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Selenium Fractionation and Cycling in the Intertidal Zone of the Carquinez Strait

Quarterly Progress Report
October 1995 through December 1995

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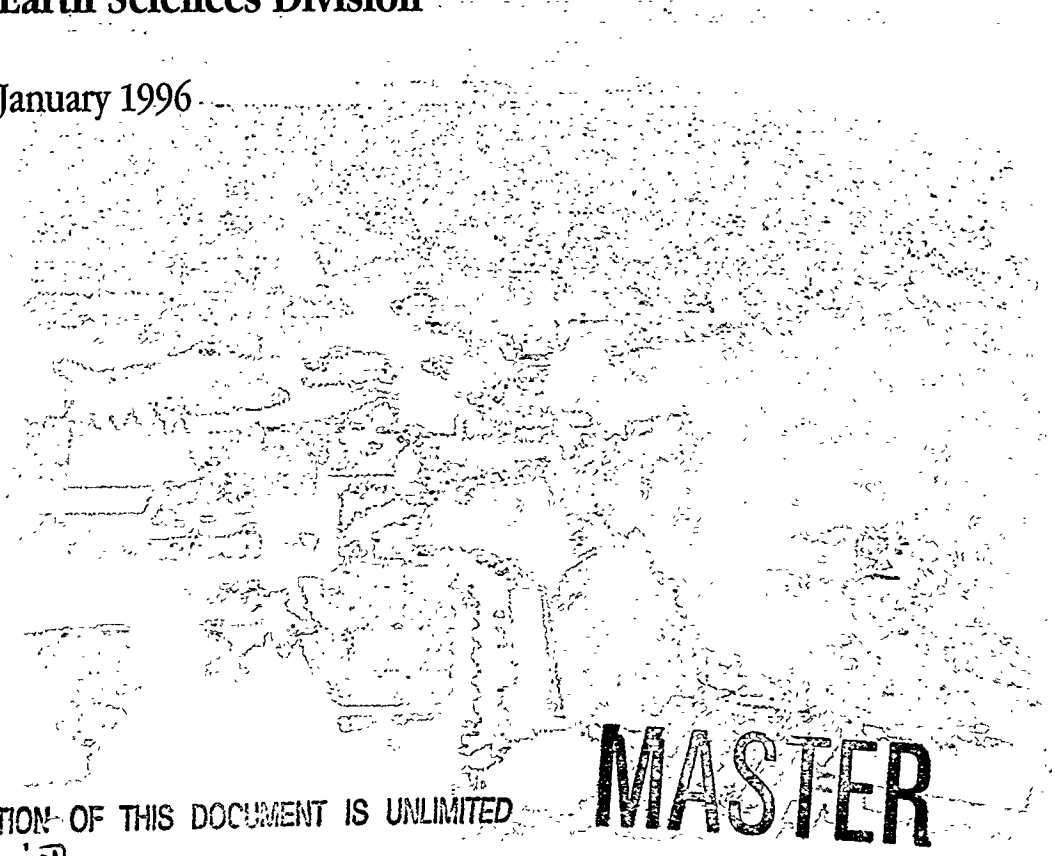
Earth Sciences Division

January 1996



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1 INTRODUCTION

This quarterly report describes the research on selenium (Se) cycling in the marshes and mudflats of the Carquinez Strait between 10/1/95 and 12/31/95. Chapter 2 contains descriptions of field activities and laboratory work related to chemical characterization of sediments and soils. Eh and pH data are presented. 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 describes advances made in the analysis of parts-per-trillion level Se, using a lanthanum hydroxide co-precipitation method, and the determination of matrix effects. Chapter 5 is an update on stable Se isotope research and Se purification techniques. The reader is referred to the 1995 Annual Report (Zawislanski et. al., 1995) for details on the project design, site selection, and methodology.

2 COLLECTION AND ANALYSIS OF INTERTIDAL SEDIMENTS

Sampling of soil and sediment at both the Martinez Regional Park (MRP) site and the Southampton Bay (SHB) site took place in early December. The goal of this sampling was to better characterize Se distribution and speciation as a function of depth, distance from shore, pH, and Eh (redox potential). Previous sampling had been done with hand augers which may have caused some disturbance and cross-contamination between different depth levels. A new sampling tool was designed and constructed at LBNL to accommodate the sampling of both very wet, almost flowing mudflat sediments and root-dominated marsh soils. This tool is described in Section 2.1. The sample locations and approach are described in Section 2.2. Results are found in Section 2.3.

2.1 New Sampling Tool Design

The new marsh core sampler design is shown in Fig. 2.1. Its main advantages over other similar tools are that it has both sharp cutting teeth, similar to a silage auger, which are capable of cutting through tough roots with minimal operator effort and disturbance to the soil profile, and a valve which can be opened when the core barrel is inserted into the soil and closed when it is withdrawn. This way, a slight vacuum is created in the core barrel preventing the often wet and slippery core from falling out. A clear butyrate liner is attached to the PVC cap, so that when the pin is pulled out, the top of the sampler is separated from the bottom and the intact core is removed while in the liner. This allows for visual inspection of the undisturbed core. The core is immediately capped and can be refrigerated or frozen in this state. Because butyrate maintains its properties when frozen, the core can be cut frozen, using a band saw, which makes a fine subdivision of the core possible.

