

Report on Sediment Samples Collected from Stewart Lake, Utah in 2002

Introduction

Samples were collected by personnel of the Bureau of Reclamation's Technical Service Center (TSC) in April, August, September, and October of 2002 from various sets of sites in the dry lake bed of Stewart Lake, Utah, (Figure 1) as part of ongoing monitoring of the remediation of selenium contaminated sediments. Sampling reports prepared by Steve Hoffman of the TSC are included as Appendix A to this report. The sampling reports also include observations and some field investigations made during the sampling trips. The purpose of this report is to document the results of laboratory analysis of the samples and to present an analysis of those data. All of the selenium analytical results from the 2002 samples are included in Appendix B.

Runoff was lacking during 2002 and the normally conducted spring flooding of Stewart Lake was foregone. The peak flow of the Green River was not great enough to provide a reasonable flushing; so the Core Team decided to pursue a plan of flooding 2 carefully prepared experimental plots.

Reclamation had planned to follow-up on an experiment conducted in 2001 in which a large 10,000 square foot plot had been treated with lime and flooded by the Green River. The plot had been treated with lime in April prior to the decision to forego Green River flooding. This large flood plot would be filled in August with water purchased from the irrigation district. Sediment samples were collected from this area before and after the application of lime in April. Additional samples were collected before and after flooding in August.

The USGS set up a highly instrumented 30' X 30' plot to monitor water and selenium movement. Construction of the flood plot is described on pages A-5 and A-6. Reclamation sampled the sediments before water was applied and after flooding once the sediments had dried. Those results are reported here.

In addition to the pre- and post-flood sediment samples, samples were collected from the 20 permanent monitoring sites that were originally established in 1998. Those samples were collected at the end of September. The samples were collected consistent with those of prior years for long-term monitoring and comparisons among years.

2002 Pre-flood Samples

Samples were collected from the large flood plot, which has been labeled as site 21 in the Reclamation numbering scheme (Figure 1). The site has been divided into 4 quadrants for sampling purposes (see Appendix). Samples were collected from the upper 6 inches of sediment from each of the 4 quadrants before and immediately after the application of lime to see if lime application by itself had any effect on selenium.

Stewart Lake, Utah
Permanent
Sediment Sampling Sites
November 2001



Figure 1: Permanent monitoring sites at Stewart Lake, Utah, as of November 2001 (S21 is the 3-acre experimental site where lime was added in April 2002)

The flooding experiments were not conducted until August. The flood plot had set undisturbed for over 3 months before the plot was to be flooded. The plot was sampled again to see if any changes in selenium had occurred during those intervening 3 months. The samples were analyzed for concentrations of various selenium species as well as for total selenium.

April 2002

The original plans were to repeat the lime experiment that was conducted at the large flood plot in 2001. Pre-flood samples were also collected from a selection of sites in the lake to review pre-flood conditions. Samples were collected from sites 1, 7, 10, 15, and 16. The first 4 sites have been used to monitor selenium through a depth profile since 2000 (site 7 was substituted for site 10 in 2001). Site 16 was sampled because it was located under a large accumulation of ice that had built up near the north-side seeps. The ice-affected speciation of selenium was to be evaluated. Only surface samples were collected for speciation. The data are shown on Figure 2.

Flooding would be expected to move the selenate from the sediments. Selenate was present at each of the sites in relatively low concentrations and as a percent of the total except at site 15 (Figure 2). At site 15, selenate made up nearly 25 percent of the total selenium. At sites 7 and 10, selenate made up between 10 and 20 percent of the total selenium, while at the remaining 2 sites, 1 and 16, selenate made up less than 5 percent of the total selenium. Under normal conditions of flooding, the selenate would be the only form that would be expected to be removed from the Stewart Lake sediments.

Elemental selenium was the predominant form of selenium at 3 of the 5 sites shown on Figure 2. Elemental selenium would be expected to remain immobile during flooding or increase in concentration as other more oxidized selenium species, such as

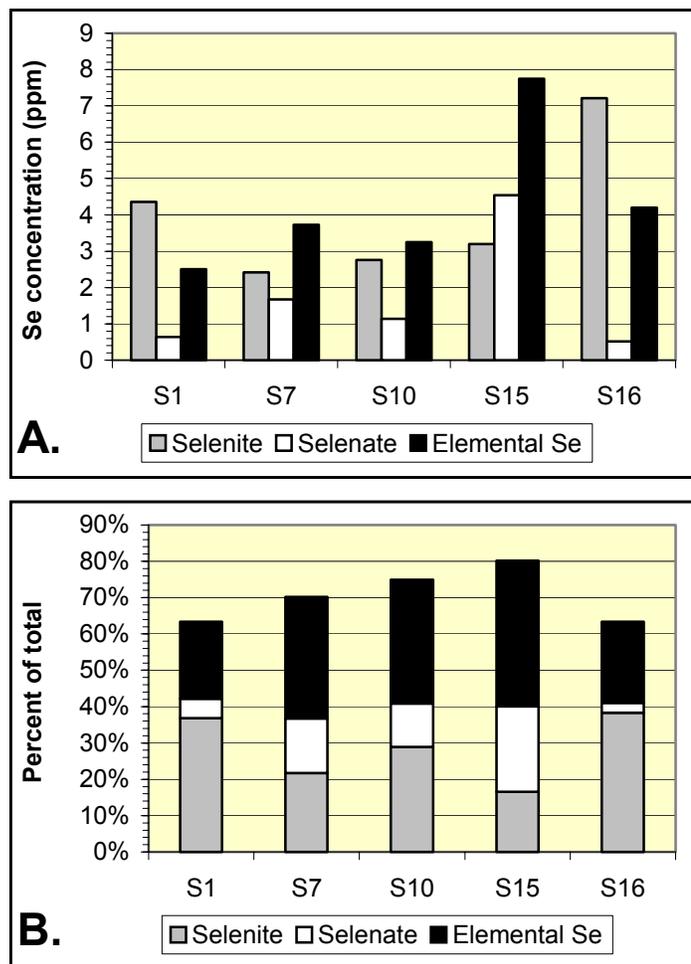


Figure 2: Concentrations and percentages of the 3 predominant selenium species in surface sediments at 5 sites in Stewart Lake during April 2002

selenate and selenite are reduced. Since elemental selenium is not soluble, it would remain in the sediments until it could somehow be oxidized.

The purpose of adding lime was to help reduce selenite adsorption. Selenite is soluble, but it is also highly adsorptive. The adsorption of selenite has been found to be strongly pH dependent (Neal *et al.*, 1987). The purpose of adding the lime was to raise the soil pH and desorb the selenite. Figure 3 shows a plot of the soluble selenite as a percent of the total selenite before the addition of lime. The percentage of soluble selenite is less than 20 percent of the total selenite at each of the sites. If the percentage could be raised, additional selenium could be mobilized and removed during flooding of Stewart Lake.

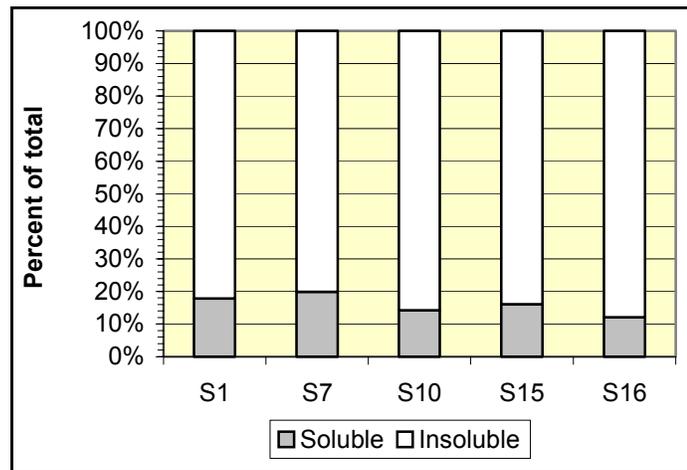


Figure 3: Soluble and insoluble selenite fractions at 5 sites at Stewart Lake during April 2002

Concentrations of various selenium species and total selenium at site 21, the large flood plot, are shown on Figure 4. Figure 4 shows the same selenium species as were earlier shown on Figure 2. In all of the quadrants at site 21, elemental selenium is the predominant species of selenium present. However, the concentration of elemental selenium is only slightly higher than the selenate concentration (< 1 ppm) in 3 of the quadrants. In those 3 quadrants selenite ranks third in abundance to selenate and elemental selenium. In the remaining quadrant selenite ranks second, while selenate ranks third.

