RECLAMATION

Managing Water in the West

Stewart Lake
Sediment Selenium – 2004

U.S. Department of the Interior
Bureau of Reclamation
Technical Service Center
Denver, Colorado

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Mission Statements

The mission of the Department of the Interior is to protect and provide access to our Nation's natural and cultural heritage and honor our trust responsibilities to Indian Tribes and our commitments to island communities.

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James W. Yahnke
Bureau of Reclamation
Denver Technical Center
Denver, Colorado

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Summary

Sediment samples for total selenium analysis were collected in August 2004 from the 20 permanent monitoring sites that were originally established in 1998. The entire data sets, including data from the sites collected in 1995 and 1997 when available, were plotted and trends over time at each of the sites are discussed. Total selenium concentrations decreased in 2004 at 14 of the 20 sites. Decreases ranged from < 1 ppm to 11 ppm (2 sites). The largest decreases were at the north end of Stewart Lake. The average total selenium concentration decreased by about 5 ppm, while the decrease in the average in the south was 1 ppm.

Temporal trends in total selenium were evaluated based on correlations with sample year for entire data sets and for a data set consisting only of samples collected since the drain water was diverted from the lake in 1997. In the complete data sets, there was 1 site that showed an increasing trend in total selenium. In the post-diversion data set, 8 sites showed a decreasing trend. Correlations of the total selenium concentrations among sites for the preceding 2 periods were also evaluated. In general, total selenium concentrations were correlated at sites that were affected by seepage or that were adjacent to the constructed channels that conveyed the seepage to the outlet. Other factors that affected the correlations were a large decrease in total selenium following the 1997 flood and a subsequent large increase in total selenium the following year.

The flood experiment that was originally conducted in 2002 was repeated in August-September 2004. There was a larger percentage of selenate present at the beginning of the 2004 experiment than there had been in 2002. Selenium removal was much more effective in 2004 than 2002. Although much of the leached selenium can be accounted for by the loss of selenate, there is evidence that some of the elemental and organic-matter associated selenium was oxidized and either converted to selenite or leached. Over 75 percent of the soluble selenium was removed from the top 2 feet of the sediments in the flood plot, and 30 to 50 percent was removed from the lower foot of sediments. Insoluble selenium was reduced by 12 to 50 percent in 4 of the layers. There was a net increase in insoluble selenium in only the 24-30 inch layer, where deposition was also observed in 2002. In 2004, areal total selenium was reduced by about 3½ times what it had been in the 2002 experiment. In 2004, there was a net areal reduction in both soluble and insoluble selenium, while in 2002, only soluble selenium showed a net reduction.

Reduction-oxidation (redox) potentials calculated from the selenate/selenite ratio indicated that the sediments were oxidizing before and after both experiments. During both experiments, the redox potential decreased. An increase in the redox potential was observed in all layers between the experiments.

Two samples collected from site 21 in April 2002 were submitted to the laboratory at the Department of Chemistry at the University of Cincinnati. The published results of the analysis of those samples were reviewed. The results are consistent with the speciation analyses received from the laboratory at the University of California at Riverside that we have used since 2000. Analysis of the organic selenium at the University of Cincinnati laboratory by high performance liquid chromatography showed that there were no significant amounts of selenocysteine, selenomethionine, or humic acid associated selenium compounds. The results indicated that organic selenium was present in higher molecular weight compounds, such as selenoproteins or peptides, most likely associated with decaying vegetation that was identified in the samples.

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Stewart Lake Sediment Selenium – 2004

Introduction

Sediment sampling for selenium analysis has been limited since 2002. No samples were collected during 2003. The 20 permanent monitoring sites (Figure 1 – figures appear at the end of the report) were sampled for total selenium analysis during August 2004 (Appendix A). Prior to being sampled at that time, Stewart Lake had not been filled since the summer of 2003, although rising ground water may have submerged low spots in the lake earlier in the spring of 2004. In addition, the seepage collection drain was completed and went into operation in June 2004. Elimination of (or at a large reduction in) the seepage entering the north end of the lake would remove the last source of selenium. The collector drain will also remove a source of inflow, further drying the lake sediments, particularly in the north end of the lake.

The flood experiment that was conducted in late August to early September of 2002 was repeated in late August to early September of 2004. In both experiments, sediment samples were collected for selenium species analysis before and after flooding the small test plot adjacent to site 15 (Figure 1). The results of those samples will be reported here. In addition, an evaluation of changes that occurred between the 2 experiments will also be reported. The selenium species samples collected in association with the flood experiment are the only speciation samples that have been collected since 2002.

Total Selenium

Twenty permanent monitoring sites were established in 1998 when remediation began. The purpose of the monitoring sites was to track changes over time as various activities were undertaken under an adaptive management remediation alternative. The protocol for sampling was established at that time and has been followed ever since. According to the protocol, at each site a set of 5 samples is composited from the top 6 inches of sediment. The samples are put on ice in plastic bags returned to Denver. The samples are air dried in the Reclamation soils laboratory. The samples are then submitted to the U.S. Geological Survey Minerals Resource Laboratory, also located in Denver. Selenium analysis is by hydride-generation atomic absorption spectrometry.

Total Selenium Trends for Each Site

This section of the report will look at the 2004 total selenium results on a site-by-site basis. In addition to the data collected since the permanent monitoring sites were formally established, there were samples collected at most of the sites in previous studies. Those data will also be included in a review of where the remediation effort stands in the context of where the total selenium concentrations were at the time of its feasibility study.

Figure 2 presents all of the surface total selenium data collected at all of the permanent monitoring sites since 1995. The 1995 samples were collected during the preparation of the feasibility study. Although a total of 45 sites were sampled in Stewart Lake in 1995, not all of the permanent monitoring sites were sampled. It should also be noted that the 1995 samples were not collected using the same protocol as later samples. In 1995, the samples were collected while the lake was flooded. There was no way to completely drain the lake at that time; water remained at the south end of the lake permanently. The samples were collected by pushing PVC tubes as far as possible into the sediments. The resulting data set consisted of a set of profiles that ranged from 12 to 42 inches in total depth. The samples included in the data set summarized on Figure 2 consist of the surface layers of that set of samples. A further complication results from the condition of the sediments at the time. The surface of the sediments was much different from the current condition in that there was a heavy organic layer that has since disappeared due to the consistent drying. For example, in 1996, when the lake was in a similar condition as in 1995, a significant percentage of the selenium was in the organic form (Zhang and Moore, 1997). As will be shown later, under current conditions, organic selenium represents only a small fraction of the total selenium.

At most of the sites at which there are samples from 1995 and 1997, there is a large decrease in total selenium (Figure 2). The 1997 samples were collected following the largest flood in Stewart Lake since sampling began in 1986. The large decrease in selenium in the sediments led to the idea that selenium could be removed by drying the sediments to promote oxidation and solubility of the sediment selenium to allow it to be subsequently removed during spring floods.

This section of the report will describe the 2004 selenium data in the context of their relationship to previous data on a site by site basis for each of the 20 permanent monitoring sites. Each of the sets of plots on Figure 2 consists of all of the surface total selenium data from 3 numerically adjacent sites in Stewart Lake. It should be noted that numerically adjacent sites are not necessarily geographically adjacent, as is evident on Figure 1. The original site numbers were a combination of the minutes and seconds of the degrees of latitude and longitude. When the site numbers were sorted, the sites ran from south to north based on the minutes and seconds of latitude. The sites were subsequently numbered from 1 to 20 on that basis. Consequently, the site numbers run from south to north.

One further note on Figure 2 before evaluating the data. The ordinates (*y*-axes) on the plots vary with the data in the plots. In general, the maximum values of the ordinates increase from the top to the bottom of the set of plots, which are arranged by increasing site number. As was just described, the site numbers run from south to north, as apparently does the total selenium concentration.

To put some emphasis on the 2004 data, all of the results are shown in Table 1. Table 1 also shows the immediately preceding samples collected in October 2002 and the average of all of the samples collected prior to that at each site. To facilitate the discussion of any

trends, Table 1 also shows the difference between the October 2002 and 2004 total selenium concentrations at each of the sites.

Table 1. Comparison of total selenium concentrations during the period 1998-2002, October 2002, and August 2004 and the 2002 to 2004 change

Site No.	Pre-Oct. 02	Oct. 2002	Sep. 2004	Change
1	16.4	15	7.9	-7.1
2	9.2	9.7	7.4	-2.3
3	12.4	15	15	0
4	9.3	8.2	9.1	0.9
5	8.1	6.6	7.6	1
6	9.4	8.1	6	-2.1
7	14.4	10	9.6	-0.4
8	8.5	11	8.9	-2.1
9	17.9	15	17	2
10	12.6	10	9.1	-0.9
11	9.0	9.4	12	2.6
12	17.0	17	16	-1
13	9.1	9.1	7.3	-1.8
14	20.5	20	17	-3
15	29.0	21	18	-3
16	23.3	22	11	-11
17	15.4	17	12	-5
18	21.5	21	17	-4
19	55.2	65	92	27
20	34.5	37	26	-11

Site 1 is the southernmost of the 20 monitoring sites in Stewart Lake and is located near its outlet (Figure 1). The total selenium at site 1 was initially at an intermediate level at 14 ppm (Figure 2). At the time, site 1 would have been in the permanently flooded section of the lake. After the 1997 flood, the concentration decreased to 10 ppm. However, the total selenium in the site 1 sediments increased dramatically to 20 ppm in the 1998 samples, at which point the selenium concentration at site 1 was among the higher concentrations in the lake and more typical of sites in the north end of the lake. Between the sets of samples, the channel down the center of the lake was excavated to facilitate draining the lake. However, the lake could not be completely drained until the outlet was replaced at a lower level. The increase in total selenium may be due to the influence of the channel, although the exact mechanism can only be a matter of conjecture. Although the Jensen Unit drains had been diverted to the Green River in the spring of 1998, the drainage channel still conveyed the seepage from the north end of the lake. Somehow the high selenium water in the channel seems to have increased the selenium concentration at site 1. The hypothetical effect of the seepage is somewhat supported by a significant correlation between the concentrations at site 1 with those at sites 16 and 18 ($r = 0.805$ and 0.885 respectively based on 1998-2004 samples). Sites 16 and 18 are located near the source of the seepage, but at the other end of the lake from site 1.

The selenium concentration at site 1 increased slightly in 1999 to 21 ppm, then decreased in 2000 (Figure 2). The total selenium concentration has fluctuated between 13 and 17 ppm in samples collected between 2000 and 2002. The total selenium concentration in the 2004 sample was 7.9 ppm (Table 1), which is the lowest concentration in any of the samples collected from site 1 since 1995 (Figure 2). The decrease of 7.1 ppm from 15 ppm in October 2002 to 7.9 ppm in September 2004 is larger than the decrease observed after the 1997 flood (4 ppm). Whether the recent decrease represents a short-term anomaly or a longer term trend is unknown.

Site 2 is located to the north of site 1, just to the east of the main channel in the lake (Figure 1). The total selenium concentration at site 2 has remained somewhat less than

10 ppm over the years, although a couple of samples have been slightly greater than 10 ppm (Figure 2). The total selenium concentration has not exceeded 10 ppm since 1999. There was only a small decrease in total selenium between October 2002 and September 2004 (Table 1). Overall, the total selenium concentration at site 2 is consistently among the lowest of all of the 20 permanent monitoring sites.

Site 3 is located to the north of site 2 and well to the west of the main channel (Figure 1). In the early part of the total selenium record at site 3, the concentration was in the intermediate part of the total selenium distribution at Stewart Lake. It was one of the few sites at which there was no decrease in total selenium after the 1997 flood (Figure 2). After 1998, there was a decline in total selenium at site 3 to its lowest point in May 2001. After the 2001 flood, the concentration at site 3 increased to its maximum in July. The concentration has remained relatively constant, but slightly below that concentration ever since. There was no change in the selenium concentration at site 3 between October 2002 and September 2004, and it is now among the sites with a higher concentration (Table 1).

Site 4 is located to the east of the main channel and is nearer to site 2 than to site 3 (Figure 1). The total selenium decreased at site 4 after the 1997 flood, but increased in 1998 back to where it had been prior to the flood. Beginning in 1999, the total selenium at site 4 dropped back below 10 ppm and has fluctuated between 8 and 10 ppm ever since (Figure 2). That trend continued between October 2002 and September 2004 with an increase from 8.2 to 9.1 ppm (Table 1).

Site 5 is the westernmost of the sites in Stewart Lake (Figure 1 – note that site 19 is not located in the lake proper). The nearest other site is site 3. The total selenium decreased following the 1997 flood and then increased in 1998 and 1999 (Figure 2). The peak concentration occurred in 1999. The total selenium decreased in 2000 and has fluctuated between about 7 and 10 ppm since then. There was an increase from 6.6 to 7.6 ppm between October 2002 and September 2004 (Table 1).

