The estuarine behavior of selenium in San Francisco Bay

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The Estuarine Behaviour of Selenium in San Francisco Bay

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In April and September 1986 concentrations of dissolved selenate, selenite and Se($-$II+O), suspended particulate selenium, nutrients, chlorophyll *a* and total suspended matter, were determined in the San Francisco Bay estuarine system. In addition, dissolved selenium speciation was determined in the Sacramento and San Joaquin Rivers between 1984 and 1987. The April 1986 estuarine sampling occurred during high river discharge, and within the Northern Reach of San Francisco Bay mid-estuarine input of selenite and Se($-$II+O) is apparent, while selenate appears to be removed. During September 1986 river discharge rates were approximately four orders of magnitude lower than in April, and the mid-estuarine production of all selenium species is apparent. In contrast, dissolved selenium in the South San Francisco Bay generally shows conservative mixing behaviour during April and September 1986. The source of dissolved selenium in the South Bay appears to be effluents from sewage treatment plants. In the Northern Reach effluents from oil refineries located in the mid-estuary may be major sources of selenium input during low river discharge periods. However, during periods of high river discharge the sources and sinks of dissolved selenium species within the Northern Reach remain unidentified.

Introduction

Selenium is an element which can exist in several oxidation states (VI, selenate; IV, selenite; O, elemental selenium; $-$II, selenide) and different chemical forms within an oxidation state (e.g. organic and inorganic). The chemical speciation of selenium is particularly important in the aquatic environment since the biotic and abiotic reactivity of selenium is a function of its chemical form (Wrench & Measures, 1982; Cutter & Bruland, 1984). Furthermore, the toxicity of selenium is also affected by its chemical form (Shamberger, 1983).

While the cycling of selenium in the world's oceans has received considerable attention (e.g. Measures & Burton, 1980; Cutter & Bruland, 1984), fewer studies have examined the estuarine geochemistry of selenium. The behaviour of selenium has been studied in several English estuaries (Measures & Burton, 1978), in the James River (U.S.A.) and lower Chesapeake Bay (Takayanagi & Wong, 1984), and in Canada's St Lawrence River estuary (Takayanagi & Cossa, 1985). The concentration of total dissolved selenium in the riverine inputs ranges from 0·62–4·94 nmol l^{-1}, with selenite averaging 4% of the total in

the English Rivers (Measures & Burton, 1978), and 70–90% of the total in the James (Takayanagi & Wong, 1984) and St Lawrence Rivers (Takayanagi & Cossa, 1985). In all of the estuaries examined thus far, total dissolved selenium displays conservative mixing behaviour. With respect to selenium speciation, low salinity (< 4 ppt) removal of selenite is reported for the James River (Takayanagi & Wong, 1984) and St Lawrence River estuaries (Takayanagi & Cossa, 1985), and selenate input at low salinities is suggested in the James River estuary (Takayanagi & Wong, 1984). Finally, selenium behaviour has been examined in the heavily polluted Scheldt River estuary (Belgium). In this study, van der Sloot and co-workers (1985) found that selenite makes up $85 \pm 6\%$ of the total dissolved selenium, with concentrations up to 30 nmol l^{-1}. Their results indicate a large, presumably anthropogenic, selenite input to the estuary near the city of Antwerp.

The San Francisco Bay has been described as an 'urbanized' estuary whose shoreline and tributaries have been extensively modified (Nichols *et al.*, 1986). Furthermore, numerous industrial and municipal discharges enter the Bay. Its major tributaries, the Sacramento and San Joaquin Rivers, have large amounts of agricultural land in their drainage basin. Elevated concentrations of dissolved selenium have been found recently in agricultural drainage water which flows into the San Joaquin River (Nichols *et al.*, 1986). Because of this potential input and those from other sources (e.g. municipal/industrial discharges), an examination of selenium in the San Joaquin and Sacramento Rivers, and the San Francisco Bay is needed. This paper presents data on selenium in the estuary, and quantitatively describes the behaviour of selenium (i.e. fluxes) using estuarine geochemical models (e.g. ~~Boyle *et al.*, 1974; Officer, 1979~~; Officer & Lynch, 1981; Kaul & Froelich, 1984).

Study area

Two major rivers enter the San Francisco Bay estuary, the southward-flowing Sacramento and the northward-flowing San Joaquin. Their drainage basin encompasses approximately 153 000 km^2 (Conomos *et al.*, 1985) and the rivers join at the 'Delta' (the easternmost end of Suisun Bay, Figure 1). During most of the year when the San Joaquin discharge rate is low, little or no water from this river enters the upper estuary (Arthur & Ball, 1979). This situation occurs when export pumping (for irrigation and municipal water supplies) from the southern Delta exceeds the San Joaquin River discharge rate. Thus, most of the freshwater entering the estuary originates from the Sacramento.

Seawater enters the estuary through the Golden Gate (Figure 1) and proceeds northward through the Central, San Pablo, and Suisun Bays (the 'Northern Reach'), or southward into the South San Francisco Bay (the 'South Bay'). The total surface area of this system is 1240 km^2, with an average depth of 6·1 m (Conomos *et al.*, 1985). The freshwater residence time of the South Bay ranges from 220 to 2700 days due to minimal input from Coyote Creek (Walters *et al.*, 1985). During summer when rainfall is low, the major 'freshwater' input to the South Bay is effluent from sewage treatment plants (Conomos *et al.*, 1979). In contrast, the freshwater residence time in the Northern Reach is 1·6 to 160 days depending on river discharge from the Delta. The freshwater residence times in the Northern Reach for April and September 1986 were calculated using methods described by Dyer (1973). The average river discharge into the estuary (as measured by the Delta Outflow Index, or DOI, obtained from the U.S. Bureau of Reclamation, Mid-Pacific Region Office, Sacramento, California) during April 1986 was 1.095×10^{14} l day^{-1}, and the calculated freshwater residence time was 9·8 days. In September 1986 the
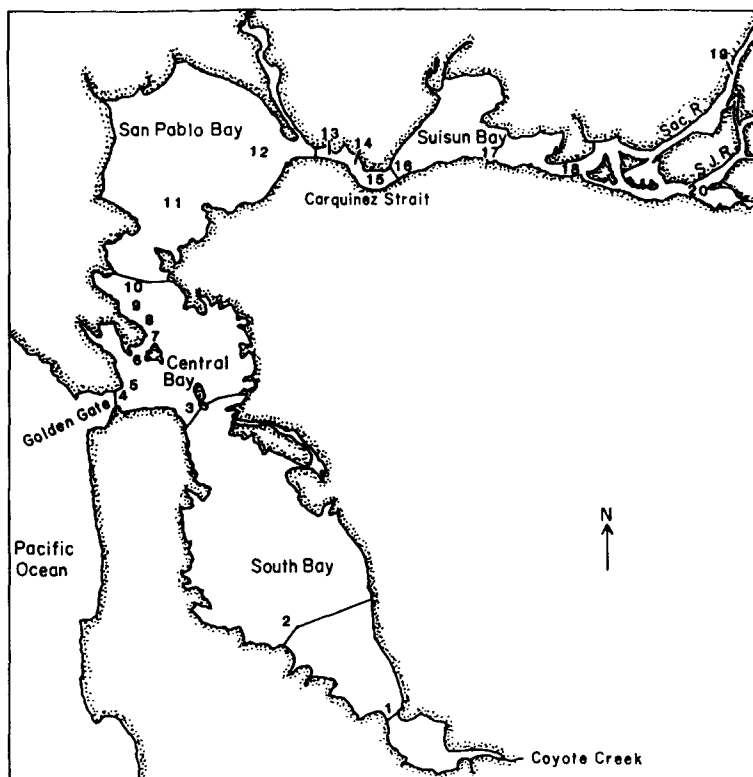
Figure 1. Station locations for the 22–23 April 1986 sampling of San Francisco Bay.

average river discharge was $2 \cdot 31 \times 10^{10} \, \mathrm{l} \, \mathrm{day}^{-1}$ and the freshwater residence time was calculated to be $24 \cdot 4$ days.

Methods

Field sampling

Estuarine samples were taken in April 22–23 and September 23–24, 1986 using the Research Vessel *Scrutiny* (U.S. Bureau of Reclamation). In April 1986, 20 stations were occupied (Figure 1), with three stations in the South San Francisco Bay, 15 in the Northern Reach, and one each in the Sacramento River (Rio Vista) and San Joaquin River (Antioch). In September 1986, a total of 26 stations were occupied, with five in the South Bay, 19 in the Northern Reach, and one each in the Sacramento and San Joaquin Rivers (Figure 2).

For the April and September 1986 field work, 5 l Go-Flo sampling bottles were used to obtain water 1 m below the surface. By pressurizing the Go-Flo bottles with nitrogen (8 psi), water was directly filtered through $0 \cdot 45 \, \mu\mathrm{m}$, pre-cleaned and -weighed Nuclepore membrane filters. Water samples were placed in 1 l linear polyethylene bottles and acidified to pH $1 \cdot 5$ with HCl. Filters were carefully folded, placed in polyethylene vials, and immediately frozen.

