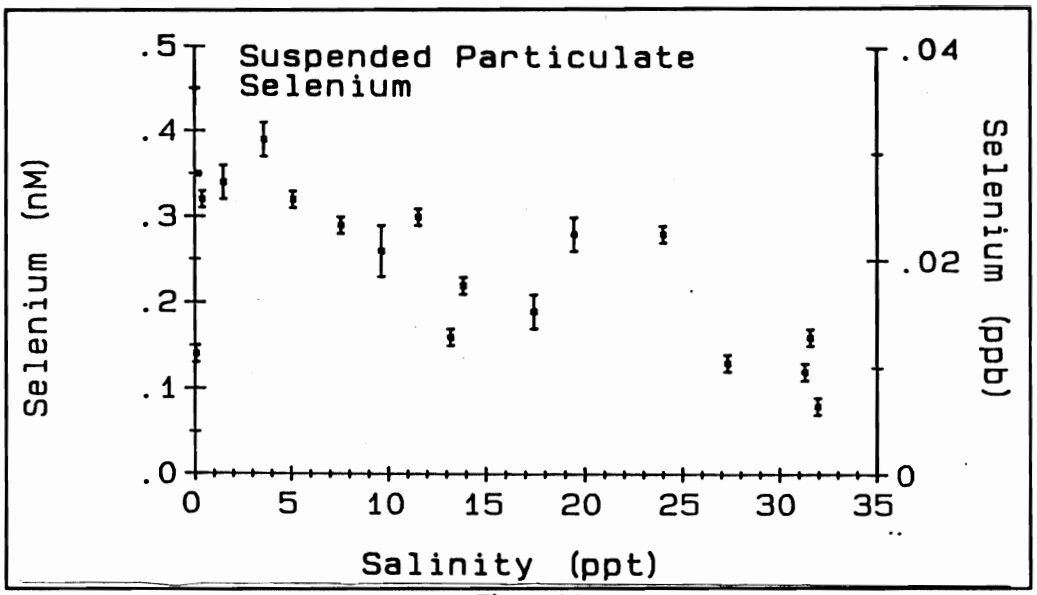

Figure 36
DISTRIBUTION OF SUSPENDED PARTICULATE SELENIUM IN SURFACE WATERS FROM THE
NORTHERN REACH OF SAN FRANCISCO BAY,
SEPTEMBER 1986

Se) centered at 8 ppt and a general decrease toward the seawater end-member thereafter. Concentrations of Se(-II + 0) in the two rivers differ markedly, but in keeping with the arguments above, the concentration in the Sacramento (0.08 nmol/L, or 0.01 ppb Se) is considered to be the correct river end-member (C_o). Se(-II + 0) is 13 percent of the total selenium in the riverine end-member but reaches 48 percent of the total in the 8 ppt maximum, and 31 percent of the total in the three highest salinity stations.

As mentioned earlier, Se(-II + 0) is operationally defined as organic selenide. Sep-Pak cartridges were again used to independently estimate the concentration of dissolved organic selenium.

For September 1986, Sep-Pak concentrations average 58 $\pm$ 32 percent (n = 21) of the Se(-II + 0) values (Table 7), a value nearly double that in April (33 percent). Again, the lack of agreement between Se(-II + 0) and Sep-Pak selenium does not preclude existence of organic selenide, since small organic molecules are not well retained by the C_{18} resin.

In the open ocean work of Cutter and Bruland *(1985),* Se(-II + 0) was found to be correlated with indicators of biological activity such as chlorophyll *a* and primary productivity. A similar correlation between chlorophyll (Figure 26) and Se(-II + 0) (Figure 35) is apparent with the September 1986 results. Using all surface data from the northern reach (Tables 6 and 7), a correlation coefficient of 0.6915 is obtained for Se(-II + 0) versus chlorophyll *a* (n = 21). If only the Se(-II + 0) maximum from Sites 15 to 22 is considered, then a correlation coefficient of 0.8528 is found (n = 8). This correlation supports the hypothesis that Se(-II + 0) is produced biologically.

To complete the description of selenium distributions in the northern reach, the concentration of selenium in suspended matter must be examined. The profile of suspended particulate selenium in the northern reach (Figure 36) shows two maxima, one at 3.6 ppt (0.39 nmol/L, or 0.03 ppb Se) and a smaller, broader peak at 22 ppt (0.28 nmol/L, or 0.02 ppb Se).

The suspended particulate selenium profile is similar to that for total suspended matter (Figure 27), although the low salinity particulate selenium peak is shifted slightly downstream relative to total suspended matter. Throughout the northern reach, suspended particulate selenium averages 13 $\pm$ 7 percent of total dissolved selenium, with a maximum value of 26 percent at Site 26. While average and maximum concentrations of total suspended matter do not change appreciably between April and September, the amount of particulate selenium relative to dissolved almost doubles from April to September.

South Bay selenium concentrations were notably elevated in April, with Se(-II + 0) being the primary species (64 percent). September sampling included more stations in the South Bay so this observation could be verified and further examined. South Bay selenium data are listed in Table 7 and shown in Figures 37-40.

As in April, linear mixing lines are seen for selenium versus salinity (total selenium, r = -0.9803; selenite, r = -0.9329; selenate, r = -0.9823; Se(-II + 0), r = -0.9003; n = 6). However, the major species in September is selenate (53 percent of total at Site 1), with selenite comprising 22 percent and Se(-II + 0) being 25 percent of total dissolved selenium at Site 1 in South Bay. Since nutrients also show linear mixing and have sewage effluent as their primary input source *(Conomos et al., 1979)*, selenium is presumably also coming from sewage outfalls (i.e., little *in situ* production of selenium). If the linear mixing curves are extrapolated back to 0 ppt salinity, the South Bay end-member would have 18.0 nmol/L total selenium (1.42 ppb Se), 3.7 nmol/L selenite (0.29 ppb Se), 9.6 nmol/L selenate (0.76 ppb Se), and 4.7 nmol/L (0.37 ppb) Se(-II + 0). This source has a significantly different selenium concentration (factor of 2 higher) and speciation than that found in April.

