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**Selenium Fractionation and
Cycling in the Intertidal Zone
of the Carquinez Strait
Quarterly Progress Report
January 1996 through March 1996**

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April 1996



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1 INTRODUCTION

This quarterly report describes research on selenium (Se) cycling in the marshes and mudflats of the Carquinez Strait between 1/1/96 and 3/31/96. Chapter 2 contains descriptions of results of extractions and analyses of sediment cores from the intertidal zone of the Martinez and Benicia field sites, including some x-ray spectroscopy data related to the characterization of the sediment Eh-pH regime. Chapter 3 contains a summary of work in progress on the extraction of various Se species from sediment/soil samples, and efforts in measuring suspended sediment Se. Chapter 4 is an update on stable Se isotope research and Se purification techniques. Chapter 5 describes the rationale, design, and preliminary results of a plant-Se study. Chapter 6 presents the design of a recently initiated sediment dynamics study. The reader is referred to the 1995 Annual Report (Zawislanski et. al., 1995) for details on the project design, site selection, and methodology.

2 EXTRACTION AND ANALYSIS OF INTERTIDAL SEDIMENTS

Soil and sediment cores collected at both the Martinez Regional Park (MRP) site and the Southampton Bay (SHB) site in early December are being characterized, extracted and analyzed. The in-situ measurements of Eh and pH in these cores were described in the previous quarterly report (Zawislanski et al., January 1996). The emphasis in the characterization of these cores is on attaining very fine vertical resolution of selenium concentrations and other properties of the sediment in order to better understand selenium transformations in this system. Samples were collected from all of the major intertidal environments: mudflat, mudflat/marsh interface, lower marsh, and upper marsh. The spatial distribution of sample points at the two sites is shown in Figures 2.1 and 2.2.

2.1 Sampling Locations

Samples were taken along two transects perpendicular to shore at each site. At each sample point, a 20 cm deep core was collected and water was sampled from the resultant hole when available. The location and elevation of the sample point was surveyed using a

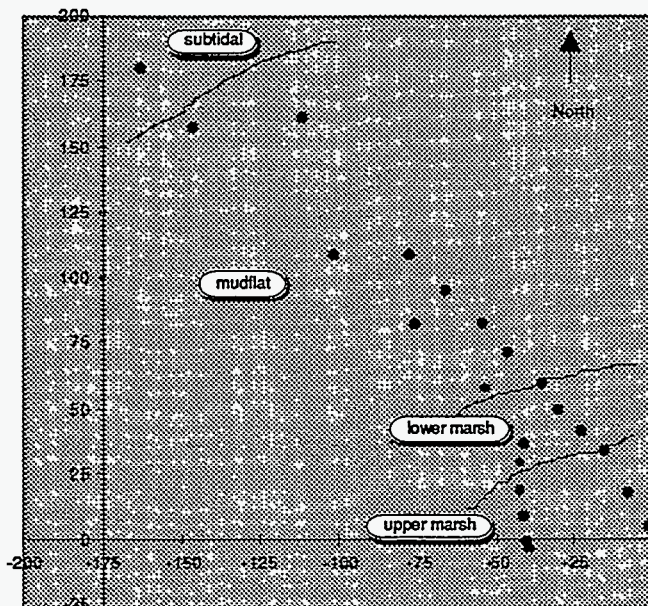


Figure 2.1 Location of core sampling points relative to the intertidal environments at MRP.

total station. This was done for both mapping purposes and to be able to correlate physical and chemical characteristics of the sample with relative degree of inundation. The locations at MRP are shown in Fig. 2.1 and at SHB in Fig. 2.2.

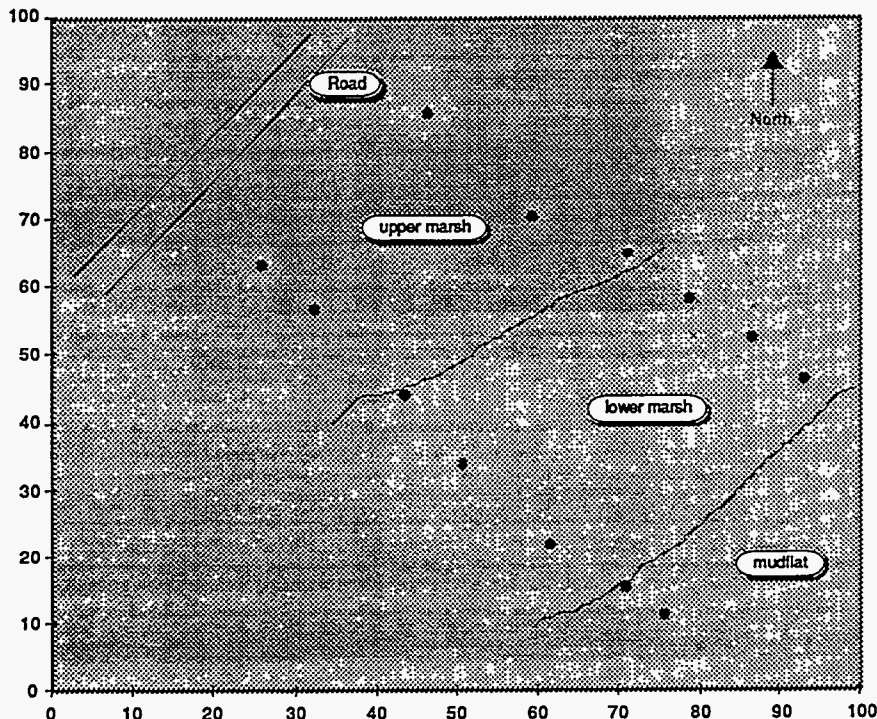


Figure 2.2 Location of core sampling points relative to the intertidal environments at SHB.

The sampling procedure and sample handling methods are described in the previous quarterly report (Zawislanski et al., January 1996).

2.2 Eh and pH Results

Some results of direct Eh measurements in the cores have been previously described (Zawislanski et al., 1995). During the last quarter, a selected core (from the MRP mudflats) was analyzed for iron speciation using x-ray (XANES) spectroscopy. This method allows for non-destructive and highly objective determination of metal speciation. Iron was analyzed in order to further establish the Eh-pH regime present in this core and compare the results with those from Pt-electrode measurement.

2.2.1 Sediment Fe-XANES and Fe (II)/Fe(III) Couple

A preliminary XANES study was conducted on mudflat samples to test the application of this technique to the interpretation of sediment redox status. The Fe K-edge XANES spectra of the sediments were collected at the SSRL, Beamline IV-2, to evaluate and compare the measured redox potentials and Fe(II)/Fe(III) ratios in the samples. The edge position of sample XANES spectra were calibrated against Fe-film (Fe-0) and compared with Fe model compounds of different oxidation states (0: Fe-film, II: FeSO₄·7H₂O, III: FeOOH).

Table 2.1 Solid phase Fe speciation of MRP mudflat sediments.

Sample Depth from Surface (cm)	Edge Position (eV)	Estimated Fe(III) (%)*	Measured Redox Eh (mV) (Pt-electrode) #
0.5	7114.8	63	367
1.5	7114.6	56	414
2.5	7114.3	47	339
4	7114.2	44	173
6.25	7114.1	41	136
8.75	7113.9	34	32
12.5	7113.6	25	115
Fe (II) in FeSO ₄ ·7 H ₂ O	7112.8	--	--
Fe (III) in FeOOH	7116	100	--

* Predicted concentrations are not corrected for ligand effects, for e.g. hydroxide versus sulfide.

Estimated Eh from Fe redox couple will be less, in the range of -150 to -300 mV.

The Fe K-edge position of Fe (III) in akaganeite was at 7116 eV and that of Fe (II) in FeSO₄·7H₂O was at 7112.8 eV and all the sediment samples exhibit intermediate values (Table 1). As the sample depth increases, Fe K-edge position shifts to lower energies (from 7114.8 eV at the top to 7113.7 eV), indicating increased Fe(II) concentrations at greater depths. When these edge positions were transformed into concentrations, Fe(III) at the top of the core was 60-65%, while the bottom-most part of the core had only 25%. These distinct changes in relative concentrations of Fe redox species relate to the sediment Eh. If Se redox speciation is at equilibrium, then Se should either be in elemental or

selenide form. However, the structural effects (mineral type), and ligand affects on edge-shift have to be considered to carefully evaluate the Fe redox couples and the sediment Eh.