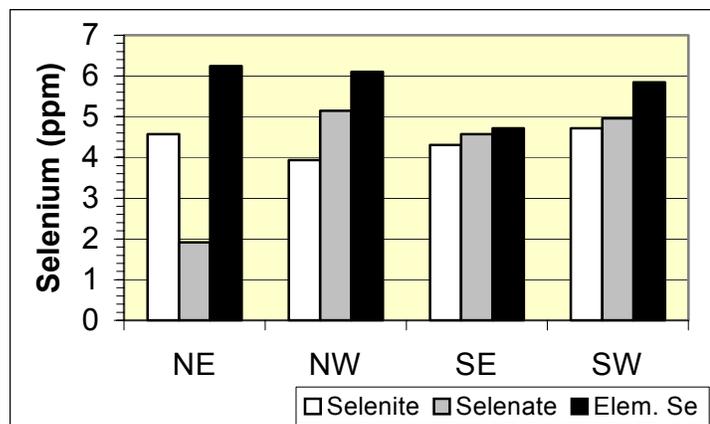


Figure 4: Concentrations of 3 selenium species in surface samples collected at site 21 during April 2002

Based on Figure 4, there is quite a bit of geochemical variation at the flood plot. The northeast quadrant differs considerably from the other 3 quadrants in that it has a very low concentration of selenate. The very low selenate concentration would indicate that conditions are less oxidizing in the northeast quadrant than in the other quadrants of site 21. Conditions in the northeast quadrant favor the stability of selenite over that of selenate. This phenomenon is explored more fully in Table 1, which presents the

Source	% Selenate	Elemental Se (%)	% Sol. Selenite	% Insol. Selenite	% Total selenite	% Org. Selenium	% OM-Se
S1	5.4%	21.2%	6.5%	30.2%	36.8%	12.9%	14.1%
S7	15.0%	33.5%	4.3%	17.4%	21.7%	3.7%	17.9%
S10	11.9%	34.0%	4.1%	24.8%	28.9%	4.7%	15.7%
S15	23.5%	40.1%	2.7%	13.9%	16.6%	1.8%	10.6%
S16	2.8%	22.3%	4.6%	33.7%	38.3%	18.2%	10.6%
S21-NE	11.6%	37.8%	3.6%	24.1%	27.7%	6.9%	13.1%
S21-NW	26.7%	31.6%	1.9%	18.5%	20.4%	5.8%	4.1%
S21-SE	25.6%	26.4%	3.1%	21.0%	24.1%	6.8%	7.7%
S21-SW	24.1%	28.4%	2.8%	20.2%	22.9%	10.1%	2.9%
S21-NE ¹	4.8%	47.8%	4.3%	19.1%	23.5%	4.6%	12.9%
S21-NW ¹	13.9%	45.3%	6.5%	13.7%	20.2%	5.7%	5.6%
S21-SE ¹	10.7%	39.7%	6.3%	20.2%	26.5%	4.5%	9.9%
S21-SW ¹	12.4%	44.1%	6.5%	18.9%	25.4%	6.3%	6.8%

¹ Post-lime application samples

percent distribution of the various selenium species of all of the April speciation samples described above.

Table 1 contains data on 2 selenium species that were not mentioned above. These include organic selenium and organic-matter associated selenium (OM-Se). Organic selenium includes organic compounds of selenium, such as selenium amino acids and methyl selenides. OM-Se has an undefined composition; it consists of selenium that is bound up in organic matter (Frankenberger and Zhang, 2001). To determine the composition of the OM-Se, the 0.1 molar sodium hydroxide extract would have to be speciated (*ibid.*).

Some of the data on the first 3 lines of Table 1 also appear on Figure 2B, where it was noted that the selenate percentages were lower at sites 1 and 16 than at other sites. From Table 1 it is also evident that the organic selenium is also higher at sites 1 and 16 than at the other sites. If the organic selenium is indicative of high organic matter content in the sediments, decomposition of greater amounts of organic matter could account for the less oxidizing conditions than at the other sites. However, correlations among the various variables do not support this hypothesis.

Lime

The application of lime to the sediments was designed to raise the pH and effect desorption of selenite. The assumption was that the majority of the insoluble selenite was adsorbed on the sediments. Selenite adsorption is pH dependent (Balistrieri and Chao, 1987; Neal *et al.*, 1987a). Prior to 2001, there was only 1 measurement of the sediment pH at Stewart Lake. The ambient pH of the Stewart Lake sediments was measured at several sites in November 2001 and at site 21 in 2002 (Table 2). According to Neal *et al.* (1987), selenite adsorption drops to a very small percentage at a pH greater than 9. The ambient pH of the Stewart Lake sediments appears to be

ordinarily between 7 and 8 based on the limited data in Table 2. The effects of the initial lime application experiment on pH and selenium leaching were reported in my previous sediment report (Yahnke, 2002).

Table 2 indicates that the pH of site 21 was stable over the 8 month period of November 2001 through July 2002. The pH in November 2001 was within the variation shown by the replicates collected in July 2002.

Selenate may also be adsorbed, but its adsorption is only significant in an acid environment, *i.e.* pH < 6.5 (Balistreri and Chao, 1987). Alternatively, Neal and Sposito (1989) showed no significant selenate adsorption at a pH greater than 4.

Lime was applied to 3 experimental plots prior to flooding by the Green River in 2001. Samples that were collected immediately after lime application, but before the flood, showed changes in both selenium speciation and the concentration of total selenium in the lime-treated plots. Samples for selenium speciation were collected immediately after lime application in April 2002 to see if changes similar to those observed in 2001 would occur again. Changes in selenium speciation and total selenium observed in 2002 are described in this section of the report. As described above, no investigations of flood effects were conducted in 2002.

The 2 sets of data for site 21 in Table 1 reflect the pre- and post-lime data sets. The application of lime was designed to simply raise the pH and desorb selenite, thus increasing the fraction of soluble selenite. However, as was the case in 2001, there were other changes as well.

As was indicated on Figure 4, elemental selenium was the predominant species in the surface sediments of all 4 quadrants of site 21. This is shown also in Table 1, although in 3 of the 4 quadrants, selenate was a close second, particularly in the southeast quadrant. Selenite was a close third in each of those 3 quadrants. The majority of the selenite was in the insoluble fraction in all 4 quadrants and represented 19 to 20 percent of the total selenium in 3 of the 4 quadrants (Table 1).