Site 6 is located on the opposite side of the lake from site 5 (Figure 1). The nearest site to site 6 is site 7, both of which would be located along the eastern shore if there were water in the lake. Site 6 is another site where selenium increased after the 1997 flood. Selenium remained constant in 1998 and then decreased below 10 ppm where it has remained since. Total selenium decreased from 8.1 to 6 ppm between October 2002 and September 2004 and now has the lowest total selenium concentration in Stewart Lake (Table 1).

The plot of total selenium at sites 4, 5, and 6 has the smallest total selenium upper limit on the ordinate of any of the plots. The 3 sites along with site 3 form a band across the lake bed (Figure 1). The total selenium at the 3 sites was rather divergent in the first several years, but converged at about 10 ppm in 1999 (Figure 2). The total selenium at the 3 sites has fluctuated between 6 and 10 ppm since 1999. However, site 3 for some reason shows a completely different pattern. The total selenium at site 2 shows a pattern that is more like that of sites 4, 5, and 6, than does that at site 3. All of these similarities

and differences serve to illustrate that the pattern of movement and deposition of selenium in the sediments of Stewart Lake is extremely complex.

Site 7 is located to the northeast of site 6 (Figure 1), There was only a slight decrease in total selenium at site 7 following the 1997 flood, followed by an increase in 1998 (Figure 2). The total selenium has remained fairly constant since then and fluctuated between about 10 and 15 ppm. Total selenium concentrations in samples collected since 1998 are significantly correlated between the 2 sites ($r = 0.832$), but the selenium concentration at site 7 is significantly higher.

Site 8 is another of those sites where little change in total selenium has been seen during attempts at remediation. Site 8 is located near the center of Stewart Lake (Figure 1). The total selenium decreased dramatically from 24 ppm to 7.5 ppm after the 1997 flood (Figure 2). Total selenium at the site has remained relatively constant between about 8 and 11 ppm ever since. There was a decrease of 2.1 ppm between October 2002 and September 2004 (Table 1), but the change is within the range of that general pattern of fluctuation.

Site 9 is somewhat centrally located just to the north of the east channel (Figure 1). Total selenium showed a small decrease after the 1997 flood (Figure 2). After that there is a lone point showing its maximum concentration in 1999. The site was not sampled in 1998 and 2000. Since 2000, the total selenium concentration has, like that at many sites simply fluctuated, but has shown little real change. In the case of site 9, the total selenium has been between 14 and 18 ppm. The most recent sample showed a 2 ppm increase within that range of fluctuation (Table 1).

Site 10 is located north of site 7 and adjacent to the east channel (Figure 1). Total selenium showed little change at the time of the 1997 flood (Figure 2). The total selenium showed a peak in 1999, but has been consistently decreasing since May 2001. The most recent sample decreased by 0.9 ppm from the previous sample (Table 1). The 2004 concentration is the minimum at the site since monitoring began.

Site 11 is isolated in the north end of the lake, to the west of the main channel (Figure 1). Total selenium decreased dramatically after the 1997 flood (Figure 2). The concentration subsequently decreased to the minimum in May 2001, but has been showing a gradual increase since then. The most recent sample showed a 2.6 ppm increase over the previous one (Table 1), but it is still well below the initial concentration. The site was probably heavily influenced by the drains and the concentration initially responded to their diversion. There is no obvious reason for the increase in the more recent samples collected since May 2001.

Site 12 is located within a cluster of sites inside the main north-south channel and the east channel (Figure 1). The sites within this cluster are among the highest in total selenium concentrations in Stewart Lake (Table 1). Site 12 is another of the few sites at which there was an increase in total selenium following the 1997 flood (Figure 2). Following a small decrease in 1998, total selenium peaked at site 12 in 1999. The total selenium has

remained relatively constant between about 15 and 18 ppm since 2000. The most recent sample at site 12 showed a decrease in total selenium of 1 ppm (Table 1).

Site 13 is located adjacent to the inlet channel to Stewart Lake (Figure 1). The site was not sampled prior to the establishment of the permanent monitoring sites in 1998 (Figure 2); so the response to the flood is unknown. Total selenium concentrations at the site have remained relatively constant since sampling began at the site in 1998. Total selenium has generally followed along the 10 ppm gridline. The minimum concentration was observed in November 2001, but 6 months later the concentration of total selenium was back to where it had been previously (Figure 2). The most recent sample showed a 1.8 ppm decrease in total selenium (Table 1).

Site 14 is located to the northwest of site 12 (Figure 12). There was a dramatic decrease in total selenium following the 1997 flood, but the next sample in 1998 had a higher total selenium concentration than was shown before the flood in 1995 (Figure 2). In 1999, the total selenium concentration dropped back to where it had been in 1995. From 1999 through 2002, the total selenium concentration generally followed the 20 ppm gridline. The 2004 sample showed a 3 ppm decrease from what had been observed in October 2002 (Table 1).

Site 15 lies adjacent to the main north-south channel near site 14 and within the cluster of sites confined by that channel and the east channel (Figure 1). Site 15 was not sampled in 1995 and the response to the 1997 flood is unknown. When it was first sampled, site 15 had the highest total selenium concentration of any site in Stewart Lake. Because of the high selenium, the site was chosen as one of the sites to be the focus of numerous experiments during remediation. As can be seen on Figure 2, there is nothing to indicate any success. However, there was a dramatic decline in total selenium in 2002 from 31 to 21 ppm. Stewart Lake was not flooded in 2002, which was an extreme drought year. By October 2002, the total selenium concentration at site 15 was about the same as that at site 14. The 2004 sample at site 15, like that at site 14, showed a 3 ppm decrease from what had been observed in October 2002 (Table 1).

Site 16 is somewhat isolated from the other sites by the channel extensions that had been dug to collect the drain water from drains J1 and J1A (Figure 1). This appeared to have an effect on total selenium at the site. Total selenium decreased from more than 20 ppm to 6 ppm after the 1997 flood, but increased to over 30 ppm in 1998 (Figure 2). In 1999, total selenium decreased to between 20 and 25 ppm and remained there through October 2002. After construction of the collector drain, a.k.a. J6, early in 2004, the pool that had been at the site dried up. Total selenium decreased by 11 ppm in 2004 from what had been observed in October 2002 (Table 1).

Site 17 is to the east of site 16 and north of site 13 (Figure 1). However, the former drainage channel from J1/J1A lies between sites 16 and 17. Total selenium at the site is intermediate between that of sites 13 and 16 on the average (Table 1). Like site 16, there was a large decline in total selenium from 11 to 4 ppm at site 17 following the 1997 flood (Figure 2). As was the case at a number of the nearby sites, the total selenium increased

to a higher concentration than was present prior to the flood, in this case, to over 14 ppm. The total selenium at site 17 remained around 15 ppm (±2 ppm) from 1998 through October 2002. The 2004 sample showed a 5 ppm decrease over what was observed in the October 2002 sample (Table 1).

Site 18 is located between and north of sites 14 and 15 (Figure 1). There was a large decrease in total selenium from 18 ppm to near 9 ppm following the 1997 flood. The next year, 1998, the total selenium increased to about 25 ppm. This was followed by a decrease in 1998, following which the total selenium remained around 20 (± 2) ppm through October 2002. There was a decrease of 4 ppm in 2004, taking the total selenium outside of that range of fluctuation (Table 1).

As was noted earlier, site 19 is not actually located in Stewart Lake (Figure 1). The site is located adjacent to the former drain channel in a pond that is dry much of the time. When it was first sampled, the total selenium at the site was relatively low (Figure 2). The total selenium increased dramatically after the drains (J2 through J4) were relocated in 1997. After the initial increase, total selenium began to decrease, but the trend reversed in 2002. In 2004, the total selenium concentration was nearly as high as the peak concentration.

Site 20 is located at the far north end of Stewart Lake at the point where the former drain channel entered the lake (Figure 1). The total selenium concentration was initially very low (Figure 2). Following the 1997 flood, total selenium decreased from 5.3 to 3.5 ppm. At the time, both of those total selenium concentrations were the lowest in the lake. As can be seen on Figure 2, there was a 2 year gap in sampling at site 20 after 1997. The reason for the gap was that the site was lost when the drains were relocated. The site was not reestablished until 2000. Prior to 2000, the sites had been surveyed in. The site was reestablished using the more accurate global positioning system (GPS) technology which had recently become available. After the site was reestablished, the initial sample was about twice as high in total selenium as the 1995 sample. The total selenium increased after that until the site had the maximum total selenium in the lake in 2001. Total selenium has decreased since then, but it is still well above what it had been in 1995. The site appeared to be affected by a nearby channel. No samples were collected from the channel, but the total selenium decreased by 11 ppm in 2004 (Table 1) after the flow to the channel was intercepted by the J6 drain. This is the same decrease as was observed at site 16 after the seepage at that site was diverted.

Sites 16, 18, and 20 are located nearest the scarp on the north end of Stewart Lake (Figure 1). The scarp is the source of the seepage that had been entering the lake. As can be seen by on Figure 1, there was standing water at site 16 when the aerial photograph was taken. There is also evidence of standing water at site 18. However, unlike the other 2 sites, site 20 appears to be dry at the time the photograph was taken.

Figure 3 shows the total selenium at sites 16, 18, and 20 since the Jensen Unit drains were diverted in 1997. The total selenium plots for sites 16 and 18 show very little difference. The similarity of the total selenium concentrations and trends in sediments at

the 2 sites lends credence that the total selenium is being controlled by a common factor, with the seepage being the most likely. Alternatively, the total selenium in the sediments at site 20 behaves differently from the other 2 sites. The one obvious difference between site 20 and the other 2 sites is that site 20 did not appear to be saturated by the seepage at the time that the aerial photograph was taken.

The largest decreases in total selenium between October 2002 and September 2004 occurred at sites 16 and 20, where there was a decrease of 11 ppm (Table 1). On average there was a decrease of about 1 ppm of total selenium per site (2.5 ppm if site 19 is not included). Total selenium decreased at 14 of the 20 sites between October 2002 and September 2004, while there was an increase at 5 sites (there was no change at 1 site). The average decrease was nearly 4 ppm per site (3.9 ppm to be exact). During the time between samples, the lake was flooded during 2003 for about 2 months, but it was dry the remainder of the time. The lake was also dry for about 2 years prior to the flood of 2003. The 2004 samples are the first after the 2003 flood.

A difference in the concentration in the north or seepage affected end the lake and the south part was noted above. The difference is illustrated on Figure 4. The much larger decrease in total selenium in the north (approximately 5 ppm) is also apparent on the figure. The decrease is despite the increase at site 19. It should be noted that the averages on Figure 4 are geometric averages, which minimize the influence of outliers like the site 19 total selenium concentration. Figure 4 only includes post-flood or autumn samples; so the May 2001 and April 2002 samples shown on figures 2 and 3 are not included. Although it is not as evident as in the north end of the lake, there is also a decrease in the south end. In the north the average total selenium concentration decreased from 26 ppm to 20.7 ppm, while in the south end the decrease in the average total selenium concentration was from 10.7 to 9.7 ppm. What is encouraging is that there are decreases in selenium throughout all areas of the lake. Although the greatest decreases occurred in the north end of the lake, the north end still has much higher concentrations than the south end (Figure 4).

Lake-Wide Total Selenium Trends

Since the time of the 1997 flood, we have been trying to manipulate the selenium in the Stewart Lake sediments. The only lake-wide method that has been tried has been draining the lake, with the goal of oxidizing and solubilizing the selenium so that it can be subsequently removed when the lake floods in the spring. Although we have seen no evidence that explicitly shows that this effort has been successful, there are indications that selenium has been declining.

Table 2 summarizes site-by-site correlations with a measure of time, the year a sample was collected. The full data sets (1995-2004) shown in Table 2 include samples that were collected during the remediation feasibility study and another set of samples collected after the 1997 flood. Those 2 sets of samples are not included the data set for the post-drain-relocation data set.