2.2.2 Preliminary Hypothesis on Sediment Redox Conditions and Se Speciation

The pore water chemistry, the sequential extracts, and the measured redox potentials of the sediment samples are not entirely consistent with each other. The pore waters exhibited minor concentrations of SeO_4 and its presence in contact with SeO_3 , elemental Se, and selenide is indicative of thermodynamic disequilibrium. Although Se redox reactions are extremely slow in pure abiotic systems and in the presence of air, Se transformations in sediments are much faster because of microbial influence. The observed variation in Se speciation estimated from different methods may be due to:

- i) Se sequential extraction procedures resulting in the release of more than one type of species.
- ii) Measured redox potentials may be incorrect either due to the poor sensitivity of Pt-electrode to sulfide rich sediments, or non-equilibrium in the system.
- iii) The measurement made using the Pt-electrode is more sensitive to dissolved species and is not indicative of the redox state of the entire sediment-plant-water system.

Although *In-situ* XANES spectroscopy provides accurate information on Fe redox couples and inferences can be made on Se speciation from these studies, the major assumption involves the system's equilibrium with respect to Se, which needs to be tested with Se-XANES. Further work is planned to examine the redox status of Se in these sediments, by evaluating the major elemental redox couples (Fe, S) of the sediments and pore waters with XAS. Se speciation will later be attempted by modeling the system with the obtained Eh-pH from the major elemental redox couples and analytically measured total Se of the samples.

Pore waters collected from cores will be divided into two parts. One sub-sample will be analyzed for its chemistry and speciation. The other will be spiked with a low Se concentration (Se VI and Se IV) (0.6 mM) and slowly injected back into the cores. These Se concentrations are below the solubility of different known selenate and selenite mineral phases and thus their precipitation can be neglected in the system. The cores will be allowed to react for 60 hours and Fe, S, and Se K-edge XANES spectra will be collected at

regular intervals. These studies will provide insight into Se speciation, and the time the Se species take to reach equilibrium with the rest of the sediment.

2.3 Selenium Distribution Along MRP Transect 1.

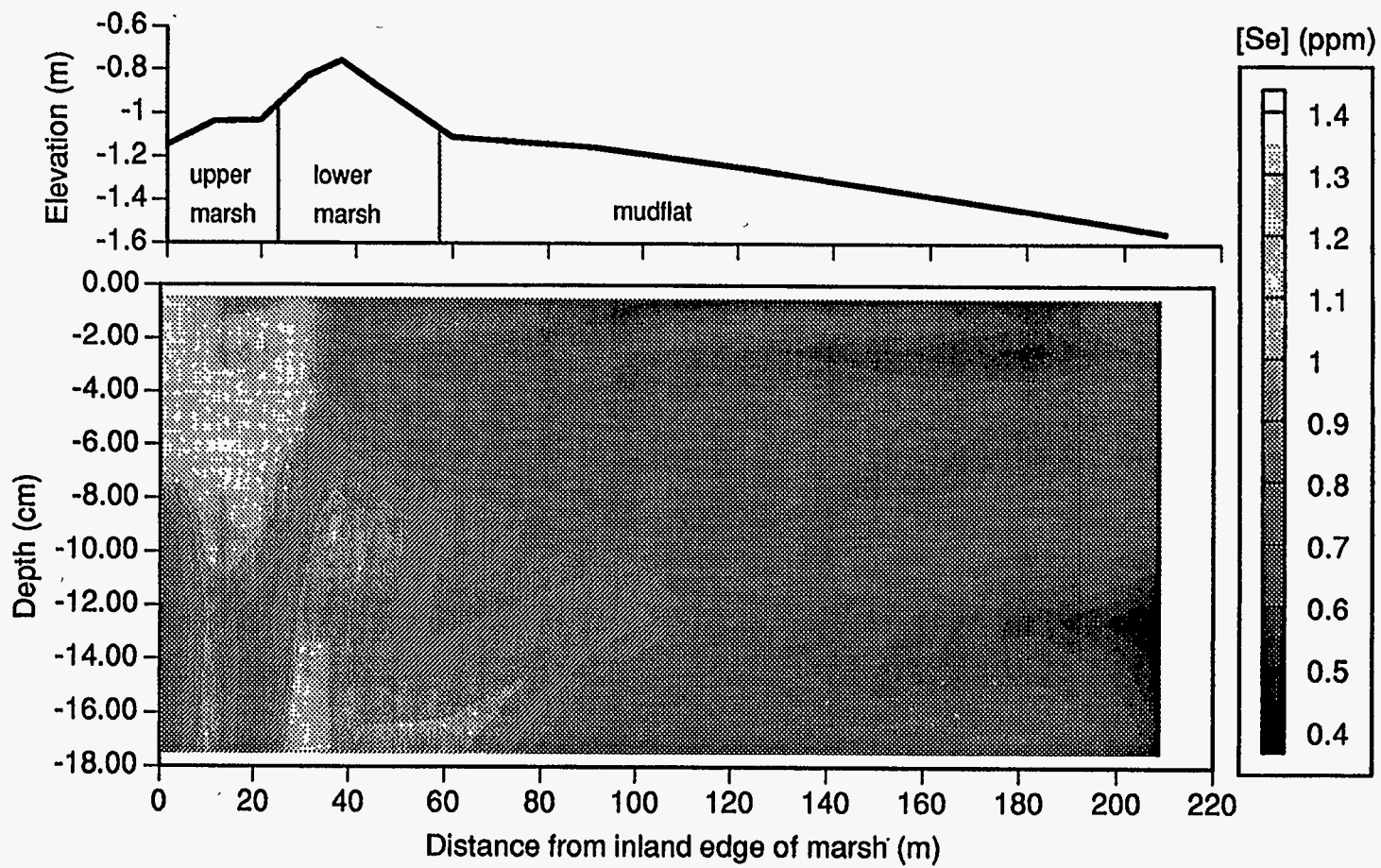
Due to the complexity of the sequential extraction procedure used to fractionate selenium in these sediment cores (see Zawislanski et al., 1995; and Chapter 3 of this report), the overall amount of time required to complete this analysis is long. Thus far, samples from both transects from MRP have been processed, although only data from Transect 1 is complete and will be summarized herein. Cores were extracted in thin horizontal slices: 0-1 cm; 1-2 cm; 2-3 cm; 3-5 cm; 5-7.5 cm; 7.5-10 cm; 10-15 cm; and 15-20 cm. These intervals coincide with the depths at which Eh and pH were measured.

2.3.1 Total Elemental Selenium

Total elemental Se was measured via the analysis of an acid digest of dried and pulverized sediment. This is the least ambiguous measurement of Se content and includes, but does not differentiate, all selenium fractions. The total Se concentrations in the top 20 cm of sediment along Transect 1 at the MRP site are shown in Figure 2.3. Because cores were collected along a 210 m long distance, but only down to a 20 cm depth, there is of course a great deal of vertical exaggeration in this representation. Nevertheless, it is very useful in discerning general trends in Se levels. Two distinct patterns are visible. First, there is a general trend of increasing Se from the mudflats to the inland edge of the marsh. Secondly, there is a very sharp increase in Se in the uppermost (i.e. inland) part of the marsh. The farthest point sampled on the mudflats represents the boundary between the intertidal and subtidal zones. The sediment-Se levels there are around 0.5 to 0.6 ppm, whereas in the upper marsh the levels are over 1 ppm, and up to 1.3 ppm at a depth of 6 cm. There are no consistent vertical trends in total Se levels, except perhaps in the upper marsh, where Se decreases with depth. However, more analysis of this data is required.