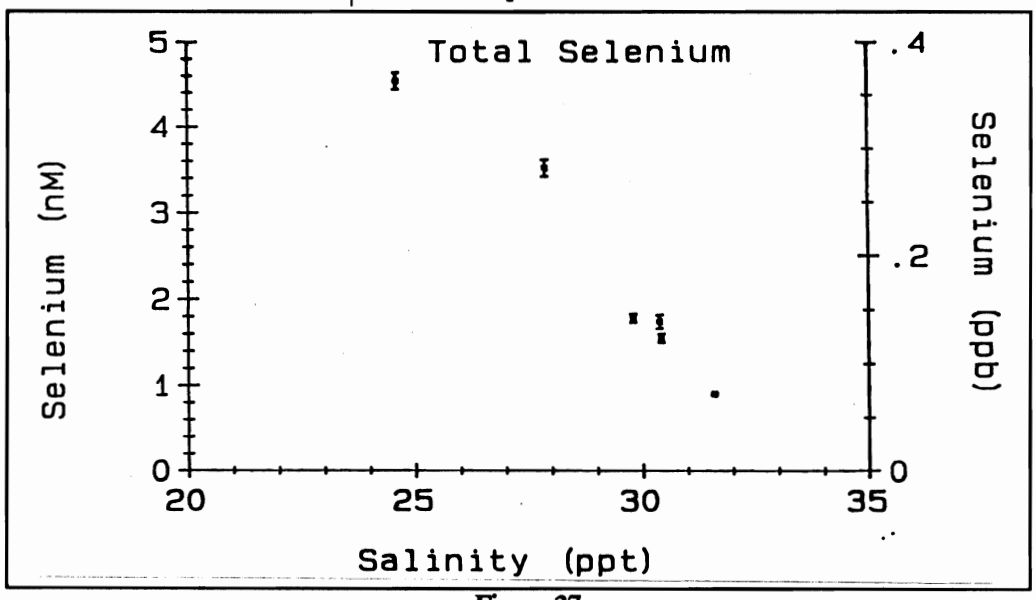

Figure 37
TOTAL SELENIUM DISTRIBUTION IN SURFACE WATERS FROM SOUTH AND CENTRAL SAN FRANCISCO BAY, SEPTEMBER 1986

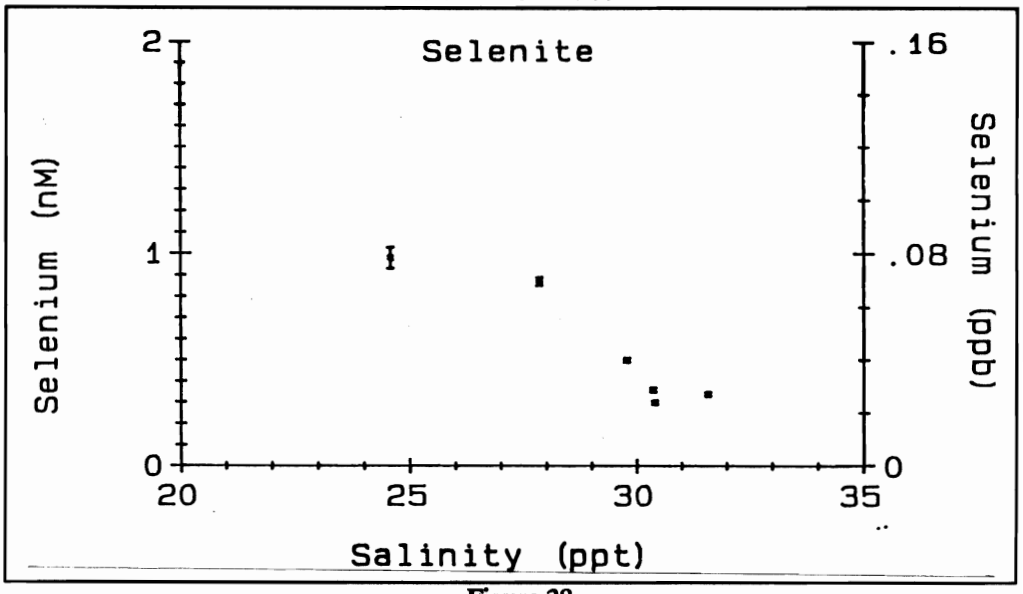

Figure 38
SELENITE DISTRIBUTION IN SURFACE WATERS FROM SOUTH AND CENTRAL SAN FRANCISCO BAY, SEPTEMBER 1986

While conclusive data are lacking, some speculation can be made with respect to the large change in South Bay selenium between April and September. It is reasonable to assume that the San Jose sewage treatment plant operates in a similar manner during both months. Therefore, any selenium speciation change in the plant effluent must represent a change in composition of water coming to the plant (i.e., from a source enriched in Se(-II + 0) in April, to one with higher total selenium and enriched in selenate in September). One mechanism to bring about such an alteration is a change in water sources between the two sampling periods. During dry summer months, water to the San Jose metropolitan area may be supplied from the Delta region (selenate-enriched); in winter, local water sources are used. Significantly, selenium concentration and speciation of the extrapolated end-member in South Bay are very similar to those in the San Joaquin and Sacramento rivers (Table 2). This explanation is merely speculative, since no confirming data have yet been obtained.