River samples were collected at Freeport or Green's Landing on the Sacramento River and at Vernalis on the San Joaquin River at various times between July 1984 and May
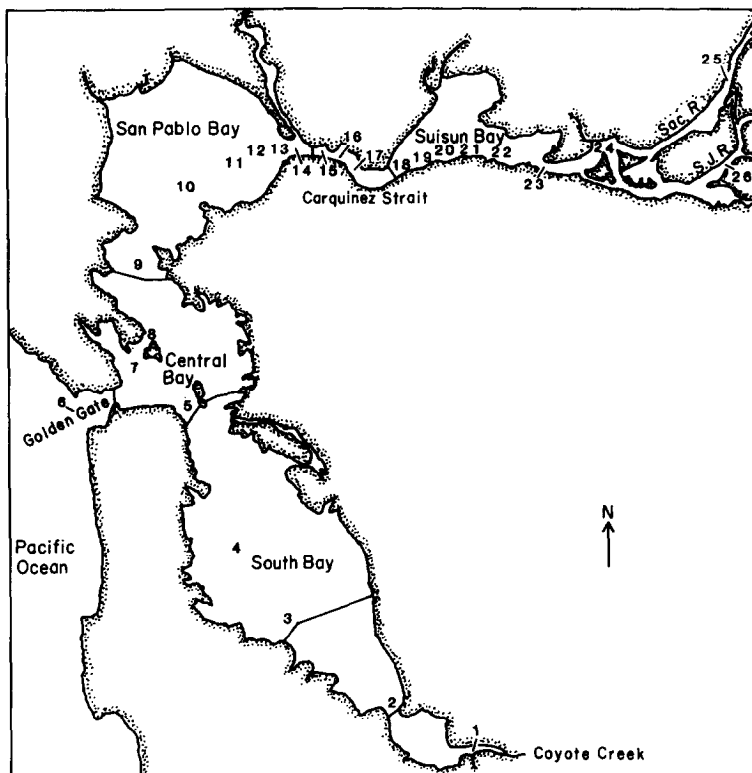
Figure 2. Station locations for the 23–24 September 1986 sampling of San Francisco Bay.

1987. For these samples, water was filtered through 0·45 μm filters, placed in linear polyethylene bottles, and acidified to pH 1·5 with HCl.

Sample analysis

Dissolved selenium speciation. The determination of dissolved total selenium, selenite, selenate, and Se(−II+O) is described elsewhere (Cutter, 1978, 1982, 1983). The technique involves selective generation of hydrogen selenide, liquid nitrogen-cooled trapping, and atomic absorption detection (0·01 nmol l^{-1} detection limit). The standard additions method of calibration is used to ensure accuracy, and all determinations are made in triplicate; precision is better than 5% at concentrations to 0·5 nmol l^{-1}. 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 at 4 M HCl acidified sample for 15 min, and then following the selenite procedure; selenate is determined by difference. The determination of total dissolved selenium entails boiling a 4 M HCl acidified sample, with potassium persulfate addition, for 1 h; the resultant solution is analyzed as a selenite sample. The difference between total selenium and selenite + selenate is the concentration of dissolved Se(−II+O). Past work has operationally called the Se(−II+O) fraction 'organic selenide' (Cutter, 1982; Cutter & Bruland, 1984).

Particulate selenium determinations. Total suspended particulate selenium determinations are made using the digestion procedure described by Cutter (1985). The pre-weighed filters are dried at 40 °C and re-weighed to determine the concentration of total suspended matter. A three step nitric-perchloric acid digestion follows, with the last step being the 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 AG1 × 8 anion exchange resin (chloride form, 100–200 mesh). After collecting the column flow-through solution, three rinses are passed through the column, and these solutions combined with the original. Experiments utilizing actual samples and standard additions of selenite and selenate show that this column procedure removes the large amounts of iron found in suspended material without affecting the speciation or concentration of selenium in the original solution (Cutter, unpublished data). Aliquots of the combined column flow-throughs are treated as total dissolved selenium samples. In this manner, the detection limit for suspended particulate selenium is $1 \cdot 0$ pmol l^{-1}, and at concentrations greater than $0 \cdot 1$ nmol l^{-1}, the precision is 8% (relative SD).

Ancillary parameters. The nutrients ammonium, nitrate, nitrite, phosphate, and silicate were determined using the colorimetric methods described by Parsons *et al.* (1984) and modified for use with an automated, continuous flow analyzer. Chlorophyll-*a* was determined on filtered material using a fluorometric method (Parsons *et al.*, 1984). Salinity was determined on a Minisal salinometer using IAPSO standard seawater as the reference.

Results and discussion

Riverine selenium

Data for dissolved selenium in the San Joaquin and Sacramento Rivers are compiled in Table 1. These results show that San Joaquin concentrations are much higher than those in the Sacramento. Total dissolved selenium in the San Joaquin ranges from $1 \cdot 72$–$36 \cdot 3$ nmol l^{-1} over a nearly three year period. In contrast, the Sacramento shows considerably less variation with time (0.50–1.40 nmol l^{-1}). With the exception of selenite, which averages $10 \pm 7\%$ of the total selenium in both rivers, the selenium speciation patterns in the Sacramento and San Joaquin also diverge. In the Sacramento River selenate is $48 \pm 15\%$ and Se($-$II$+$0) is $40 \pm 15\%$ of the total, while selenate averages $74 \pm 13\%$ and Se($-$II$+$O) averages $19 \pm 14\%$ of the total dissolved selenium in the San Joaquin.

As noted above, most of the water in the San Joaquin River is diverted from the estuary. For the period examined here, San Joaquin River water entered the Delta only during April and May 1986. Since the Sacramento and San Joaquin join near the head of the estuary, the riverine selenium data for these two periods can be combined via weighting the selenium concentration by the river discharge, adding the two together and re-computing a ' single ' river end-member concentration. For April 16, 1986 the discharge-weighted selenium concentrations are $4 \cdot 06$ nmol l^{-1} total selenium, $0 \cdot 25$ nmol l^{-1} selenite, $3 \cdot 28$ nmol l^{-1} selenate and $0 \cdot 53$ nmol l^{-1} Se($-$II$+$O). The discharge-weighted values for May 1, 1986 are $1 \cdot 95$ nmol l^{-1} total selenium, $0 \cdot 22$ nmol l^{-1} selenite, $1 \cdot 13$ nmol l^{-1} selenate and $0 \cdot 60$ nmol l^{-1} Se($-$II$+$O).

A continuous seasonal data set for riverine selenium is not yet available. However, the Sacramento data in Table 1 (recall that the primary water input is from the Sacramento) and the two discharge-weighted river inputs for April and May 1986 can be used to initially describe the temporal variability of riverine selenium input to San Francisco

TABLE 1. Selenium in the Sacramento and San Joaquin Rivers

Date	DOI[a]	Total Se (nmol l^{-1})	Se(IV) (nmol l^{-1})	Se(VI) (nmol l^{-1})	Se($-$II$+$0) (nmol l^{-1})
Sacramento River (Freeport/Green's Landing)					
24/7/84	2·70	0·65 $\pm$ 0·01	0·09 $\pm$ 0·01	0·29 $\pm$ 0·04	0·27 $\pm$ 0·04
6/9/84	2·50	0·81 $\pm$ 0·05	ND	0·35 $\pm$ 0·05	0·46 $\pm$ 0·07
23/10/84	2·20	0·71 $\pm$ 0·05	0·11 $\pm$ 0·01	0·33 $\pm$ 0·01	0·27 $\pm$ 0·05
8/1/85	3·46	1·04 $\pm$ 0·05	0·07 $\pm$ 0·02	0·92 $\pm$ 0·03	ND
20/6/85	0·92	0·50 $\pm$ 0·03	0·13 $\pm$ 0·01	0·25 $\pm$ 0·01	0·12 $\pm$ 0·03
16/4/86	10·00	1·40 $\pm$ 0·02	0·14 $\pm$ 0·006	0·94 $\pm$ 0·04	0·32 $\pm$ 0·04
1/5/86	3·39	1·32 $\pm$ 0·05	0·21 $\pm$ 0·007	0·60 $\pm$ 0·02	0·51 $\pm$ 0·05
29/8/86	1·20	1·18 $\pm$ 0·09	0·09 $\pm$ 0·03	0·68 $\pm$ 0·04	0·41 $\pm$ 0·09
17/9/86	2·05	1·12 $\pm$ 0·06	0·17 $\pm$ 0·01	0·57 $\pm$ 0·04	0·38 $\pm$ 0·07
29/9/86	4·23	1·21 $\pm$ 0·08	0·44 $\pm$ 0·02	0·15 $\pm$ 0·08	0·73 $\pm$ 0·10
15/10/86	3·04	0·86 $\pm$ 0·03	0·03 $\pm$ 0·00	0·25 $\pm$ 0·02	0·58 $\pm$ 0·04
9/12/86	2·86	0·69 $\pm$ 0·01	0·07 $\pm$ 0·00	0·43 $\pm$ 0·01	0·19 $\pm$ 0·01
23/12/86	2·77	0·64 $\pm$ 0·02	0·06 $\pm$ 0·00	0·34 $\pm$ 0·03	0·24 $\pm$ 0·04
9/1/87	4·27	1·00 $\pm$ 0·03	0·14 $\pm$ 0·01	0·40 $\pm$ 0·01	0·46 $\pm$ 0·03
28/1/87	2·64	0·84 $\pm$ 0·04	ND	0·42 $\pm$ 0·01	0·41 $\pm$ 0·04
9/2/87	2·46	1·27 $\pm$ 0·02	0·08 $\pm$ 0·01	0·73 $\pm$ 0·01	0·46 $\pm$ 0·02
23/2/87	3·07	1·00 $\pm$ 0·02	0·06 $\pm$ 0·01	0·48 $\pm$ 0·03	0·46 $\pm$ 0·04
12/3/87	4·35	0·84 $\pm$ 0·01	0·12 $\pm$ 0·03	0·30 $\pm$ 0·03	0·43 $\pm$ 0·03
1/4/87	2·35	0·93 $\pm$ 0·02	0·11 $\pm$ 0·01	0·41 $\pm$ 0·02	0·41 $\pm$ 0·03
20/4/87	1·47	0·98 $\pm$ 0·04	0·12 $\pm$ 0·01	0·39 $\pm$ 0·01	0·47 $\pm$ 0·04
San Joaquin River (Vernalis)					
24/7/84	2·70	9·06 $\pm$ 0·23	0·94 $\pm$ 0·05	8·38 $\pm$ 0·47	ND
6/9/84	2·50	5·61 $\pm$ 0·34	1·22 $\pm$ 0·10	3·59 $\pm$ 0·13	0·80 $\pm$ 0·35
23/10/84	2·20	1·72 $\pm$ 0·05	0·27 $\pm$ 0·01	1·23 $\pm$ 0·01	0·22 $\pm$ 0·05
8/1/85	3·46	5·10 $\pm$ 0·36	0·19 $\pm$ 0·01	4·44 $\pm$ 0·08	0·47 $\pm$ 0·37
20/6/85	0·92	28·6 $\pm$ 0·09	1·07 $\pm$ 0·04	16·9 $\pm$ 0·10	10·6 $\pm$ 0·90
16/4/86	10·00	7·69 $\pm$ 0·52	0·40 $\pm$ 0·03	6·48 $\pm$ 0·14	0·81 $\pm$ 0·54
1/5/86	3·39	4·76 $\pm$ 0·16	0·28 $\pm$ 0·02	3·46 $\pm$ 0·06	1·02 $\pm$ 0·17
29/8/86	1·20	18·7 $\pm$ 0·5	1·75 $\pm$ 0·13	15·3 $\pm$ 0·6	1·67 $\pm$ 0·75
17/9/86	2·05	6·59 $\pm$ 0·30	0·77 $\pm$ 0·06	5·84 $\pm$ 0·27	ND
29/9/86	4·23	8·05 $\pm$ 0·02	0·43 $\pm$ 0·03	4·88 $\pm$ 0·21	2·74 $\pm$ 0·21
15/10/86	3·04	6·90 $\pm$ 0·18	0·58 $\pm$ 0·02	5·72 $\pm$ 0·04	0·60 $\pm$ 0·18
21/11/86	2·20	9·29 $\pm$ 0·24	0·70 $\pm$ 0·02	8·39 $\pm$ 0·30	ND
4/12/86	2·39	11·3 $\pm$ 0·4	0·54 $\pm$ 0·00	10·9 $\pm$ 0·7	ND
16/12/86	2·36	5·78 $\pm$ 0·05	0·68 $\pm$ 0·01	3·60 $\pm$ 0·02	1·50 $\pm$ 0·05
6/1/87	4·52	14·2 $\pm$ 0·8	0·74 $\pm$ 0·02	10·4 $\pm$ 0·02	3·06 $\pm$ 0·85
22/1/87	2·31	20·5 $\pm$ 0·7	1·08 $\pm$ 0·01	13·9 $\pm$ 0·9	5·54 $\pm$ 1·17
6/2/87	4·82	31·3 $\pm$ 1·9	1·41 $\pm$ 0·04	16·9 $\pm$ 0·1	13·0 $\pm$ 1·9
19/2/87	7·05	31·1 $\pm$ 2·0	1·40 $\pm$ 0·04	19·3 $\pm$ 0·3	10·4 $\pm$ 2·1
10/3/87	6·76	29·4 $\pm$ 1·5	1·20 $\pm$ 0·01	16·8 $\pm$ 0·1	11·4 $\pm$ 1·5
25/3/87	5·20	36·3 $\pm$ 1·5	1·93 $\pm$ 0·02	23·0 $\pm$ 2·0	11·4 $\pm$ 2·5
9/4/87	1·52	22·6 $\pm$ 1·3	1·85 $\pm$ 0·07	17·9 $\pm$ 1·1	2·83 $\pm$ 1·73
23/4/87	1·64	12·1 $\pm$ 0·1	1·34 $\pm$ 0·02	8·19 $\pm$ 0·50	2·57 $\pm$ 0·50