Absolute and percent changes in the predominant selenium species (selenate, selenite, and elemental selenium) for each of the quadrants at site 21 are shown in Table 3. There was an increase in soluble selenite in all 4 of the quadrants. The size of the changes in terms of both percentages and ppm were highly variable, with a range in percentages from about 26 to an over 200 percent increase and in ppm from 0.15 to 0.774 (Table 3). This variability indicates that there were other significant factors controlling the chemical reaction, *i.e.* desorption, aside from pH. For example, Neal *et*

Site	Nov-01	Jul-02	
		Rep. 1	Rep. 2
S1	7.04		
S7	7.75		
S10	7.66		
S15	7.70		
S21-NE	7.76	7.5	7.8
S21-NW	7.89	8.0	7.9
S21-SE	7.80	8.2	7.6
S21-SW	7.71	7.7	8.0

* A sample composited from sediment from numerous sites in 2000 had a pH of 7.48

Table 3. Post-lime changes in predominant selenium species and total selenium at site 21 during April 2002						
Percent	Se^{IV}		Change in % total Se^{IV}	Δ % Se^{VI}	Change in % Elem. Se	Change in % Total Se
Quadrant	Δ sol.	Δ Insol				
NE	25.9%	-18.4%	-12.7%	-57.8%	30.1%	2.9%
NW	208.6%	-32.0%	-9.3%	-52.4%	31.2%	-8.3%
SE	68.8%	-20.5%	-9.1%	-65.4%	24.2%	-17.3%
SW	104.0%	-17.7%	-2.9%	-55.0%	35.7%	-12.4%
ppm	Se^{IV}		Change in total Se^{IV}	Δ Se^{VI}	Change in Elem. Se	Change in Total Se
Quadrant	Δ sol.	Δ Insol				
NE	0.152	-0.732	-0.580	-1.108	1.883	0.484
NW	0.774	-1.141	-0.367	-2.697	1.902	-1.602
SE	0.380	-0.770	-0.390	-2.986	1.141	-3.093
SW	0.596	-0.732	-0.136	-2.727	2.088	-2.555

al. (1987a) showed a great deal of adsorptive variation among soils; selenite adsorption is also greatly affected by phosphate (Balistrieri and Chao, 1987; Neal *et al.*, 1987b).

The changes in the solubility fractions of selenite were accompanied by an overall decrease in selenite (Table 3). The magnitude of the decrease also showed a decreasing trend from northeast to southwest. The largest decrease in the percent of selenite was in the northeast quadrant (Table 3), where the lowest concentration (and percentage) was present before the lime was added (Figure 4). The general direction of decrease is away from the seeped area, which is generally along the scarp at north end of the Stewart Lake Waterfowl Management Area. Evidence for the effect of seepage on the northeast quadrant of site 21 is described on page A-5 (see paragraphs 5 and 6).

Among the other changes in selenium speciation accompanying the application of lime was a very large decrease, *i.e.* from at least 1 ppm to nearly 3 ppm, in selenate in all 4 quadrants. The decrease in selenate was much greater than any of the increases in soluble selenite. Overall there was a relatively large net decrease in soluble selenium. Accompanying the large decrease in soluble selenium was a rather significant increase in elemental selenium, a highly insoluble form of selenium. On the other hand, there was a net decrease in total selenium in 3 of the 4 quadrants of site 21 and a small increase in the other quadrant. The decreases in total selenium ranged from 1.6 to 3.1 ppm (Table 3). Similar decreases in total selenium were noted following the lime application in 2001. The decreases can only be accounted for by volatilization. The increase cannot be accounted for on the basis of the available data, but the northeast quadrant is nearest the only remaining source of selenium in Stewart Lake.

August 2002

In wet or normal flow years, the Green River floods and enter Stewart Lake. During these high flow periods, ground water rises under Stewart Lake. The high ground water would inhibit the downward movement of selenium during the Green River flood. To investigate whether selenium leaching would be enhanced by flooding when the ground

water was deeper below the lake, berms were constructed around 2 experimental areas in the north end of Stewart Lake. These areas were flooded with water from Red Fleet Reservoir when the ground water was several feet below the lake bed to evaluate how well selenium was leached.

Pre-flood samples were collected during August at each of the sites that had been sampled in April because of the long period (4 months) since the previous samples had been collected. The results of the speciation and total selenium analyses of the samples from April and August (pre-flood) are shown on Figure 5. The total selenium analyses include those from both the UC Riverside (UCR) and USGS laboratories, although only total selenium analyses were run at the UCR laboratory on samples from sites 1, 10, and 15. No lime was applied to these sites and they can act as something of a control in evaluating changes at site 21. There were no samples collected from site 7 in August. However, of even more interest to this section of the report are the changes in concentrations of the various species and the total selenium shown on Figure 6. The changes in total soluble and total insoluble selenium are also shown on Figure 6, although these selenium measures are not explicitly included on Figure 5.

Soluble selenite decreased at sites 1 and 10, but increased at site 15 (Figure 6). All of the changes were small at 0.5 ppm or less. Insoluble selenite increased at sites 1 and 15, but decreased at site 10. The pattern of changes in soluble and insoluble selenite was different at each of the 3 sites. In other words, there was a decrease in soluble selenite at site 1 accompanied by an increase in insoluble selenite, while at site 10 there was a decrease in both fractions, and at site 15, there was an increase in both fractions. At either of these latter 2 sites, whatever happened to one fraction did not happen at the expense of the other. Whatever changes occurred were more complex than that.

The selenite changes in the 4 quadrants just add to the complexity of the sediment chemistry of the Stewart lake sediments. In the northeast quadrant there were decreases in both the soluble and insoluble fractions of selenite; the decrease in insoluble selenite in the northeast quadrant was the largest change in selenite in any of the samples on Figure 6. In the remaining 3 quadrants of site 21, there were increases in soluble selenite and decreases in insoluble selenite, although the magnitude of the changes varied. As was noted in the effects of lime application, there is a difference in the sediment chemistry of selenite in the northeast quadrant of site 21 from that of the other 3 quadrants.

Organic selenium is present in much lower concentrations than selenite, as is indicated by the difference in scale of their respective sets of graphs on figures 5 and 6. In addition, soluble organic selenium is present in much lower concentrations than the insoluble fraction as is very evident from the scale of the respective plots on Figure 5. This solubility distribution is consistent with the solubility of the organic component of the organoselenium molecule. Organic compounds generally tend to be somewhat limited in solubility in water although this is not universally true.