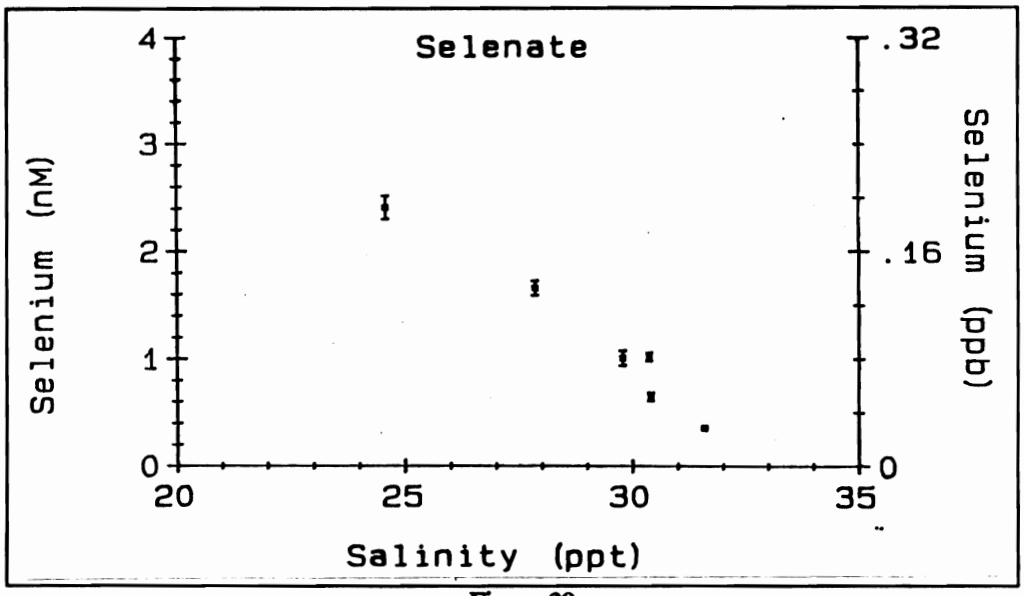

Figure 39
SELENATE DISTRIBUTION IN SURFACE WATERS FROM SOUTH AND CENTRAL SAN FRANCISCO BAY, **SEPTEMBER 1986**

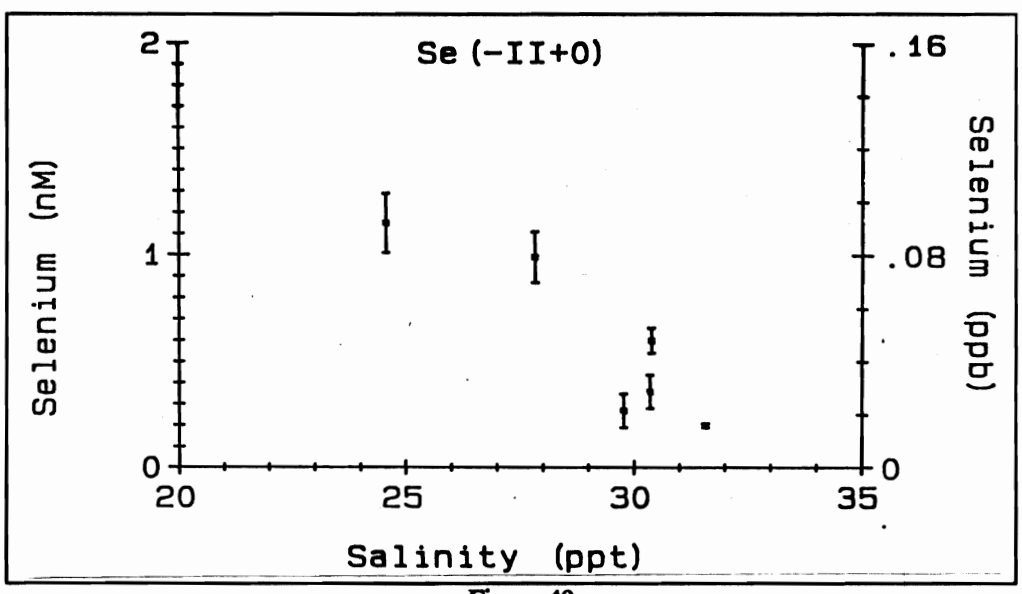

Figure 40
Se(-II + 0) DISTRIBUTION IN SURFACE WATERS FROM SOUTH AND CENTRAL SAN FRANCISCO BAY, SEPTEMBER 1986

Flux Estimates Based on the 1986 Selenium Data

In a qualitative sense, the estuary's northern reach appears to be a source for total dissolved selenium and selenite and a mixture of source and sink for selenate and Se(-II + 0). Selenium derived from South Bay that flows through the Golden Gate appears to be primarily affected by physical dilution and, thus, is conservative (i.e., no *in situ* removal or production).

To rigorously describe selenium behavior in San Francisco Bay, selenium's removal and production terms must be quantified. In this section, the selenium speciation data are modeled to derive flux estimates (riverine, internal, and estuarine). Equations given in the discussion of June 1985 data (above) are used. However, the effect of variations in riverine selenium concentrations on the salinity/selenium profiles must be considered first.

Depending on the period and magnitude of river source variations and an estuary's freshwater residence time, constituent/salinity mixing plots can be nonlinear yet still show conservative behavior. The data in Table 2 show that riverine concentrations of selenium vary with time. To correct for the effects of such source variations, the model of Officer and Lynch *(1981)* is employed. This model assumes a sinusoidally varying river source with time. Model inputs are:

- Period of riverine fluctuation;
- Amplitude of river variation;
- Mean riverine concentration about which the variation is occurring;
- Time relative to the variation when estuarine samples were taken;
- Freshwater residence time during sampling; and
- Salinities of the riverine and oceanic end-members.

Freshwater residence times for April and September 1986 were calculated using methods described by Dyer *(1973)*. Average river discharge (R) into the estuary (Delta Outflow Index) during April 1986 was 1.095×10^{14} liters/day, and freshwater residence time was calculated to be 9.8 days. In September 1986, average river discharge was 2.31×10^{10} liters/day, and freshwater residence time was 24.4 days.

Estimates of the variability with time of riverine selenium were already discussed. Since a complete yearly description of riverine selenium is not yet available, correlations between selenium and other known variables were sought. In brief, total selenium and selenate concentrations correlate with river discharge (DOI); Se(-II + 0) concentrations are highest in spring and summer; and selenite shows little variation compared to concentrations in the main estuary (i.e., selenite variations will be ignored). These results provide the information for the Officer and Lynch *(1981)* model.

For total dissolved selenium and selenate:

- The period of the source variation (1) is one year (same as DOI),
- The amplitudes (2) are 1.04 nmol/L (0.08 ppb Se) and 0.80 nmol/L (0.06 ppb Se) respectively,
- The mean riverine concentrations (3) are 1.32 nmol/L (0.10 ppb Se) and 0.80 nmol/L (0.06 ppb Se) respectively, and
- Time (4) is measured relative to October 15 (when concentrations equal the mean).

The highest Se(-II + 0) concentrations occur in spring and summer, when plankton blooms are also abundant *(Ball and Arthur, 1979)*. This is in accord with findings of Cutter and Bruland *(1984)*, and with the September 1986 data, where the maximum in Se(-II + 0) coincides with the maximum in chlorophyll *a*. If it is assumed that the concentration is correlated with biological productivity, then the riverine Se(-II + 0) maximum occurs in May and June, when chlorophyll is also at a maximum *(Ball and Arthur, 1979)*. Thus:

- The period of variation (1) for Se(-II + 0) is one year,
- The time from which it is measured (4) is February 15,
- The mean Se(-II + 0) (3) is 0.37 nmol/L (0.03 ppb Se), and
- The amplitude of the variation (2) is 0.20 nmol/L (0.02 ppb Se).

The Officer and Lynch *(1981)* model-generated total selenium, selenate, and Se(-II + 0) concentrations versus salinity were computed for April and September 1986, and these are plotted with the linear, conservative mixing lines in Figure 41 (April) and Figure 42 (September).

The model plots for all three species display nonlinear patterns, but in this situation the nonlinearity is due to physical (conservative) processes. When corrections are applied to the observed concentrations, the largest effect (12 percent correction for selenate) is in September, when freshwater residence time is longest. The largest correction in April is 5 percent for selenate.

Now that the data have been corrected for river source variations, the results can be modeled. The relationship between C^* and C_o has already been discussed, and the principle task is computing C^* values for all selenium species. While the graphical tangent method can be used (e.g., Table 3), more accurate fluxes are desired.