Table 2. Pearson correlations of total selenium on year – comparison of the trends for all data (1995-2004) and for the period since the drain outlets were relocated (1998-2004) [significant correlations are highlighted]

Sites 1-10		**1995-2004**	**1998-2004**	**Sites 11-20**		**1995-2004**	**1998-2004**
Site 1	r	-0.2650	-0.8945	Site 11	r	-0.5993	0.0932
	Prob. > r	0.431010	0.001133		Prob. > r	0.051362	0.811563
Site 2	r	-0.2099	-0.5930	Site 12	r	0.2804	-0.2885
	Prob. > r	0.535598	0.092399		Prob. > r	0.403664	0.451448
Site 3	r	0.2324	0.2139	Site 13[1]	r	-0.6768	-0.6768
	Prob. > r	0.491654	0.580594		Prob. > r	0.045263	0.045263
Site 4	r	-0.5529	-0.5768	Site 14	r	-0.0577	-0.7946
	Prob. > r	0.077731	0.103996		Prob. > r	0.866192	0.010509
Site 5	r	-0.2271	-0.1349	Site 15	r	-0.6047	-0.5458
	Prob. > r	0.501962	0.729241		Prob. > r	0.064005	0.128502
Site 6	r	-0.4789	-0.8440	Site 16	r	-0.0799	-0.8444
	Prob. > r	0.136158	0.004222		Prob. > r	0.815327	0.004189
Site 7	r	0.0889	-0.8133	Site 17	r	0.4936	-0.1216
	Prob. > r	0.794938	0.007667		Prob. > r	0.122823	0.755286
Site 8	r	-0.5237	0.5509	Site 18	r	0.1898	-0.8975
	Prob. > r	0.098248	0.124270		Prob. > r	0.576118	0.001024
Site 9	r	-0.3839	-0.7366	Site 19	r	0.5656	-0.0909
	Prob. > r	0.243817	0.023586		Prob. > r	0.069781	0.816176
Site 10	r	-0.0813	-0.3492	Site 20	r	0.7515	0.6206
	Prob. > r	0.812100	0.357059		Prob. > r	0.007660	0.074529

[1] All samples were collected after the drain relocation

As shown in Table 2, there are only 2 statistically significant correlations (probability of a greater $r < 0.05$) in the complete 1995-2004 data set. One is positive (site 20) indicating increasing selenium over time and one is negative (inverse – site 13) indicating decreasing total selenium. However, the inverse correlation for site 13 is based on a data set that included no samples in 1995 or 1997. In other words, the 1995-2004 data set is identical to the 1997-2004 data set and is in reality a post-relocation data set. Alternatively, there are 8 statistically significant correlations in the post-relocation data set, despite the fact that there is a smaller number of samples and statistical significance requires a higher r-value to be significant (statistical significance means that the trend is not likely to be random). Interestingly, there are 8 other sites in the post-relocation data set that have negative r-values, indicating a decreasing trend (albeit, possibly random). Although there are only 2 pre-relocation sets of samples, these seem to be sufficient to detrend the apparent trend of decreasing selenium at those 8 sites. If the trends are real, then the indication is that the relocation of the drains was working to decrease the selenium at some of the sites.

The data that went into the correlations in Table 2 are the same that were plotted on Figure 2 and described on a site by site basis. Recall that in many cases, the conclusion was that there appeared to be little change in total selenium at many of the sites following

the flood. To explore this further, the total selenium data from the sites with significant correlations are plotted with trend lines on Figure 5.
The total selenium at site 1 showed one of the most significant trends in Table 2. The trend line on Figure 5 has a slope of approximately -2. The slope of the trend line represents the decrease in total selenium in ppm/year. In other words, the total selenium has decreased by an average of 2 ppm/year since 1998. The line ends in 2004 at a total selenium concentration of just below 10 ppm. If the trend is projected into the future, the total selenium would meet the 4 ppm goal in about 3 years, or 2007. Alternatively, the slope of the trend at site 13 is only about ½ ppm/year. However, the trend line in 2004 shows a total selenium concentration of less than 8 ppm. At a rate of decrease of ½ ppm/year, the total selenium at site 13 would meet the 4 ppm goal in 2008. Now for the bad news. If we take site 16 as an example, the slope of the line is -1. However, the trend line in 2004 shows a total selenium concentration of about 20 ppm. At the rate of decrease of 1 ppm/year, the goal would not be met until 2020. The rates of decrease at sites 14 and 18 are even lower, while the total selenium concentration at those sites is also shown as being about 20 ppm in 2004. For sites 14 and 18, at the rates of total selenium decrease shown, the goal would not be met until sometime beyond 2020. The goal at the time that remediation was initiated was to complete the sediment cleanup well before 2020.

In addition to the 8 sites where there are significant decreasing trends, there are 8 others that show nonsignificant decreasing trends (Table 2). From a statistical perspective, these are not really trends. The statistical nonsignificance reflects a trend with either no slope or so much variation in the data such that no trend can be discerned. The total selenium at site 5 (slope < 0.1 ppm/year) is an example of the former, while the total selenium at site 15 (slope = -1.5 ppm/year) is an example of the latter. However, the negative correlation coefficients indicate that there was a decrease in total selenium over the period 1998 through 2004, although the decrease may be extremely small.

Figure 4 showed the average selenium in 2 areas of Stewart Lake for each sampled year. Figure 6 shows a similar plot of the lake-wide average total selenium in Stewart Lake. There are several things of note on Figure 6. First, even at its lowest in 1997, the lower confidence limit about the mean was still about twice the cleanup goal, which is also shown on Figure 6. Second, the increase in the average total selenium in 1998 was even greater than the decrease in 1997. Third, the average total selenium in 2004 is about the same as it was in 1995. The last observation can be extrapolated to conclude that it took 6 years to recover from the 1998 increase. The cause of the 1998 increase is unknown.

Relationships of Total Selenium between Sites

Significant correlations in the total selenium concentrations were noted above in the site-by-site overview presented above. Complete correlation matrices for total selenium among the sites are included in Appendix B. There are correlation matrices in the appendix, corresponding to the breakdown in Table 2. That is, there is a set of correlations for the complete record of 1995 through 2004 and another for the subset of data for the post-drain relocation period of 1998 through 2004 Significant correlations are highlighted in Appendix B and listed in Table 3. It should be noted that the r-value shown with the correlation matrices is based on the number of observations in the table titles. If there are samples missing in some years, the r-value at the selected significance level would be greater. The r-value in the matrices is included as a point of reference only. SYSTAT, which was used to generate the correlations, reports a probability for each correlation and that probability was used to flag significant correlations. Significance was based on a probability of a greater r occurring by chance alone being less than 1 in 100 ($\alpha = 0.01$), rather than the more common 1 in 20 ($\alpha = 0.05$). Because there were well over 100 correlations (190 to be exact) in each matrix, the chance of correlations incorrectly being flagged as significant at $\alpha = 0.05$ was rather great; at that α-level, at least 9 spurious correlations would be expected. At $\alpha = 0.01$, only 1 would be expected.

Table 3. Summary of significant correlations of total selenium concentrations among sites

Since relocation		All samples	
Site with	Sites	Site with	Sites
1	6, 16, 18	1	7, 16, 18
4	9	7	1, 16, 18
6	7, 18	8	11
7	6	11	8
9	4	14	16, 18
14	16, 18	16	1, 7, 14, 18
16	1, 14, 18	17	18
18	1, 6, 14, 16	18	1, 7, 14, 16

In generating the correlations, it was expected that the response to the flood in 1997 would be an influential factor in the correlations based on the complete record. A review of Figure 2 indicates that the response is a factor in some of the correlations. For example, the total selenium at sites 8 and 11 showed a very large decrease in 1997, but did not show the subsequent increase in 1998 that was so common that it shows up greatly on Figure 6. Large common responses can have an undue influence on a correlation (or a regression for that matter), and appears to be a factor in the significant correlation between the total selenium at the 2 sites. In SYSTAT, such an influence is flagged in regression output, but not in the correlation output. Although the locations of sites 8 and 11 would appear to have nothing in common (Figure 1), the common response appears to be the flood and the currents that it induced. In 1997, both the Green River and Ashley Creek flooded Stewart Lake. There was a convergence zone near the center of the lake that could have influenced the 2 sites, but this is only speculation.

The total selenium at sites 16, 17, and 18 showed the common response to the 1997 flood, but the 1998 increase at site 17 was much smaller than that at the other 2 sites. The total selenium at sites 1 and 7 showed a similar response (Figure 2). It would appear that the response to the 1997 flood was the factor controlling the correlations for site 17, which no longer shows a relationship when 1995 and 1997 are dropped from the input

data (Table 3). The flood appears to be a factor in the correlation of total selenium between sites 7 and 16, but not between 7 and 18 (Table 3). The correlations of total selenium at sites 1, 16, and 18 are unaffected by dropping the early data.

The point of including the correlations of total selenium among the sites is to illustrate the variability and complexity of the controls on total selenium concentrations at Stewart Lake. On the other hand, the response of selenium to the various attempts to enhance its removal during spring floods have already illustrated the same result quite well.

Selenium Species Data – Flood Plot

The pre- and post-flood selenium species samples were collected as described in Appendix A, although only the pre-flood samples are described there. The post-flood samples were collected as soon as the site was dry enough to work. Samples were submitted to the laboratory at the Department of Environmental Sciences at the University of California at Riverside and analyzed as described in Frankenberger and Zhang (2001).

Species Distributions – 2004

The flooding focuses on dissolving and transporting soluble selenium to the deep ground water. The most soluble form of selenium is selenate. Figure 7 shows a selenate profile from the flood plot from before and after the flood experiment. Selenate is also the most highly oxidized form of selenium. Consequently, the highest concentration of selenate would be expected to be at or near the surface of the profile. Before the experiment, there was about 3 ppm of selenate in the top 12 inches of the profile (Figure 7). Selenate decreased to about 2 ppm between 12 and 18 inches of depth and to about 1 ppm between 18 and 24 inches before flooding. Below 24 inches the pre-flood selenate was < 1 ppm.

The greatest reduction in selenate during the flood experiment occurred near the surface, where over 90 percent was removed. In the top 24 inches, an average of about 90 percent removal was achieved. In the deeper layers of the profile, where the selenate concentration was lower, removal was about 80 percent. In all layers, the selenate concentration was < 0.5 ppm after the experiment was concluded (Figure 7).

The other oxidized form of selenium is selenite. Selenite concentrations before and after flooding are shown on Figure 8. Unlike selenate, there are 2 sets of selenite plots on Figure 8. The upper set of plots is labeled soluble, while the lower set is labeled insoluble. These are functional definitions related to the analytical technique. The soluble fractions are extracted with deionized water. The insoluble fractions are extracted with any of several solvents, including sodium hydroxide, sodium sulfite, and hydrogen peroxide. The extraction scheme is shown on Figure 9. Although selenite is considered soluble, it is readily adsorbed onto clay particles and iron oxides in the sediments. Presumably, the soluble fraction is deposited in the sediments as evaporite minerals, while the insoluble fraction is adsorbed. As can be seen on Figure 8, the

majority of the selenite is in the insoluble fraction. In both cases, the highest selenite concentration is in the surface layer.

Both selenite fractions increased in the near-surface sediments during the flood experiment (Figure 8). The increase in soluble selenite was relatively small with a maximum of 0.2 ppm. Alternatively, insoluble selenite increased by about 1.5 ppm. The likely reason for this would be reduction of some of the selenate to selenite as more reducing conditions developed as the flood experiment progressed. However, this may not be the case, or as is more likely, it is only part of the story.

Figure 8 indicates that there were also increases in soluble selenite in 4 of the 5 layers beneath the surface. The changes between 12 and 24 inches include a very small increase and a very small decrease, but these very small changes probably represent random variation in the samples and should be considered no change. There are small increases (< 0.1 ppm) in soluble selenite in the remaining 3 subsurface layers.

Insoluble selenite increased in only 2 of the subsurface layers, the 6-12 and 24-30 inch layers. Insoluble selenite decreased in the 2 intervening layers. There was essentially no change in insoluble selenite in the deepest layer.

The increases and decreases in selenite with depth show no pattern that would readily lend itself to interpretation. There may be some relatively complex pathways that involve water movement and determine the distribution of selenium with depth in the sediments. Table 4, which shows the percent distribution of the various selenium species with depth before and after the flood experiment, would indicate that this is true. For example, the most highly oxidized species, selenate, is not present as the highest percentage of the total near the surface, as would be expected. Actually, the surface percentage of selenate is one of the lowest percentages in the pre-flood profile (Table 4). The peak in the percentage of selenate is in the 12-18 inch layer, followed by that in the deepest layer. This would indicate that oxidizing conditions prevail throughout the profile. The distribution of selenite would support that. The highest percentages of insoluble selenite in the pre-flood profile are in the layers between 12 and 30 inches, while the percentages of insoluble selenite in the surface layers are among the lowest in the profile (Table 4).

Table 4 indicates that the predominant selenium species in both the pre-flood and post-flood profile was elemental selenium. Its percentage increased slightly after the flood. However, the overall concentration of elemental selenium decreased (Figure 10). Elemental selenium is insoluble in water. The decrease in elemental selenium would indicate that some had been oxidized. The oxidation of elemental selenium would account for some of the increase in selenite after the flood (Figure 8), with the remainder of the selenite increase due to selenate reduction. The obvious conclusion would seem to be that the overall decrease in selenium, as shown on Figure 11, would be due to leaching of selenate, except for 1 thing – the overall decrease in selenium was greater than the decrease in selenate (Figure 7).