2.2 Soil Sampling Procedure and Eh/pH Measurement

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 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. Samples were taken close to low tide, in order to be able to sample the largest expanse of mudflat

possible. In the laboratory, small holes were drilled in every core at depths of 0.5, 1.5, 2.5, 4.0, 6.25, 8.75, 12.5, and 17.5 cm, in order to accommodate the insertion of Eh and pH electrodes. Banks of platinum and antimony electrodes were used to measure Eh and pH, respectively. Both Eh and pH were recorded directly in mV. Subsequently, Eh, which was measured referenced to a calomel electrode, was adjusted by adding 245 mV to reference it to a standard hydrogen electrode (Light, 1972). pH was calculated using a linear correlation derived by Schaller and Fischer (1981) and calibrated to readings taken with a glass pH electrode in pH 7 and 10 buffers. After the measurement, the cores were re-sealed and frozen for further processing, which will include x-ray spectroscopy for redox couples and sequential extraction for Se.

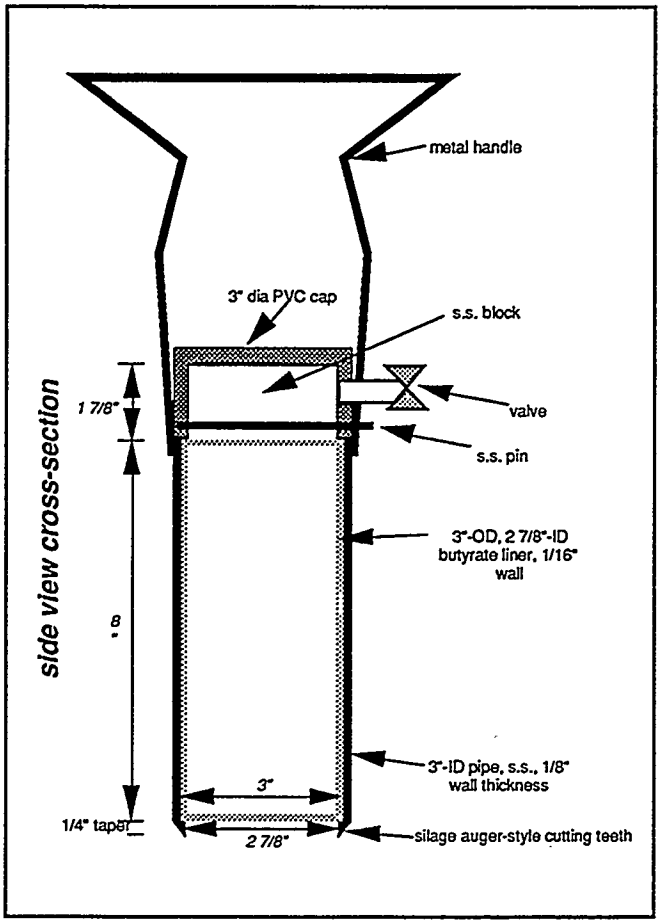

Figure 2.1 Schematic diagram of new marsh core sampler design.

2.3 Eh and pH results

The results of the Eh measurements have shed light on the redox conditions at the two sites. Overall, soils and sediments for MRP were more oxidized than those from SHB. This may have to do with sediment texture, where MRP sediments are generally coarser than those at SHB; finer sediments retain more water, resulting in more reducing conditions. The most significant trend at both sites was the expected decrease in Eh with depth, with soils at 17.5 cm being around Eh = 0. With a few exceptions, surface soils at both sites had Eh in the range of + 100 to 300 mV. The sharpest decrease in Eh occurs at a depth of approximately 3 to 4 cm. However, soils which contain a high density of plant roots, as found in the lower and upper marsh, are generally more reduced due to organic matter decay. Because of an absence of plants, it is easier to resolve Eh trends in the mudflats. pH in MRP soils was generally between 6.5 and 7.5 in the marsh and up to 8.5 in the mudflats. At SHB, pH was much higher, up to 10, both in the marsh and the mudflats.