Figure 2.3 also contains a graph of the surface elevation along the transect. This is particularly interesting because the elevation of the "lower" marsh is in fact higher than that of the "upper" marsh, by as much as 30 cm. This is probably due to the trapping of sediment in the thickly-vegetated lower marsh. Although this results in a very gentle slope which is difficult to discern in the field, it is certainly significant in the hydrologic cycle of this system. Namely, the lower elevation of the upper marsh results in post-high-tide ponding in this area, during which water becomes stagnant. This may lead to chemically

Figure 2.3 Total Se distribution measured along Transect I at site MRP. The top graph shows the surface elevation of the transect.



more reducing sediments, as well as the deposition of very fine suspended sediment under more or less quiescent conditions. Both processes would result in elevated Se concentrations. This in fact is observed in Figure 2.3 and the coincidence between the boundary of the lower elevation area and the elevated Se is striking.

2.3.2 Chemical vs. Physical Control of Se Deposition

The overall lateral pattern of Se levels is somewhat at odds with the working hypothesis of Se cycling. First of all, the assumption has been that Se reduction in the organic-rich sediments of the lower marsh would dominate the cycle. Although marsh Se levels are higher than mudflat concentrations, the most organic-rich part of the marsh, or the lower marsh dominated by cattail and rushes, does not contain the highest Se. Figure 2.4 presents a conceptual distribution of Se concentrations following the working hypothesis. Given that the approximate mean Se concentration on suspended particulates is around 1 ppm, no sediments would be expected to contain lower levels. As conditions are more reducing in the lower marsh than in the mudflats, additional input of dissolved Se is expected as it is adsorbed, chemically reduced, and immobilized. In the upper marsh, Se reduction was assumed to be less efficient because of the lower density of plants (i.e. lower organic carbon) and the loss of some of the dissolved Se to the lower marsh, bringing the sediment-Se levels to slightly above SPM-Se concentrations.

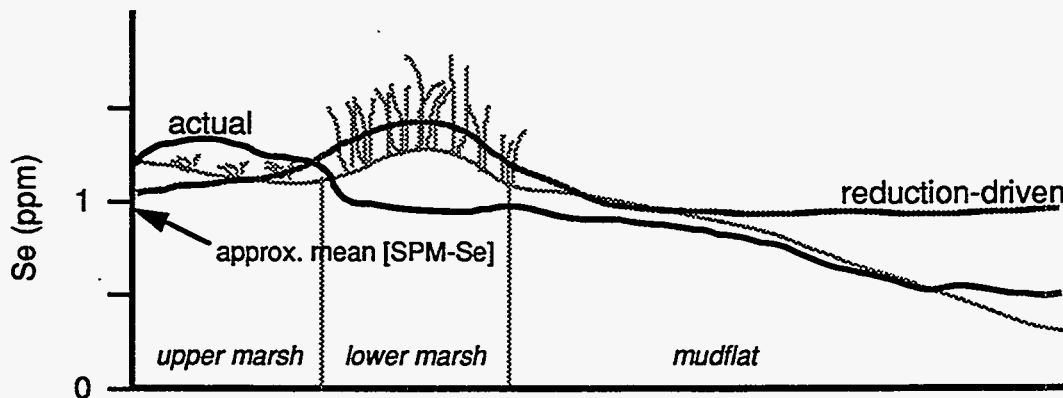


Figure 2.4 Conceptual (reduction-driven) versus actual distribution of Se in the intertidal zone of MRP, following the results of Transect 1 analysis. There is significant vertical exaggeration in the elevation of the surface.

The actual observed sediment-Se distribution is quite different and suggestive of some other controlling factor. Given that observed sediment-Se levels in the mudflats are lower than SPM-Se, it could be hypothesized that the sediment-Se distribution is controlled mostly by the energy of the depositional regime. Water overlying the mudflats is generally at a higher energy than that overlying the marsh, where quiescent conditions dominate. This should theoretically result in the deposition of coarser particles in the mudflats and finer, more clayey, particles in the marsh. In fact, the farther inland, the lower the energy of the system and potentially the more fine sediment should be deposited. It is well known that finer particles provide a larger surface area and more sorption sites than sandy and silty material. Therefore, it may be assumed that the coarser particles which are being deposited in the mudflats will have lower-than-average Se concentrations, while the more clayey particles falling out inland will have higher-than-average Se levels. This is supported by the fact that mudflat sediments at MRP are indeed coarser-grained than the adjacent marsh soils.

In order to test this revised hypothesis, a number of projects have been initiated. These include a study of sedimentation dynamics in the intertidal zone, which is described in Chapter 6; a study of plant biomass and turnover, described in Chapter 5; measurements of particle-size distribution in the system; and a laboratory microcosm study aimed at measuring rates of Se reduction in each of the major environments under consideration.

3 METHODS FOR SE EXTRACTION FROM SEDIMENTS

In an effort to increase the efficiency of the extraction of OM-associated Se, several experiments were performed to determine whether repeated sodium hydroxide (OHx, 0.02 M NaOH) extracts would significantly increase the amount of OM-Se extracted. The extraction method was also tested to determine if sonication would significantly alter the amount of OM-Se released. Finally we ran several experiments to determine if drying of soils changed the extractability of OM-Se and other Se fractions. The experiments were intended to address concerns on the use of sonication, and a general concern about the extractability of organic fractions as demonstrated by the spiked extractability samples reported in the Zawislanski et al. (1995).

3.1 Extraction Procedures

Extraction procedures for the different OHx tests were altered to include the following changes:

- 1) Two extractions using 0.02 M NaOH were used, with 1 hr of heating at 85 °C each. The supernatant liquid was filtered and analyzed separately.
- 2) Single extractions on wet field soils and dried field soils (freeze-dried) using the procedure outlined in the 1995 Annual Report.
- 3) Single extractions were run with 1 hr sonication and 1 hr bath heating only at 85 °C.

These alterations of procedures were run in triplicate with a control for each experiment.

Extracting the soils twice greatly increased the amount of OM-Se released, but an inventory of the total Se extracted demonstrated that the extraction efficiency was greater than 110% (Table 3.1). This overestimation of the total Se brings into question the veracity of the numbers determined. OM-Se alone extracted using the repeated extractions was between 84 and 109% (total Se = 539 ppb for MRP 12-2). One of the problems may be errors in the HG-AAS analysis of the extracts due to the ten fold dilution used for the acid boil and analysis.

Table 3.1. Repeated OHx of Martinez Regional Park Sample 12, 10-20 cm depth.

Soil/Replicate	Dx+Px ppb	OHx (1) ppb	OHx (2) ppb	Sx ppb	Total ppb
MRP 12-2 (1)	102	265	188	177	544
MRP 12-2 (2)	110	322	196	183	616
MRP 12-2 (3)	125	384	156	180	690
MRP 12-2 (4)	121	355	235	174	650

The results of wet sample analysis (311 ± 29) versus that of freeze-dried samples (275 ± 19 ppb) was not statistically different for OM-Se, and essentially identical for Dx+Px combined extraction (83 ± 5 versus 76 ± 7 ppb, respectively). This demonstrates that freeze-drying may have a slight impact on Se fractionation, but the effect cannot be distinguished from the error in analysis for this sample.

Sonication made little difference on the amount of Se released by the OHx, with both the sonicated and normally extracted soils yielding OM-Se within the error of analysis for MRP 12-2 soil averaged over four replicates (sonicated average: 316 ± 44 ppb; reference average: 311 ± 29 ppb). This clearly shows that sonication is not solubilizing significant quantities of OM-Se or fractions other than elemental-Se in the sulfite extraction (where sonication is used to increase extraction efficiency).

3.2 Pyrite Se Analysis

Pyrite-Se was determined using the apparatus based on a design by Velinsky and Cutter (1990) described in the 1/96 quarterly report (Zawislanski et al., 1996). Samples from surface soils in Martinez and Southampton Bay had pyrite-Se concentrations which were at the limits of detection (around 20 ppb Se relative to soil mass, or generally less than 5% of the total Se inventory). It will require improvement in the chromatography of separation to improve resolution such that the pyrite-Se in these samples is easily quantifiable. At present the combination of the large hydrogen sulfide peak and the dispersion of the hydrogen selenide peak, make it disappear after passing through the chromatographic column. Increasing sample size only increases the amount of interference from hydrogen sulfide. Using a different packing material or longer column may improve chromatographic separation, but that may be complicated by the added dispersion of the peaks. Increasing the flow rate through the column in combination with increasing the column length is most likely the best combination for aiding in the separation.