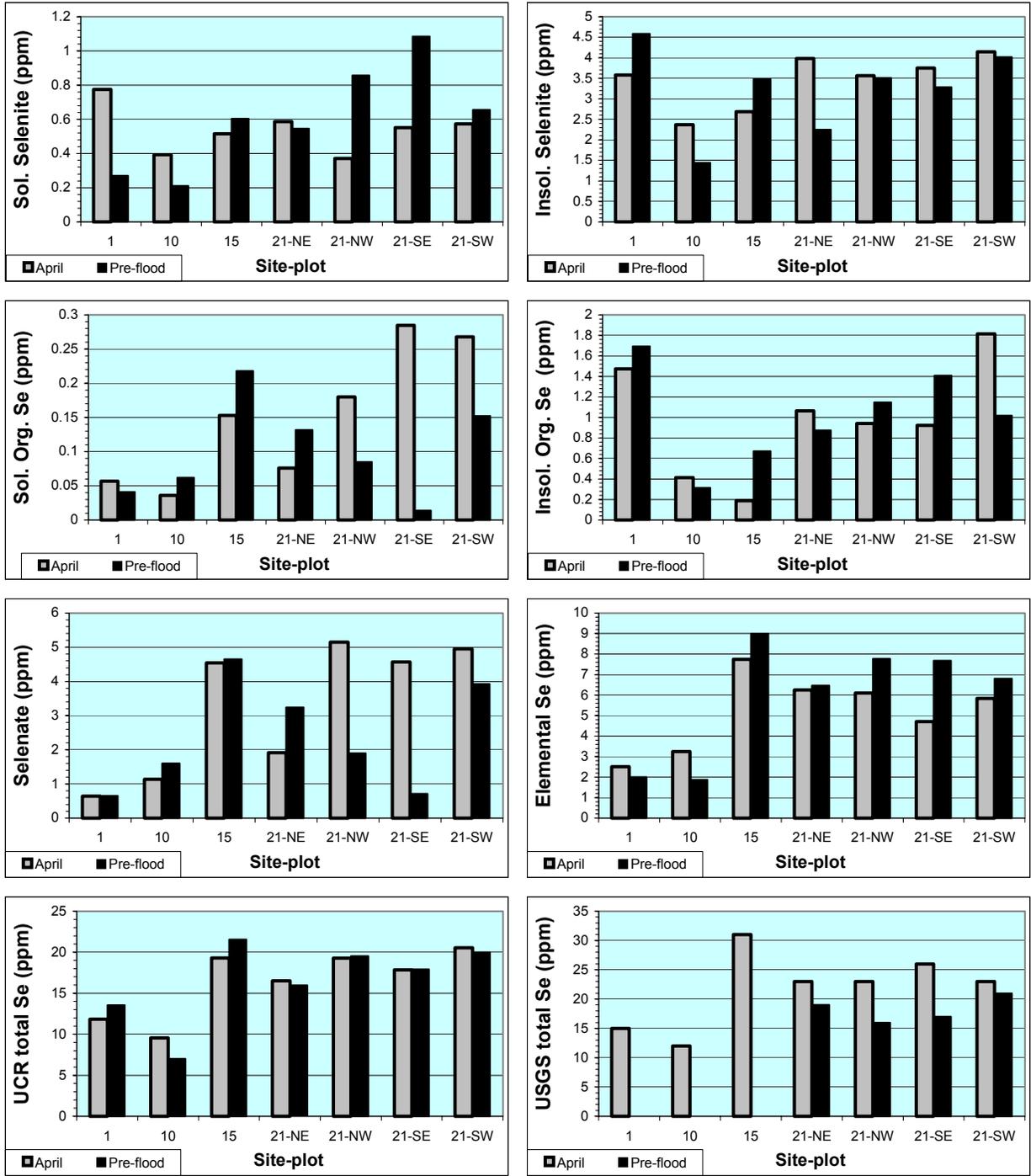


Figure 5: Concentrations of total selenium and its species in sediment samples collected from Stewart Lake in April and August 2002

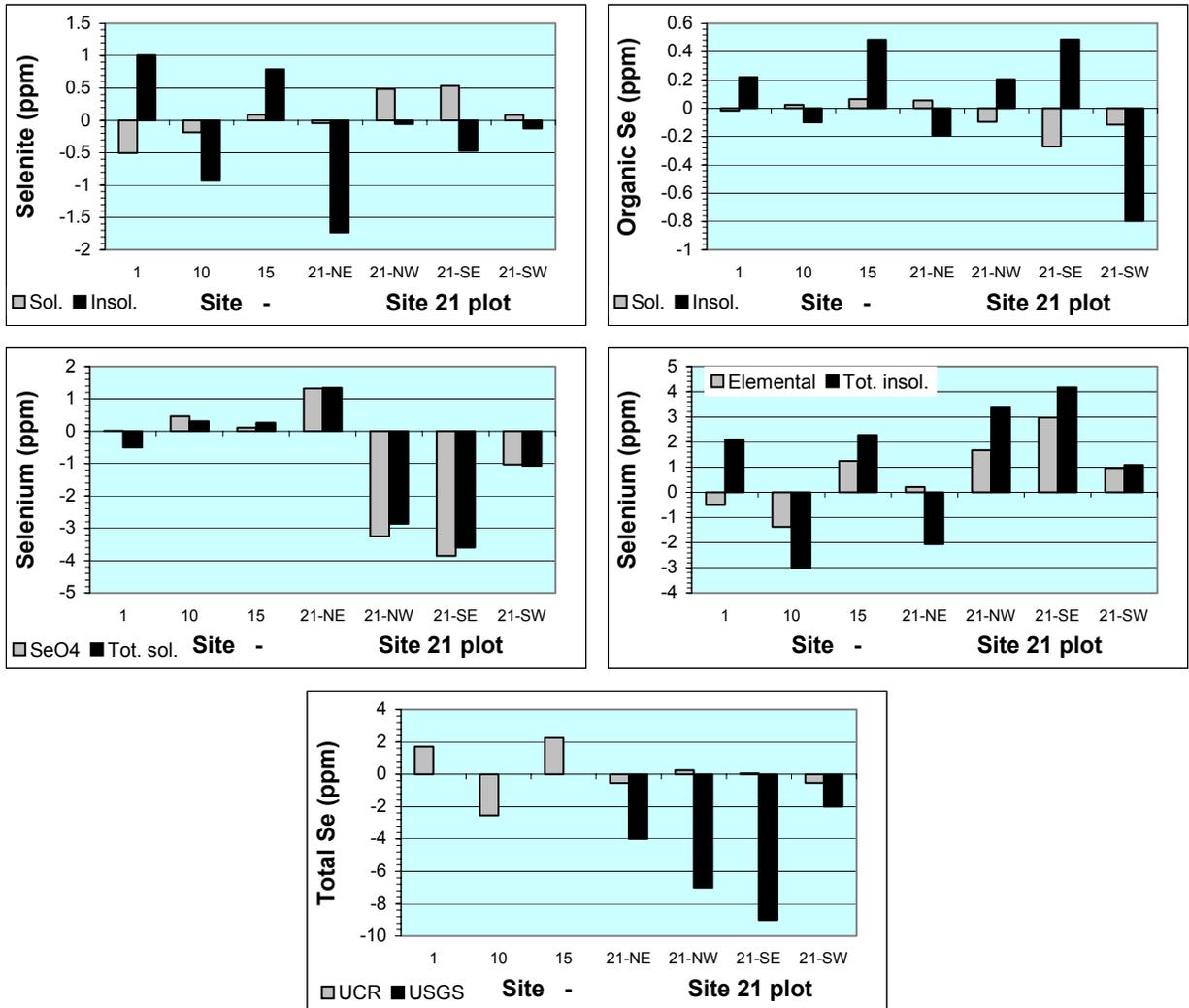


Figure 6: Changes in the concentrations of total selenium and its species in samples collected from Stewart Lake in April and August 2002

Organic selenium changes also varied from site to site and quadrant to quadrant. There was an increase in the insoluble fraction at site 1, coupled with a decrease in the soluble fraction. The opposite was true at site 10, while both fractions increased at site 15. There was also variety in the changes at site 21. There was an increase in the soluble fraction of the organic selenium in the northeast quadrant, coupled with a decrease in the insoluble fraction. The opposite was true, *i.e.* decreases in soluble and increases in insoluble organic selenium, in the northwest and southeast quadrants, while both fractions decreased in the southwest quadrant. In all cases the change in the insoluble fraction was much larger than that in the soluble fraction, presumably reflecting the magnitude of their respective initial concentrations.

Selenate (SeO_4) is generally the largest component of the soluble selenium. The 2 variables are plotted together on Figure 6. For the most part the changes are consistent, with the change in total soluble selenium generally somewhat smaller than

the similar change in selenate (Figure 6). The one big exception to this generalization is at site 1, where there is a small increase in selenate, but a very large decrease in soluble selenium. The decrease in soluble selenium appears to reflect the 0.5 ppm decrease in soluble selenite, which is also shown on Figure 6. Overall there are small increases in soluble selenium at sites 10 and 15 and the northeast quadrant of site 21. Alternatively, there are relatively large decreases (2-3 ppm) in soluble selenium in the northwest and southeast quadrants of site 21 and a smaller (1 ppm) decrease in the southwest quadrant. Overall there appeared to be a net decrease in soluble selenium in Stewart Lake between April and August despite the fact that the lake had been dry throughout that period. It is noteworthy that the selenate concentration decreased in site 21, although the reason for the decrease cannot be determined. This result would seem to lessen the effectiveness of flooding site 21 over what it had been during April.

Total insoluble selenium changes track with the changes in elemental selenium almost as well as those of soluble selenium with the changes in selenate (Figure 6). The 2 sites at which the changes in the 2 variables differ include site 1 and the northeast quadrant of site 21. At site 1, elemental selenium decreased by less than 1 ppm, while the total insoluble selenium increased by more than 2 ppm. In the northeast quadrant of site 21, elemental selenium increased by a fraction of a ppm, while the total insoluble selenium decreased by about 2 ppm. Both elemental and total insoluble selenium decreased at site 10, with the insoluble selenium decreasing by about twice that of the elemental selenium. Both variables increased in the remaining 3 quadrants of site 21. The maximum increase in insoluble selenium was over 4 ppm in the southeast quadrant, coinciding with a 3 ppm increase in elemental selenium.