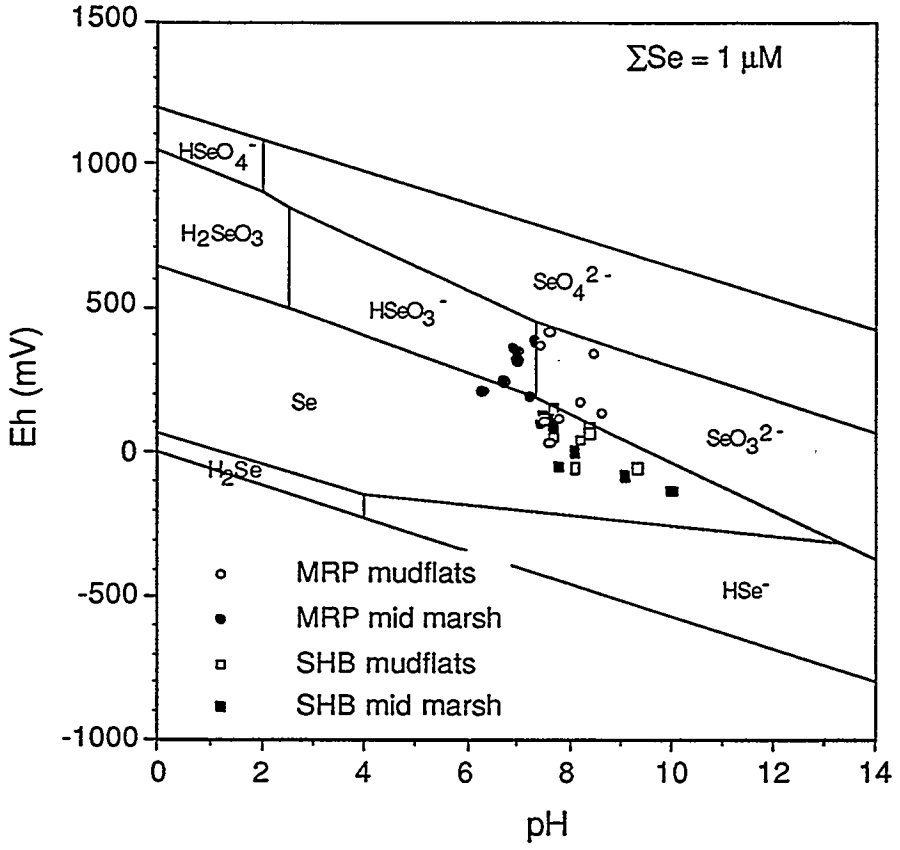

Figure 2.2 Eh-pH diagram for the Se-H_2O system with data from four soil/sediment profiles.

By superimposing Eh-pH data onto a Se stability diagram (Fig. 2.2 and 2.3, after McNeal and Balistrieri, 1989), it can be seen which Se species are to be expected in this environment *under equilibrium conditions.* Due to the presence of plants, animals, and the action of waves and tides, resulting in changes in moisture conditions, these sediments are not likely to be in chemical equilibrium. However, this representation is helpful in understanding which Se species are *most likely* to be present.

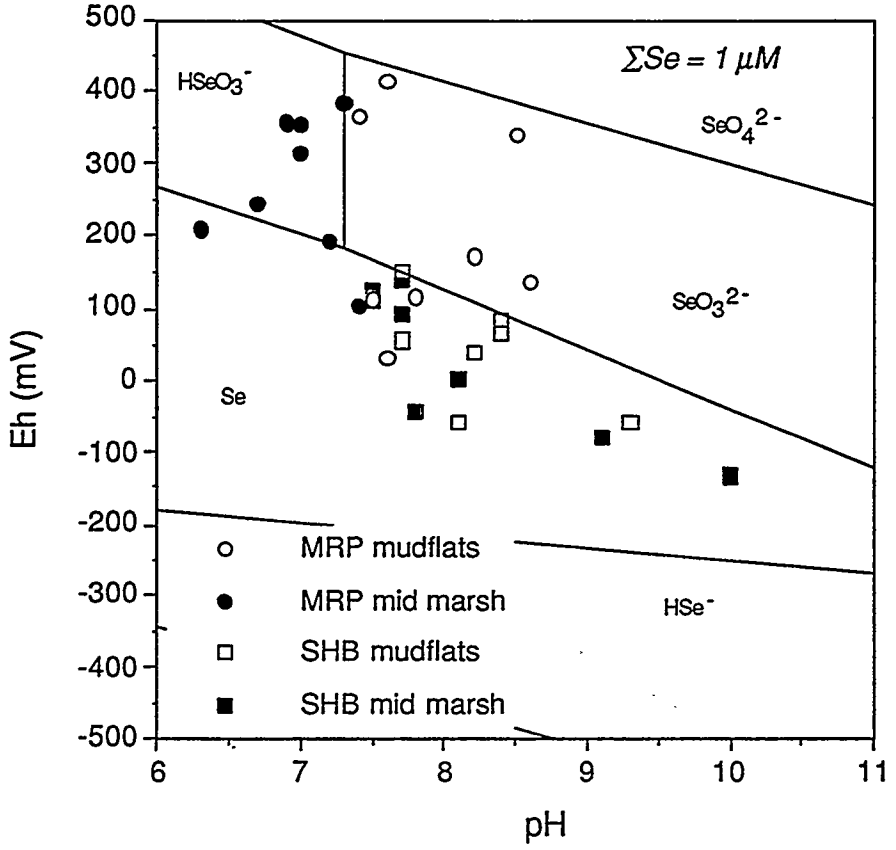

Figure 2.3 Eh-pH diagram for the Se-H_2O system with data from four soil/sediment profiles -- close-up view.