3.3 Experimental Plan for Determining the Role of SPM in the Movement of Refinery Selenite into Intertidal and Marsh Sediments

It has been suggested that suspended particulate matter (SPM) plays a critical role in the food web with regard to Se (S. Luoma, personal communication). SPM is composed of mineral and organic colloids, and microorganisms (phytoplankton and diatoms). Processes affecting the Se content of the SPM include: mineral dissolution/precipitation; adsorption/desorption; and microbial metabolism of Se. Therefore, Se may be present in a variety of forms, and its bioavailability is governed by what form it is in. Mineral Se is predominantly in the form of adsorbed selenite (selenate is a poor ligand) but can also be in ferroselite, similar iron-sulfur-selenides, and/or co-precipitated into carbonates and a variety of evaporites/precipitates (as selenite). Organic Se includes both metabolized and adsorbed Se, such as selenides produced by microbial processes (seleno-cystein or -methionine) or selenite adsorbed from aqueous solution.

Given that adsorption is such an important process, selenite released by refineries (the strongest inorganic ligand containing Se) increases the surface concentration of Se on SPM (Cutter, 1989). Organic colloids adsorb high concentrations of selenite, and phytoplankton will also concentrate Se from selenite in their biomass. The result is a Se-enriched SPM that is transported through the estuary .

Luoma's hypothesis is that Se enriched SPM is ingested by surface feeding clams in the mudflats, which increases the Se concentration in these clams. This typically occurs when water flows are low and refinery-Se drastically increases the total Se and selenite concentrations in areas such as the Carquinez Strait. Diving ducks, feeding off the clams, are therefore the species most affected by elevated Se concentrations in the Bay.

Phytoplankton and diatoms growing in the Carquinez Strait take up Se, transforming selenite into organic Se or just by adsorbing selenite onto tissues. USGS data shows that phytoplankton concentrations are highest in high flow years, and that at low flow phytoplankton concentrations are low. This population fluctuation complicates the model for Se uptake because high phytoplankton populations can result in greater Se uptake in high flow years, and result in a greater percentage of phytoplankton (and phytoplankton Se) in SPM. Our hypothesis is that in low-flow years, the high selenite concentration of

waters in the Carquinez Strait results in increased Se concentrations of the phytoplankton, despite lower concentration of phytoplankton in the water.

In order to determine what mechanisms control Se adsorption/incorporation into SPM, we are undertaking a series of experiments. The first phase of these experiments is to collect samples of SPM and surface clams on a monthly basis from the Carquinez Strait (at the MRP site). Total clam-Se and SPM-Se fractionation will be done to determine what Se fractions (adsorbed, OM-associated Se, elemental-Se, pyrite-Se) correlate best with total clam Se.

The second phase of experiments involves a series of adsorption and speciation experiments with SPM and synthetic mineral colloids in solution with extracted humic and fulvic acids, and varying selenite concentrations. Using mineral colloids, and sulfide-reacted humic and fulvic acids, mechanisms of adsorption and changes in oxidation states will be monitored. Final experiments will involve changes in organically associated-Se with sedimentation and burial (decreasing redox potentials) in microcosm studies.

I. Field sampling of water, SPM and clams.

- A. Monthly sampling of water and SPM (5 days/month) and clams (1 to 2 days/month during the SPM sampling period).
- B. Measurement of EC, pH, dissolved Se, and phytoplankton concentration in solution.
- C. Total Se and fractionated Se from SPM, TOC, metals, and mineral composition.
- D. Clam total Se (measured by Luoma at USGS).

II. Se adsorption and speciation in SPM.

- A. Synthetic colloid experiments determining adsorption/desorption coefficients for Se onto humic and fulvic acid coated clays.
 1. Batch experiments determining adsorption/desorption coefficients from simulated estuarine solutions.
 2. Batch experiments determining adsorption/desorption coefficients for hydrogen sulfide-altered humic and fulvic acid coated clays.
- B. Selenite adsorption/desorption properties of SPM.
 1. Batch experiments determining adsorption/desorption coefficients from simulated estuarine solutions.

2. Batch experiments determining adsorption/desorption coefficients for hydrogen sulfide-altered SPM.

II. Speciation studies.

A. Incubation of selenite adsorbed onto sulfide-reacted humic and fulvic acid.

B. Incubation of selenite adsorbed onto sulfide-reacted SPM.

3.3.1 Preliminary Results

Analysis of Se in SPM has been ongoing with total Se measurements being taken monthly on between two and five samples. The SPM total Se concentrations fluctuate between 700 and 2,000 ppb. It is unclear whether the high SPM concentrations result in diminished total Se concentrations, although it is suggested by the presently available data.

Figure 3.1 shows the data collected to date for the SPM concentrations in the Carquinez Strait from 12/1/95 - 1/29/96, with the mass of SPM per liter plotted against total organic carbon (TOC).

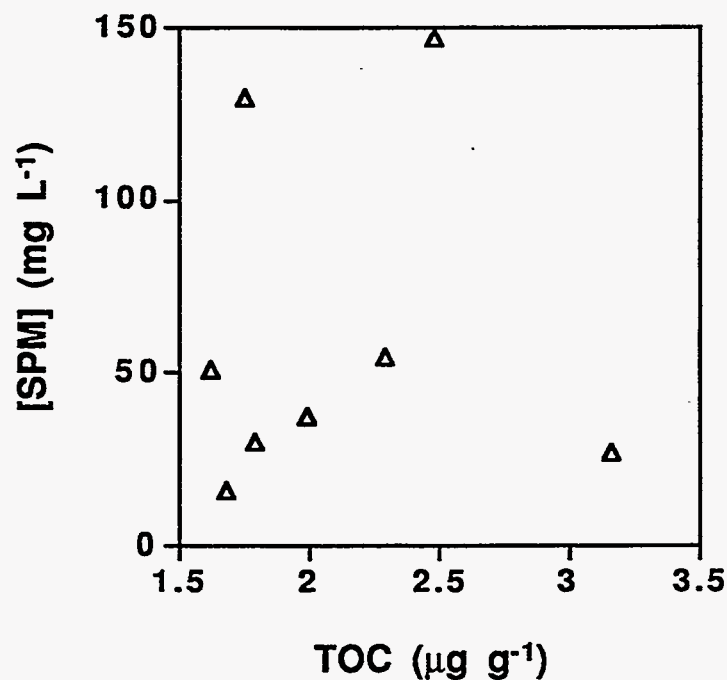


Figure 3.1. Suspended particulate matter (SPM) concentrations from 12/1/95-1/29/96, plotted versus the total organic carbon concentration (TOC).

An interesting, though noisy, relationship between SPM-Se and TOC is observed (Figure 3.2).

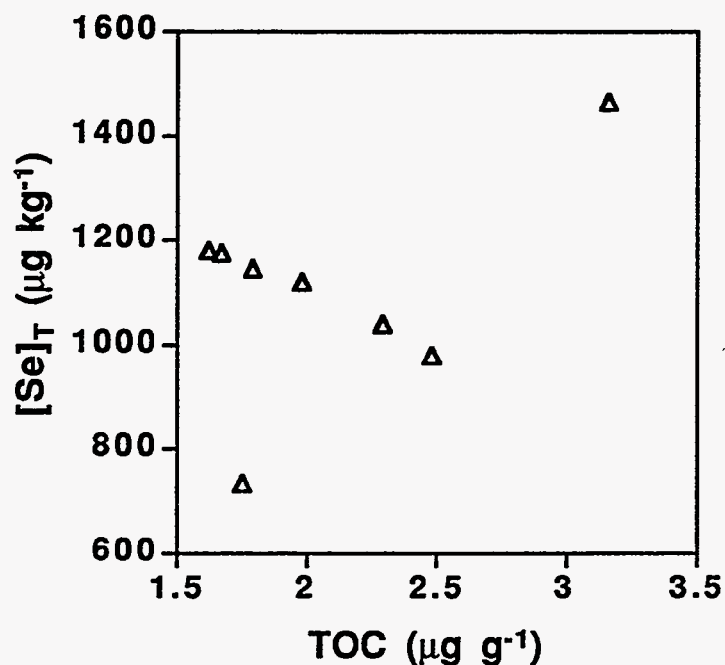


Figure 3.2 Total Se ([Se]_T) in SPM versus SPM-TOC.