Table 4. Percent distribution of selenium species before and after the 2004 flood experiment								
Time	Selenium analyte	Depth Increment						Average
		0-6"	6-12"	12-18"	18-24"	24-30"	30-36"	
Pre-flood	Soluble Se^{IV}	2.0%	1.3%	1.8%	3.3%	11.4%	7.7%	2.6%
	Soluble Se^{VI}	16.9%	21.0%	26.1%	18.9%	15.4%	23.5%	20.0%
	Soluble Organic Se	0.3%	0.4%	0.5%	0.7%	1.4%	1.5%	0.5%
	Total Sol. Se	19.2%	22.7%	28.4%	22.9%	28.2%	32.7%	23.1%
	Insoluble Se^{IV}	16.2%	15.3%	19.2%	24.4%	19.8%	16.9%	17.7%
	Insoluble Se^{VI}	2.3%	1.6%	0.0%	2.1%	1.0%	-0.2%	1.5%
	Insoluble Organic Se	6.3%	3.8%	4.2%	4.4%	6.3%	7.1%	5.1%
	Elemental Se	27.7%	28.4%	27.4%	20.9%	19.1%	16.0%	26.1%
	OM-Se[1]	25.9%	27.8%	19.9%	20.2%	13.8%	18.1%	23.9%
	Total Insoluble Se	80.8%	77.3%	71.6%	77.1%	71.8%	67.3%	76.9%
Post-flood	Soluble Se^{IV}	4.1%	1.8%	2.8%	6.1%	10.3%	11.8%	4.2%
	Soluble Se^{VI}	1.5%	3.9%	4.4%	3.2%	2.7%	5.5%	3.1%
	Soluble Organic Se	0.3%	0.5%	0.6%	1.2%	1.6%	2.0%	0.6%
	Total Sol. Se	5.8%	6.2%	7.9%	10.5%	14.6%	19.3%	7.9%
	Insoluble Se^{IV}	30.8%	21.3%	18.6%	26.8%	22.3%	19.1%	24.7%
	Insoluble Se^{VI}	1.7%	0.9%	-0.1%	0.5%	1.8%	0.6%	1.1%
	Insoluble Organic Se	8.3%	6.8%	7.1%	2.8%	6.2%	3.0%	6.8%
	Elemental Se	28.5%	30.9%	31.7%	25.0%	19.3%	22.0%	28.5%
	OM-Se[1]	20.9%	28.0%	22.6%	19.2%	21.4%	19.8%	23.2%
	Total Insoluble Se	94.2%	93.8%	92.1%	89.5%	85.4%	80.7%	92.1%

[1] OM-Se – organic-matter associated selenium

Table 4 also indicates that a high percentage of the total selenium is in the form of organic-matter-associated selenium (OM-Se). OM-Se is of unknown and probably variable composition. As can be seen on Figure 9, the OM-Se is extracted with 30 percent H_2O_2 (hydrogen peroxide), which oxidizes organic matter. Frankenberger and Zhang (2001) indicate that the OM-Se would have to be independently speciated to determine its composition. Since the OM-Se is not extracted in the water extraction, it is included in the insoluble species. However, as is shown on Figure 12, the OM-Se decreased throughout much of the profile just as the elemental selenium did. The decrease on OM-Se is actually larger than the decrease in elemental selenium at the surface and accounts for most of the OM-Se decrease. The added decrease in total selenium over and above what can be accounted for by the decrease in selenate appears to be due to the decreases in elemental selenium and OM-Se.

Selenium Mass Changes – 2004

Table 5 shows areal changes in the mass per unit area of selenium in the flood plot. The data in Table 5 were calculated by first calculating the mass of selenium in each layer of the flood plot. To do this, the selenium concentration was multiplied by the density of the sediments (0.91 g/cm^3) and the volume of sediment in each layer. The selenium under an area as shown in the table was then calculated by summing the layer data and converting to a unit area from the total size of the flood plot (900 ft^2).

Table 5. Areal changes in selenium during the 2004 flood experiment

Selenium form	Total Profile		Top 6 inches	
	(mg/cm^2)	mg/ft^2	(mg/cm^2)	mg/ft^2
Total Se	-0.1327	-123.3	-0.0463	-43.0
Soluble Se	-0.1100	-102.2	-0.0336	-31.2
Insoluble Se	-0.0695	-64.6	-0.0232	-21.6

Table 5 shows that the net change in total selenium, total soluble selenium, and total insoluble selenium during the 2004 flood experiment are all decreases. The data in Table 5 represent the total selenium in the top 3 feet of sediment. The data show that the change in total selenium is greater than the decrease in soluble selenium, which as was shown above, is mostly selenate. The total decrease in the 2 fractions of selenium in Table 5, *i.e.* soluble and insoluble, appears to be larger than the decrease in the total selenium.

The insoluble fraction represents the sum of the selenium species presented above, *i.e.* selenate, selenite, elemental selenium, and OM-Se. The difference is represented by the last form of selenium shown on Figure 9, the residue. The residue is the difference between the sum of the individual species concentrations and the total selenium concentration. The residue selenium increased in all layers after the flood experiment. The actual mineral composition of the residue, like that of the OM-Se, is unknown, but because it is only extracted by the combination of H_2O_2 and 1 + 1 HCl (hydrochloric acid), it should be the most inert form of selenium present. As noted above, H_2O_2 is used to oxidize organic matter. Alternatively, 1 + 1 HCl is used as a surrogate for stomach acid. What this means from a biological perspective is that even the most inert form of selenium could become biologically available under the right circumstances.

Comparison of the 2002 and 2004 Flood Experiments

The reason for repeating the flood experiment was to verify the results and to carry on the experiment somewhat longer to see if the selenium would be driven deeper. In both cases, sediments were sampled using the same sampling protocol and were analyzed in the same laboratory using the same an analytical procedures. The comparison will be based on the summary results as presented for the 2004 experiment in Table 5. In addition, the selenium concentrations and changes in each of the layers will be evaluated.

The 2002 experimental mass changes are shown in Table 6. These results were previously presented in Yahnke (2004). The overall amount of soluble selenium

and 6). In 2002, the total and soluble selenium removed from the surface layer were almost equal, but the soluble selenium removed from the total profile was much greater than the total selenium removed (Table 6). There was a net increase in insoluble selenium in the profile, although there was a decrease in insoluble selenium in the surface sediments (Table 6). Taken together, the evidence is overwhelming that there was selenium deposition in the profile, most likely due to chemical reduction of selenate and/or selenite in the lower layers of the profile.

Table 6. Areal change in total selenium during the 2002 flood experiment

Selenium form	Total Profile		Top 6 inches	
	(mg/cm^2)	mg/ft^2	(mg/cm^2)	mg/ft^2
Total Se	-0.0372	-34.5	-0.0762	-70.9
Soluble Se	-0.1136	-105.6	-0.0716	-66.5
Insoluble Se	0.0610	56.7	-0.0156	-14.5

The 2004 experiment gave different results in that the total selenium reduction in the total profile was much greater than that in the surface sediments (Table 5). As was the case in 2002 (Table 6), the total selenium removed in 2004 from the surface sediments was greater than the soluble selenium removed (Table 5). The difference in the 2 experiments relates to the removal of insoluble selenium from both the surface sediments and total profile (compare tables 5 and 6).

Table 7 shows the total amount of 3 categories of selenium in each of the layers in the flood plot before and after the flood experiments of 2002 and 2004. There was somewhat more selenium in the surface layer of the flood plot in 2002 than in 2004 before the experiment. Much of the difference in total selenium relates to the amount of soluble selenium in the 2 years. There was nearly twice as much soluble selenium in the surface sediments in 2002 as in 2004, although below the surface, concentrations of soluble selenium were lower in 2002. In 2004, the soluble selenium removal was between 76 and 80 percent in the top 2 feet of sediments; this level of selenium removal was only achieved in the surface layer in 2002. Nevertheless, over 50 percent soluble selenium removal was still achieved in the other 3 layers in the top 2 feet of sediments in 2002.

The amount of insoluble selenium in each of the layers in the flood plot prior to the 2002 and 2004 experiments were remarkably similar (Table 7). However, the response of the insoluble selenium in the 2 experiments was quite different. In 2002, there was a low level of removal insoluble selenium in 3 of the layers, but these reductions were more than offset by increases in 2 layers, in particular in the 6-12 inch layer, where the already large amount of selenium was increased by over 50 percent. Alternatively, in 2004, there were losses of significant amounts of insoluble selenium in 3 of the layers.

The net effect of the above changes in soluble and insoluble selenium was an increase of over 50 grams of selenium in the 6-12 inch layer in 2002 that was not seen in 2004 (Table 7). However, while there was a reduction in selenium in the 6-12 inch layer in 2004, it was much smaller than the reduction in the adjacent layers and reflected the absence of a change in insoluble selenium in that layer. In 2004, there was a much greater removal of selenium in all layers where there was removal. The only layer that showed selenium deposition (increase) was the 24-30 inch layer, where deposition also occurred in 2002.

Table 7. Selenium mass and its changes in each of the flood plot layers in 2002 and 2004									
	Depth Interval	Total Se 2002 (g)		Se 2002 change		Total Se 2004 (g)		Se 2004 change	
		Pre-flood	Post-flood	(g)	%	Pre-flood	Post-flood	(g)	%
Total Selenium	0 - 6 "	227	163	-64	-28.1%	193	154	-39	-20.1%
	6 - 12 "	134	190	55	41.1%	151	135	-16	-10.8%
	12 - 18 "	96	73	-23	-24.1%	85	60	-25	-29.6%
	18 - 24 "	72	58	-14	-19.9%	69	36	-33	-47.5%
	24 - 30 "	24	35	11	43.4%	22	28	7	30.2%
	30 - 36 "	21	26	4	20.9%	26	22	-4	-16.8%
Soluble Selenium	0 - 6 "	76	16	-60	-79.3%	37	9	-28	-75.7%
	6 - 12 "	24	9	-15	-63.1%	34	8	-26	-75.7%
	12 - 18 "	20	6	-14	-72.1%	24	5	-20	-80.5%
	18 - 24 "	9	4	-5	-52.6%	16	4	-12	-76.1%
	24 - 30 "	4	3	-1	-30.7%	6	4	-2	-32.8%
	30 - 36 "	3	3	0	0.0%	9	4	-4	-50.9%
Insoluble Selenium	0 - 6 "	149	136	-13	-8.7%	156	137	-19	-12.4%
	6 - 12 "	111	170	59	53.5%	117	117	1	0.5%
	12 - 18 "	64	61	-3	-4.4%	61	48	-13	-21.5%
	18 - 24 "	53	47	-6	-12.1%	53	27	-26	-49.7%
	24 - 30 "	17	30	14	81.3%	16	20	4	25.5%
	30 - 36 "	18	19	1	3.1%	18	14	-4	-21.1%

Reduction-Oxidation Potential

The goal of the flood experiment, like that of the prior attempts to remove selenium from the sediments, was to dry the sediments and oxidize the selenium to selenate. The measure of success in the above description was based on the selenate concentration. The actual measurement of how oxidizing a chemical environment may be is known as the reduction-oxidation potential (redox potential or Eh). Direct measurement of Eh is made using a platinum electrode. However, indirect measurements can be made using ratios of redox couples. The most commonly used redox couple consists of ferrous and ferric iron. In Stewart Lake, the sediment monitoring data consist solely of selenium concentrations; so there are no iron data to with which to work.

Selenate and selenite are a redox couple. The selenate/selenite couple is not used very often in geochemical studies because the selenium species are too redox sensitive and rarely come to an equilibrium (Ball and Nordstrom, 1991). However, in Stewart Lake sediment rehabilitation, the goal had nothing to do with achieving a chemical equilibrium. The goal was to promote oxidation. A redox potential based on the selenate/selenite couple should provide a reasonable estimate of conditions at the time the samples were collected. This section will provide estimates of the redox environment based on estimates of the Eh as calculated from the selenate/selenite couple. In this case, the Eh was calculated from the total selenate and selenite (soluble plus insoluble) concentrations.

The interrelationships between species are not just dependent on the Eh. The speciation is also dependent on pH. To further complicate matters, the relationship of the chemical species to the pH and Eh conditions of the geochemical environment changes with the total concentration of the element in question, in this case selenium. In the case of Stewart Lake, the individual selenium species concentrations are known, but the speciation cannot be directly compared to a theoretical Eh-pH phase diagram.