As can be seen from these diagrams, most of the MRP soils fall above or just below the selenite-elemental Se line, whereas all of the SHB soils fall into the elemental Se stability field, but still close to the selenite field. This agrees qualitatively with prior results of fractionation, which showed selenate concentrations to be between 0 and 5% of total, adsorbed selenite to be on the order of 10 to 20% of the total, and organically-associated and elemental Se to comprise most of the remainder. Because organically-associated Se may contain a number of Se species, this analysis cannot be taken much further, but it is

clear that reduced forms of Se dominate. In fact, the above stability diagrams are for a Se-H_2O system only, and organic Se species are not considered.

The next step in the analysis of these cores is sequential extraction. The way in which these cores will be subdivided will be based on the available Eh-pH data, which will help define the correlation between Eh-pH and Se fractionation. Both wet chemistry and x-ray spectroscopy will be used to determine ratios of redox couples, such as Fe and Mn. This will define the relevance of in-situ measurements.

3 METHODS FOR SE EXTRACTION FROM SEDIMENTS

Speciation studies have followed three routes during the past quarter: 1) improvement of the extraction methods for elemental Se, 2) development of the pyrite Se extraction method, and 3) application of extraction methods to suspended particulate matter. Below is a summary of the results in these three areas. In addition to the extraction method research, a collaborative project with Dr. Sam Luoma at the USGS, Menlo Park, has been undertaken to determine the role of different selenium fractions in SPM (extracted by the sequential extraction technique) on the uptake of Se by surface feeding clams (*Macoma balthica*). The basic outline of the mechanism by which refinery Se enters the food web is presented, and the role of SPM and clams hypothesized.

Additional effort has been made to further perfect the extraction methodology for Se speciation, with improvements in the sulfite extraction (Sx) and preparation of the pyrite extraction (CrX) method. The sequential extraction procedure has a limited efficiency with the original procedure for elemental Se, and improvements in the sulfite analysis has proven to drastically improve Se recovery, making the sequential extraction process significantly more efficient.

3.1 Sulfite Extraction

Initial tests of the sulfite extraction appeared to demonstrate that longer duration sonication did not significantly alter elemental Se solubilization. More comprehensive testing has shown that 6 hr of sonication, rather than the 1 to 2 hr used previously, drastically enhances solubilization, improving the efficiency of the sulfite extraction. Additional work needs to be done to determine if additional sonication is merely resulting in dissolution of all residual Se fractions, or merely improving the solubilization of elemental Se. Velinsky and Cutter (1990) did not observe increased solubilization of non-target Se fractions due to sonication, but did report that sulfite does solubilize organic and inorganic Se species (Se IV and Se VI). Sequential extraction has been shown to remove the bulk of the organic, selenite, and selenate species (Zawislanski et al., 1995). Therefore, interference from other residual Se species in the elemental Se extraction should be minimal in comparison to elemental Se concentrations. Mineral dissolution of silica species in sulfite and all other extractions appears to be low for silicates. Dissolution of non-silicate minerals is apparently taking place given the high concentration of Fe and Al in sodium

hydroxide extracts, but sulfite does not appear to be removing high concentrations of metals.

Results from the new extraction method have revealed that the residual fraction is actually much lower than previously determined using the old sulfite method, and elemental-Se measured by the new method are 50-300% higher. The new method still has to be tested for problems with increased mineral dissolution (due to the sonication) and increased release of residual Se fractions such as organically bound Se, but it does appear to be improving the overall removal of Se.

3.2 Pyrite Extraction

Testing of the pyrite-Se extraction and of the apparatus for the procedure was done in preparation for analysis of the residual soils and sediments from the sequential extraction procedures. The pyrite-Se method apparatus is similar to that developed by Velinsky and Cutter (1990). A diagram of the apparatus is included in the Figure 3.1, as we have now reconfigured the system.

The procedure is as follows: a sample of soil is placed in the reactor vessel and suspended in 10 mL of 6 M HCl. After purging for 3 min with helium, the valve is positioned such that the reactor vessel is connected to the Se trap and vented to the atmosphere. The trap is placed in liquid nitrogen and the chrome solution is added to the reactor vessel. After addition of the required chrome solution the reactor is allowed to react and purge for 20 min. Then the valve is turned such that the reactor vents directly to the atmosphere, and the trap is connected to the column and AA loop. After the baseline is established, the trap is removed from the liquid nitrogen, and the hydrogen selenide is separated by the Porapak column as it travels to the AA. The system is calibrated using the low level Se measuring system.

An error in the original publication led to problems in our system because it was designed on the specifications in the paper. The detailed description and method below outlines the procedure as it is followed in our laboratory. The error was found regarding the diameter of the Porapak column used to chromatographically separate hydrogen sulfide from hydrogen selenide (tubing diameter cited as 1/4" instead of 1/8"). The larger tubing diameter specified in the paper led to poorer peak resolution, and as a result, insufficient separation to allow for quantification. The new column diameter is now being tested, and should provide better separation.