[a]—Delta Outflow Index ($\times 10^{10}$ l day^{-1}). Data obtained from the U.S. Bureau of Reclamation, Mid-Pacific Region, Sacramento, CA.
ND = non-detectable ($< 0·01$ nmol l^{-1}).

Bay. First, the concentrations of total selenium and selenate appear to be related to river discharge. When the total selenium and selenate concentrations are plotted against the DOI at the time of sampling, a roughly linear relationship (increased DOI, increased selenium concentration) is obtained (total selenium, $r = 0·8388$, $n = 20$, mean

TABLE 2. San Francisco Bay ancillary data (22–23 April 1986)

Station no.	Salinity ppt	Chlorophyll-a (μg l^{-1})	TSM (mg l^{-1})	PO$_4^{3-}$ (μmol l^{-1})	NO$_2^{-}$ (μmol l^{-1})	NO$_3^{-}$ (μmol l^{-1})	NH$_3$ (μmol l^{-1})
1	17·54	49·23	64·60	5·81	0·64	7·14	0·50
2	20·40	10·74	35·72	2·90	0·57	3·50	1·07
3	24·06	5·89	16·60	2·10	0·71	12·14	2·07
4	26·82	4·72	24·64	1·94	0·79	7·14	1·64
5	25·72	4·08	24·64	2·06	0·70	14·29	1·71
6	25·74	3·32	17·52	1·90	0·71	15·00	1·36
7	23·73	4·00	29·91	1·90	0·79	15·71	1·93
8	20·96	3·20	27·49	1·81	0·70	13·57	1·60
9	20·19	3·12	26·57	1·74	0·71	12·86	0·71
10	17·67	4·31	25·35	1·65	0·64	11·43	0·64
11	16·49	12·23	31·64	1·90	0·71	15·00	1·57
12	14·62	12·28	17·92	2·29	0·71	15·71	2·29
13	12·30	9·71	13·88	2·00	0·71	17·14	2·79
14	9·15	13·78	23·90	1·97	0·71	17·86	3·36
15	7·67	14·37	27·65	2·06	0·79	18·57	4·07
16	6·06	12·16	58·86	2·23	0·60	20·71	6·80
17	2·11	9·21	63·69	2·06	0·64	20·71	5·00
18	0·53	3·92	41·86	2·06	0·60	21·42	5·90
19	0·09	2·50	20·13	1·58	0·40	17·86	7·00
20	0·09	2·24	27·90	2·03	0·60	20·71	4·90

All samples taken 1 m below surface, TSM = total suspended matter.

concentration $= 1\cdot11 \pm 0\cdot76$ nmol l^{-1}; selenate, $r = 0\cdot8540$, $n = 20$, mean concentration $= 0\cdot61 \pm 0\cdot61$ nmol l^{-1}). Historical data (Conomos *et al.*, 1979) show that the maximum river discharge occurs in January-February, and that the minimum discharge is during July-August. Therefore, maximum riverine concentrations of total selenium and selenate would be anticipated in the winter months. Selenite and Se($-$II$+$O) do not display this strong correlation with river discharge (selenite *vs.* DOI, $r = 0\cdot4220$, $n = 20$; Se($-$II$+$O) *vs.* DOI, $r = 0\cdot2160$, $n = 20$). Se($-$II$+$O) concentrations are actually highest in the spring and summer, while variations in selenite concentration are minimal compared to downstream values (i.e. have little effect on the estuarine distribution).

April 1986 transect

The April sampling was designed to examine the behaviour of selenium during high river discharge. Since freshwater residence time changes dramatically with discharge, the net effect of estuarine reactions (removal, production) on selenium can also vary. While data from April represent high discharge conditions, they may be slightly atypical due to severe flooding in Northern California in February 1986. The exact effect of this flood on the estuarine behaviour of selenium is difficult to predict, but it must be kept in mind when examining the data.

Ancillary data. The ancillary data for the April 1986 sampling include nutrients, chlorophyll a, salinity and total suspended matter; these data are contained in Table 2. In general, the concentration and distributions of the nutrients ammonium, nitrate, and phosphate are similar to those presented by Peterson *et al.* (1985) for typical ' wet ' May-June periods. The data for chlorophyll-a in the Northern Reach (Figure 3) show a pronounced maximum in the 2–12 ppt salinity range, corresponding to the San Pablo
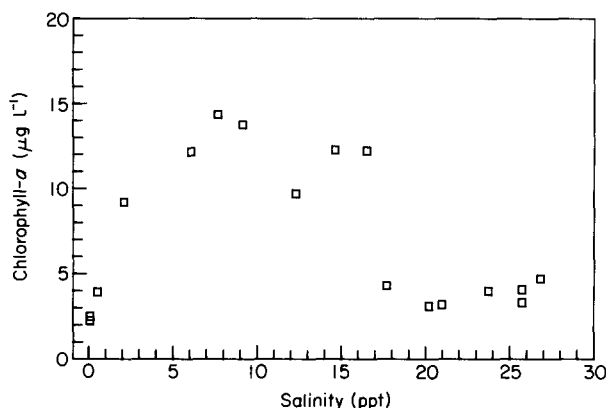
Figure 3. Surface water distribution of chlorophyll-*a* in the Northern Reach of San Francisco Bay, April 1986. There are two concentrations at ' 0 ' salinity, and represent data from the two river stations (Stations 19 and 20, Figure 1).

Bay and Carquinez Strait. These data are consistent with those presented by Ball and Arthur (1979) for high river discharge conditions. Finally, total suspended matter (Table 2) has a maximum of $63 \cdot 7$ mg l^{-1} which occurs in Suisun Bay and an average of $24 \cdot 3$ mg l^{-1} in the rest of the Northern Reach. The location of the TSM maximum is similar to that found by Arthur and Ball (1979) for periods of high river discharge.

Selenium data. Selenium speciation data for all stations are listed in Table 3 and displayed in Figures 4–6. Total selenium concentrations in the two rivers (Stations 19 and 20) differ by over a factor of two (Table 3), with the higher concentration in the San Joaquin being consistent with the previous riverine data (Table 1). As in the riverine discussion above, if the Sacramento and San Joaquin concentrations are discharge-weighted and conservatively mixed, then total selenium in the ' single ' riverine end-member is $2 \cdot 02$ nmol l^{-1}. Throughout the Northern Reach total dissolved selenium (Figure 4) is nearly conservative, but shows some production in the upper estuary (Suisun Bay) and elevated concentrations at the two stations nearest the Golden Gate (Stations 4 and 5 in Figure 1).

The concentrations of selenite at the river stations (Table 3) are nearly identical, and the discharge-weighted selenite concentration is calculated to be $0 \cdot 21$ nmol l^{-1}. The selenite-salinity distribution for the Northern Reach (Figure 4) has a maximum centered at approximately 9 ppt salinity (Stations 14–16 in the Carquinez Strait), with selenite making-up 23% of the total dissolved selenium. In contrast to selenite, selenate concentrations are very different in the two rivers (Table 3), with the San Joaquin value over twice that in the Sacramento; the discharge-weighted riverine selenate concentration is calculated to be $1 \cdot 51$ nmol l^{-1}. Selenate displays non-conservative behaviour in the Northern Reach, with apparent removal in the 6–12 ppt salinity range dominating the profile (Figure 4). At its low salinity maximum (Stations 16–18) selenate averages 82% of the total, and then averages 49% in the rest of the Northern Reach.