If the two outlying data points (which need to be verified) are removed, an excellent correlation between SPM-Se and TOC is observed (Figure 3.3). The reason for removing the outliers is that their values may not represent the accurate TOC concentration, and all these samples will be reanalyzed. The goodness of fit for these preliminary data points may only be fortuitous especially since two out of eight points may be outliers; further measurements will likely increase the total amount of scatter. If this correlation does hold, TOC may be an excellent tool for predicting total Se in SPM.

The data presented over time shows the variation in total Se, TOC, and SPM concentration during the three months. This data does not reflect the continuous fluctuations in SPM concentrations in the Carquinez Strait inter-tidal zones, but it does provide an excellent approximation of how the total Se concentrations change over time.

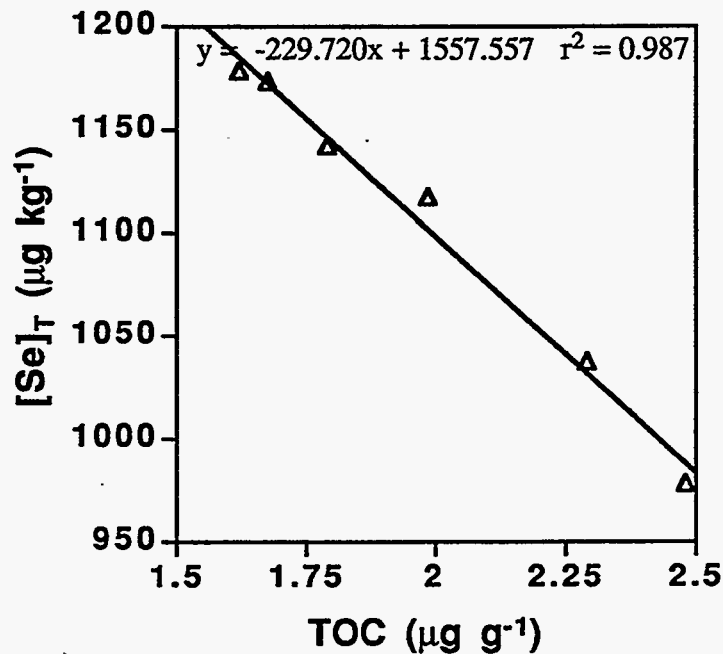


Figure 3.3 Total Se ($[Se]_T$) is plotted versus TOC with the points for 12/1/95 and 12/15/95 removed as outliers.

Water concentrations of Se are being measured using the cold-trap-AAS method (Cutter, 1978). The large number of samples and the attempts to measure pyrite-Se have prevented analysis of the filtered and preserved waters. Analysis of these waters is expected to be completed by the end of May, for samples taken through March.

3.3.2 SPM-Se Speciation

The extraction procedure has been altered to allow analysis of SPM-Se fractions. SPM is freeze-dried and extracted first with Px (for adsorbed *and* soluble species). OHx and Sx are done to complete the Se extraction sequence. Preliminary results show that the amended methods provide solutions which are easily analyzed for total, OM-, and Se (IV) selenium. Further analysis is required to determine whether this method is going to be successful.

4 STABLE ISOTOPE METHODS

The first analysis of selenate from San Joaquin River water was carried out. Purification of one microgram of selenium from selenate in river water was much harder to attain than expected; considerable experimentation and research were carried out to resolve problems that were not encountered with the higher concentration selenite-dominated samples analyzed earlier. The basic problem is the large volume of water that must be processed to produce the one microgram of purified selenium needed for each analysis, and the concomitant processing of large amounts of various chemical species that interfere with the purification and mass spectrometry of selenium. Several strategies are being pursued (discussed below), and some combination of these will allow us to complete the reconnaissance analyses and lead to more efficient analysis procedures in the future.

The river water sample was taken at Antioch, and according to its chloride and sulfate concentrations (measured by ion chromatography), it was fresh water with little or no salt water component. Accordingly, it may serve as a representative sample of the riverine selenium input into the estuary further west. However, because of complicated flow dynamics near Antioch, it is not entirely clear that the water sampled came from the San Joaquin River. Further work will be carried out to better characterize the riverine inputs. The selenium concentration was about 500 pptr, and two liters of water were processed to yield one microgram of purified selenium.

The result of this first river water analysis do not provide evidence for the hoped-for large, systematic difference between refinery effluent selenium and river-borne selenium that would enable isotopic tracing of refinery effluent in the estuary (Table 4.1). Further work will include duplicate analysis of this sample, and collection and analysis of a few more river samples to characterize the riverine input.

Table 4.1 Se isotope ratios of refinery effluent and river water.

Sample	$^{80}\text{Se}/^{76}\text{Se}$ ratio	$\delta^{80}\text{Se}$ (per mil)
Chevron Effluent	5.3198	$+4.4 \pm 1$
Shell Effluent	5.3229	$+4.9 \pm 0.4$
UNOCAL Effluent	5.3134	$+3.2 \pm 0.4$
Exxon Effluent	5.3249	$+5.3 \pm 0.2$
Antioch Water	5.3258	$+5.5 \pm 1$

Initial Se isotope measurements on refinery effluent samples were completed with the analysis of Chevron effluent obtained on 2/1/96. Chevron refines North Slope crude, whereas the other refineries accept large amounts of San Joaquin crude. However, despite the difference in the source of the selenium, the Chevron effluent analysis indicated that its $^{80}\text{Se}/^{76}\text{Se}$ ratio is within the range spanned by the other refinery effluent samples (Table 4.1).

4.1 Selenium extraction and purification

Because natural selenium isotope ratio measurements have not been developed previous to this work, there are no previous techniques to draw upon directly. Consequently, continued methods development has been necessary to enable processing of the river water samples, because of low concentrations of selenium and the fact that the selenate form dominates. The methods development work concentrated on the following goals:

1) Preconcentrate selenate.

We have already succeeded in preconcentrating selenite (SeIV) from Bay water, but the majority of the riverine selenium input is in the selenate (SeVI) form. Initial attempts at recovering the selenate involved reducing the volume of the sample by evaporation and converting selenate to selenite by adding large amounts of concentrated hydrochloric acid and heating. The solution was then neutralized and the selenite recovered in the usual way. These steps consume huge quantities of time and reagents, and are not desirable for larger-scale processing of samples.

Techniques for preconcentrating selenate prior to its reduction to selenite were researched. A technique that uses lanthanum hydroxide co-precipitation to preconcentrate the selenate was pursued and found to be promising except for one major flaw. A large mass of added lanthanum is required, and concerns were raised over possible traces of selenium in the reagent and the difficulty of removing the lanthanum later in the process.

Preconcentration of selenate by adsorption onto anion exchange resin is currently under development and the first natural samples will be processed by this method in the coming weeks. This procedure is effective for the dilute waters of the upper parts of the Bay system; all of the anions in one liter of water are adsorbed onto a small column (a few cubic

centimeters) of anion exchange resin. This procedure could ultimately be carried out in the field concurrent with filtration of the samples. After collection of all anions, phosphate and organic acid anions can be flushed from the column with dilute acid. The remaining anions (e.g., chloride, sulfate, and selenate) are then removed from the column by 30 mL of hydrochloric acid and this small volume is then processed via the usual methods.

2) Remove organic molecules from solutions.

Some types of organic acid molecules appear to have similar properties to selenite in the anion exchange chromatography procedure and thus are not separated well from the selenite. The traces of organic molecules in the final purified selenium solution interfere with the mass spectrometry, and this problem is especially severe with large samples of fresh water. Organic molecules can be oxidized with hydrogen peroxide or perchloric acid. This treatment leads to oxidation of the selenite to selenate, and this transformation would be advantageous in later processing of the solutions. However, our experiments and literature search reveal that the kinetics of this transformation are slow. Presently, an overnight digestion of solutions with organic residue problems is proposed, but faster oxidation methods are being sought.

3) Decrease the required sample size by optimizing mass spectrometry technique.