To accomplish this, the observed selenium species versus salinity curves were fitted using a least squares, polynomial curve fitting routine similar to that performed by Kaul and Froelich *(1984)* for

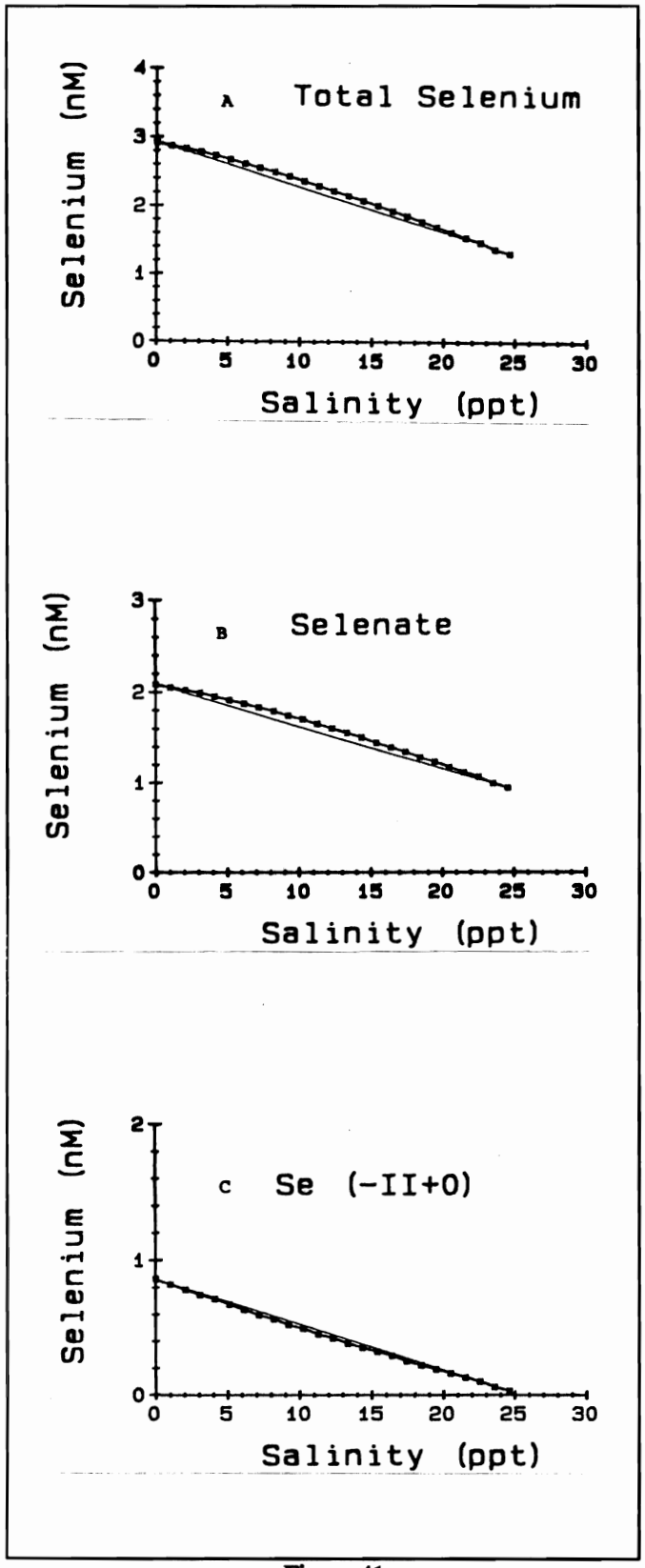

Figure 41
CONSERVATIVE MIXING LINES FOR
SAN FRANCISCO BAY,
APRIL 1986
Lines include river end-member variations.
Linear mixing lines are included for comparison.

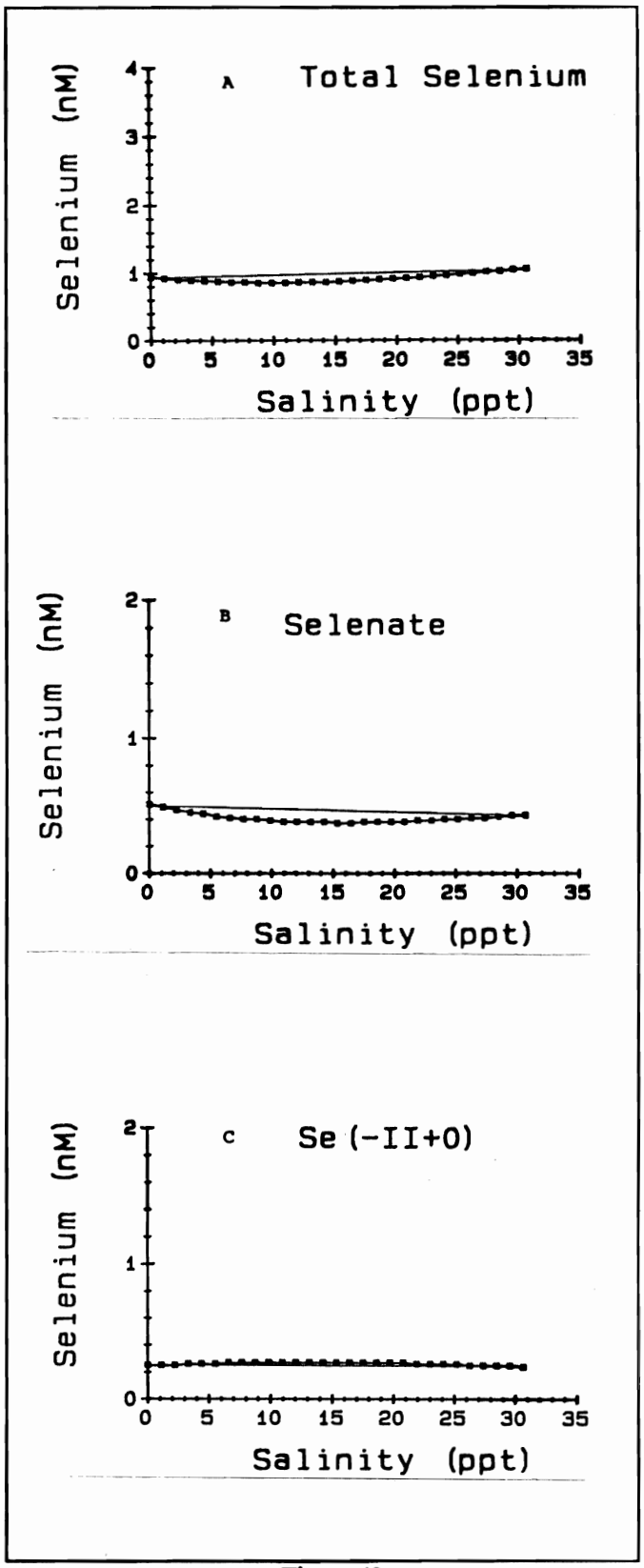

Figure 42
CONSERVATIVE MIXING LINES FOR
SAN FRANCISCO BAY
SEPTEMBER 1986
Lines include river end-member variations.
Linear mixing lines are included for comparison.

nutrients. Since the selenium results (Tables 5 and 7) have random errors due to analytical procedures and sample handling (i.e., noise), the data were smoothed prior to fitting by averaging every three successive values (e.g., points 1, 2, and 3, then 2, 3, and 4, etc.). In this manner, an equation relating selenium concentration to salinity for each species was computed, and this equation was used in the flux expressions described previously. As before, a test of the data fitting is the flux balance between total selenium and the individual selenium species.