Total selenium changes at sites 1, 10, and 15 are based on UCR data only (Figure 6). There is a decrease of more than 2 ppm at site 10 and decreases of about the same size at sites 1 and 15. Alternatively there is essentially no change in the UCR total selenium concentrations within site 21. However, there are relatively large decreases in the USGS determined total selenium in all 4 quadrants. The decreases range from about 2 ppm in the southwest quadrant to as much as 9 ppm in the southeast quadrant. Differences in changes in the 2 measures of total selenium have been noted in previous reports on sediment selenium (see, for example, Yahnke, 2002).

Flooding Effects on Sediment Selenium

The flood experiment was conducted during the period of August 26 through September 2, 2002. The experiment was conducted at 2 sites in the northern part of Stewart Lake (Figure 7). Day-by-day activities, including sample collection and handling, are described in Appendix A beginning on page A-7. All samples were composited to better represent site conditions. Surface samples (0-6 inches) consisted of composites of 10 samples collected randomly over each site; subsurface samples (6-36 inches in 6-inch increments) consisted of composites of 3 samples each. Post-flood samples were collected on September 13, 2002, after the plots had dried enough to provide access. Pre-flood speciation samples consisted of surface samples from the flood plot and each

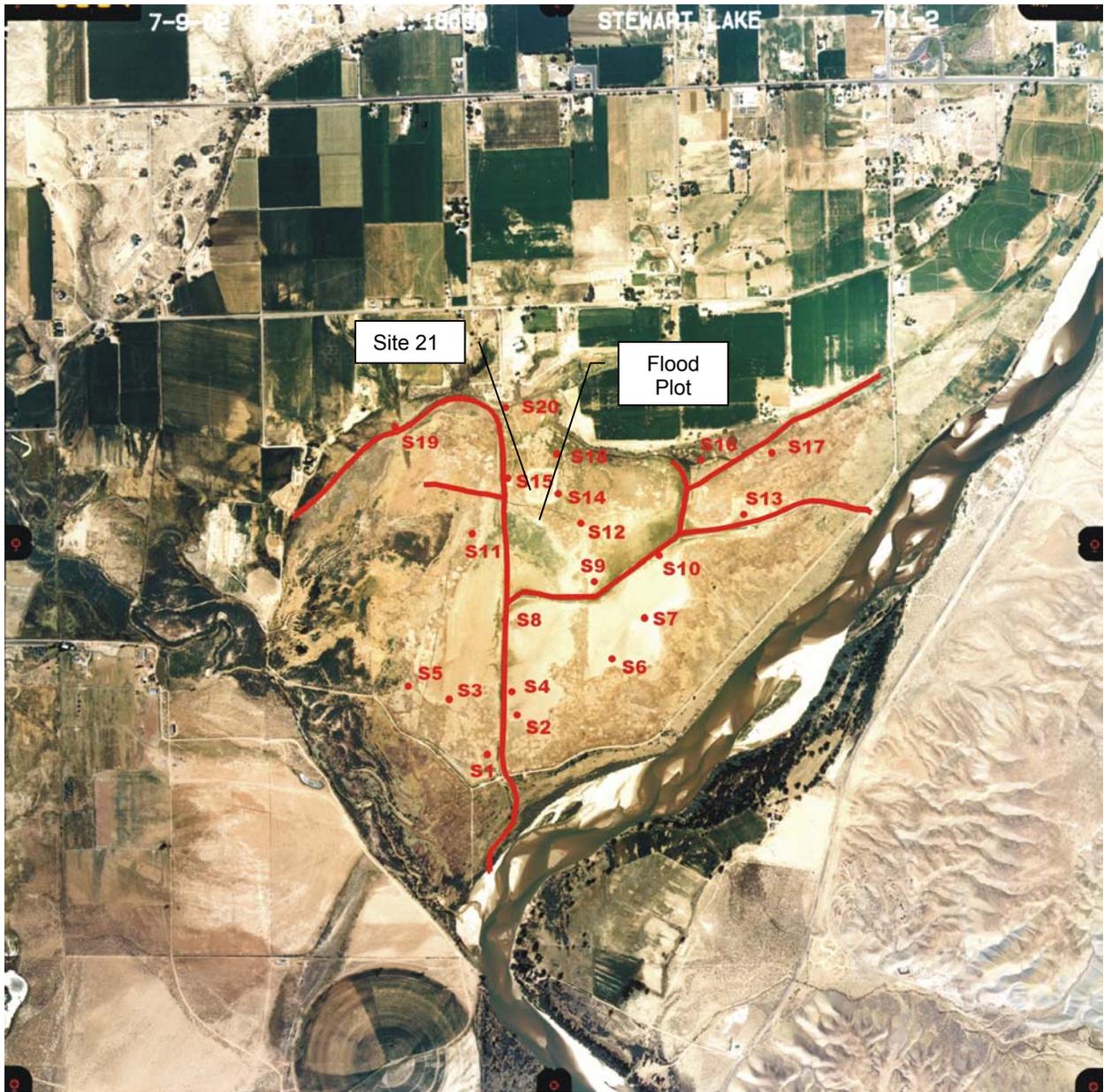


Figure 7: Location of the 2002 experimental flood plots at Stewart Lake

of the 4 quadrants of site 21 and sediment profiles to a depth of 36 inches from the flood plot and 1 quadrant of site 21 for submittal to UCR. Post-flood speciation samples consisted of 36-inch profiles from the flood plot and each of the 4 quadrants of site 21. Identical sets of samples were collected for total selenium analysis at the USGS laboratory in Denver, Colorado. This section of the report will present a comparison of the pre-flood samples with the post-flood samples to note any changes. Comparisons of pre- and post-flood selenium for each of the site 21 quadrants will be made on the basis of surface samples and the profile from the southwest quadrant only.

Surface Sediment Selenium

Concentrations of selenium species in surface sediments of the USGS flood plot (for this report site FP) and the 4 quadrants of site 21 are shown on Figure 8. Changes in the concentrations of the selenium species are shown on Figure 9. Figure 8 will better show the variability in concentrations among sites, while Figure 9 will show the relative magnitude of changes. The pre-flood data shown on Figure 8 were presented in the previous section. These will not be described further, but comparisons to the flood plot will be made.

There was generally a higher concentration of soluble selenite at site 21 than at site FP, but insoluble selenite concentrations were similar at the 2 sites (Figure 8). Site FP is located just to the south of site 21 (Figure 7), and similarities to the south quadrants of site 21 would be expected if there is variation among the site 21 quadrants. Site FP has a much higher concentration of soluble organic selenium than site 21, but the concentration of insoluble organic selenium is about the same as that of the northeast quadrant and lower than that of the other 3 quadrants of site 21. Site FP is also higher than any of the site 21 quadrants in selenate by nearly 2 ppm. Elemental selenium was virtually absent from site FP prior to the flood and obviously much lower than any of the quadrants of site 21 (Figure 8).