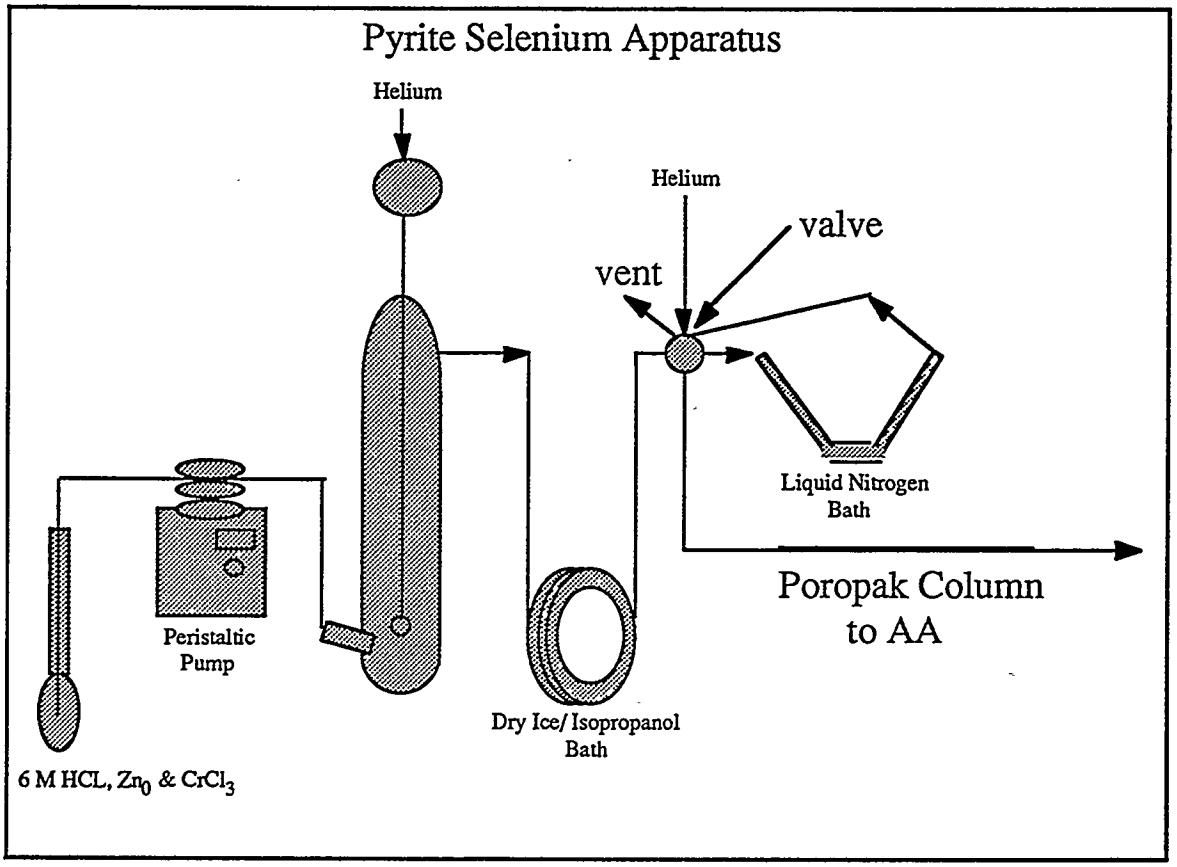

Figure 3.1 Pyrite Se extraction apparatus.

Tests to determine if hydrogen selenide is present, and whether the reduction reaction works as well as shown by Velinsky and Cutter (1990) appear to be promising given that peak heights cannot be quantified yet. Work with the larger diameter column showed that selenium is present in the residual soils and sediments in significant concentrations, and that the technique is able to remove it. Improved removal of elemental Se should make this method more reliable because there will then be less interference from elemental Se. Velinsky and Cutter (1990) found that there was no interference from non-elemental Se fractions.

3.3 Sequential Extraction of Suspended Particulate Matter Se

The difficulty of analyzing Se in suspended particulate matter (SPM) Se stems from the variability of sediment loading in the Bay, and the variability of Se concentrations in the SPM. At high SPM loading, it is presumed that considerable amounts of sediments on the surface of mudflat region are resuspended, and that storm run-off is introducing

considerable amounts of clays from streams and soils surfaces. As a result, total Se concentrations are presumed to decrease with increasing loading of SPM. At low SPM loading, processes that concentrate Se in SPM are significant contributors to SPM levels in the Bay. Diatoms and microscopic organisms can take up Se, and increase the Se concentration in the SPM. As a result, total Se concentrations in SPM are expected to be highest with low energy, low SPM loading. Unfortunately, during the settling periods between storm events, low Se-sediments can dominate the watershed and convolute verification of this assumption.

Limited total Se analyses of SPM measured at the Martinez Regional Park location (MRP) do not prove the operating assumptions concerning Se concentrations in SPM. The table below summarizes the SPM measurements taken in December as part of the study of the effects of SPM on clam Se concentrations.

Table 3.1 SPM Se concentrations at MRP during the month of December.