Figure 13 presents Eh estimates for samples collected before and after the 2002 and 2004 flood experiments. The estimated Eh for each of the depth intervals are shown on the figure. Figure 13 also shows the change between samples on a separate plot, as was done for the selenium species data above.

The range in Eh shown on Figure 13 is relatively small. The minimum and maximum Eh both occur in the surface sediments. The maximum Eh, 0.431V, occurred in the surface layer at the beginning of the 2002 flood experiment, while the minimum Eh, 0.395V, occurred at the end of the 2004 flood experiment in the same layer. Figure 13 also indicates that in all instances, the entire profile is relatively oxidizing. The Eh of the deeper layers at the beginning of the 2004 flood experiment were particularly high, which may have been a factor in the particularly effective selenium removal during that experiment.

Figure 13 indicates that the estimated Eh decreased in all layers during both flood experiments. The decrease in the Eh was particularly large in the deeper layers in 2004. Recall from Figure 7 that a large proportion of the selenate was removed from all layers of the sediments in 2004. Alternatively, there were relatively small changes in selenite (Figure 8). The Eh was estimated from the selenate/selenite ratio. The large change in the estimated Eh may be more of a reflection of the selenate removal than any actual change in Eh.

Figure 13 also indicates that there was a relatively large increase in Eh between the experiments. Based on the preceding, the increased Eh may be a reflection of an increase in selenate associated with an increase in total selenium. Although the seepage was removed prior to the flood experiment, there was still a selenium source for much of the time between experiments. Figure 14 indicates that total selenium did increase in some layers of the sediments in the flood plot. The maximum increase was about 2 ppm at the surface. None of the decreases in the deeper layers were greater than 1 ppm. There were also decreases in total selenium in 2 of the layers. Since the Eh increased in all layers, at least some of the increase in Eh based on the selenate/selenite ratio must be real. In the case of the layers where the total selenium decreased, all of the Eh increase must be real. However, it is impossible to tell exactly how is real in the other layers based on the available data.

Elemental selenium was present as a relatively high percentage of the total selenium in all layers of the flood plot both before and after the experiment (Table 4). Elemental selenium (Se^0) is a reduced form of selenium, at least relative to the selenium oxyanions used to estimate the Eh. This raises the question as to the validity of the Eh estimates.

However, microbially driven selenate reduction results in the precipitation of elemental selenium (Stolz *et al.*, 2002). While remobilization of selenium through oxidation does occur, the rates are 3 to 4 orders of magnitude less than the reductive part of the cycle (Dowdle and Oremland, 1998). Consequently, microbial activity could cause a buildup of elemental selenium. Its presence in the oxidizing environment sediments may be a matter of chemical kinetics, *i.e.* rate determined.

University of Cincinnati Results

In 2002, we submitted 2 samples from the site 21 to Joseph Caruso at the Department of Chemistry, University of Cincinnati (U Cinn). The results were provided to us in a draft paper to be submitted for publication. The paper was an early draft without an abstract or introduction. The paper was also flagged do not cite. The paper has since been published (Ponce de León *et al*., 2003). Regrettably, we never had a chance to review the abstract or introduction and Stewart Lake has been moved from Utah to California in both sections of the paper. Despite this geographical error, there are some interesting results that I will summarize here.

The analytical methodology of Ponce de León *et al*. (2003) includes many of the same extractions as those of Frankenberger and Zhang (2001). The analytical methodology also includes some additional analyses using high performance liquid chromatography (HPLC). However, none of the reports that we received from the U Cinn laboratory included the speciation of the individual samples. What we received was more of a lumped result with references to the percentages of some of the analytes in the individual samples. The total selenium results were reported and showed good agreement with other analyses of the samples from the USGS and UC Riverside laboratories. The total selenium samples were analyzed by a method similar to that of the UC Riverside (UCR) laboratory.

Ponce de León *et al*. (2003) found that the predominant species were selenate, selenite, and elemental selenium. The agrees with the above results from UCR. They also found small concentrations of organic selenium, also in agreement with UCR. About 10 percent of the selenium in the samples was labeled as being refractory, which is the equivalent to the UCR residual selenium, and not out of line with previous results from UCR.

The interesting part of the Ponce de León *et al*. (2003) results concern the analysis of the organic fraction of the selenium. They found none of the selenium was associated with humic acids, which are common in wetlands. However, our draining the lake and oxidation of the sediments over a number of years would likely have allowed for the oxidation of any humic acids that had been present. The analytical results showed that selenomethionine and selenocysteine were not present in detectable concentrations. Although they could not specifically identify the organic compounds present, Ponce de León *et al*. (2003) indicate that the results are consistent with some higher molecular weight compounds, such as selenoproteins or peptides. Their likely source was decaying vegetation identified in the samples.

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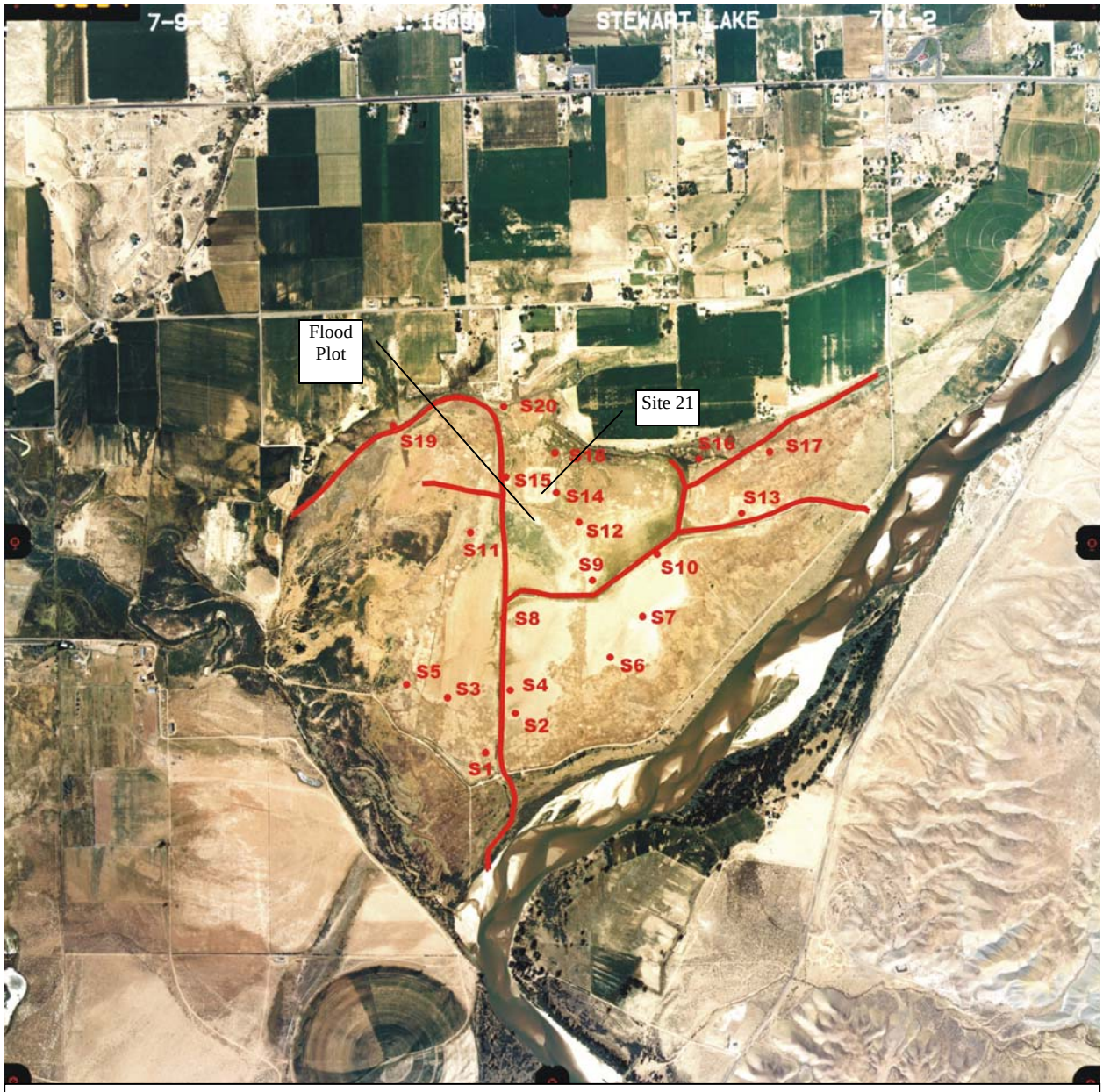

Figure 1: Aerial photograph of Stewart Lake bed showing channels and site locations

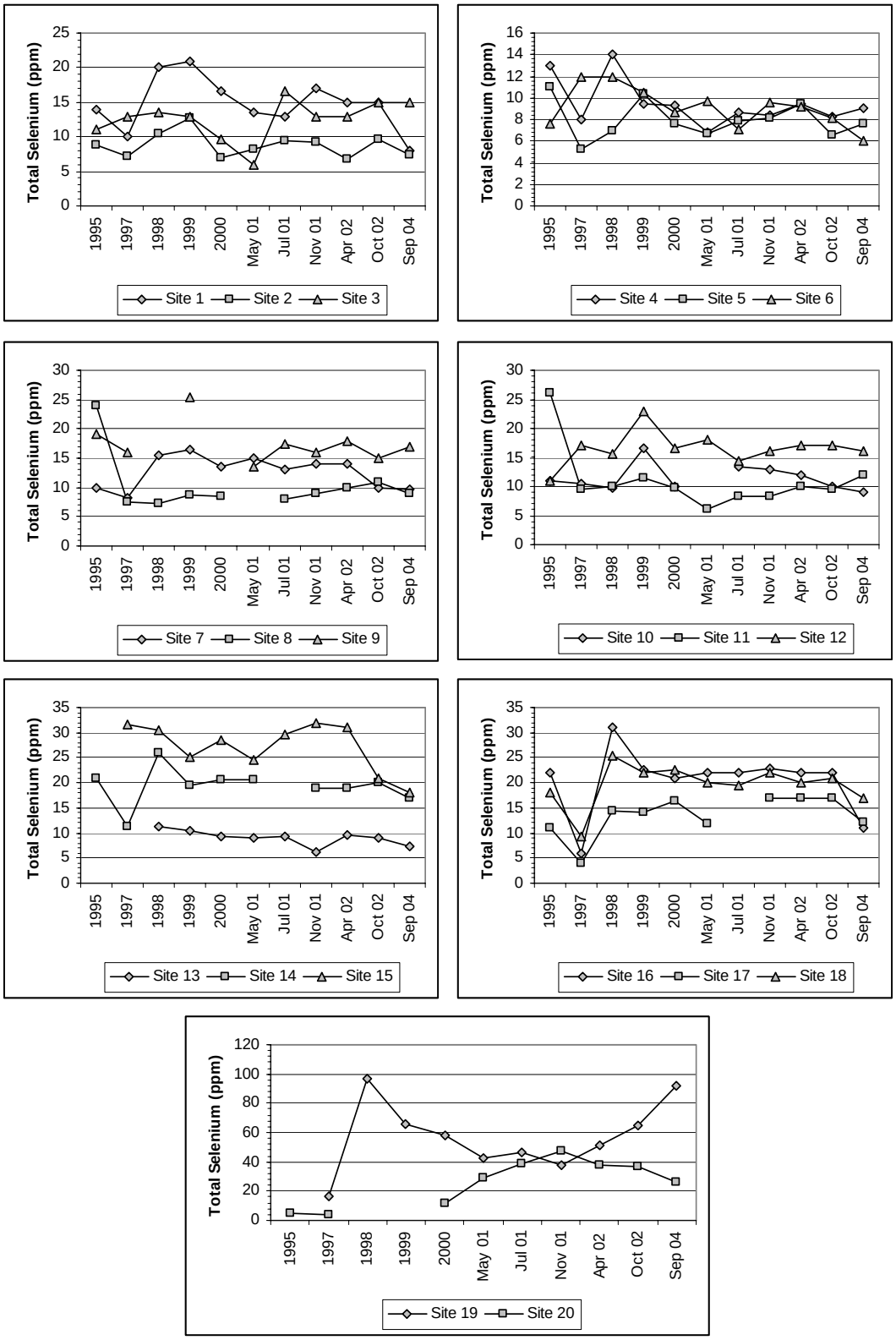

Figure 2: Plots of the complete total selenium data sets for each of the 20 permanent monitoring sites