Since $Se(-II+O)$ is determined as the difference between total selenium and selenite + selenate, the observed precision is poorer (larger error bars). When the error is larger than the calculated concentration, $Se(-II+O)$ is considered non-detectable (e.g. Table 3, Station 16). The $Se(-II+O)$-salinity distribution (Figure 4) displays two maxima, one centered at 10 ppt salinity and another near the Golden Gate. The discharge-
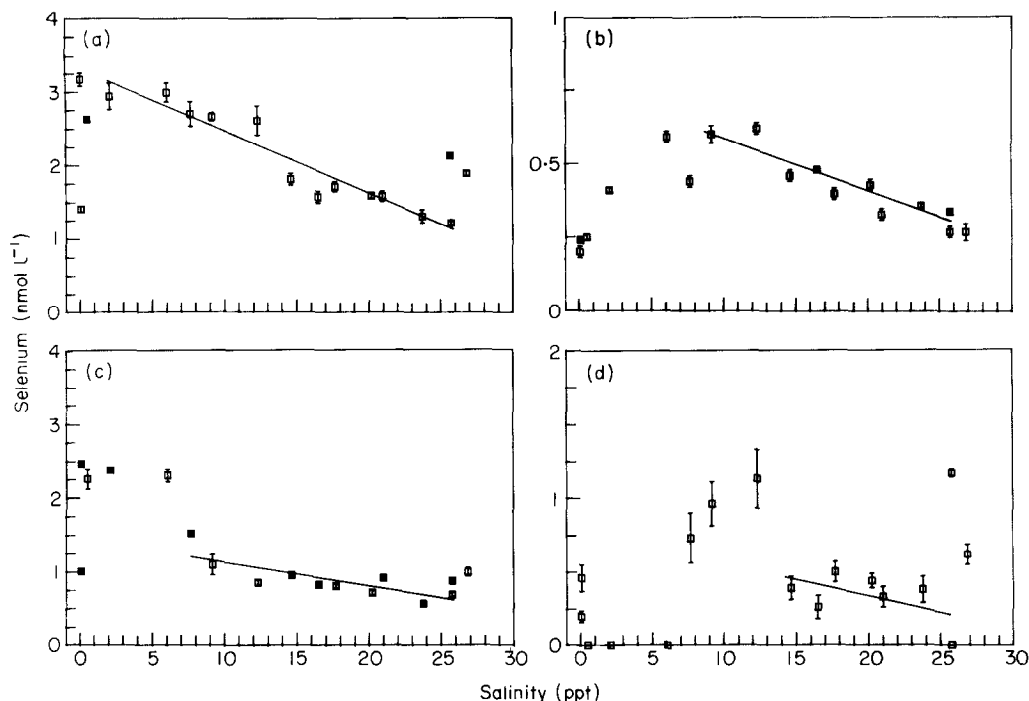
Figure 4. Distributions of (a) total dissolved selenium, (b) selenite, (c) selenate and (d) Se ($-$II$+$O) in surface waters from the Northern Reach of San Francisco Bay, April 1986. Straight lines show the best linear regression fits to the data over the following salinity ranges: total selenium, 2·11–25·74 ppt; selenite, 9·15–25·74 ppt; selenate, 7·67–25·74 ppt; Se($-$II$+$O), 14·62–25·74 ppt. Selenium data from the two stations nearest the Golden Gate (Stations 4 and 5, Figure 1) are not included in these regressions. There are two concentrations at '0' salinity, and represent data from the two river stations (Stations 19 and 20, Figure 1).

weighted riverine Se($-$II$+$O) concentration is 0·29 nmol l^{-1}, and amounts to 14% of the total dissolved selenium. In its low salinity maximum Se($-$II$+$O) reaches 35% of the total, while the high salinity maximum is 44% of the total selenium.

An examination of estuarine selenium cannot be simply restricted to dissolved species. The concentration–salinity profile for suspended particulate selenium in the Northern Reach shows a maximum, like that for total suspended matter, in the low salinity region (Figure 5). Throughout the Northern Reach's surface waters, suspended particulate selenium averages 7·1 $\pm$ 1·7% ($n=13$) of the total dissolved selenium. In terms of the selenium concentration on the particles themselves (Figure 5, the results were calculated using the TSM data in Table 2 and particulate selenium data in Table 3), the highest values are found near the Carquinez Strait (average of 0·64 µg Se g^{-1} for Stations 12–15), with the particulate selenium concentration averaging 0·33 µg Se g^{-1} at the remaining stations in the Northern Reach.

As noted above, anomalously high concentrations of total selenium and Se($-$II$+$O) are found near the Golden Gate (Stations 4 and 5), especially in comparison to typical Pacific Ocean concentrations (e.g. 0·75 nmol l^{-1} total selenium, Cutter & Bruland, 1984). In addition to water from the Northern Reach, the South and Central Bays contribute to the outflow through the Golden Gate. When selenium data from the South Bay transect
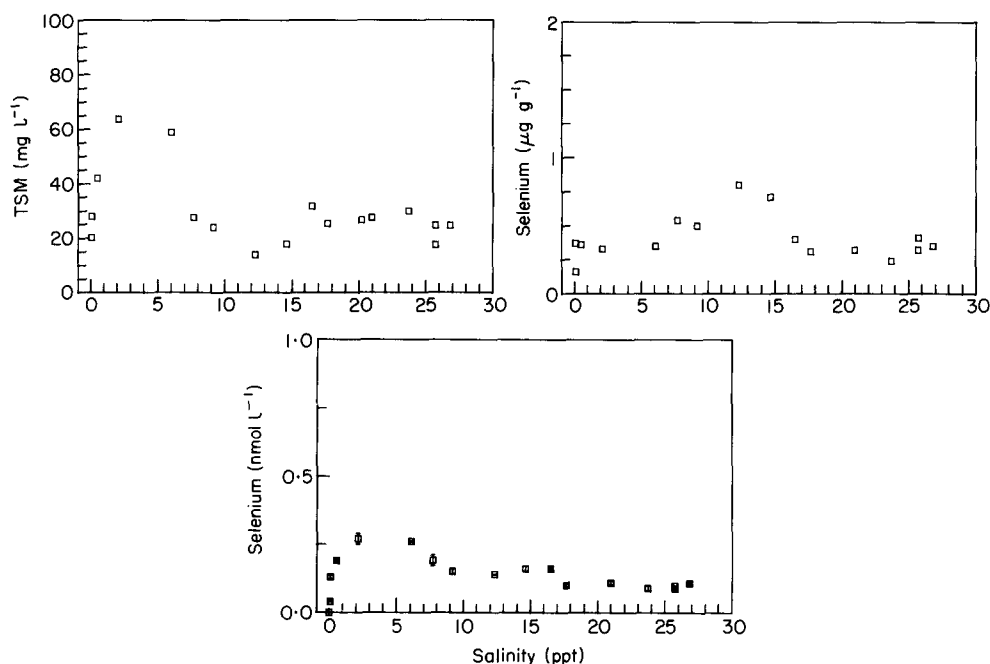
Figure 5. Distributions of total suspended matter (TSM), the selenium concentration in the suspended matter, and the total concentration of suspended particulate selenium in surface waters from the Northern Reach of San Francisco Bay, April 1986. There are two concentrations at '0' salinity, and represent data from the two river stations (Stations 19 and 20, Figure 1).

(Stations 1–5, Figure 1) are plotted against salinity (Figure 6), linear mixing lines are obtained for Se($-$II$+$O) ($r = 0.9631$, $n = 5$) and total selenium ($r = 0.9771$, $n = 5$); the behaviours of selenite and selenate are more complex. These results strongly indicate that the elevated total selenium and Se($-$II$+$O) concentrations at the Golden Gate originate in the South Bay. With respect to the selenium concentration in the South Bay's freshwater end-member, extrapolating the linear mixing lines to zero salinity yields a total selenium concentration of 8.2 nmol l^{-1} and a Se($-$II$+$O) concentration of 6.2 nmol l^{-1}. The sources of this selenium input may be effluents from sewage treatment plants since they are the dominant source of water and dissolved nutrients to the South Bay during much of the year (Conomos *et al.*, 1979); this topic will be discussed below.

September 1986 transect

The primary emphasis in the September 1986 field work was to obtain selenium data during a period of low river discharge (longer freshwater residence time), to perform more detailed surface water sampling (closer salinity spacing), and to make a more thorough survey of selenium in the South Bay.