	Units	*12/1/95*	*12/12/95*	*12/15/95*	*12/20/95*
Σ Se	*$\mu g\ g^{-1}$*	1.463	0.978	0.735	1.082
SPM Load	*$g\ L^{-1}$*	0.0268	0.147	0.130	0.0183
SPM-Se Load	*$\mu g\ L^{-1}$*	0.0392	0.144	0.096	0.0198

Sequential extraction procedures for SPM-Se are presently under development, and are being tested for quantifiability of low levels using the FIAS analytical method. Difficulty of analyzing the low mass of SPM removed from waters makes quantification problematic. Sediments are removed from water using a centrifugation method developed for this study. Water centrifuged at 10,000 rpm for 30 min has little or no >0.45 μm particles in suspension, making this method an efficient and clean method for removing SPM. Sequential extraction of the freeze-dried residue requires exact measurements of liquid masses. Liquid to solid ratios have to be very high to have sufficient volume for analysis. Given that the typical mass for extraction is between 0.1 and 0.5 g, small volumes are required and significant dilution of the extracted Se is unavoidable.

3.4 SPM-Se Correlation with Clam Se

Luoma et al. (1992) demonstrated that surface sediment feeding clams, such as *Macoma balthica*, take up organic Se in the form of phytoplankton biomass with an 86 % efficiency, whereas dissolved selenite and particulate elemental Se are taken up at much

lower efficiency (<25 %). These studies were done in laboratory tanks where conditions were carefully monitored and controlled. In estuarine sediments, determination of the role of SPM Se on the Se concentrations in clams is not as easily demonstrated. It is also not clear how refinery effluent Se, released as selenite, might influence the concentration of Se in clams given the poor efficiency of selenite uptake by clams.

One route by which clams are likely to ingest selenite through a high efficiency absorption pathway is through SPM. SPM traveling into the Carquinez Strait adsorbs selenite, which then undergoes reduction on the surface of the organically coated colloids or is ingested and absorbed by phytoplankton associated with SPM. The SPM, with the organically associated Se is then ingested by clams and the reduced organic Se is efficiently absorbed by the clams. Once in the clams, Se will further affect the food web.

Testing this hypothesis is the goal of our collaboration with Dr. Luoma. It is our hope that by studying the adsorption properties of organic matter associated with SPM, we will be able to determine the affinity of selenite for these surfaces under estuary salt concentrations and pH. In addition, field measurements of SPM concentrations and Se fractionation within the SPM will help correlate clam Se concentrations with individual SPM Se fractions. It is presumed that clam Se concentrations will most closely correlate with organic Se concentrations in the SPM. The absorption efficiency of *organically associated* Se by clams is not known, but certainly *organic* Se is absorbed very efficiently (77-96%).

4 ANALYTICAL PROCEDURES

4.1 Low-level Se Analysis Procedure Development

The analysis of seawater samples and soil extracts has often posed a problem. By conventional flame atomic absorption (FLAA) methods, extracts for selenite analysis are difficult to analyze. The original Cutter method (Cutter, 1978) was set up for the analysis of water samples, but was not intended for the analysis of large numbers of samples. The Cutter method takes at least fifteen minutes per sample to analyze and requires constant supervision by a chemist. After examining the literature, a recently published method by Tao and Hansen (1994), which utilizes flow injection (FIAS) hydride generation atomic absorption spectrometry with on-line pre-concentration by co-precipitation with lanthanum hydroxide, was found. The paper reported a method detection limit of 0.001 mg/L. The most interesting aspect of this method is that it is run by an autosampler and the analysis takes only 2 minutes. We thought the method should be examined since a FIAS system was already available. In the long run it could prove a more cost effective method of analysis.

The co-precipitation method was relatively easy to set up. There were some problems going from the paper to the actual method, but a working method was achieved. The main concerns are the pH adjustment of samples, the stability of the buffer, and the time for co-precipitation.

Samples must be adjusted to a pH of 3.0 prior to analysis. The pH adjustment is critical because the co-precipitation will not be as effective if the pH is not at 3.0 ± 0.2. Lanthanum nitrate is naturally at a pH of 3.2 when in solution. This set our upper limit for the pH. When the lower end of the pH was examined the co-precipitation efficiency dropped off when the pH was below 2.8. This was primarily because the buffer could not be as effective at co-precipitating the lanthanum hydroxide and selenite.

The buffer, ammonium chloride/ammonium hydroxide, is at a pH of 9.1. Unfortunately, when the pH reaches 8.3, carbonate forms from carbon dioxide, CO_2, in the air. CO_2 interferes with the analysis. When the buffer is exposed to CO_2, the efficiency drops off significantly and the pH of the buffer solution begins to lower with the formation

of bicarbonate in solution. The buffer must be kept in a inert atmosphere. Once the buffer was kept in a tightly sealed bottle with a layer of argon over the top, pH remained steady and the efficiency was consistent.

The time for allowing the co-precipitation of the selenite and lanthanum hydroxide was looked at next. Using a two-meter knotted reactor, a 1.0 ppb standard was analyzed several times for different time intervals. The knotted reactor reaches a level of saturation after a certain pre-concentration interval.