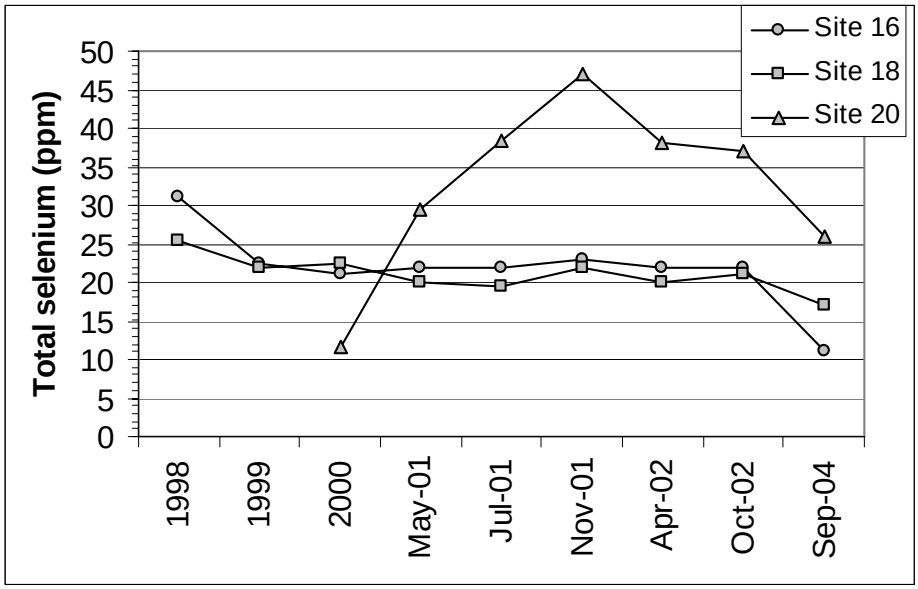

Figure 3: Total selenium at sites 16, 18, and 20 since diversion of the Jensen Unit drains

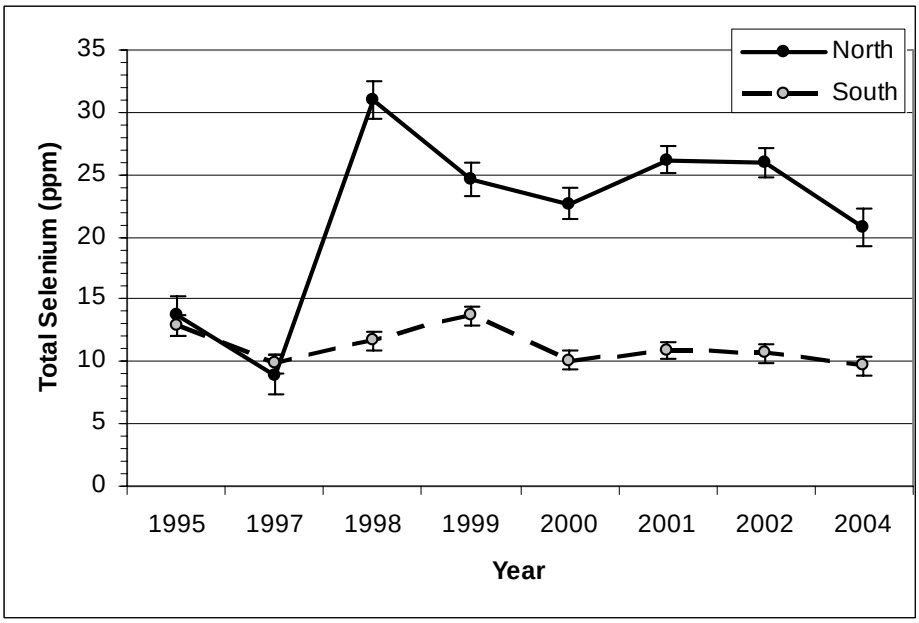

Figure 4: Average total selenium in the north and south parts of Stewart Lake from 1995 through 2004

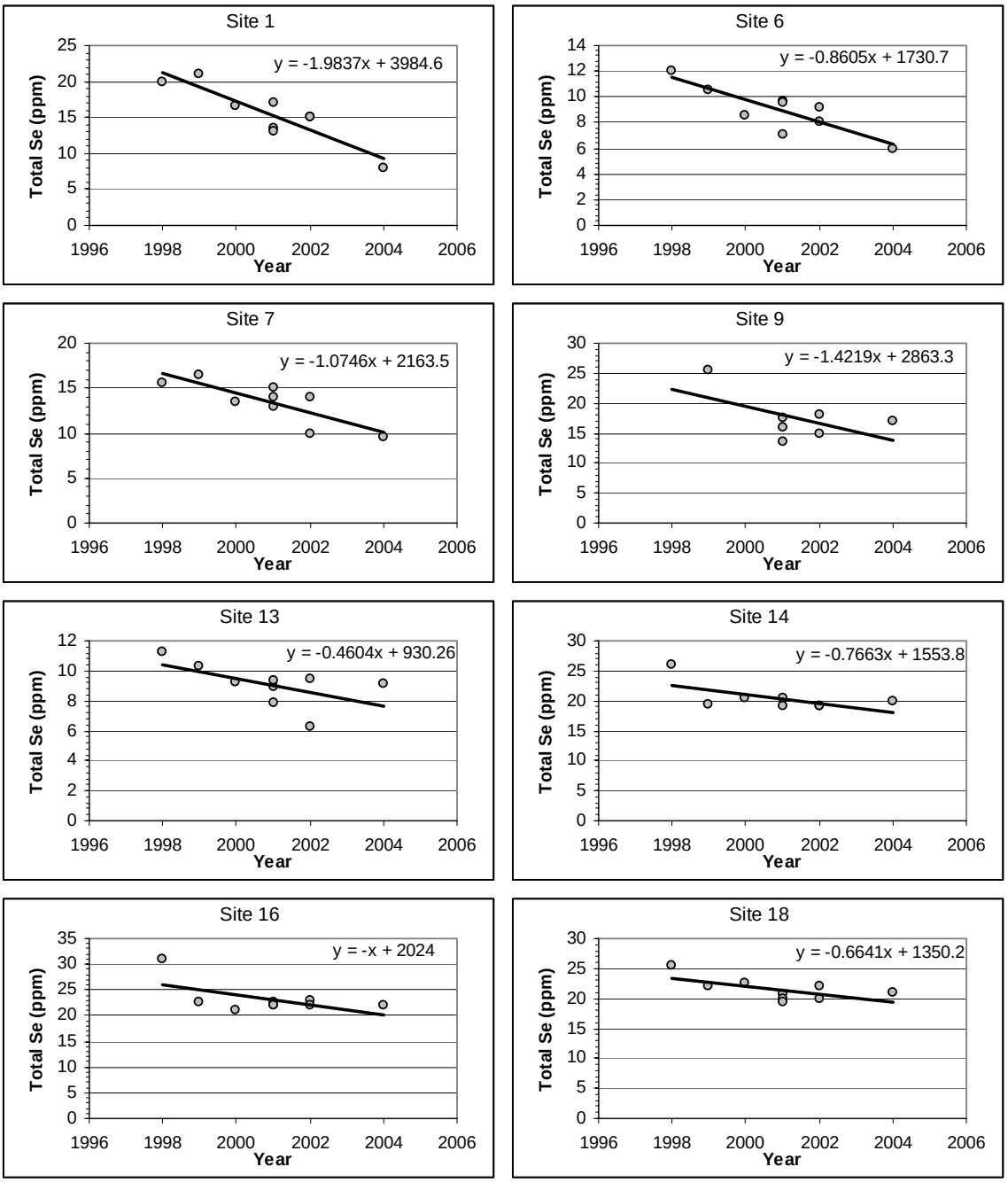

Figure 5: Plots of trends for significant correlations of total selenium on year

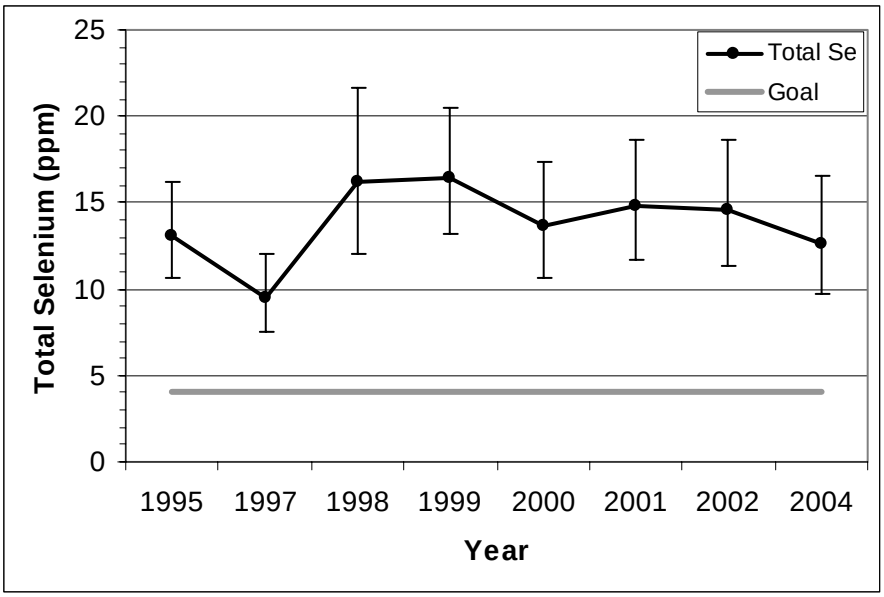

Figure 6: Geometric mean total selenium concentrations in Stewart Lake from 1995 though 2004

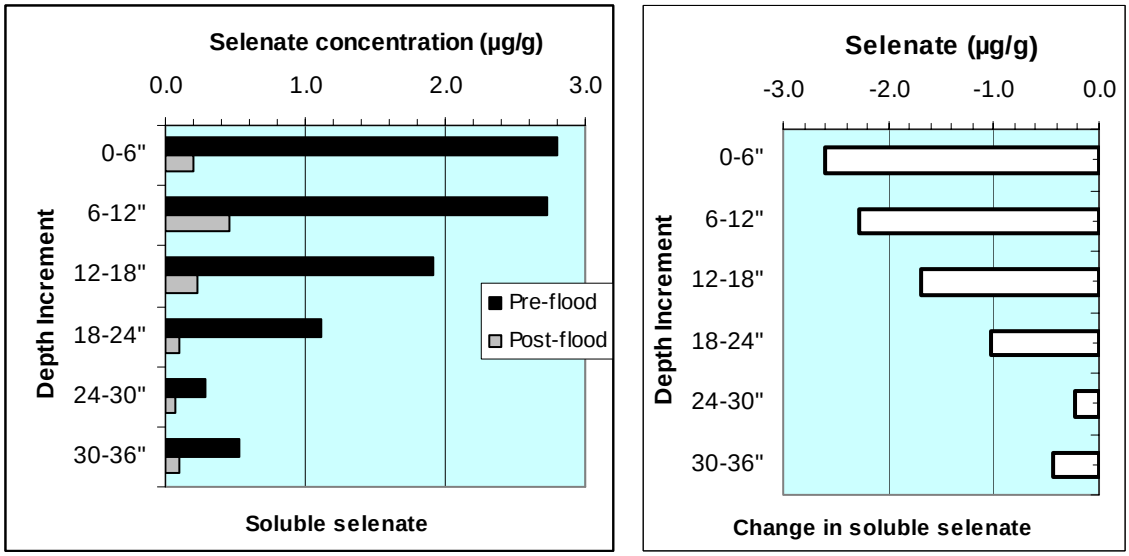

Figure 7: Selenate concentrations before and after the flood experiment and the estimated change in selenate during the experiment