April 1986

The selenium/salinity plots from April (Figures 12-19) clearly show selenium input from the South Bay. To derive flux estimates for the northern reach, only data from the riverine end-member to Site 6 (not affected by South Bay input) were considered. Therefore, the computed estuarine fluxes are not entirely accurate, because they do not extend to outside the Golden Gate. (Also, no samples outside the Gate were acquired.) Aside from data at Sites 4 and 5, the plots of total selenium (Figure 12), selenite (Figure 13), and Se(-II + 0) (Figure 15) are dominated by apparent estuarine input (i.e., selenium-salinity plot concave up). Selenite input is occurring between 5 and 12 ppt salinity and Se(-II + 0) input between 7 and 13 ppt. In contrast, the selenate-salinity profile (Figure 14) bows downward, indicating apparent removal between 5 and 8 ppt salinity. These types of behavior can be simulated by second order polynomial equations. The smoothed data and model fits are shown in Figure 43; curve fitting parameters and corresponding fluxes are listed in Table 8.

Table 8 shows that the estuary itself appears to be a source for total selenium, selenite, and Se(-II + 0). The internal flux of total selenium (F_{int}) is roughly equivalent to the riverine input (F_{riv}), and the estuarine export of selenium (F_{est}) is consequently doubled. For selenite and Se(-II + 0), export fluxes are dominated by their internal estuarine inputs. On the other hand, the riverine flux of selenate appears to be almost completely removed in the estuary, with the export flux almost a tenth of the riverine input. The sum of the internal fluxes for selenite, selenate, and Se(-II + 0) agree within 8 percent of that for total selenium, while the estuarine fluxes balance within 4 percent. This indicates that the fluxes are at least internally consistent (i.e., valid).

Finally, it is noteworthy that the April 1986 sampling followed a period of extremely high river discharge (Figure 6). While the data were corrected for a varying riverine end-member using the Officer and Lynch *(1981)* model, flood control diversions (e.g., the Yolo Bypass) and the complicated mixing pattern of the two rivers may affect the behavior of selenium. Estuarine sources and sinks of selenium are examined in a later section.

September 1986

The selenium/salinity plots from the September transects (Figures 32-40) do not indicate a significant effect from South Bay input. September results for the northern reach (Sites 6-25) are similar to those in June 1985 (Figure 5). Total selenium (Figure 32) and selenite (Figure 33) show input between 9 and 21 ppt salinity. Selenate input seems to occur between 9 and 13 ppt (Figure 34). Se(-II + 0) shows low salinity input and then removal from about 8 to 15 ppt (Figure 35).

A third order polynomial was chosen to represent the broad maxima (total selenium, selenite, and selenate) and combination of input and removal (Se(-II + 0)) seen in these data. The model fits to the smoothed data are shown in Figure 44; curve fitting parameters and computed fluxes are listed in Table 9.

Fluxes for September 1986 (Table 9) are similar to those in June 1985 (Table 3), with input for all species except Se(-II + 0). Internal estuarine fluxes for total selenium, selenite, and selenate are 7 to 9 times greater than the riverine fluxes. As in June 1985, all of the Se(-II + 0) river flux is removed in the northern reach. Since each profile was fitted individually, comparing the sum of the selenite, selenate, and Se(-II + 0) fluxes to the total selenium flux provides a good check of the fitting routine. For September results, internal fluxes and computed estuarine fluxes agree within 0.3 percent.

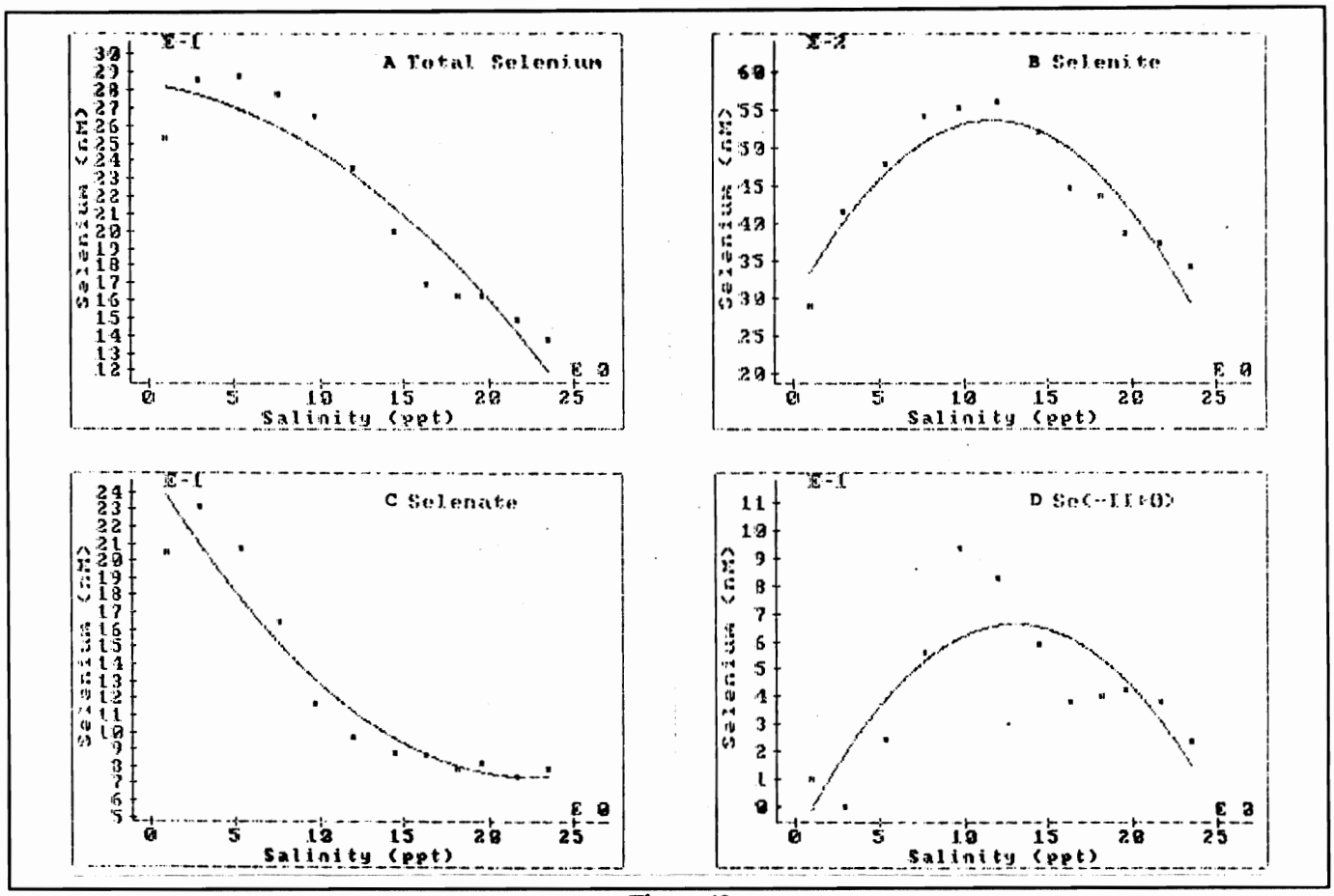

Figure 43
POLYNOMIAL FIT OF APRIL 1986 SELENIUM DATA
(3-Point Smoothed)
(Resulting flux data are listed in Table 8)