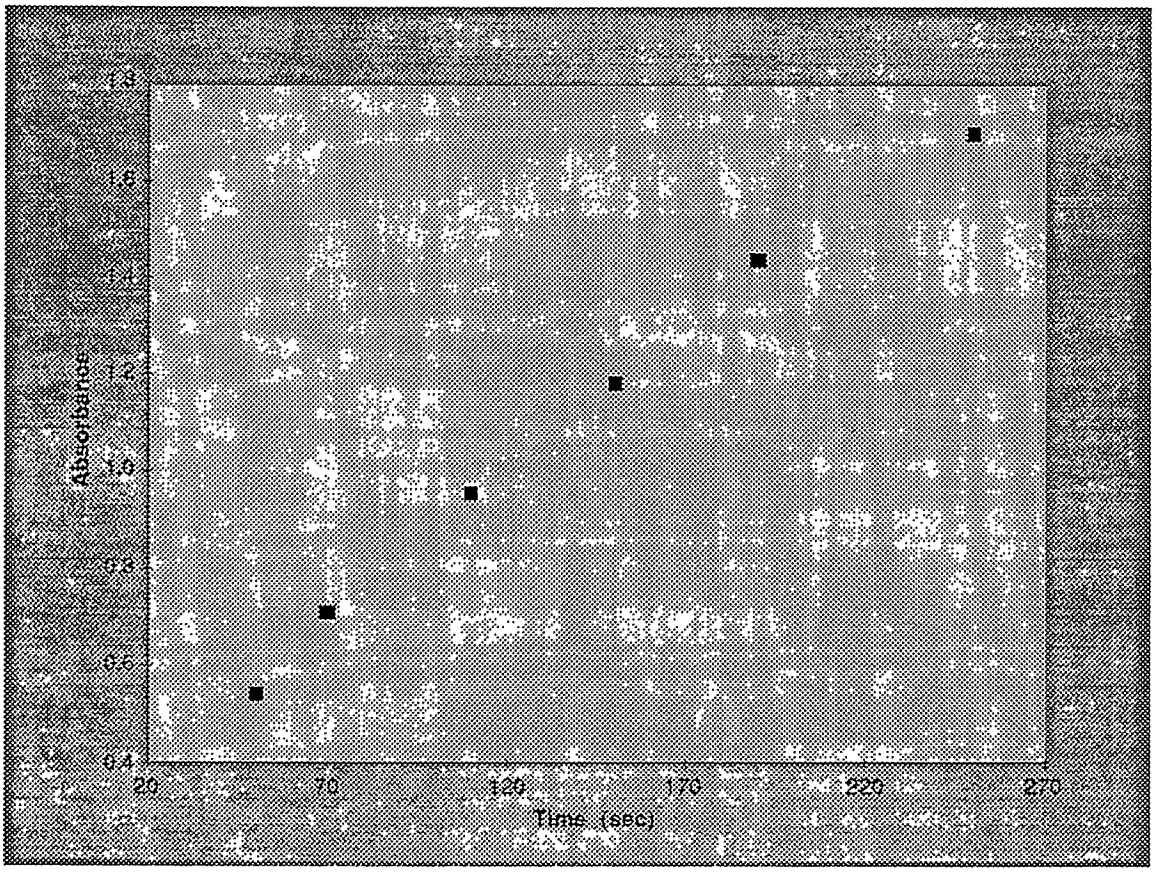

Figure 4.1 Absorbance for a 1 ppb selenite standard at different time intervals.

Figure 4.1 is a plot of a 1.0 ppb selenite standard pre-concentrated for different time intervals to figure out the saturation and most efficient pre-concentration time. The curve is has a fit of $r^2 = 0.994$ for all five points. When the last point at t = 250 sec is removed the $r^2 = 0.9995$. (Note: each point is an average of three replicates.) This indicates that there is the beginning of saturation at 250 seconds of pre-concentration time.

When everything is considered, the optimum working parameters are a two-meter knotted reactor with a pre-concentration time of 190 seconds (Table 4.1). This makes the total run time 221 seconds per sample for a 50 pptr detection limit for a seawater matrix. 16 samples can be abalyzed per hour.

Table 4.1 Absorbance as a function of a range of pre-concentration time.

Time (sec)	Sample Consumed (ml)	Selenium Trapped (ng)	Absorbance	Total Time of Analysis (sec)
70	4.67	4.67	0.709	101
110	7.33	7.33	0.960	141
150	10.0	10.0	1.184	181
190	12.7	12.7	1.435	221

The QA/QC for this analytical method does not need to differ from the existing QA/QC protocol with regards to matrix spikes, replicates, standards, blanks, and check samples. The frequency should remain the same, but the level of the matrix spikes should not exceed 1.00 mg/L.