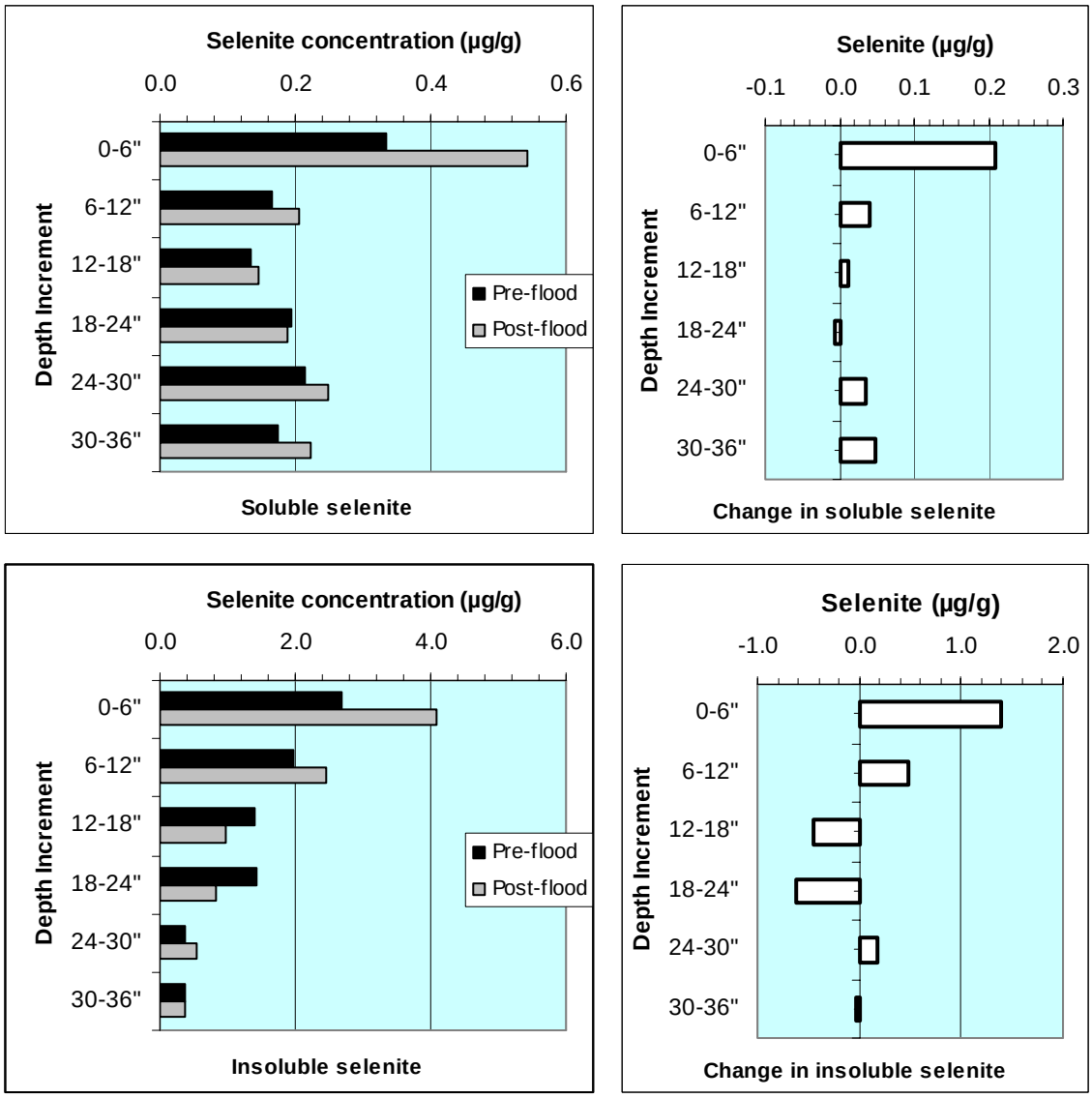

Figure 8: Selenite concentrations before and after the flood experiment and the estimated change in selenite during the experiment

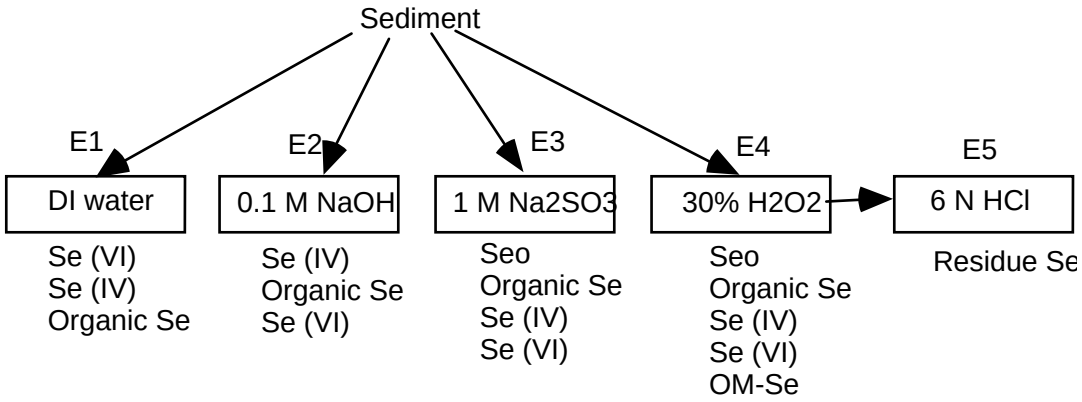

Figure 9: Selenium fractions present in the extractions with various solvents (after Frankenberger and Zhang, 2001)

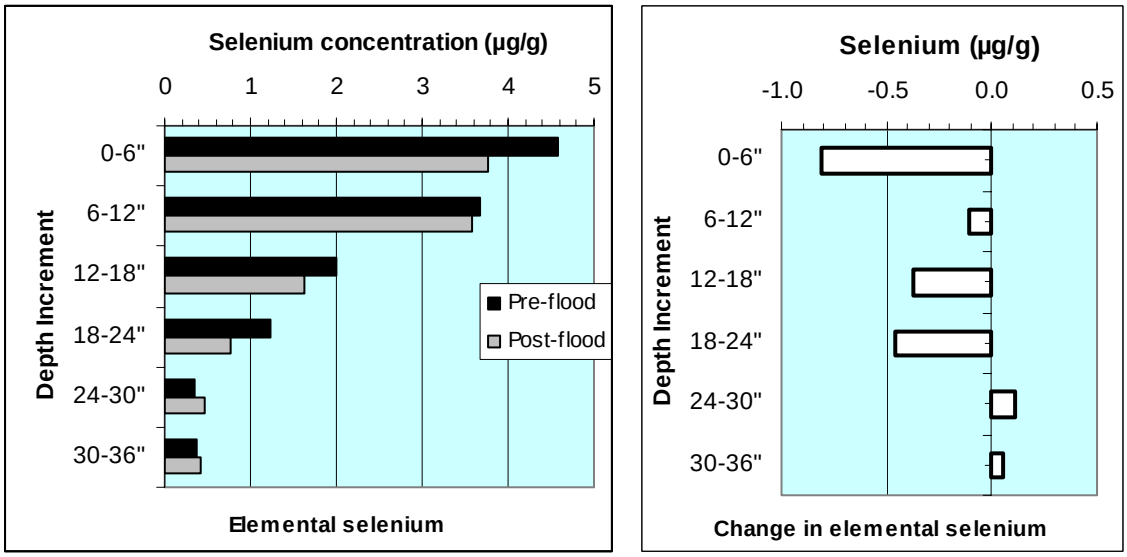

Figure 10: Elemental selenium concentrations before and after the flood experiment and the estimated change in elemental selenium during the experiment

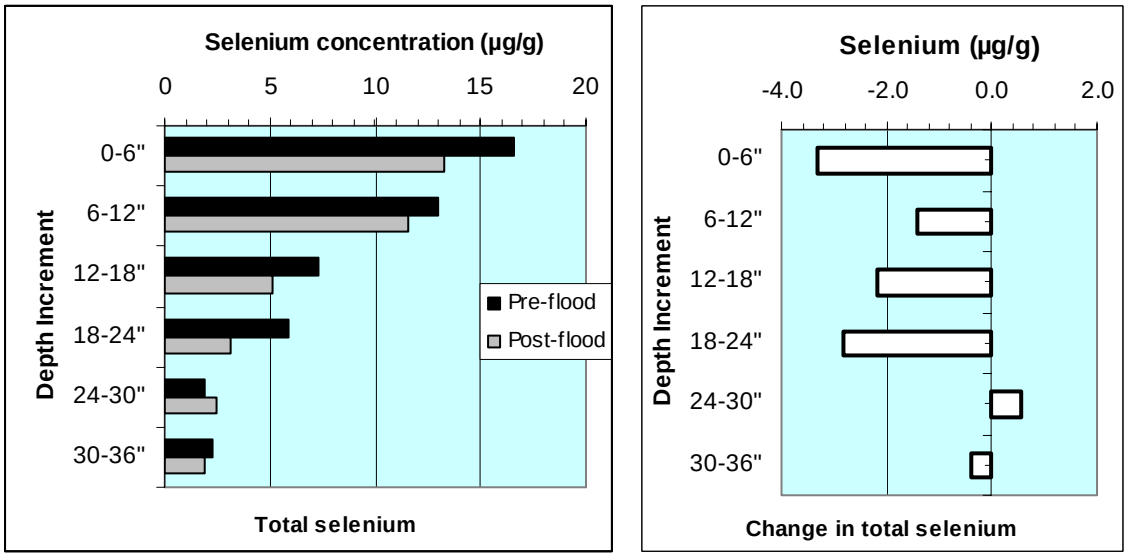

Figure 11: Total selenium concentrations before and after the flood experiment and estimated changes in total selenium during the flood experiment

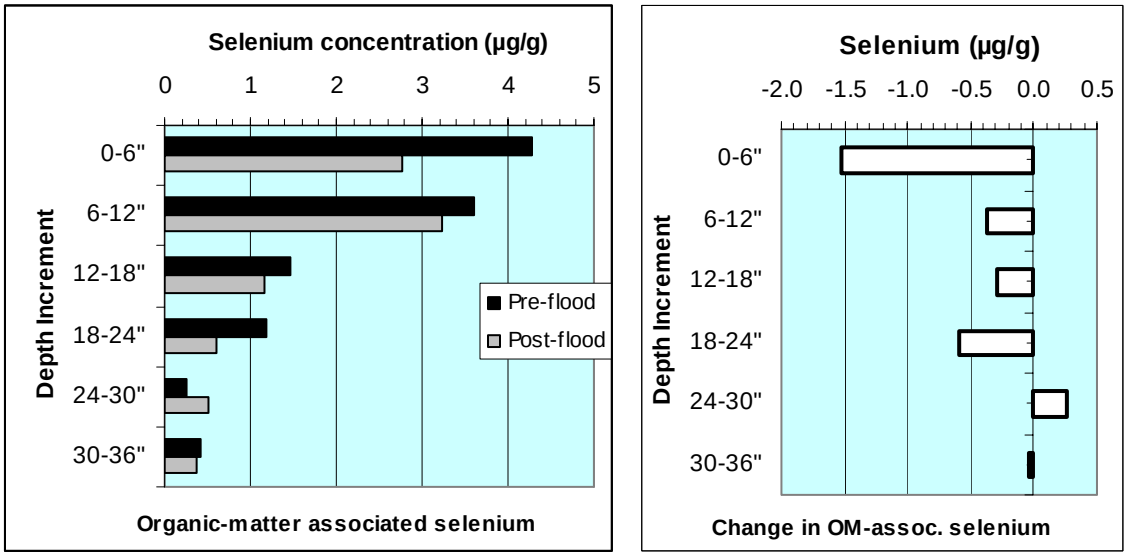

Figure 12: OM-Se concentrations before and after the flood experiment and estimated changes in OM-Se during the experiment

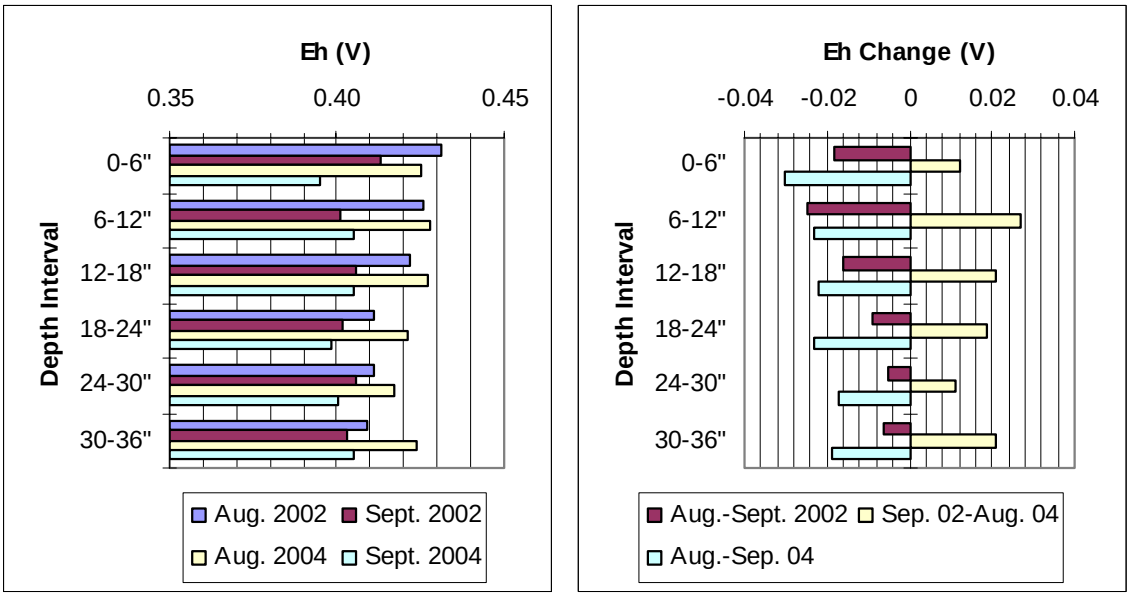

Figure 13: Estimated Eh of the flood plot before and after the 2002 and 2004 flood experiments and changes in Eh between and during experiments (Eh estimated from the Se^{VI}/Se^{IV} ratio)