A three fold increase in the ion production efficiency has been achieved through ongoing experimentation, but it is likely that a further ten fold increase can be obtained. In one run, an ion beam of this size was observed, but the exact conditions have not yet been duplicated. Experimentation with the configuration of the instrument and the proportions of the various reagents involved in the technique should ultimately lead to much stronger ion beams. This would in turn lead to processing of 100 mL to 500 mL of Bay water, instead of the present 1 to 5 L sample size. The amounts of phosphate and organic anions processed would thus decrease and make the entire purification process easier and more reliable.

A technique for amplifying the output of the ion beam detector has also been employed. This technique probably decreases the precision of the measurements, but in cases where only a small amount of selenium (e.g., 0.2 μg) can be recovered from natural samples it allows measurements to be made. Testing of this method gave surprisingly precise results (0.05% uncertainty) for one sample, but further use of this technique awaits repair of the amplifying circuit in the coming weeks.

5 PLANT-SE: DESIGN, COLLECTION, AND ANALYSIS

Vertical selenium fluxes in the upper and lower marsh is largely dependent on plant uptake and assimilation. Assimilation is defined as one of three known fates for Se once it passes from the interstitial water into the root; Se can be:

1. volatilized as dimethyl selenide and thereby eliminated from the system,
2. assimilated into amino acids such as selenomethionine or selenocysteine, or
3. (temporarily) accumulated in inorganic form, primarily in the form of selenate.

Most of the selenium is eventually converted into amino acid form (Gissel-Nielsen, 1979) and consequently has the potential of adding organo-Se to the existing pool through the degradation of plant material. To investigate the role of marsh plants in selenium cycling, the following components are being addressed:

- aboveground biomass of six predominant marsh plant species: *Scirpus robustus*, *Scirpus californicus*, *Salicornia sp.*, *Typha latifolia*, *Distichlis spicata*, *Spartina foliosa*;
- total Se concentrations in above-ground and below-ground plant components;
- total Se concentrations for root-associated soils;
- litter bag study to determine the decomposition rates for plant material in the marsh and to account for lost material between samplings.

Based on the biomass data, turnover rate of plant material will be estimated. The calculation is based on annual production and mean yearly live biomass. The Se data will help develop a species-specific correlation between root and shoot Se, as well as a correlation between available soil Se and plant Se. It will also quantify the relative contribution of plant material to the overall Se mass balance. By measuring the turnover rate, the amount of Se returned to the marsh through decomposition will be estimated.

5.1 Methods

5.1.1 Biomass Sampling

Sampling consists of clipping all of the aboveground material falling within a 0.25 m² area at 5 randomly selected sites for each species. All vegetation is clipped to ground level and placed in a plastic bag for transport. Site selection, for quadrat placement, is based on the level of disturbance and species homogeneity and is otherwise random. Samples are then rinsed, dried at 70°C for 72 hours, and weighed. All reported weights are for dry tissue.

5.1.2 Total Selenium Determination in Plant Tissues

Total selenium values in both above- and below-ground tissues are determined through a wet ashing procedure modified from Ganje and Page (1974).

5.1.3 Total Selenium Determination in Root-Associated Soil

Soil-root composites for each quadrat are taken from the marsh and frozen until the time of extraction. Two subsamples of soil are removed from the composite as determined by their affiliation with the roots. Only soil contacting the roots will be investigated. The total selenium concentration in the soils is determined by a standard acid digestion procedure.

5.1.4 Litter Bag Study

The litter bag method (White et al., 1978; White and Trapani, 1982) will be used to account for material lost between sampling and to determine the rate of decomposition. Plant material from the biomass study will be cut and weighed before being placed into nylon litter bags (with a yet to be determined mesh diameter). 5 bags will be placed aboveground, containing aboveground components, and 5 belowground, containing belowground components, for each species. This represents a functional test to determine the effects of redox potential on decomposition rate. Bags will be collected at approximately 1 month intervals starting 1 month after insertion. Upon collection, the bags will be cleaned, rinsed, material dried and weighed to account for material lost.

5.2 Preliminary Results

The first sets of plant and associated soil samples were collected at MRP and SHB on 1/18/96 and 1/23/96, respectively. Along with live above- and belowground parts for all the species listed above, dead aboveground parts were sampled for *S. foliosa*, as these were significant at the time of collection.

Above-ground biomass was measured and is shown in Figure 5.1. As expected, the greatest biomass was observed in the lower marsh region, vegetated by *Scirpus* and *Typha*. The mean biomass for these species at the MRP site ranged from 1,100 g m⁻² to 1,600 g m⁻²; at SHB that range was from 750 g m⁻² to 1,250 g m⁻². The next highest biomass was observed in the upper marsh, where mean values for *D. spicata* were similar for both sites (around 750 g m⁻²). *Salicornia sp.* biomass, however, was significantly higher at SHB than at MRP (950 g m⁻² compared with just over 100 g m⁻², respectively). The smallest biomass was measured in the transition from the lower marsh to the mudflats, an area dominated by *S. foliosa*. Values were similar for both sites, with the mean biomass of the standing dead higher than the alive plant parts (150 to 200 g m⁻² vs. 50 to 100 g m⁻²). There are no plants in the mudflats.

Se concentrations in the aboveground plant tissues were measured and are shown in Figure 5.2. All values in the upper and lower marsh fall between 0.1 and 0.2 ppm, except for *T. latifolia* at SHB, where the mean concentration is at 0.7 ppm. This is unusual in that the range of values for this species is very broad compared to all other species. *S. foliosa*, at the marsh/mudflat interface, contains Se in concentration ranging from 0.3 ppm in the standing dead at SHB to 0.65 ppm in the live plants at MRP. Data for the belowground parts is not yet available.

By combining the biomass and tissue-Se data, Se mass per area can be calculated. The result is shown in Figure 5.3. Values for most species fall in the range of 100 to 200 µg m⁻². Because of the anomalously high tissue-Se in *Typha* at SHB, the Se mass per area for this species at SHB is anomalously high (mean around 725 µg m⁻²). *Spartina foliosa*, representing the marsh/mudflat interface contains low Se-mass due to its very low biomass, and despite higher than average tissue-Se concentrations. Relatively speaking, aboveground plant-Se comprises a small, yet not negligible fraction of the total Se