Table 8
SELENIUM FLUX DATA, APRIL 1986

Species	Curve Fit Degree	Curve Fit r^2	C_o (nmoles/L)	C^* (nmoles/L)	F_{riv} ($x\ 10^5$ moles/d)	F_{int} ($x\ 10^5$ moles/d)	F_{est} ($x\ 10^5$ moles/d)
Total Se	2	0.9020	2.02	4.43	2.21	2.64	4.85
Selenite	2	0.8530	0.21	1.45	0.22	1.37	1.59
Selenate	2	0.9173	1.51	0.17	1.65	-1.46	0.19
Se(-II+0)	2	0.6470	0.29	2.97	0.32	2.93	3.25

NOTES:

For curve fitting parameters, the degree of the polynomial and the degree of correlation are given.

A negative F_{int} indicates removal within the estuary; a positive F_{int} indicates production within the estuary.

To convert fluxes (F_{riv}, F_{int}, F_{est}) from moles Se/d to kg Se/d, multiply by 0.079.

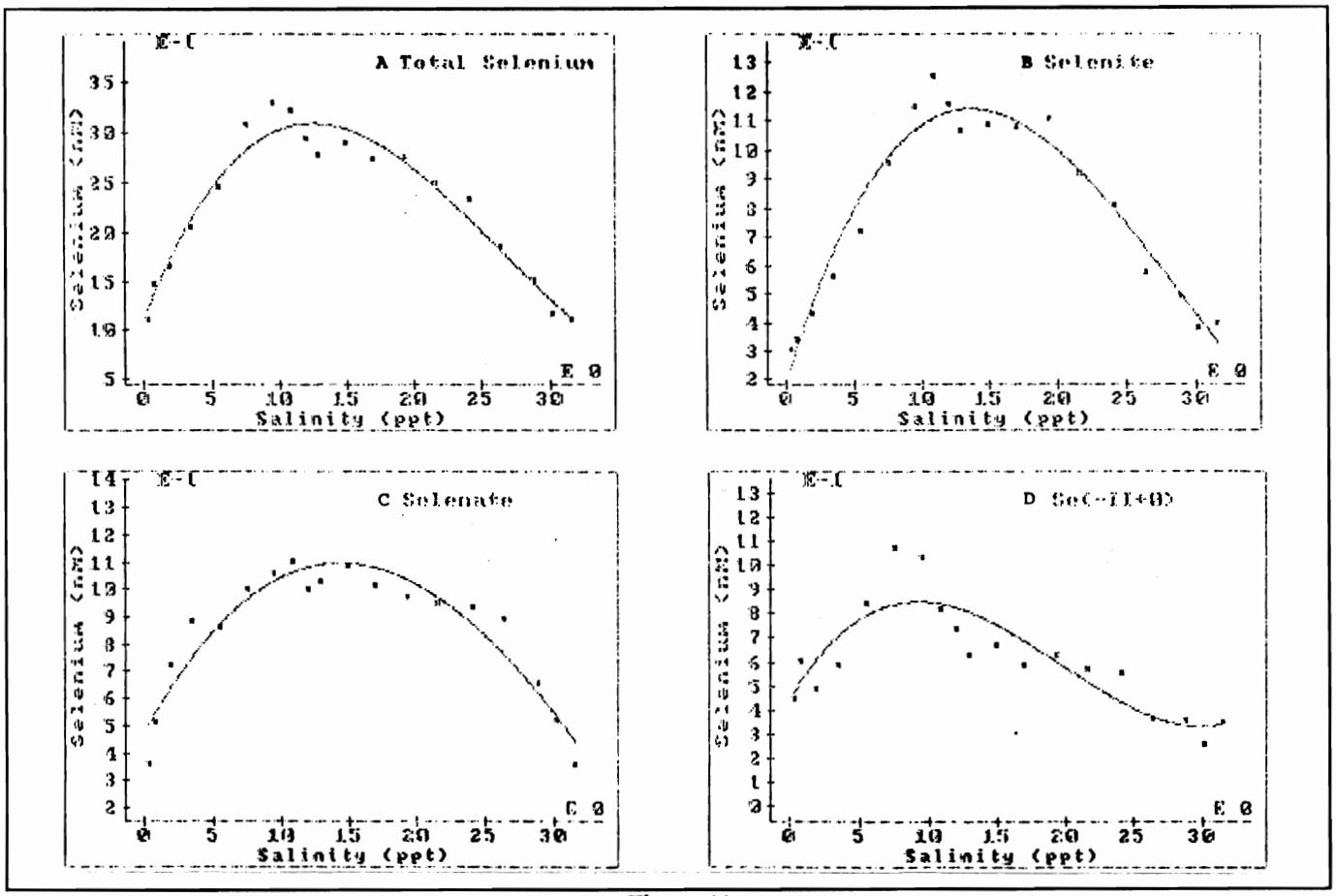

Figure 44
POLYNOMIAL FIT OF SEPTEMBER 1986 SELENIUM DATA
(3-Point Smoothed)
(Resulting flux data are listed in Table 9)

Table 9
SELENIUM FLUX DATA, SEPTEMBER 1986

Species	Curve Fit Degree	Curve Fit r^2	C_o (nmoles/L)	C^* (nmoles/L)	F_{riv} (moles/d)	F_{int} (moles/d)	F_{est} (moles/d)
Total Se	3	0.9553	0.61	4.91	14.1	99.3	113.4
Selenite	3	0.9570	0.24	2.29	5.5	47.4	52.9
Selenate	3	0.9065	0.29	2.63	6.7	54.1	60.8
Se(-II+0)	3	0.7601	0.08	0.0	1.9	-1.9	0.0

NOTES:

For curve fitting parameters, the degree of the polynomial and the degree of correlation are given.

A negative F_{int} indicates removal within the estuary, while a positive F_{int} indicates production within the estuary.

To convert fluxes (F_{riv}, F_{int}, F_{est}) from moles Se/d to kg Se/d, multiply by 0.079.

Potential Selenium Sources and Sinks in the Northern Reach

Interpretation of estuarine data with respect to input or removal of an element is based on deviations from ideal, conservative mixing (dilution). Variations in the riverine or oceanic end-members can, therefore, cause apparent nonconservative behavior (e.g., input, output). Every effort has been made to correct for such artifacts in the data presented here, but there is still a degree of uncertainty in the assessment of an *apparent* input or output of selenium.