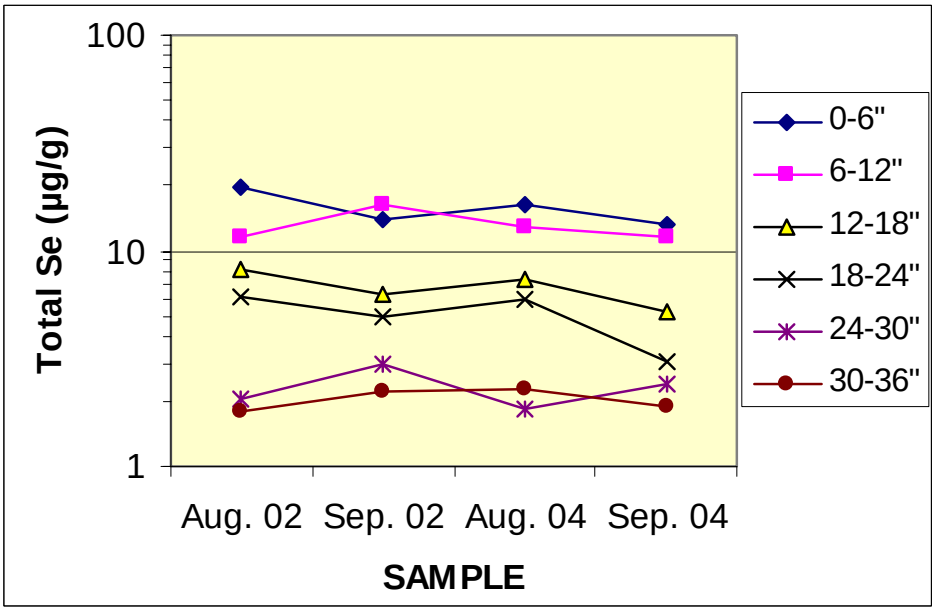

Figure 14: Total selenium concentrations in the flood plot in 2002 and 2004

APPENDIX A

SAMPLING REPORT

9/29/2004

Bureau of Reclamation
Denver Office – Technical Service Center
Denver, Colorado

TRAVEL REPORT

To: James Yahnke, Hydrologist, Land Suitability and Water Quality (D-8570)

From: Del Smith

Subject: Sediment Sampling for Selenium Analysis and Flood Plot Pipeline Installation at Stewart Lake, Utah

1. *Travel Period:* August 2nd through August 5th, 2004

2. *Synopsis of the Trip:* On Monday Afternoon, August 2, Del Smith traveled to Vernal, Utah, stopping at Stewart Lake to see if the gate key worked. It did not so I went to the Utah Division of Wildlife Resources (UDWR) office in Vernal, Utah, on Tuesday morning to get the right gate key.

On Tuesday, August 3rd, I picked up a gate key from UDWR at 7:30 AM and purchased 1,560 feet of 2-inch diameter plastic irrigation pipe (PIP) from Intermountain Farm Association, along with a 2-inch diameter PIP valve, 2-inch diameter PIP elbow and PIP reducers for 6-inch PIP to 2-inch PIP. After discovering that the Stewart Lake gate key did not work I, returned to UDWR in Vernal to get the right key. While waiting for the pipe to be delivered from Vernal to Stewart Lake, I glued the PIP fittings together for the reducer and elbow and collected soil samples from sites S-15 and S-20. A composite of five samples, 0 to 6 inches in depth, were collected using an Oakfield Probe push tube and placed in zip lock bags. All samples were collected within a 3-foot radius of the permanent steel pole markers. A summary of the cover material growing on the dry lake bed surrounding each site can be found in Table 1. I also pulled weeds from the perimeter of the flood plot for one hour and keyed in the 20-mil PVC plastic liner that was used in 2002 for decreasing later seepage out of the flood plot through the earth dikes.

On Wednesday, August 4th, I collected soil samples from sites, S-1, S-5, S-10, S-7, S-14, S-12, S-9, S-6, S-18, S-19, S-16, S-17, and S-13. Note I found all the permanent markers for these sites except S-16, which was near the alignment of the new 24-inch diameter drainage pipeline that crosses Stewart Lake. I did collect a sample at S-16, using the GPS coordinates with an accuracy reading of ± 9-feet. I also punctured a tire on my pickup truck with a tamarisk stem that went through the sidewall. Dave Naftz from the USGS in Salt Lake City arrived mid morning and started setting up his flood plot test equipment.

We spent several hours in the afternoon hauling and connecting the 20-foot section of 2-inch diameter PIP.

On Thursday, August 5th, I finished collecting soil samples from the 20 permanent sites. Samples were collected from S-2, S-3, S-4, S-8, and S-11. I collected one soil profile sample from the flood plot, in 6-inch increments, down to a depth 36 inches for speciation. This sample was collected using an open faced 4-inch diameter soil auger and the samples were kept on ice until they were put in a freezer in the Denver TSC soils lab. Steve Noyes showed up late in the day and he and John Hunting tested the water delivery system to the flood plot through the new 2-inch diameter PIP.

On Friday, August 6th I returned to Denver, Colorado, dropping off the soil samples at the TSC soils lab.

General Observations: The river outlet of the new 24-inch drainage pipeline was half submerged at a Green River flow rate of 1,290 ft^3/sec on Monday August 2nd, 2004.

Table 1. Ground Cover at Sample Locations

Sample No.	**Date Collected**	**Surrounding Ground Cover**
S-1	8/4/2004	3-foot tall Tamarisk & 2-foot tall bulrush
S-2	8/5/2004	2-foot tall Tamarisk (sparse)
S-3	8/5/2004	Dead bulrush with 2-foot tall tamarisk (sparse)
S-4	8/5/2004	3-foot tall Tamarisk (sparse)
S-5	8/4/2004	2-foot tall Tamarisk
S-6	8/4/2004	Bare ground
S-7	8/4/2004	10-foot tall cottonwoods ~ 50 foot apart
S-8	8/5/2004	3-foot tall Tamarisk
S-9	8/4/2004	1-foot tall weeds (sparse)
S-10	8/4/2004	1-foot tall Tamarisk
S-11	8/5/2004	2-foot tall White top
S-12	8/4/2004	3-foot tall bulrush (sparse)
S-13	8/4/2004	2-foot tall dense weeds
S-14	8/4/2004	1-foot tall Tamarisk (sparse) and dead bulrush
S-15	8/3/2004	1-foot tall Tamarisk
S-16	8/4/2004	3-foot tall bulrush & 4-foot tall cattails
S-17	8/4/2004	3-foot tall bulrush (sparse)
S-18	8/4/2004	4-foot tall cattails
S-19	8/4/2004	Sparse weeds
S-20	8/3/2004	5-foot tall bulrush
Flood Plot	8/5/2004	1-foot tall bulrush and weeds

APPENDIX B

TOTAL SELENIUM CORRELATIONS AMONG SITES AT STEWART LAKE

Correlations: 1995-2004 – n = 11

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*
20	-0.0339	0.0186	0.2526	-0.5284	0.0181	-0.3834	0.2124	-0.2687	-0.4044	0.2828	-0.4750	0.1201	-0.7605	0.0248	-0.1961	0.1861	0.6052	0.2622	0.0734
19	0.2431	0.2579	0.3041	0.2545	-0.1096	-0.0853	0.3329	-0.4388	0.3111	-0.2084	-0.3047	0.2816	-0.1883	0.4875	-0.5557	0.3204	0.4409	0.5687	
18	0.7754	0.4693	-0.0741	0.3578	0.2999	0.0051	0.7673	-0.0967	0.3678	0.1848	-0.1437	0.1256	-0.1781	0.8988	-0.0310	0.9133	0.8450		
17	0.5498	0.2221	0.1298	0.0671	0.3252	-0.2813	0.5495	-0.0971	0.1617	0.1799	-0.2118	0.0968	-0.4529	0.6275	-0.0946	0.7077			
16	0.7968	0.5028	-0.1110	0.4870	0.3603	0.1264	0.7353	0.0965	0.3164	0.2345	0.0058	-0.0506	0.0786	0.9377	0.2245				
15	0.2988	-0.0965	-0.0970	0.3418	0.1747	0.4713	0.1658	0.1731	0.1263	0.1909	0.1754	-0.3438	0.3594	0.0455					
14	0.6524	0.4122	-0.1362	0.6025	0.3099	-0.0111	0.6212	0.1503	0.3066	-0.0050	0.1087	-0.1691	0.0990						
13	0.2144	0.1805	-0.0795	0.5221	0.0949	0.4748	-0.0542	0.2868	0.4108	-0.0037	0.3899	-0.0640							
12	0.3730	0.4158	-0.0859	-0.4416	-0.0744	0.4059	0.4735	-0.6005	0.3638	0.5469	-0.5510								
11	-0.0571	0.0353	-0.0217	0.6288	0.6522	-0.2866	-0.3569	0.9414	0.2854	-0.1031									
10	0.4972	0.6342	0.0375	-0.1848	0.5084	0.1767	0.5793	-0.0889	0.4951										
9	0.6449	0.5923	0.1721	0.5405	0.5901	0.2285	0.4660	0.0623											
8	-0.0648	-0.0021	-0.1299	0.4759	0.6269	-0.3557	-0.3463												
7	0.7822	0.4852	-0.2856	0.1158	0.2987	0.3393													
6	0.4835	0.2440	-0.2356	0.1317	-0.2931														
5	0.3642	0.3139	-0.0005	0.4328															
4	0.3950	0.2519	0.1447																
3	-0.1043	0.2332																	
2	0.6836																		

$r_{\alpha=0.01} = 0.73$

Correlations: 1998-2004 – n = 9

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*
20	-0.3715	-0.1697	0.2535	-0.6264	0.0557	-0.3998	-0.3263	0.5065	-0.5978	0.2187	-0.3939	-0.2282	-0.6345	-0.5785	0.0855	-0.2425	0.2877	-0.4996	-0.6630
19	-0.0125	0.1481	0.3355	0.7132	-0.1628	0.0610	-0.2216	-0.1560	0.3755	-0.4835	0.6999	-0.0402	0.3529	0.3586	-0.4112	-0.0405	-0.3162	0.1664	
18	0.8851	0.4395	-0.1474	0.6568	-0.0470	0.8528	0.6097	-0.3235	0.4375	0.0621	-0.0530	0.0914	0.5323	0.8461	0.5662	0.8855	0.3904		
17	0.4134	-0.0700	0.2411	0.0809	0.1881	0.1483	-0.0261	0.5012	0.0469	0.0399	0.0351	-0.1282	-0.0394	0.0435	0.5141	0.3413			
16	0.8052	0.4378	-0.1119	0.5511	-0.0608	0.8500	0.6675	-0.3149	0.2523	0.1791	-0.3336	0.0008	0.6158	0.8669	0.6766				
15	0.5393	-0.0053	-0.0626	0.3328	0.2595	0.5227	0.6248	-0.3774	0.1755	0.2969	-0.3263	-0.2384	0.1705	0.4152					
14	0.6055	0.3075	-0.1407	0.7386	-0.3395	0.7426	0.4865	-0.4947	0.2352	-0.1945	-0.1769	-0.1509	0.6955						
13	0.5527	0.3876	-0.0290	0.5823	0.1252	0.5435	0.4897	-0.2673	0.5592	0.1214	0.1177	0.2799							
12	0.4721	0.5655	-0.2673	-0.1489	0.6061	0.3660	0.4650	0.1607	0.5752	0.6515	0.2662								
11	0.0396	0.1360	0.5125	0.4550	0.4566	-0.1392	-0.2251	0.1769	0.6398	-0.0661									
10	0.4736	0.6232	0.0276	-0.2094	0.7483	0.2818	0.6156	-0.0916	0.4926										
9	0.6469	0.5746	0.2049	0.5608	0.6851	0.4234	0.5287	-0.2831											
8	-0.1785	-0.1304	0.2442	-0.4184	0.0731	-0.3305	-0.5542												
7	0.7616	0.4343	-0.4406	0.2956	0.4394	0.8320													
6	0.8704	0.4799	-0.3598	0.5278	0.1566														
5	0.3520	0.2794	0.1863	0.0459															
4	0.4790	0.2531	0.3081																
3	-0.1175	0.2575																	
2	0.6460																		

$r_{\alpha=0.01} = 0.80$