Both the soluble and insoluble fractions of selenite at site FP showed a very small decrease during the flood (~ 0.1 ppm - Figure 9). There was an increase in soluble selenite in all of the quadrants of site 21. However, insoluble selenite showed a variable response to the flood in site 21. In the northeast quadrant there was a relatively large increase (> 1 ppm) in insoluble selenite. Insoluble selenite decreased in each of the other 3 quadrants of site 21, but the magnitude of the decrease varied considerably. In the southeast quadrant the decrease in insoluble selenite was only slightly greater than that at site FP. The decrease in insoluble selenite in the southwest quadrant was about double that in the southeast quadrant (~ 0.2 ppm), while the decrease in the northwest quadrant was the largest of all at 0.7 ppm. Once again, as was the case with the effects of lime application, the sediment selenite behaved differently in the northeast quadrant of site 21 from that of the other quadrants. Furthermore, the changes in selenite were independent of the initial concentration. In other words, whatever selenite-related

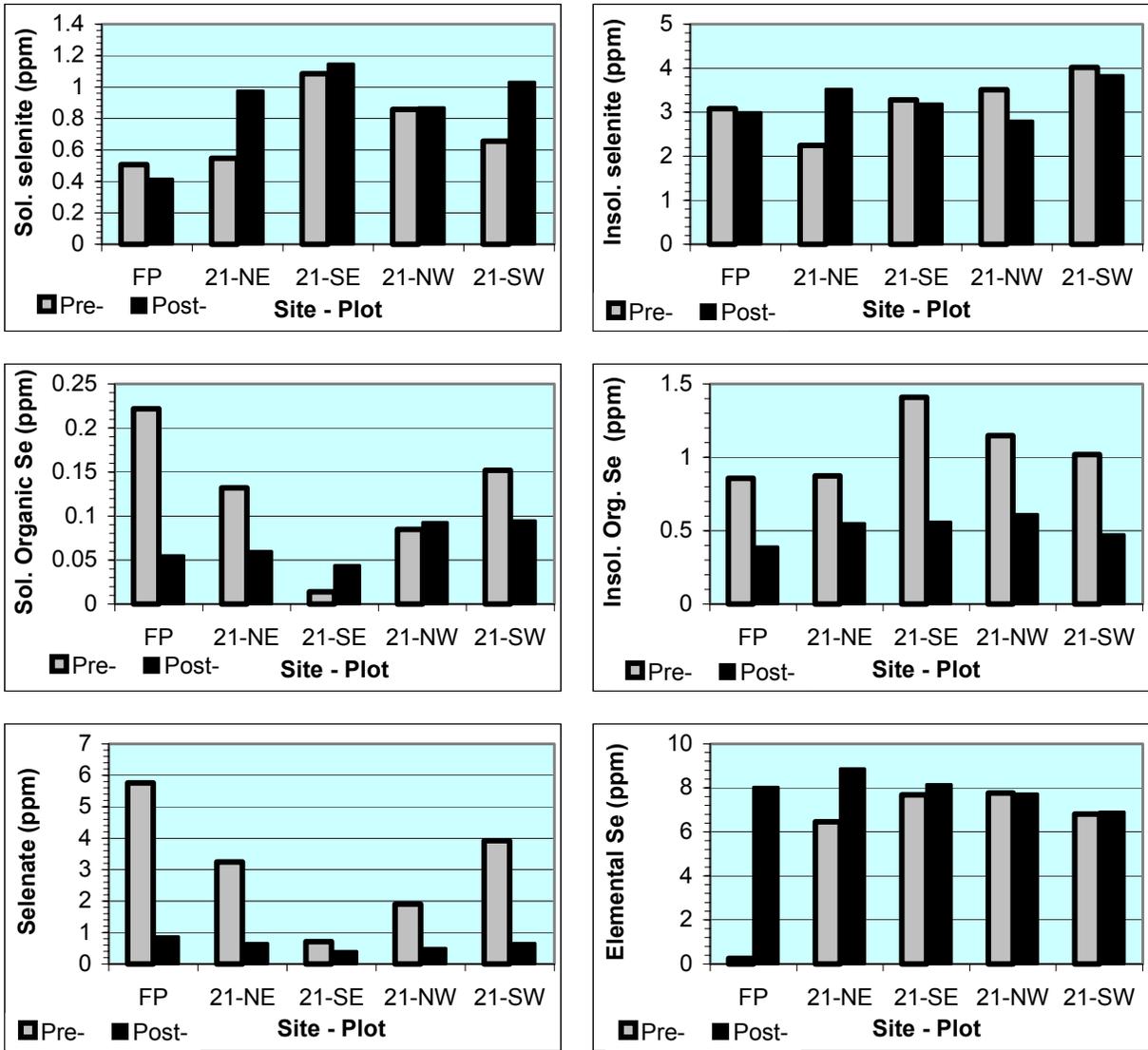


Figure 8: Concentrations of selected selenium species before and after the flood experiment in the USGS flood plot and Reclamation's experimental site 21

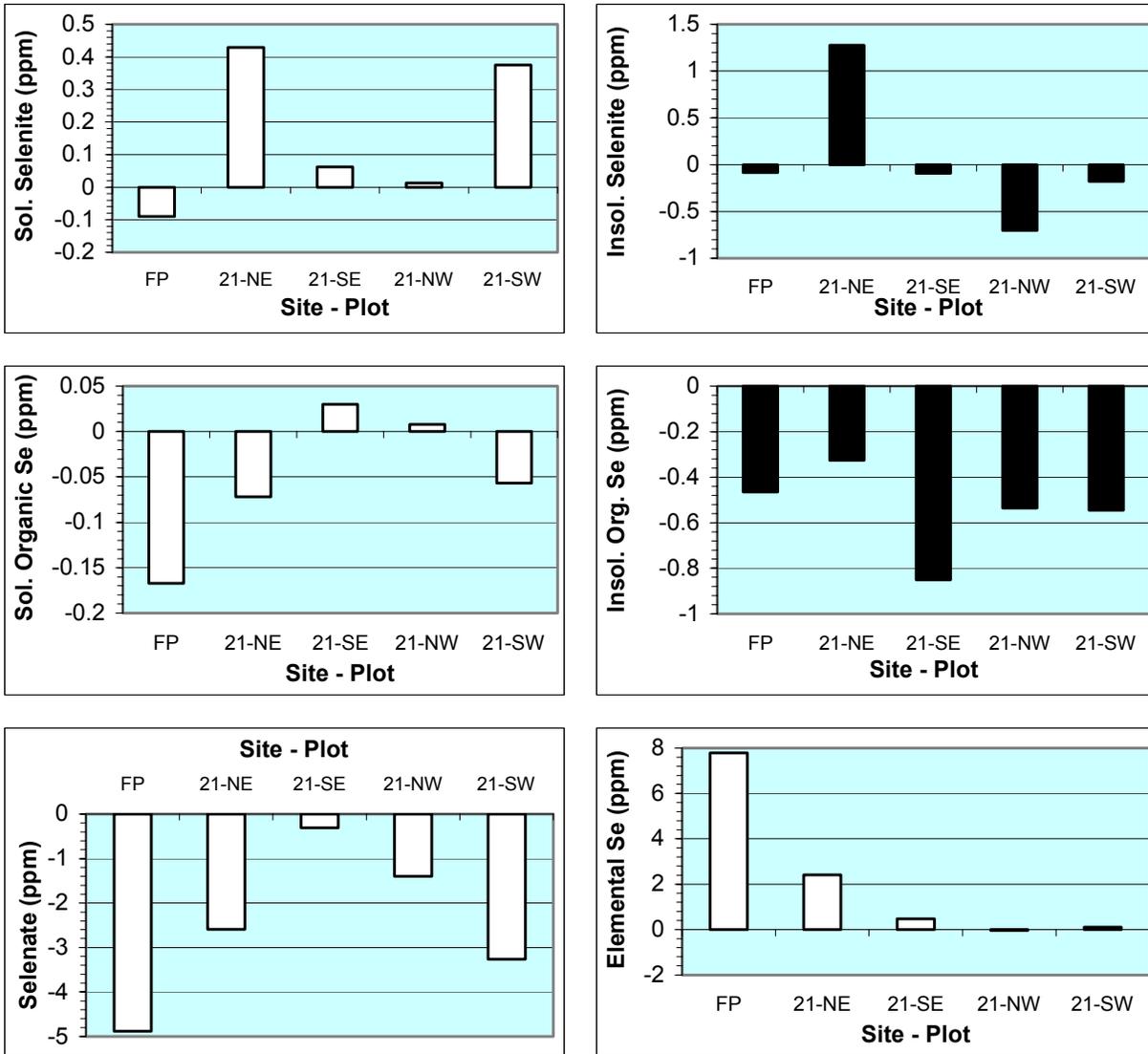


Figure 9: Changes in concentrations of various selenium species during the 2002 flood experiments at Stewart Lake

reactions occurred in the sediments during the flood, they were not concentration-dependent.