Ancillary data. The ancillary data for the September 1986 sampling includes nutrients, chlorophyll-*a*, and total suspended matter; these data are found in Table 4. The concentrations and estuarine distributions of ammonium, nitrate, phosphate, and silicate in the Northern Reach are essentially the same as those described by Peterson *et al.* (1985) for a typical September with an intermediate river discharge.
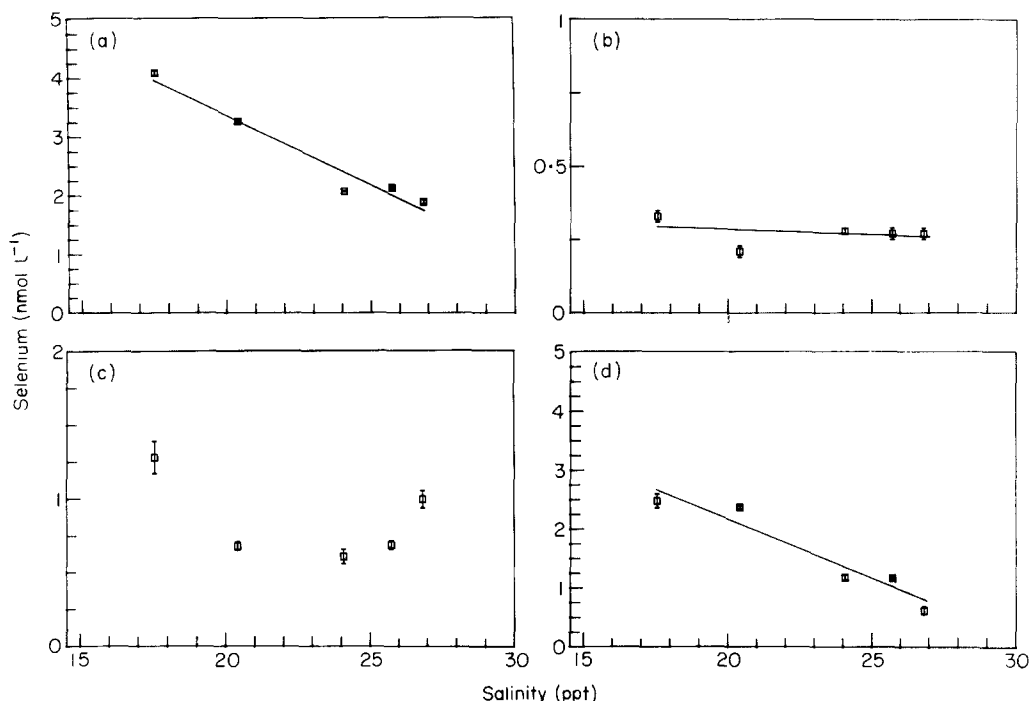
Figure 6. Distributions of (a) total dissolved selenium, (b) selenite, (c) selenate and (d) Se($-$II+0) in surface waters of the South and Central San Francisco Bay, April 1986. Straight lines indicate the best linear regression fits to the data (none plotted for selenate).

The distribution of chlorophyll-a in September 1986 (Figure 7) displays a maximum concentration in western Suisun Bay (average of $7 \cdot 1 \mu g \ l^{-1}$), with a second, smaller maximum in San Pablo Bay. Compared to a September with similar river discharge (Ball & Arthur, 1979), the observed chlorophyll maximum is a factor of four lower in concentration and shifted slightly downstream. The highest concentrations of total suspended matter (Table 4) are also found in the upper portion of the estuary (Station 24, $59 \cdot 53 \ mg \ l^{-1}$) and in San Pablo Bay ($63 \cdot 75 \ mg \ l^{-1}$, Station 12). Excluding data from the two stations above and below these maxima, total suspended matter averages $19 \cdot 8 \ mg \ l^{-1}$ in the Northern Reach. It should be noted that the upper San Pablo Bay (Stations 11–13) was sampled on a high slack tide in high winds. Under these conditions, Arthur and Ball (1979) report 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.

Selenium data. Data for selenium species at all September 1986 stations can be found in Table 5; Figures 8–10 show these data versus salinity. The 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. Since the major riverine input is the Sacramento (refer to the discussion above), the riverine end-member for total dissolved selenium in September is taken to be $0 \cdot 61 \ nmol \ l^{-1}$. Proceeding down the estuary, the concentration of total dissolved selenium (Figure 8) increases to a broad maximum

TABLE 3. San Francisco Bay selenium data (22–23 April 1986)

Station no.	Total Se (nmol l^{-1})	Se(IV) (nmol l^{-1})	Se(VI) (nmol l^{-1})	Se($-$II$+$0) (nmol l^{-1})	Part. Se (nmol l^{-1})
1	4·09 ± 0·05	0·33 ± 0·02	1·28 ± 0·11	2·48 ± 0·12	0·31 ± 0·02
2	3·26 ± 0·02	0·21 ± 0·02	0·68 ± 0·03	2·37 ± 0·03	0·03 ± 0·02
3	2·07 ± 0·01	0·28 ± 0·01	0·61 ± 0·05	1·18 ± 0·05	0·10 ± 0·004
4	1·89 ± 0·04	0·27 ± 0·02	1·00 ± 0·06	0·62 ± 0·07	0·11 ± 0·003
5	2·13 ± 0·02	0·27 ± 0·02	0·69 ± 0·03	1·17 ± 0·03	0·10 ± 0·001
6	1·22 ± 0·03	0·34 ± 0·006	0·88 ± 0·02	ND	0·09 ± 0·005
7	1·31 ± 0·09	0·36 ± 0·01	0·57 ± 0·02	0·38 ± 0·09	0·09 ± 0·01
8	1·58 ± 0·07	0·33 ± 0·02	0·92 ± 0·02	0·33 ± 0·07	0·11 ± 0·007
9	1·59 ± 0·04	0·43 ± 0·02	0·72 ± 0·04	0·44 ± 0·05	NS
10	1·71 ± 0·07	0·40 ± 0·02	0·81 ± 0·03	0·50 ± 0·07	0·10 ± 0·006
11	1·57 ± 0·08	0·48 ± 0·005	0·83 ± 0·02	0·26 ± 0·08	0·16 ± 0·004
12	1·81 ± 0·08	0·46 ± 0·02	0·96 ± 0·02	0·39 ± 0·08	0·16 ± 0·01
13	2·61 ± 0·20	0·62 ± 0·02	0·86 ± 0·04	1·13 ± 0·20	0·14 ± 0·001
14	2·66 ± 0·06	0·60 ± 0·03	1·10 ± 0·14	0·96 ± 0·15	0·15 ± 0·01
15	2·70 ± 0·17	0·44 ± 0·02	1·53 ± 0·02	0·73 ± 0·17	0·19 ± 0·02
16	2·99 ± 0·13	0·59 ± 0·02	2·31 ± 0·09	ND	0·26 ± 0·002
17	2·94 ± 0·18	0·41 ± 0·01	2·38 ± 0·02	ND	0·27 ± 0·02
18	2·63 ± 0·02	0·25 ± 0·01	2·26 ± 0·14	ND	0·19 ± 0·004
19	1·41 ± 0·04	0·20 ± 0·02	1·01 ± 0·02	0·20 ± 0·04	0·04 ± 0·002
20	3·17 ± 0·09	0·24 ± 0·006	2·47 ± 0·02	0·46 ± 0·02	0·13 ± 0·007

ND = non-detectable (< 0·01 nmol l^{-1}), NS = no sample.

between 10–20 ppt (average concentration, 2·79 nmol l^{-1}, $n = 9$), with a decrease thereafter to the seawater end-member. Unlike April 1986, no total selenium anomaly is observed near the Golden Gate.

The distribution of selenite $vs.$ salinity in the Northern Reach (Figure 8) is very similar to the distribution of total dissolved selenium. Selenite differs by 27% in the two river stations, and the riverine concentrations are higher than those found in April by approximately 40%. The single riverine end-member is 0·24 nmol l^{-1} and is 39% of the total selenium. The large selenite maximum located between 9–20 ppt has an average concentration of 1·13 nmol l^{-1} ($n = 9$), and is 41% of the total selenium in this region. In the lower estuary selenite decreases in concentration, making up 38% of the total dissolved selenium in the seawater end-member.

The profile of selenate $vs.$ salinity in the Northern Reach (Figure 8) for September is very different than that in April 1986. Selenate concentrations in the two river stations are identical (Table 5), and the riverine end-member is thus 0·29 nmol l^{-1} (48% of the total selenium). Selenate increases with salinity to a maximum between 10–14 ppt, and then decreases towards the seaward end-member. Selenate concentrations change rapidly near the Golden Gate, a feature reminiscent of the April total selenium and Se($-$II$+$O) data (Figure 4). In the three highest salinity stations (Stations 6–8) selenate averages 0·36 nmol l^{-1}, or 33% of the total dissolved selenium.

Like the April 1986 data set, error bars for Se($-$II$+$O) are larger than those of the other species because it is calculated as the difference between two typically large numbers. For the Northern Reach, the Se($-$II$+$O)-salinity distribution (Figure 8) displays one prominent maximum (1·32 nmol l^{-1}) centered at 8 ppt, and a general decrease towards the seawater end-member thereafter. The concentrations of Se($-$II$+$0) in the two rivers differ markedly (Table 5), but in keeping with the arguments above, the concentration in

TABLE 4. San Francisco Bay ancillary data (23–24 September 1986)

Stn. no.	Salinity (ppt)	Chlorophyll-a ($\mu g\,l^{-1}$)	TSM ($mg\,l^{-1}$)	PO_4^{-3} ($\mu mol\,l^{-1}$)	NO_3 ($\mu mol\,l^{-1}$)	NH_3 ($\mu mol\,l^{-1}$)	Si ($\mu mol\,l^{-1}$)
1	24·58	3·86	42·05	33·7	149	16·4	173
2	27·85	2·95	32·42	22·8	67·9	10·3	128
3	29·78	1·39	21·41	11·9	31·4	12·4	98·0
4	30·36	1·63	22·67	7·0	23·6	10·3	61·6
5	30·40	1·61	18·24	3·1	12·1	7·6	20·0
6	31·58	3·45	10·72	2·1	8·6	5·5	15·0
7	31·95	2·42	11·96	1·8	7·9	5·2	6·7
8	31·30	2·44	13·47	2·2	10·0	6·6	15·0
9	27·77	4·73	25·60	2·8	12·1	4·1	28·3
10	27·33	3·69	14·36	3·0	10·0	4·4	28·3
11	24·01	3·59	31·78	3·2	14·3	3·8	33·3
12	20·97	4·89	63·75	3·2	14·3	3·6	46·7
13	19·46	4·50	44·16	3·1	15·0	4·6	49·9
14	17·45	3·13	23·60	3·2	15·7	4·6	63·5
15	13·89	2·75	16·76	3·1	15·7	4·4	78·4
16	13·22	4·29	16·20	3·3	16·4	4·5	83·5
17	11·56	3·06	22·70	3·1	16·4	4·3	88·2
18	11·06	5·46	15·12	3·1	17·1	5·1	177
19	9·65	7·52	18·04	3·2	17·1	4·1	107
20	7·57	6·84	30·71	3·0	17·1	2·9	119
21	5·10	6·87	33·46	3·0	18·6	3·4	155
22	3·61	3·57	42·84	3·0	20·7	2·6	228
23	1·51	2·78	49·24	3·2	22·1	3·7	93·3
24	0·39	2·20	59·53	3·0	20·7	0·9	248
25	0·07	0·65	28·42	2·3	9·3	7·4	247
26	0·19	NS	28·87	2·9	21·4	0·4	243

All samples taken 1 m below surface, NS—no sample, TSM = total suspended matter, Si = dissolved reactive silicate.