4.2 Analytical Method Testing -- Matrix Effects

When this analysis was performed on water samples collected from Martinez Regional Shoreline Park (MRP) and the Monterey Bay there were some remarkably different matrix effects. Martinez Bay contained high concentrations of dissolved organics. This interfered with the generation of the hydrogen selenide. When ten samples were spiked with 1.0 mg/L the average recovery was 46%. The addition of sulfanilamide did not help the recovery in this method as it did with the Cutter's method. But when the sample was degassed with argon for 10 min. the recovery jumped to 87% for an average of six samples with a %RSD of 7.20%. When the MRP water was filtered through a 0.45 μm filter and degassed, the recovery for ten samples was 107% with a %RSD of 10.8%. For the Monterey seawater the recovery for ten samples was 94% with a %RSD of 6.98% when degassed with argon. When the sample was not degassed the percent recovery for ten samples was 101% with a %RSD of 4.76%. Therefore we are not seeing any dissolved organics interfering with the analysis of the Monterey Bay samples. When more areas are available for analysis we will look at the effect of dissolved organics so that a prep method can be tailored for each individual area in the bay.

Labwork has also begun to include the analysis of extracts for metals and interstitial samples for anion analysis. The metals analysis is following SW-846 protocols for ICP methodology (method 6010). The analysis of the interstitial waters is done by ion chromatography. The analysis is done using an HPLC with a conductivity detector for the major anions: F, Cl, Br, NO_2, NO_3, SO_4, and PO_4. This work will continue into the next quarter.

5 STABLE ISOTOPE METHODS

At the close of fiscal year 1995, techniques for purifying Se and obtaining precise measurements on the mass spectrometer had been worked out, and the first measurements of actual samples were under way. Since that time, a few additional measurements were made, analysis of the more problemmatic Bay water samples was begun, and procedures were adapted to enable measurements of Bay water and streamline processing of all types of samples.

The analysis of a Shell Refinery effluent sample reported in last year was confirmed by a duplicate measurement. A soil water sample from the San Joaquin Valley (Kesterson area), chosen as a first example of the riverine input to the Bay, was also analyzed. The internal standard, MH495, was analyzed at the beginning of each mass spectrometry session, and now enough duplicate measurements have been performed to establish moderate-term (one month) reproducibility (Table 5.1).

Table 5.1 Results of Se isotope ratio analyses.

Sample	$^{80}Se/^{76}Se$ ratio
MH495-1	5.2982
MH495-2	5.2966
MH495-3	5.2958
MH495-4	5.2966
MH495-5	5.2969
Mean	5.2968
Std. Dev.	±0.0008 (0.16 per mil)
Oil Refinery Effluent	5.3213 ($\partial^{80}Se$= +4.6)
Kesterson groundwater	5.3156 ($\partial^{80}Se$= +3.6)

The ∂ notation used above is standard for stable isotope analysis reporting. It gives the per mil deviation from a standard, and is defined by:

$$\partial^{80}Se = \frac{r_{sample} - r_{standard}}{r_{standard}} \times 1000$$

where r refers to the $^{80}Se/^{76}Se$ ratio. The results above indicate that the Kesterson sample is signficantly different from the refinery sample, but it remains to be seen whether the Kesterson sample is representative of the entire river system.

Large-volume water samples were collected at Antioch, McEvoy, and Martinez Regional Park. The Antioch water was chosen as a fresh or nearly fresh water sample, and the other two samples are brackish and closer to the refinery outfalls. These ten liter samples contain enough Se for a few isotope ratio measurements each (depending on prevailing concentrations at sampling time). Two liters of each sample was carefully evaporated to approximately 0.2 liters under a heat lamp, and the selenate in the sample was converted to selenite by addition of 100 ml concentrated HCl, followed by heating at 95°C for 30 min. The selenite was then selectively removed from solution using the $Fe(OH)_3$ precipitation method (Zawislanski et. al., 1995). At this point, further processing was hampered by organic molecules removed with the selenium from the large volume of water.

This problem was attacked by designing new chemical purification techniques, which have the added benefit of simplifying processing of all types of samples. The organic molecules can be destroyed by oxidation with perchloric acid. The sample, in selenite form, is oxidized to the selenate form quantitatively. The anion exchange techniques previously designed for selenite purification have been redesigned for selenate purification, and the current technique is simpler and more reliable than the older one. Based on published work, it was expected that the selenate would not be acceptable for loading in the mass spectometer. However, modification of the reported technique produced good results with Se loaded in the selenate form. The end result is a more efficient purification technique with greater tolerance of organic contaminants. The new method is in the testing stage and new bay water and refinery samples are being collected to be analyzed in the coming weeks.

A new technique to eliminate the need to evaporate bay water samples to reduce their volume is being evaluated. Hydrazine sulfate and sodium tellurite are added to the samples. This reduces both selenate and selenite to elemental selenium, and creates a tellurium precipitate with which the selenium is co-precipitated. This can then be redissolved and processed according to existing procedures. The potential exists for

fractionation of the isotopes if reduction of the selenium is not complete. If this is found to be a problem, the $^{82}Se + ^{74}Se$ spike (Zawislanski et. al., 1995) can be added to the sample to compensate.

In the next few weeks, the purification techniques will be finalized, and the recent modifications should greatly enhance the efficiency of the isotope ratio analyses.

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