Soluble organic selenium tends to be present in the lowest concentrations of any of the selenium species for which there are analyses, with maximum concentrations on the order of 0.2 ppm (Figure 8). Although soluble organic selenium showed some variability among the various sample sources, insoluble organic selenium decreased in the sediments of both sites and those in all 4 quadrants of site 21 (Figure 9). The decreases in insoluble organic selenium ranged from about 0.4 ppm to a little over 0.8 ppm. The smallest decrease occurred in the northeast quadrant of site 21, followed closely by that at site FP. The decreases in insoluble organic selenium in the northwest and southwest quadrants of site 21 were about the same size, while the largest decrease was in the southeast quadrant (Figure 9). There were decreases in soluble

organic selenium in the sediments from site FP and the northeast and southwest quadrants of site 21. Both of the decreases in the site 21 sediments were somewhat smaller than that at site FP, *i.e.* < 0.1 ppm vs. ~ 0.2 ppm. The increases in soluble organic selenium in the southeast and northwest quadrants of site 21 were quite small and amounted to 0.03 and 0.008 ppm respectively. Because of their low concentrations in the Stewart Lake sediments, changes in organic selenium species probably contribute little to the overall selenium response to any experiments related to selenium removal.

Selenate is the most soluble of the selenium species. For purposes of this report, all selenate is considered soluble, although small amounts may be adsorbed under the right conditions. Selenate decreased in all of the sources of samples (Figure 9). The pre- and post-flood concentrations of total soluble selenium are shown on Figure 10. The decreases in selenate are essentially the same as those of the total soluble selenium. This result supports the hypothesis behind the drying and flooding effort, which was predicated on the oxidation and flushing of selenate from the sediments. The flood experiments were designed to flush the selenate to the deeper ground water. The data on Figure 8 indicate that about 5 ppm of selenate (and total soluble selenium as well – Figure 10) were flushed from the surface sediments of site FP. The maximum decrease in selenate in the site 21 sediments was in the southwest quadrant, where the decrease was just over 3 ppm. The decreases in selenate in the remaining 3 quadrants of site 21 amounted to 2.6, 1.4, and 0.3 ppm in the northeast, northwest, and southeast

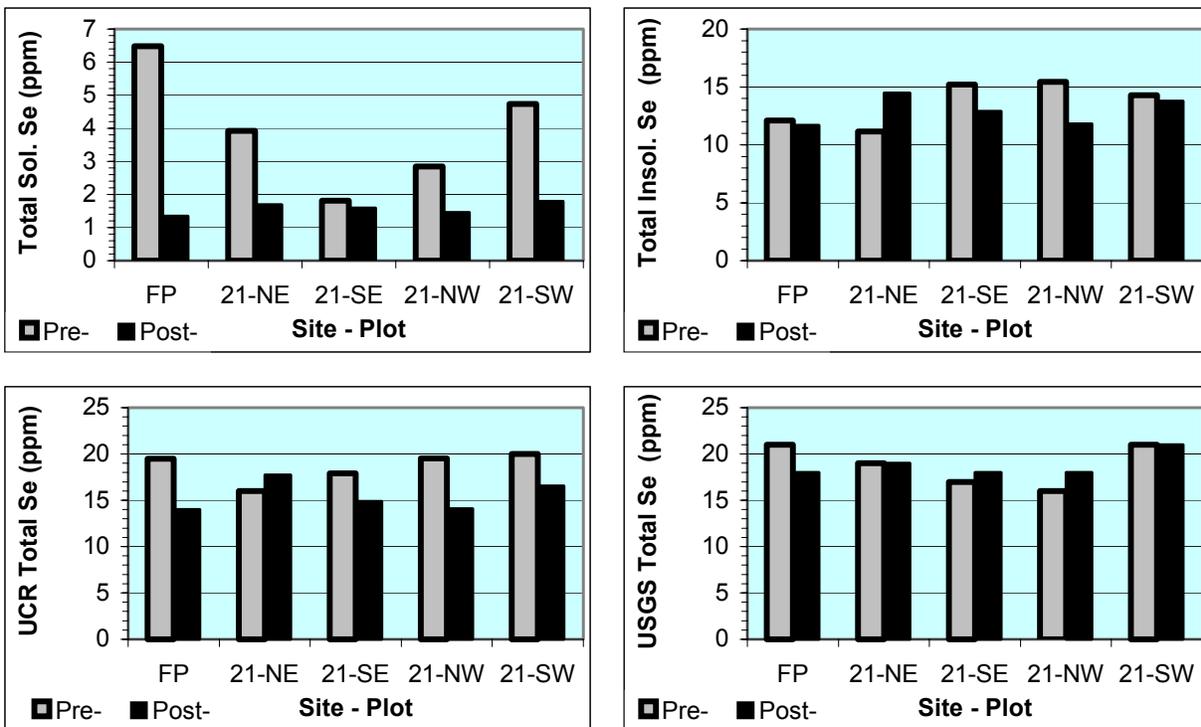


Figure 10: Pre- and post-flood concentrations of total selenium and its soluble and insoluble fractions in the flood plot and site 21 sediments in 2002

quadrants, respectively. The decreases in total soluble selenium were somewhat smaller than those of selenate in all 4 quadrants (figures 8 and 10), reflecting the above described increases in soluble selenite (Figure 9).

Elemental selenium is the predominant insoluble species at each of the sites. The total insoluble selenium concentrations in each of the source sediments are shown on Figure 10. Unlike the changes in selenate and soluble selenium, the changes in elemental selenium and insoluble selenium do not track at all (figures 8 and 10). At site FP there is a large (8 ppm) increase in elemental selenium coupled with a small (0.4 ppm) decrease in insoluble selenium. Obviously the change in total insoluble selenium is not being controlled by elemental selenium at the site. Both the elemental and total insoluble selenium increased in the northeast quadrant of site 21 with the increase in total soluble selenium only slightly greater than that of the elemental selenium. However, the total insoluble selenium decreased in the other 3 quadrants. There was a slight increase (~ 0.5 ppm) in elemental selenium in the southeast quadrant (figures 8 and 9), while the changes in elemental selenium in the other 2 quadrants were negligible ($< \pm 0.1$ ppm) and probably reflect random analytical error, rather than any actual change.

There was a large decrease in OM-Se at site FP (Figure 11). The decrease in OM-Se at FP is almost as large as the increase in elemental selenium and accounts for the lack of a net change in insoluble selenium despite the large increase in elemental selenium. Smaller decreases in OM-Se were noted at site 21. Changes in OM-Se were negligible in the northeast and southwest quadrants, while there were decreases of approximately 2 ppm in the southeast and northwest quadrants (Figure 11B).

The remaining plots on Figure 10 are of the concentrations of 2 measures of total selenium. The pre- and post flood concentrations generally show that the total selenium concentrations as determined by the USGS laboratory are slightly higher than those from the UCR laboratory. As has been discussed in previous reports, the USGS laboratory uses a somewhat more rigorous digestion and higher concentrations of selenium are not unexpected.