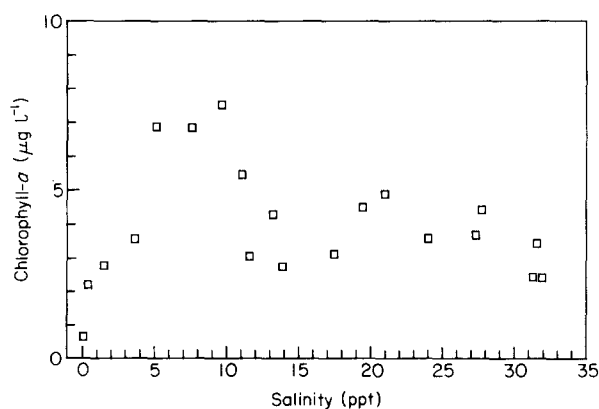
Figure 7. Surface water distribution of chlorophyll-a in the Northern Reach of San Francisco Bay, September 1986. There are two concentrations at ' 0 ' salinity, and represent data from the two river stations (Stations 25 and 26, Figure 2).
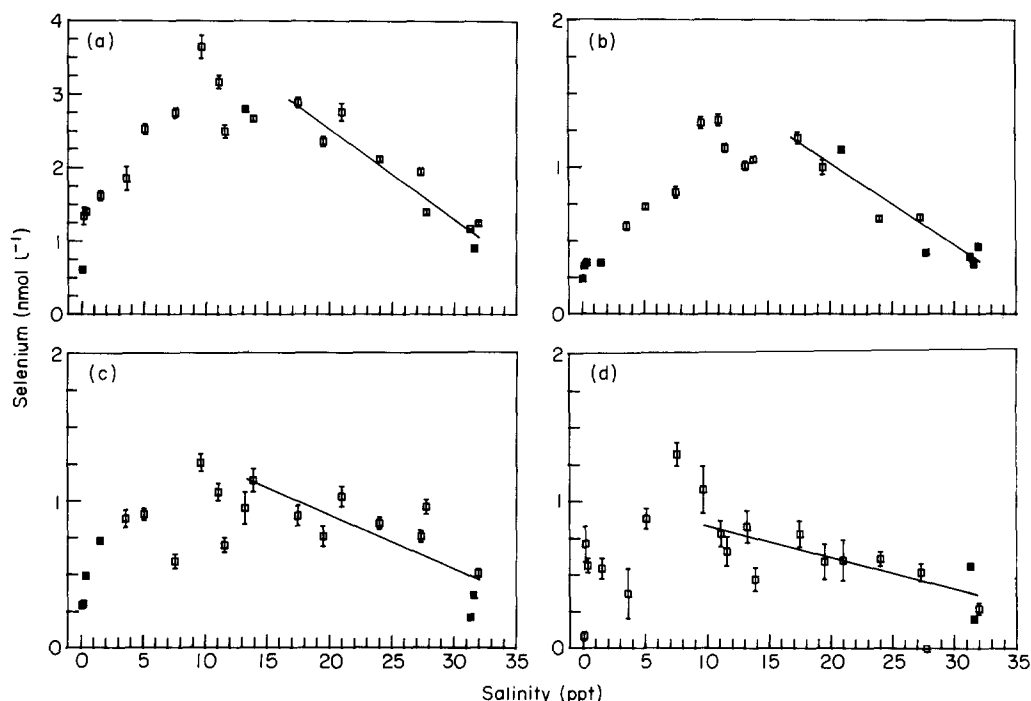
Figure 8. Distributions of (a) total dissolved selenium, (b) selenite, (c) selenate and (d) Se($-$II$+$0) in surface waters from the Northern Reach of San Francisco Bay, September 1986. Straight lines show the best linear regression fits to the data over the following salinity ranges: total selenium, 17·45–31·58 ppt; selenite, 17·45–31·58 ppt; selenate, 13·87–31·58 ppt; Se($-$II$+$0), 9·65–31·58 ppt. There are two concentrations at ' 0 ' salinity, and represent data from the two river stations (Stations 25 and 26, Figure 2).

the Sacramento (0·08 nmol l^{-1}) is considered to be the dominant riverine end-member. While Se($-$II$+$O) is 13% of the total selenium in the riverine input, this selenium fraction reaches 48% of the total in the 8 ppt maximum, and 31% of the total in the three highest salinity stations. In April 1986 (Figure 4) and September 1986 (Figure 8) the maxima in Se($-$II$+$O) occur in the same region as the maxima in chlorophyll-*a* (Figures 3 and 7, respectively). This observation is similar to that made by Cutter and Bruland (1984), who found Se($-$II$+$O) was correlated with indicators of biological activity such as chlorophyll-*a* and primary productivity.

To complete the description of selenium distributions in the Northern Reach, the profile of suspended particulate selenium in the Northern Reach (Figure 9) generally decreases with increasing salinity. Like the April 1986 results, the distribution of suspended particulate selenium is similar to the abundance of total suspended matter (Figure 9). Throughout the Northern Reach suspended particulate selenium averages 13±7% of the total dissolved selenium, with a maximum value of 26% at Station 26. While the average concentration of total suspended matter does not change appreciably between April and September 1986, the amount of particulate selenium relative to dissolved almost doubles from April to September. Similarly, the concentration of selenium in the suspended particles increases to an average of 0·75 μg Se g^{-1} in the Northern Reach during September, with the highest concentrations primarily in Suisun Bay (Figure 9).

TABLE 5. San Francisco Bay data (23–24 September 1986)

Station no.	Total Se (nmol l⁻¹)	Se(IV) (nmol l⁻¹)	Se(VI) (nmol l⁻¹)	Se(−II+0) (nmol l⁻¹)	Part. Se (nmol l⁻¹)
1	4.54 ± 0.10	0.98 ± 0.05	2.41 ± 0.11	1.15 ± 0.14	0.28^{a}
2	3.52 ± 0.10	0.87 ± 0.02	1.66 ± 0.07	0.99 ± 0.12	0.33 ± 0.01
3	1.78 ± 0.05	0.50 ± 0.01	1.01 ± 0.07	0.27 ± 0.08	0.15 ± 0.01
4	1.74 ± 0.08	0.36 ± 0.01	1.02 ± 0.04	0.36 ± 0.08	0.10 ± 0.01
5	1.55 ± 0.05	0.30 ± 0.01	0.65 ± 0.04	0.60 ± 0.06	0.11 ± 0.01
6	0.90 ± 0.01	0.34 ± 0.01	0.36 ± 0.01	0.20 ± 0.01	0.16 ± 0.01
7	1.24 ± 0.03	0.46 ± 0.01	0.51 ± 0.03	0.27 ± 0.04	0.08 ± 0.01
8	1.16 ± 0.003	0.39 ± 0.01	0.21 ± 0.01	0.56 ± 0.01	0.12 ± 0.01
9	1.39 ± 0.04	0.42 ± 0.01	0.96 ± 0.05	ND	NS
10	1.94 ± 0.05	0.66 ± 0.02	0.76 ± 0.04	0.52 ± 0.06	0.13 ± 0.01
11	2.11 ± 0.04	0.65 ± 0.02	0.85 ± 0.04	0.61 ± 0.05	0.28 ± 0.01
12	2.75 ± 0.12	1.12 ± 0.01	1.03 ± 0.07	0.60 ± 0.14	NS
13	2.35 ± 0.07	1.00 ± 0.05	0.76 ± 0.07	0.59 ± 0.12	0.28 ± 0.02
14	2.88 ± 0.07	1.20 ± 0.04	0.90 ± 0.07	0.78 ± 0.09	0.19 ± 0.02
15	2.66 ± 0.04	1.05 ± 0.02	1.14 ± 0.08	0.47 ± 0.08	0.22 ± 0.01
16	2.79 ± 0.02	1.01 ± 0.03	0.95 ± 0.11	0.83 ± 0.11	0.16 ± 0.01
17	2.49 ± 0.09	1.13 ± 0.03	0.70 ± 0.05	0.66 ± 0.10	0.30 ± 0.01
18	3.16 ± 0.09	1.32 ± 0.04	1.06 ± 0.06	0.78 ± 0.09	NS
19	3.64 ± 0.16	1.30 ± 0.04	1.26 ± 0.06	1.08 ± 0.16	0.26 ± 0.03
20	2.74 ± 0.07	0.83 ± 0.04	0.59 ± 0.05	1.32 ± 0.08	0.29 ± 0.01
21	2.52 ± 0.07	0.73 ± 0.02	0.91 ± 0.04	0.88 ± 0.07	0.32 ± 0.01
22	1.85 ± 0.16	0.60 ± 0.03	0.88 ± 0.06	0.37 ± 0.17	0.39 ± 0.02
23	1.62 ± 0.07	0.35 ± 0.01	0.73 ± 0.01	0.54 ± 0.07	0.34 ± 0.02
24	1.40 ± 0.05	0.35 ± 0.01	0.49 ± 0.01	0.56 ± 0.05	0.32 ± 0.01
25	0.61 ± 0.02	$0.24 + 0.01$	0.29 ± 0.02	0.08 ± 0.03	0.14 ± 0.01
26	1.34 ± 0.12	0.33 ± 0.01	0.30 ± 0.02	0.71 ± 0.12	0.35^{a}

^{a}Some difficulties were encountered with these sample analyses and no replicates were run.
ND = non-detectable (<0.01 nmol l⁻¹), NS = no sample.