Potential inputs of dissolved selenium species include regeneration from suspended particulate or sedimentary selenium, species interconversions (e.g., selenite oxidation to selenate), and inputs from tributaries or industrial/ municipal effluents. The first two inputs would represent nonconservative processes, while the mixing of multiple end-members (e.g., tributaries) is a conservative process. With respect to the 1986 results, inputs for selenite, selenate, and Se(-II + 0) and outputs for selenate and Se(-II + 0) need to be identified.

In terms of selenium addition or removal through particulate materials, both the estuarine sediments and the suspended matter should be considered. Since suspended matter can be affected by gravitational settling, which does not equivalently affect the water and its dissolved components, it is not possible to mass balance suspended particulate selenium with the dissolved selenium inventory.

During both sampling periods, suspended particulate selenium was a small part of the total water column selenium (dissolved + particulate). Thus, it would seem difficult to derive the needed input fluxes (via particulate to dissolved selenium regeneration) and output fluxes (via adsorption or biogenic incorporation) through changes in the concentration of suspended particulate selenium. However, particulate selenium in sediments certainly must be considered as a potential source and sink.

Kaul and Froelich *(1984)* have shown estuarine sediments to be important sources of nutrients to the overlying water column. Velinsky *(1987)* found that dissolved selenium can be mobilized from coastal salt marsh sediments under oxidizing conditions and removed when the sediments are anoxic. No estuarine results are yet available, and the role of sediments as potential sources or sinks must remain speculative.

Conversion of one selenium form to another could be a source/sink for individual species. Using regeneration experiments, Cutter *(1982)* has shown the conversion of Se(-II + 0) to selenite. The data presented here do not uniquely document such a process, since total selenium is not conserved in the estuary. Specifically, when the total concentration is changing, it is not possible to resolve *in situ* species interconversions from the input/output of individual selenium forms.

Finally, a potentially major selenium input that must be considered for San Francisco Bay is that from industrial effluents, tributaries, and sewage effluents. The South Bay data clearly show the effects of selenium input via sewage treatment effluent. Throughout the northern reach, numerous industrial and municipal effluents enter the estuary. In April and September 1986, the geographic position of the salinity changes, but the location of apparent selenium input remains at or near Carquinez Strait. This is also where most of the region's oil refineries are located.

To examine the potential input of selenium from oil refinery effluent, filtered (0.45 μm) water samples from waste discharge of the following refineries were obtained on February 24, 1987:

Chevron (Richmond),
Exxon Corp. (Benicia),
Pacific Refining Co.,
Shell Oil (Martinez),
Tosco Corp. (Avon), and
Union Oil (San Francisco).

Selenium data for these samples and the discharge rates for February 1987 are shown in Table 10.

Compared to selenium concentrations in the rivers (Tables 1 and 3), the northern reach (Tables 1, 5, and 7), and South Bay (Tables 5 and 7), the refinery effluent concentrations are extremely high. Furthermore, selenite is enriched in these effluents (48 percent of total for all samples and 72 percent in the three highest concentration effluents) relative to the other estuarine selenium inputs. Certainly more data are needed over a longer time scale, but the results shown in Table 10 can be used to initially estimate the importance of refinery effluents to selenium in the estuary.

Multiplying the monthly discharge rates for February 1987 by the selenium concentrations, the following combined input fluxes are obtained:

78.2 moles/day (6.18 kg Se/d) total selenium
49.8 moles/day (3.93 kg Se/d) selenite
16.9 moles/day (1.33 kg Se/d) selenate
11.0 moles/day (0.87 kg Se/d) Se(-II + 0).

Assuming these fluxes are representative of other months (more data are needed, but the flow rates only vary by about 30 percent over the year), then during periods of low river discharge, these fluxes would rival riverine input. Compared to the internal estuarine fluxes (F_{int}) in June 1985 (Table 3) and September 1986 (Table 9), most of the calculated selenite and selenate input fluxes can be attributed to refinery discharge. Thus, estuarine input of these selenium forms during low flow is actually a conservative (mixing) process.

In addition, input of Se(-II + 0) from the refineries suggests that the internal removal flux of Se(-II + 0) is underestimated in Tables 2 and 9 (i.e., refinery input is larger than the calculated F_{int}'s).

Overall, the data in Table 10 demonstrate the potentially significant input of selenium from refinery operations and point to the critical need for more data. In this respect, the internal source of selenium to the estuary during high river discharge is still ambiguous. The refinery effluents can account for only about 0.02 percent of the selenium flux during these periods (e.g., April 1986).

Table 10
SELENIUM IN DIRECT DISCHARGES NEAR CARQUINEZ STRAIT

Identification	Total Se *(nmol/L)*	Se(IV) *(nmol/L)*	Se(VI) *(nmol/L)*	Se(-II + 0) *(nmol/L)*	Average Discharge *($x10^6 L/d$)* Feb 1986
Chevron, Richmond Refinery	165 ± 2.7	99.4 ± 4.9	10.1 ± 7.1	56.0 ± 5.8	62.5
Exxon, Benicia Refinery	823 ± 6.1	698 ± 32.0	63.0 ± 58.0	62.0 ± 49.0	12.3
Pacific Refining Co.	83.2 ± 3.2	ND	46.3 ± 3.3	36.9 ± 3.3	0.91
Shell Oil, Martinez Refinery	1671 ± 32	1213 ± 26	309 ± 89.0	149 ± 91.0	17.9
Tosco Corp., Avon Refinery	276 ± 5.1	40.0 ± 1.6	69.4 ± 6.2	167 ± 7.8	24.0
Union Oil, S.F. Refinery	1978 ± 162	1153 ± 46	772 ± 87.0	ND	10.7

ND - Not detectable
To convert to ppb Se, multiply by 0.079

Chapter 4. CONCLUSIONS

Data acquired from 1984 to the present have gone a long way toward defining the estuarine behavior of selenium in San Francisco Bay. Within the bay, several sources can contribute dissolved selenium. Sources include: the Sacramento and San Joaquin rivers; South Bay (probably sewage effluent); oil refinery effluents near Carquinez Strait; and internal production, presumably through dissolution of particulate selenium.

The riverine sources of dissolved selenium display temporal variability, which appears to be related to discharge and seasonal biological cycles.

Selenate is the predominant selenium species in both the Sacramento and San Joaquin rivers; selenite and Se(-II + 0) are in roughly equivalent proportions. During high streamflow, selenate is also the dominant species in the northern reach, and the concentration of selenite is about half that of selenate. However, selenite and selenate are roughly equimolar in this same region during low streamflow.

The selenium speciation pattern in the South Bay undergoes large changes with time. Se(-II + 0) was the dominant form in April 1986, but selenate predominated in September 1986.

In terms of the export of selenium from the bay to coastal waters, selenite sources within the estuary add from 1 to 32 times the amount of this species brought in by the rivers.

Both estuarine removal and production of selenate and Se(-II + 0) are seen. During low streamflow, Se(-II + 0) is lost in the estuary and selenate is produced; the reverse is true under high streamflow conditions.