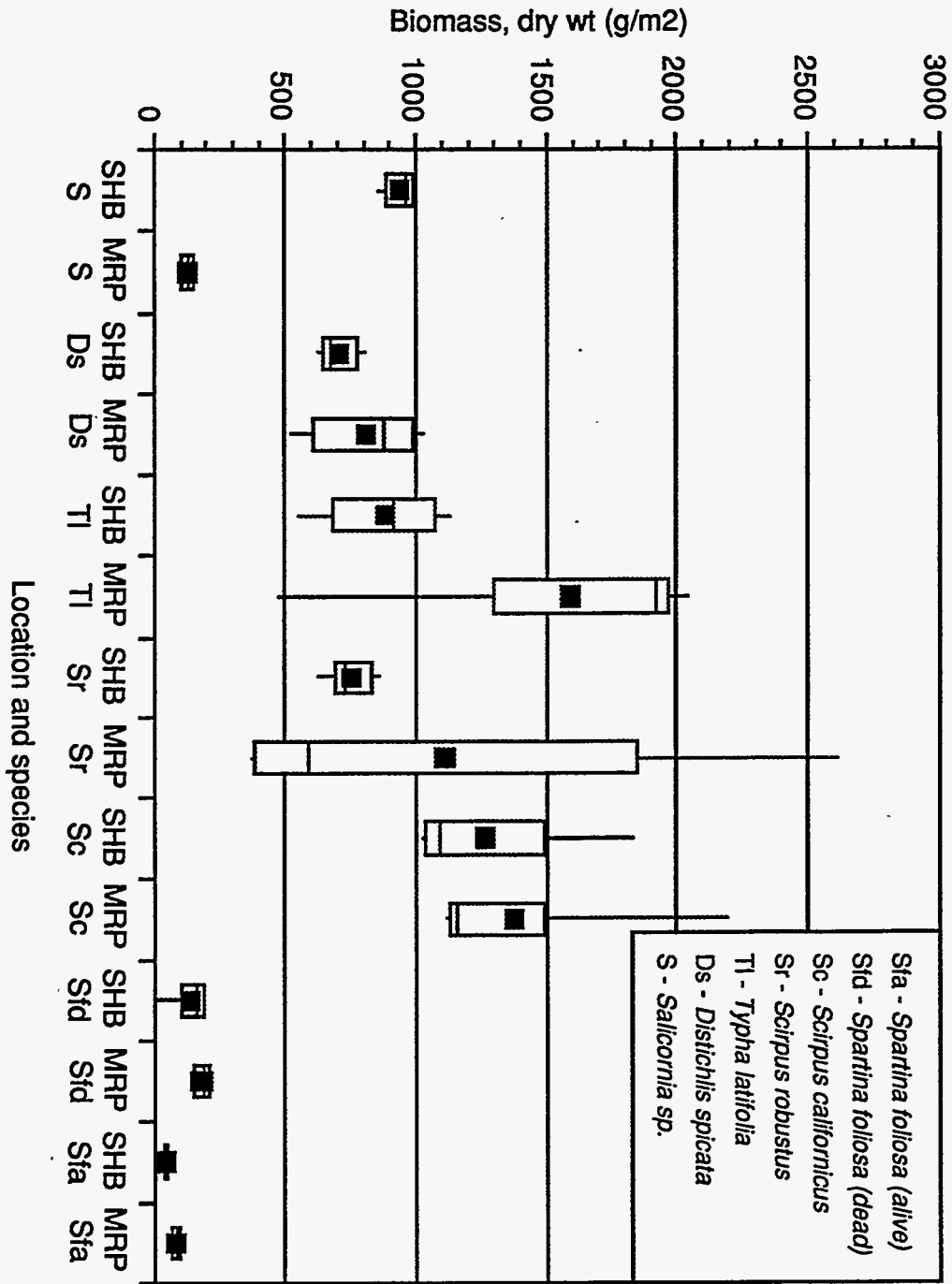


Figure 5.1 Species-specific biomass of aboveground parts at sites MRP and SHB. The filled square represents the arithmetic mean of five values; the box represents one standard deviation; the whiskers show the range of values; the line inside the box is the median value.

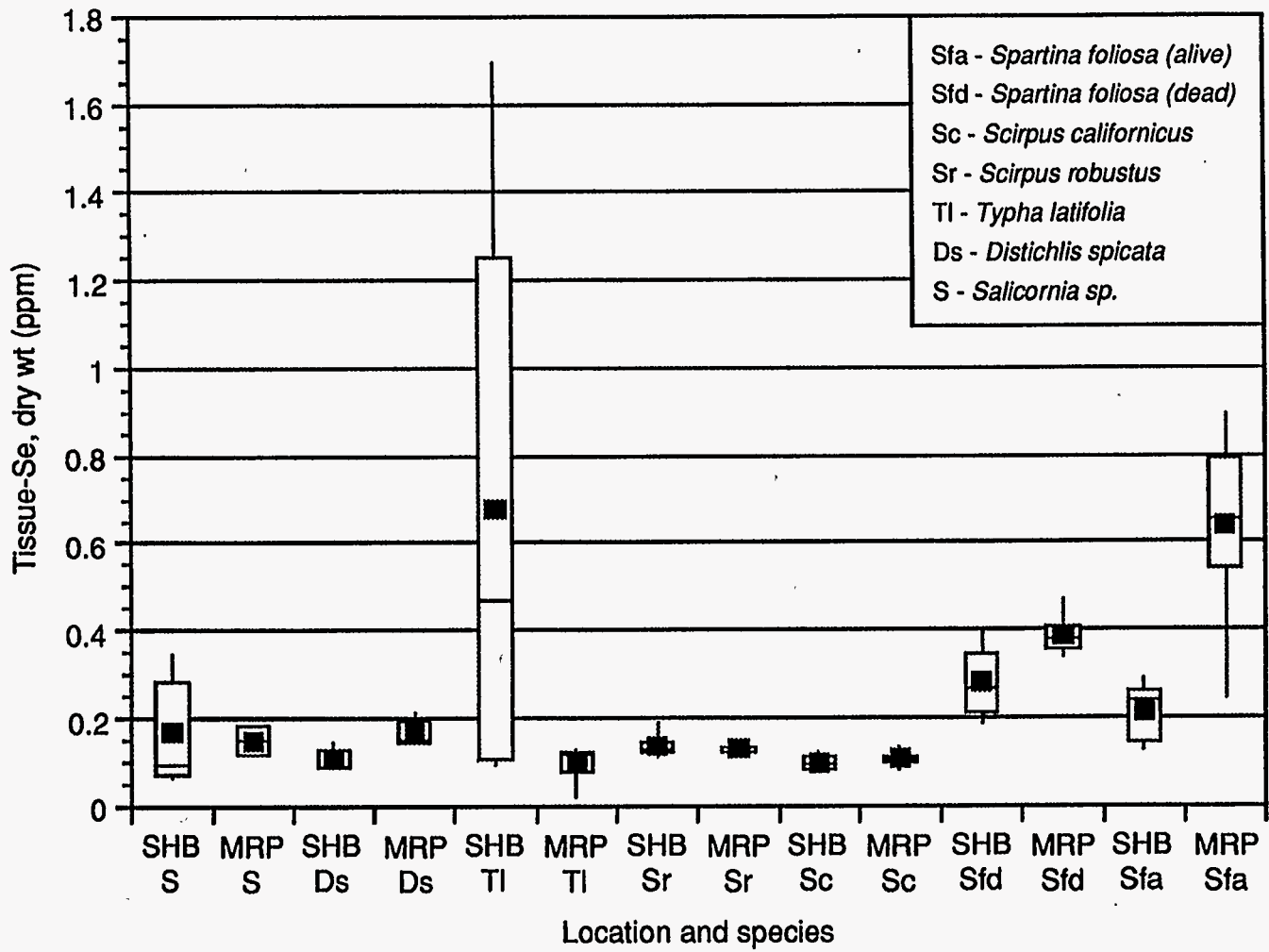


Figure 5.2 Species-specific tissue-Se concentrations of aboveground parts at sites MRP and SHB.