South Bay selenium concentrations were notably elevated in April, with Se(−II+O) being the primary species (64%). The South Bay selenium data for September 1986 are listed in Table 5 and shown in Figure 10. Like April, linear mixing lines are observed for selenium *vs.* salinity (total selenium, $r = -0.9803$; selenite, $r = -0.9329$; selenate, $r = -0.9823$; Se(−II+O), $r = -0.9003$; $n = 6$ for all). However, the major species in September is selenate (53% of total at Station 1), with selenite comprising 22% and Se(−II+O) being 25% of the total dissolved selenium at Station 1 in the South Bay. Since nutrients (Table 4) show linear mixing ($n = 6$; phosphate, $r = -0.9782$; nitrate, $r = -0.9888$; ammonium, $r = -0.8681$; silicate, $r = -0.9287$) and have effluent from sewage treatment plants as their primary input source (Conomos *et al.*, 1979), selenium is also presumably coming from these outfalls (i.e. little *in situ* production of selenium). If the linear mixing curves are extrapolated back to zero salinity, the South Bay end-member would have 18·0 nmol l⁻¹ total selenium, 3·7 nmol l⁻¹ selenite, 9·6 nmol l⁻¹ selenate, and 4·7 nmol l⁻¹ Se(−II+O). This source has a significantly different selenium concentration (factor of 2 higher) and speciation than that extrapolated from the April 1986 data.

Flux estimates

In a qualitative sense, the estuary's Northern Reach appears to have an internal source of total dissolved selenium, selenite, and Se(−II+O), and a mixture of source and sink for
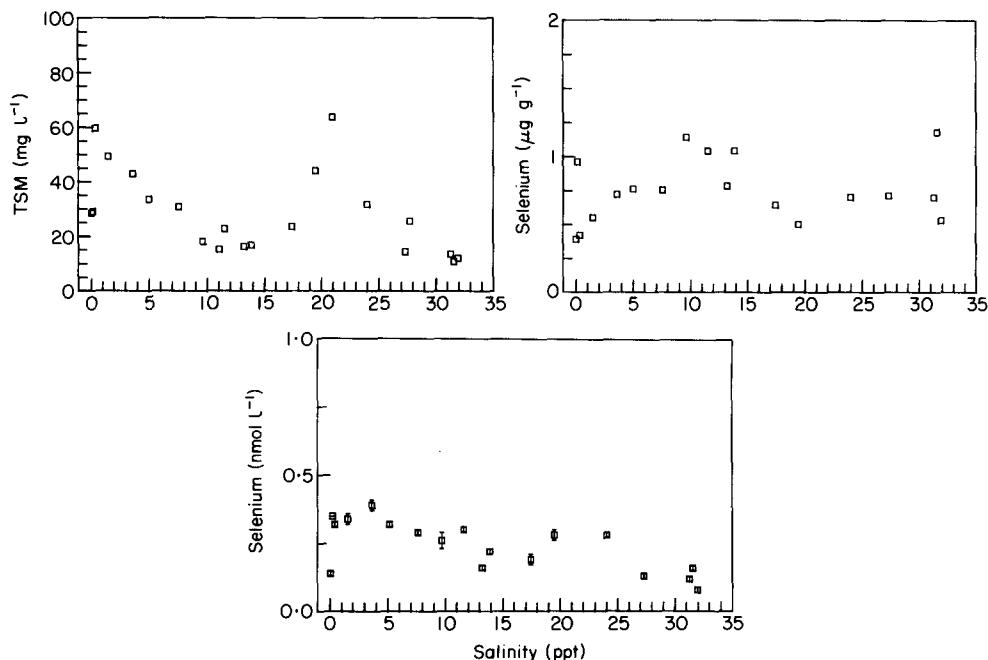
Figure 9. Distributions of total suspended matter (TSM), the selenium concentration in the suspended matter, and the total concentration of suspended particulate selenium in surface waters from the Northern Reach of San Francisco Bay, September 1986. There are two concentrations at '0' salinity, and represent data from the two river stations (Stations 25 and 26, Figure 2).

selenate. Selenium in the South Bay appears to be primarily affected by physical dilution and thus is conservative (i.e. no *in situ* removal or production). In order to rigorously describe selenium behaviour in the Northern Reach, selenium's removal and production fluxes must be quantified through modeling. ~~Boyle et al. (1974) and Officer (1979)~~ thoroughly describe the estuarine mixing behaviour of non-conservative constituents. The flux of a dissolved constituent from a river into an estuary is simply $F_{riv} = RC_O$, where R is the river discharge (1 day^{-1}) and C_O is the riverine concentrations (nmol l^{-1}). The flux from an estuary is $F_{est} = RC_*$, where C_* is the concentration of a hypothetical river end-member that would explain the observed concentration of the seawater end-member if only conservative mixing was present (i.e. C_* is the concentration calculated by extending a tangent to the concentration–salinity curve at the seawater end-member back to zero salinity). Thus, the net removal or production within an estuary is $F_{int} = R(C_* - C_O)$.

So that estuarine fluxes can be estimated, a value for C_* at the seaward end-member must be derived through modeling. This can be accomplished by fitting either functional equations (Kaul & Froelich, 1984) or a series of straight lines (e.g. Froelich *et al.*, 1985) to the constituent-salinity profiles. The April and September 1986 data suggest primarily point sources and sinks for dissolved selenium in the Northern Reach. Therefore, the straight-line method which has been used successfully with similar data sets (e.g. Froelich *et al.*, 1985) was employed. The primary interest in this work is to obtain estimates for the net export of selenium species from the estuary (and thereby the total input or output within the estuary). Extrapolating the best-fit line at the seaward end-member back to zero salinity yields a value for C_* and thus F_{est} (as well as F_{int}). However, the potential effect of
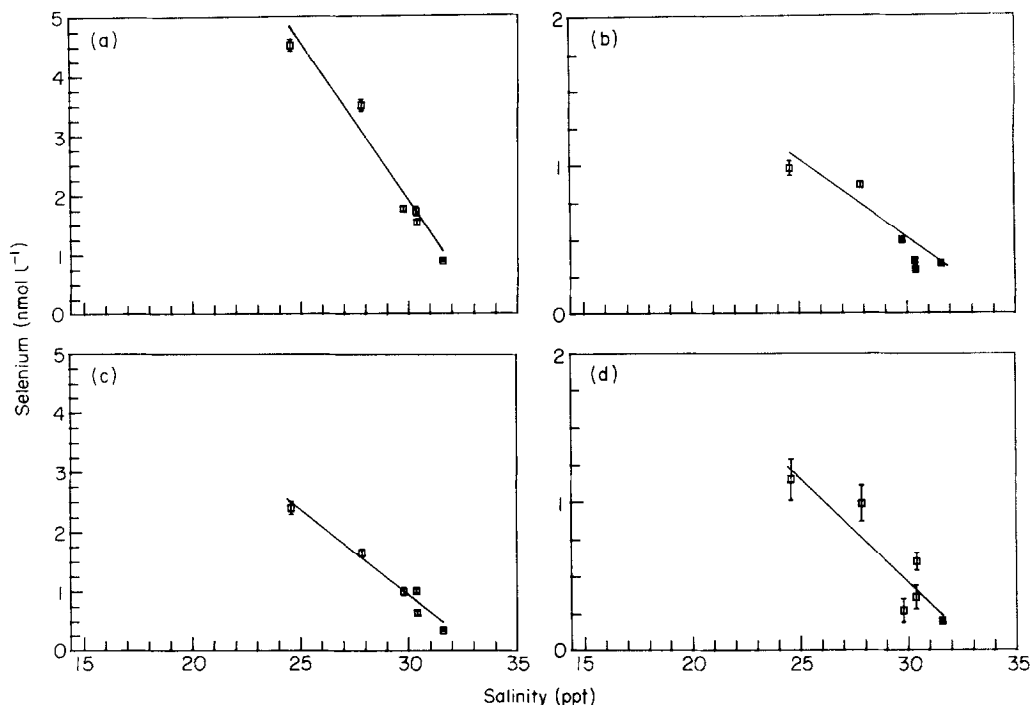
Figure 10. Distributions of (a) total dissolved selenium, (b) selenite, (c) selenate and (d) Se($-$II$+$0) in surface waters of the South and Central San Francisco Bay, September 1986. Straight lines indicate the best linear regression fits to the data.

variations in riverine selenium concentrations on the salinity-selenium profiles was first considered. Depending on the period and magnitude of river source variations, and an estuary's freshwater residence time, constituent-salinity mixing plots can be non-linear, yet still show conservative behaviour (Loder & Reichard, 1981). The data in Table 1 clearly show that the riverine concentrations of selenium vary with time.

To correct for the effects of riverine source variations, the model of Officer and Lynch (1981), which assumes a sinusoidally varying river end-member with time, was employed. The river data in Table 1 and associated correlations (described above) provide information on the timing and magnitude of riverine variability. In April and September 1986 the estuarine residence times were very short relative to the river source variations, minimizing the effect of a varying river end-member. The largest correction computed using the Officer and Lynch model is 12% for selenate in September 1986 (the corrections for the other selenium species are less than 4%). The largest correction for the April results is 5% for selenate. Thus, the apparent behaviour of selenium during the two sampling periods does not appear to be an artifact of river end-member variability.