Thus, the cycling of selenium within San Francisco Bay is complex, with the different chemical forms displaying large temporal and spatial variability. Moreover, industrial discharges of selenium in the northern reach are significant when river discharge is low.

In spite of anthropogenic selenium inputs to San Francisco Bay, the highest concentrations found in this estuarine system (4.54 nmol/L [0.36 ppb] total selenium in South Bay and 3.64 nmol/L [0.29 ppb] total selenium in the northern reach, Table 7) are within the ranges measured in other estuaries. Further, selenium concentrations in the San Francisco Bay estuary are orders of magnitude below any used in toxicology studies. Thus, no conclusion can be made regarding the potential toxicity of selenium in the bay.

This description of selenium behavior in San Francisco Bay is by no means complete, and several topics still need to be addressed:

- Since changes in river discharge appear to alter the concentration and speciation of selenium in the bay, river monitoring of selenium should continue.
- Monitoring of industrial and municipal discharges throughout the estuary should be undertaken to accurately assess their effects on the bay's selenium cycle. In particular, these inputs potentially alter selenium behavior in South Bay and Carquinez Strait.
- Data acquired thus far have raised several questions related to the sources of selenium in the bay. River and effluent monitoring can quantify these inputs, but the role of estuarine sediments as sources and sinks of selenium needs careful study. Sediment cores (taken with a box corer) and sediment porewaters need to be acquired from throughout the estuary, but particularly in regions where apparent selenium input occurs (Suisun Bay, San Pablo Bay, and Carquinez Strait). Resulting data would allow calculation of sedimentary selenium fluxes (in and out).
- Since the April 1986 sampling occurred after unusually high river discharge, another estuarine transect during "normal" high flow conditions should be undertaken to verify the April findings. In particular, flood control measures (e.g., water bypass) and atypical flow patterns for the Sacramento and San Joaquin rivers may have induced artifacts in the estuarine distribution and speciation of selenium.

BIBLIOGRAPHY

Arthur, J. F. and M. D. Ball. 1979. Factors influencing the entrapment of suspended material in the San Francisco Bay-Delta Estuary. In San Francisco Bay: The Urbanized Estuary, T. J. Conomos, Ed. (AAAS, Washington, D.C.), pp.143-174.

Ball, M. D. and J. F. Arthur. 1979. Planktonic chlorophyll dynamics in the northern San Francisco Bay and Delta. In San Francisco Bay: The Urbanized Estuary, T. J. Conomos, Ed. (AAAS, Washington, D.C.), pp.265-286.

Boyle, E., R. Collier, A. T. Dengler, J. M. Edmond, A. C. Ng, and R. F. Stallard. 1974. On the chemical mass-balance in estuaries. Geochim. Cosmochim. Acta 38, 1719-1728.

Conomos, T. J., T. E. Smith, D. H. Peterson, S. W. Hager, and L. E. Schemel. 1979. Processes affecting seasonal distributions of water properties in the San Francisco Bay estuarine system. In San Francisco Bay: The Urbanized Estuary, T. J. Conomos, Ed. (AAAS, Washington, D.C.), pp.115-142.

Cutter, G. A. Submitted. Selenium in fresh water systems. In Distribution and Speciation of Selenium, M. Ihnat, Ed. (CRC Press, Florida), Chapt. 10.

_____. 1985. Determination of selenium speciation in biogenic particles and sediments. Anal. Chem. 57, 2951-2955.

_____. 1983. Elimination of nitrite interference in the determination of selenium by hydride generation. Anal. Chim. Acta 149, 391-394.

_____. 1982. Selenium in reducing waters. Science 217, 829-831.

_____. 1978. Species determination of selenium in natural waters. Anal. Chim. Acta 98, 59-66.

Cutter, G. A. and K. W. Bruland. 1984. The marine biogeochemistry of selenium: a re-evaluation. Limnol. Oceanogr. 29. 1179-1192.

Dyer, K. R. 1973. Estuaries, a Physical Introduction. (Wiley, London), 140 pp.

Howard, J. H., III. 1977. Geochemistry of selenium: formation of ferroselite and selenium behavior in the vicinity of oxidizing sulfide and uranium deposits. Geochim. Cosmochim. Acta 41, 1115-1678.

Kaul, L. W. and P. N. Froelich. 1984. Modeling estuarine nutrient geochemistry in a simple system. Geochim. Cosmochim. Acta 48, 1417-1433.

Measures, C. I. and J. D. Burton. 1978. Behavior and speciation of dissolved selenium in estuarine waters. Nature 273, 293-295.

Officer, C. B. 1979. Discussion of the behavior of nonconservative constituents in estuaries. Estuarine Coastal Mar. Sci. 9, 91-94.

Officer, C. B. and D. R. Lynch. 1981. Dynamics of mixing in estuaries. Estuarine Coastal Shelf Sci. 12, 525-533.

Peterson, D. H., R. E. Smith, S. W. Hager, D. D. Harmon, R. E. Herndon, and L. E. Schemel. 1985. Interannual variability in dissolved inorganic nutrients in Northern San Francisco Bay Estuary. Hydrobiologia 129, 37-58.

Shamberger, R. J. 1983. The Biochemistry of Selenium (Plenum, New York), 334pp.

Takayanagi, K. and G. T. F. Wong. 1984. Total selenium and selenium (IV) in the James River Estuary and southern Chesapeake Bay. Estuarine Coastal Shelf Sci. 18, 113-119.

Takayanagi, K. and D. Cossa. 1985. Speciation of dissolved selenium in the upper St. Lawrence Estuary. In Marine and Estuarine Geochemistry, A. C. Sigleo and A. Hattori, Eds. (Lewis Publishers, Michigan), Chapt. 19.

van der Sloot, H. A., D. Hoede, J. Wijkstra, J. C. Duinker, and R. F. Nolting. 1985. Anionic species of V, As, Se, Mo, Sb, Te and W in the Scheldt and Rhine Estuaries and the Southern Bight (North Sea). Estuarine Coastal Shelf. Sci. 21, 633-651.

Velinsky, D. J. 1987. Geochemistry of selenium and sulfur in a coastal salt marsh. Ph.D. Thesis, Dept. of Oceanography, Old Dominion Univ.

Walters, R. A., R. T. Cheng, and T. J. Conomos. 1985. Time scales of circulation and mixing processes of San Francisco Bay waters. Hydrobiologia 129, 13-36.

Wrench, J. J. 1978. Selenium metabolism in the marine phytoplankters Tetraselmis tetrathele and Dunaliella minuta. Mar. Biol. 49, 231-236.

Wrench, J. J. and N. C. Campbell. 1981. Protein bound selenium in some marine organisms. Chemosphere 10, 1155-1161.

Wrench, J. J. and C. I. Measures. 1982. Temporal variations in dissolved selenium in a coastal ecosystem. Nature 299, 431-433.