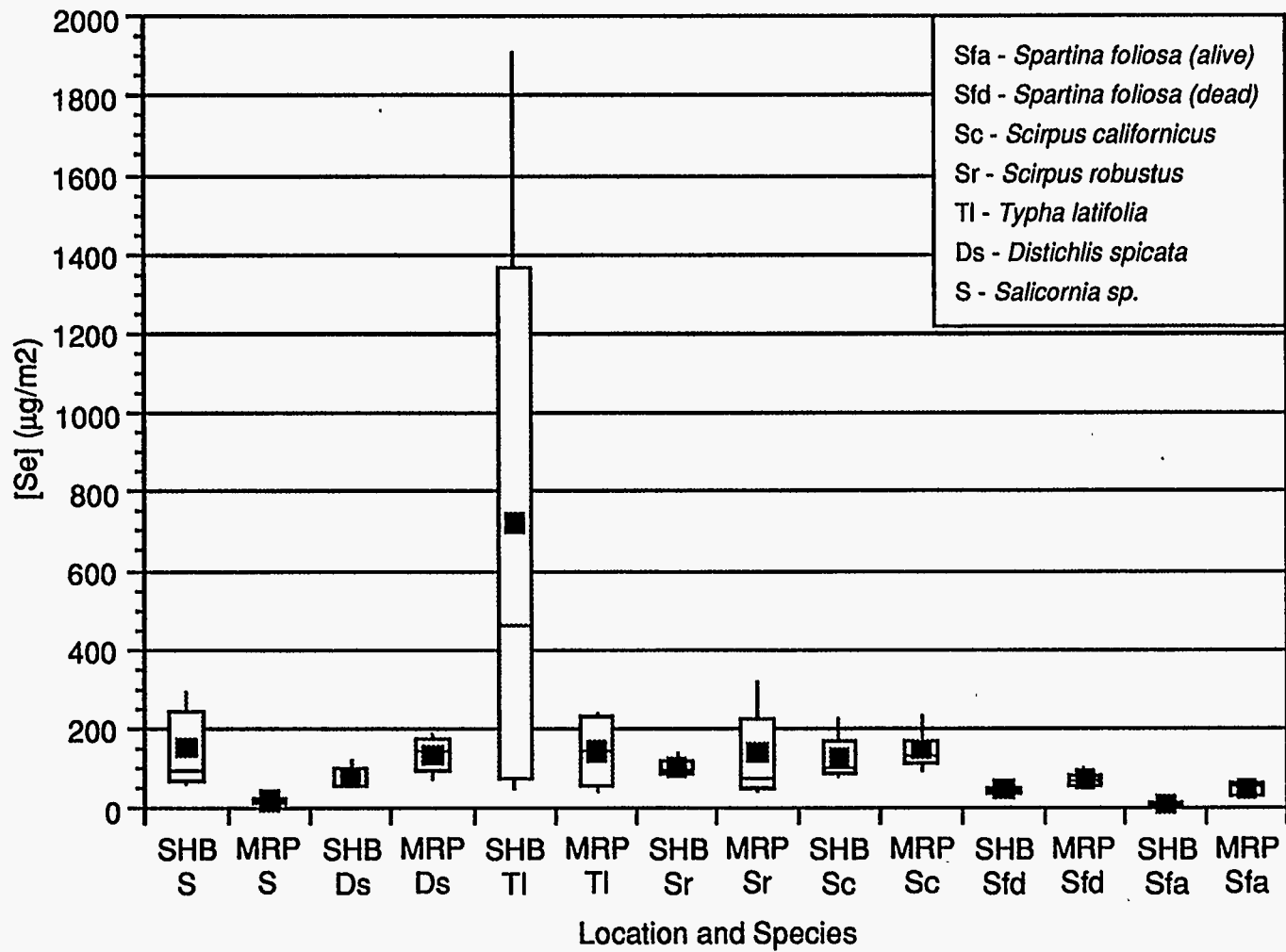


Figure 5.3 Species-specific Se-mass of aboveground parts at sites MRP and SHB.

inventory. For example, the top 10 cm of marsh sediment at either site contains around 8,000 $\mu\text{g m}^{-2}$. However, the annual contribution of plants to the system is yet to be determined; the annual influx of Se on sediment, assuming a sedimentation rate of 2 mm yr⁻¹, is on the order of 1,000 $\mu\text{g m}^{-2}$. Depending on the plant turnover and litter decomposition rates, plant-Se may be an important link in the Se cycle in these environments. Furthermore, below-ground parts, the biomass and plant-tissue Se of which are currently being measured, may be an even more significant pool of Se.

6 SEDIMENT DYNAMICS

Previous work has shown that suspended sediments carry significant amounts of Se (Cutter, 1989). As pointed out in Chapter 2 of this report, sediment deposition may in fact control sediment concentration patterns in the intertidal environment. Therefore, a study to evaluate the rates of sediment deposition in the upper marsh, lower marsh, and mudflat environments is underway.

There are two reasons for calculating a sediment budget for the marshes. The first is to measure rates of sedimentation on the mudflats and the marsh plain and to determine how these rates change seasonally. It is hypothesized that the rates are higher in the winter when the suspended sediment concentration is high and storm surges lengthen the periods of inundation of the marsh.

The second reason for studying the sediment budget is to identify the nature and origin of the sediments. It is hypothesized that sediments deposited on the mudflats are primarily mineral while the sediments on the marsh plain have a higher percentage of organic material derived in situ from plant litter. Furthermore, it is hypothesized that some sediments from the mudflats may become remobilized by waves and re-deposited onto the marsh plain.

To test these hypotheses, erosion pins and sediment traps were put in place at both the Martinez and Southampton sites on March 23, 1996. The erosion pins are stainless steel rods that are two feet long. They were inserted into the mudflats and marsh plains so that only the top 30 centimeters of each pin remained unburied. The sediment traps consist of 10 x 10 cm squares of plastic with long bolts at each corner to serve as anchors. The plastic surfaces were roughened by gluing fine sediment on them. These traps were then installed as flush to the ground surface as possible. Twelve erosion pins and sediment traps were installed at evenly spaced intervals along a transect in Martinez Marsh. The transect is perpendicular to the shoreline and spans from the high marsh to the mudflats (Figure 6.1). Similarly, twelve pins and traps were installed at evenly spaced intervals along a transect in Southampton Marsh. There is only one station in the mudflats at this site because walking on the mudflats is treacherous (Figure 6.2).

The pins will be measured on a monthly basis. These will indicate whether any sedimentation or erosion has occurred. Sediments from the traps will be analyzed to determine whether they are organic or mineral sediments.

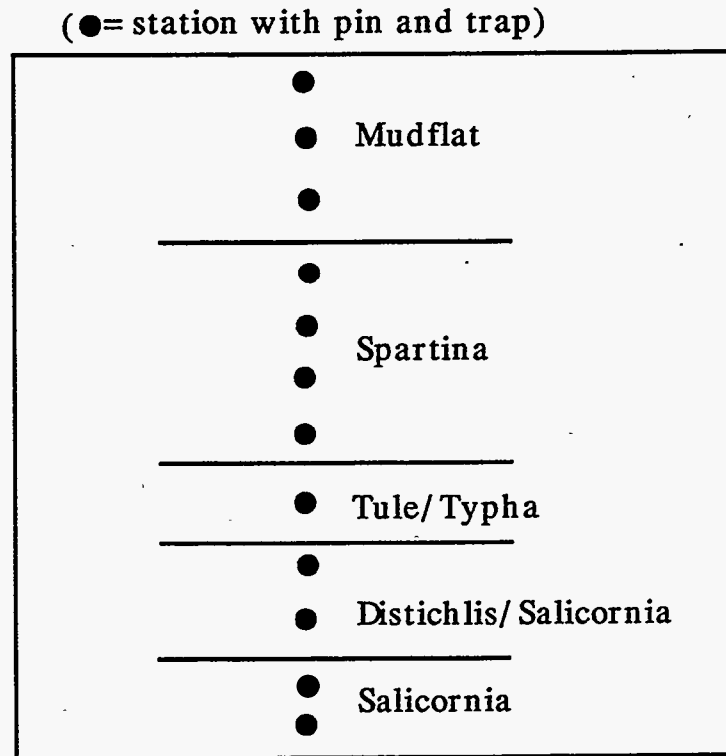


Figure 6.1 Distribution of pins and traps within different environments at Martinez Regional Park.

(●= station with pin and trap)

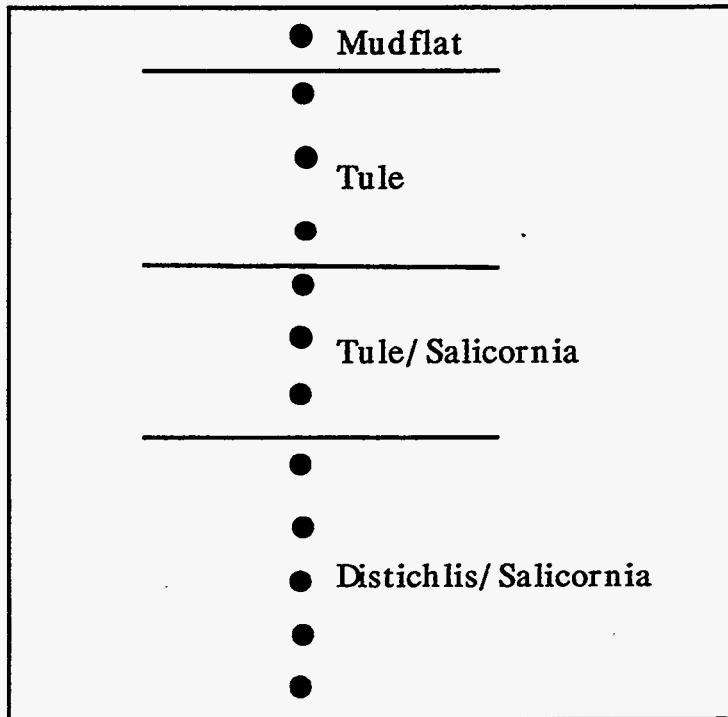


Figure 6.2 Distribution of pins and traps within different environments at the Southampton Bay site.

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