April 1986. The selenium-salinity plots from April (Figures 4 and 6) clearly show selenium input from the South Bay. In order to derive flux estimates for the Northern Reach, only data from the riverine end-member to Station 6 (not affected by South Bay input) were considered. Therefore, the computed estuarine fluxes are not entirely accurate since they do not extend to outside the Golden Gate. The plots of total selenium, selenite, and Se($-$II$+$O) (Figure 4) are dominated by apparent estuarine input at salinities of approximately 2, 9 and 13 ppt, respectively. In contrast, the selenate–salinity

TABLE 6. Selenium fluxes in the Northern Reach

Species	C_0 (nmol l^{-1})	C_* (nmol l^{-1})	F_{riv} (mol day^{-1})	F_{int} (mol day^{-1})	F_{est} (mol day^{-1})
Period: April 1986[a]					
Total Se	2·02	3·22	$2·21 \times 10^5$	$1·31 \times 10^5$	$3·53 \times 10^5$
Selenite	0·21	0·77	$0·22 \times 10^5$	$0·62 \times 10^5$	$0·84 \times 10^5$
Selenate	1·51	1·45	$1·65 \times 10^5$	$-0·06 \times 10^5$	$1·59 \times 10^5$
Se($-$II$+$O)	0·29	0·78	$0·32 \times 10^5$	$0·53 \times 10^5$	$0·85 \times 10^5$
Period: September 1986[b]					
Total Se	0·61	5·06	14·1	102·8	116·9
Selenite	0·24	2·16	5·5	44·4	49·9
Selenate	0·29	1·66	6·7	31·6	38·3
Se($-$II$+$O)	0·08	1·05	1·9	22·4	24·3

[a]For April 1986 the average river discharge (R) was $1·10 \times 10^{14}$ l day^{-1}. The estuarine flux, F_{est}, is calculated at 25·74 ppt salinity. [b]For September 1986 the average river discharge (R) was $2·31 \times 10^{10}$ l day^{-1}. The estuarine flux, F_{est}, is calculated at 31·58 ppt salinity.
A negative F_{int} indicates removal within the estuary, while a positive F_{int} indicates production with the estuary.

profile (Figure 4) indicates apparent removal between 5–8 ppt salinity. Again, the primary objective is estimating F_{est} for the whole Northern Reach, and therefore flux calculations are based only on lines fitted to the seaward end-members; the best-fit lines are plotted in Figure 4 and the corresponding fluxes are listed in Table 6.

The results in Table 6 show that the internal flux of total selenium (F_{int}) in April 1986 increases the estuarine export (F_{est}) by 60%, while the export fluxes of selenite and Se($-$II$+$O) are dominated by their internal estuarine inputs. On the other hand, the export flux of selenate is 4% lower than that of the riverine flux due to internal estuarine removal. As an internal test of the data fitting procedure, the estuarine fluxes (F_{est}) for total selenium and the individual selenium species which comprise it can be compared (i.e. the sum of the individual species should equal the total). The sum of the estuarine fluxes for selenite, selenate, and Se($-$II$+$O), $3·28 \times 10^5$ mol Se day^{-1}, agrees within 7% of that for total selenium ($3·53 \times 10^5$ mol Se day^{-1}), indicating that the estimated fluxes are at least internally consistent. Finally, it should again be pointed out that the April 1986 sampling followed a period of extremely high river discharge. While the effects of a varying riverine end-member were considered, flood control diversions (e.g. the Yolo Bypass on the Sacramento) and the complicated mixing pattern of the two rivers may affect the apparent behaviour of selenium.

September 1986. The selenium-salinity plots from the September transects (Figures 8 and 10) do not indicate a significant effect from South Bay input, and flux calculations for the Northern Reach can be made to a higher salinity than those for April 1986. In September 1986 total selenium and selenite (Figure 8) show input between 10–17 ppt salinity. Selenate input appears to occur between 10–13 ppt (Figure 8), while Se($-$II$+$O) shows input at approximately 8 ppt salinity. Since the primary focus is determining the total estuarine production and consumption of selenium species, fluxes are based on the best linear fit to the data near the seaward end-member; the corresponding lines are plotted in Figure 8 and the flux estimates are listed in Table 6. In comparison to the fluxes in April 1986, those in September are orders of magnitude lower in size. This is primarily

TABLE 7. Selenium in some direct discharges to the San Francisco Bay

ID	Date	Total Se (nmol l^{-1})	Se(IV) (nmol l^{-1})	Se(VI) (nmol l^{-1})	Se($-$II$+$0) (nmol l^{-1})	R[a]
Publicly Owned Treatment Works in the South Bay						
Palo Alto/	21/12/87	27·7±1·3	4·58±0·08	8·32±0·60	14·8±1·4	
Mountain View	19/1/88	14·0±0·7	5·19±0·26	9·21±0·75	ND	
San Jose/	21/12/87	8·90±0·53	3·32±0·16	5·47±0·48	ND	
Santa Clara	19/1/88	10·3±0·3	0·97±0·07	7·14±0·17	2·19±0·34	
Sunnyvale	21/12/87	5·60±0·28	0·40±0·02	4·76±0·26	0·77+0·38	
	19/1/88	8·83±0·44	0·25±0·03	8·20±0·72	ND	
Refinery Effluents near Carquinez Strait						
Chevron,	24/2/87	165±3	99·4±4·9	10·1±7·1	55·3±5·8	49·6
Richmond Refinery	7/5/87	336±17	236±12	94·3±20·6	ND	
Exxon,	24/2/87	823±6	698±32	62·4±58·8	61·9±49·5	7·65
Benicia Refinery	7/5/87	1064±44	771±18	308±59	ND	
Pacific	24/2/87	83·2±4·0	ND	46·3±3·3	36·9±5	0·78
Refining Co.	7/5/87	110±6	ND	102±7	ND	
Shell Oil,	24/2/87	1671±33	1213±27	309±89	149±91	14·2
Martinez Refinery	7/5/87	1898±95	1622±9	224±47	ND	
Tosco Corp.,	24/2/87	276±5	40·0±2·0	69·4±3·5	167±8	9·50
Avon Refinery	20/5/87	330±15	15·4±0·8	220±14	95·1±21	
Union Oil,	24/2/87	1978±162	1153±55	772±92	ND	9·01
S.F. Refinery	20/5/87	1422±71	1148±35	ND	313±100	

[a]Average discharge rate of refinery effluent for September 1986 ($\times 10^6$ l d^{-1}). Data obtained from the State of California Water Resources Control Board.
ND = non-detectable (<0·01 nmol l^{-1}).

due to the almost 10 000 fold decrease in river discharge between April and September 1986. Within the Northern Reach in September 1986, the production of the three major forms of dissolved selenium ranges from 5 to 12 times higher than the respective riverine inputs (Table 6). Compared to the estuarine flux for total dissolved selenium (116·9 mol Se day^{-1}), the sum of the estuarine fluxes for selenite, selenate, and Se($-$II$+$O), 112·5 mol Se day^{-1}, agrees within 4%.

Potential sources of selenium. Data from the South Bay indicate that the source of selenium appears to be the effluents from municipal/industrial discharges rather than *in situ* production (i.e. dissolved selenium primarily displays conservative behaviour). This is perhaps not unexpected since these effluents are also the major source of 'freshwater' and nutrients to the South Bay (Conomos *et al.*, 1979). Table 7 contains recent selenium data for several of the municipal discharges to the South Bay. While these data do not overlap with the sampling periods, it is significant that the concentration and speciation of selenium in these effluents is similar to the zero salinity end-members extrapolated from the South Bay results (e.g. 8·2 nmol l^{-1} total Se in April; 18·0 nmol l^{-1} total Se in September).

In the Northern Reach the behaviour of selenium is more complex, and potential inputs of dissolved 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 are due to non-conservative processes, while the mixing of multiple end-members (e.g. tributaries) is a conservative process. The inputs of selenium in the Northern Reach appear as point sources (i.e. three end-member mixing). More importantly, the geographic position of these sources is relatively constant in spite of large changes in river discharge and the

corresponding position of the salinity gradient (i.e. selenium maxima occur near Carquinez Strait regardless of the salinity). This suggests either a large input of dissolved selenium from sediments, or additional end-members (tributaries or municipal/industrial effluents). While a sediment source for dissolved selenium cannot be discounted, the concentration of porewater selenium would have to be orders of magnitude higher than that in the overlying water column to maintain a large diffusional flux.

There are numerous industrial and municipal effluents entering the Northern Reach, with most of the region's oil refineries located near the Carquinez Strait. In order to examine the potential input of selenium from oil refinery effluent, filtered water samples from the waste discharge of the refineries were obtained on February 24 and May 7, 1987; selenium data for these samples are presented in Table 7. Compared to selenium concentrations in the rivers, the Northern Reach, and the South Bay (Tables 1, 3, and 5), concentrations in the refinery effluents are extremely high. Furthermore, selenite is enriched in these effluents (50% of total for all samples and 76% in the three highest concentration effluents) relative to the other estuarine selenium inputs.

While the refinery effluents and the estuary were not sampled concurrently, the results in Table 7 can be used to initially estimate the importance of refinery effluents. Assuming that the concentration of selenium in the effluents varies little during the year (the flowrates themselves changed by at most 32% during 1986), then this selenium input should have the largest effect during periods of low river discharge (i.e. September 1986). Using the data in Table 7, the following combined inputs fluxes for all six refineries are derived: 63.3 mol total selenium day^{-1}, 44·7 mol selenite day^{-1}, 12·7 mol selenate day^{-1}, and 5·3 mol Se($-$II$+$O) day^{-1}.

In September 1986 the input of selenium species from refineries can be a factor of 2–8 greater than the riverine fluxes (Table 6). Compared to the internal estuarine fluxes (F_{int}) for September 1986 (Table 6), the flux from refineries accounts for virtually all of the selenite flux, 62% of the total selenium flux, 40% of the selenate flux, and 24% of the flux for Se($-$II$+$O). Thus during low river discharge, a substantial portion of the selenium input to the estuary is actually due to the mixing of a 'third' end-member (refinery effluent), rather than *in situ* (non-conservative) processes. Correspondingly, the flux of selenium to the coastal ocean is dominated by anthropogenic sources. During high river discharge the identity of the internal selenium source within the estuary is still ambiguous. The refinery effluents can only account for approximately 0·02% of the selenium flux during these periods (e.g. April 1986). The export of selenium from San Francisco Bay to the coastal ocean is controlled by riverine sources during high discharge periods.

Conclusions

Within the San Francisco Bay estuary several sources can contribute dissolved selenium, including: the Sacramento and San Joaquin Rivers; the South Bay (probably effluent from sewage treatment plants); oil refinery effluents near the Carquinez Strait; and internal production, presumably through the dissolution of particulate selenium. The riverine sources of dissolved selenium display temporal variability which appears to be related to discharge rate and seasonal biological cycles. Thus, the cycling of selenium within the 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 the San Francisco Bay, the highest concentrations found in this estuarine system (4·54 nmol l^{-1}

total selenium in the South Bay and 3.64 nmol l^{-1} total selenium in the Northern Reach) are within the ranges measured in other estuaries.

Acknowledgements

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