The changes in the 2 measures of total selenium are somewhat different (Figure 12). At site FP there is a decrease of nearly 6 ppm in total selenium as measured by the UCR laboratory, while the decrease in total selenium as determined in the USGS laboratory is only about 3 ppm. The differences in

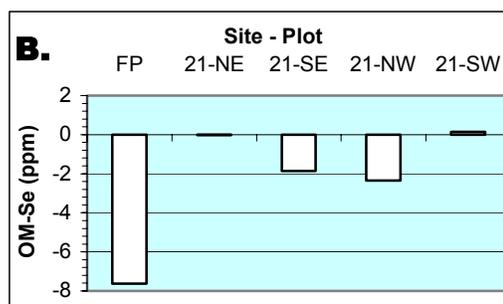
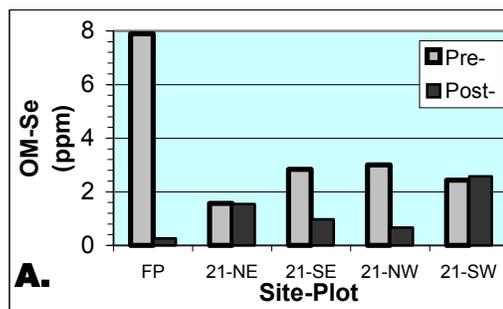


Figure 11: Organic-matter associated selenium concentrations and changes in the flood plot and site 21

the results from site 21 are even more dramatic. The largest difference in total selenium is in the result from the northwest quadrant of site 21, where there was a decrease of about the same size as at site FP based on the UCR data, but an increase of about 2 ppm based on the USGS data (Figure 12). Overall there is only an increase in total selenium in the northeast quadrant of site 21, but decreases in the other 3 quadrants based on the UCR data. Alternatively, based on the USGS results, there was an increase in 2 quadrants and no change in the other 2 quadrants. The net change of total selenium in the 2 sites would be different based on the 2 data sets. Based on the UCR data, there was a net decrease in surface sediment total selenium during the flood, while on the basis of the USGS data there was no change.

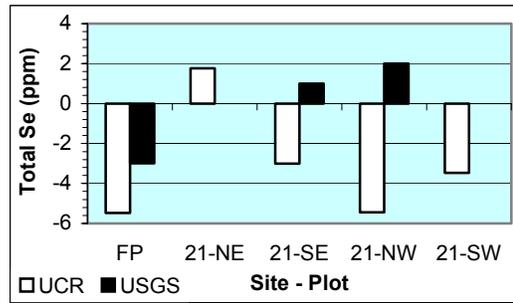


Figure 12: Changes in the concentrations of 2 measures of total selenium in the flood plot and site 21

Sediment Selenium Profiles

Post-flood total selenium profiles were sampled and submitted to the USGS from all 4 quadrants of site 21 and site FP (Figure 13). Sediment profile samples for selenium speciation were collected only from the southwest quadrant of site 21 and from site FP. These latter 2 sets of samples will constitute the basis for the pre- and post-flood comparison of selenium. Since no pre-flood profiles from site 21 for total selenium analysis were submitted to the USGS laboratory, no comparison can be made against the post-flood profiles. However, the post-flood profiles can be compared to each other to look at variation among the 4 quadrants in site 21.

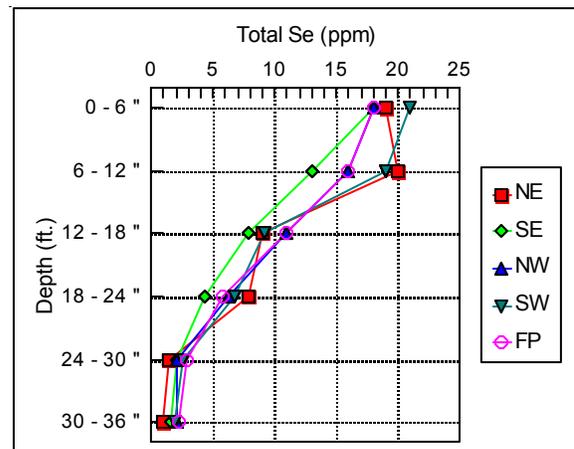


Figure 13: Post-flood total selenium profiles at sites 21 and FP

Figure 13 shows total selenium profiles from the 4 quadrants of site 21 and from site FP. There are differences in the total selenium concentrations at the surface among the quadrants. There is an increase in total selenium the 6-12 inch layer of the northeast quadrant of site 21, but decreases in the other quadrants and site FP. There are decreases below that level in all 5 profiles. For 0 to 18 inches, the total selenium profiles from site FP and the northwest quadrant of site 12 are completely overlain. Below 12 inches all but the profile from the southeast quadrant are nearly overlain. Below 24 inches there is little difference in total selenium among the 5 profiles. The important point is that the profile from the southwest

quadrant fits well within the others and appears representative of the site. The profile from site FP also fits well within the spread of the other quadrants of site 21.

Figure 14 shows pre- and post-flood profiles of the concentrations of selenate and selenite at sites FP and the southwest quadrant of site 21 (from hereon, simply site 21). Changes in the concentrations of the various species are shown on Figure 15. The surface samples at these sites were described in the preceding section.

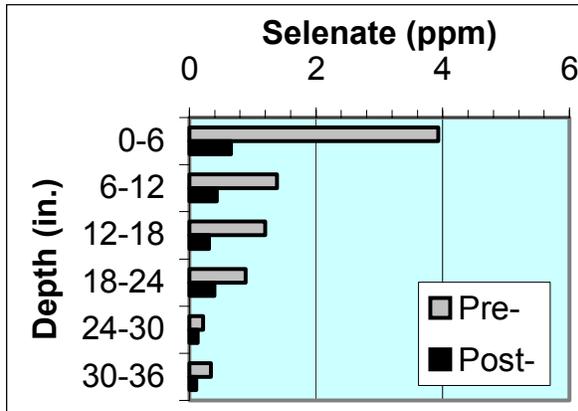
At both sites FP and 21, there was a decrease in selenate in all layers, but the greatest decrease occurred at the surface, where the pre-flood concentration was the highest (figures 14 and 15). At both sites the post-flood selenate concentration was reduced to less than 1 ppm in all of the layers (Figure 14). Since selenate is the most soluble of the selenium species, reduction in selenate is to be expected if leaching were to occur. As was noted in the discussion of the surface samples, selenate constituted the majority of the total soluble selenium. The reduction in selenate accounted for the majority of the reduction in total soluble selenium and in some cases exceeded the loss in total soluble selenium (Figure 16). The remarkable thing about the selenate results is that the profiles showing the changes in the 2 sites are very much alike.

Soluble selenite concentrations were much lower at the 2 sites than the selenate concentrations (Figure 14). The pre-flood soluble selenite concentrations in both sets of profiles ranged from about 0.1 ppm at the base of the profile to about 0.5 ppm at the surface. Except at the surface, the changes in soluble selenite within the respective profiles were also remarkably similar (Figure 15). At both sites there was an increase in soluble selenite in the 6-12 inch layer, but little change in the remaining layers. The increase in soluble selenite in the 6-12 inch layer was about 5 times as great at site FP as that at site 21, the latter of which should probably be included within the category of little change, *i.e.* 0.036 ppm.

The insoluble selenite profiles also show a great deal of similarity in terms of both their concentrations and changes (figures 14 and 15). Both sites show a small decrease in insoluble selenite at the surface, a comparatively large increase (> 1 ppm) in the 6-12 inch layer, followed by a small decrease in the 12-18 inch layer. There is a bit of a difference in the 18-24 inch layer, where there was little change at site 21, but a decrease at site FP (Figure 15). Both sites showed an increase in the 24-30 inch layer, but the increase was much larger at site 21. Finally, at the base of the profiles, there was a small decrease at site 21, but no change at site FP. With the exception of the 18-24 inch layer, the results related to insoluble selenite are similar with minor differences where changes were relatively small (Figure 15).

Organic selenium represents the last of the soluble selenium species. Concentrations of soluble and insoluble organic selenium at sites FP and 21 are shown on Figure 17. The changes in their concentrations during the flood experiment at the 2 sites are also shown on Figure 17 at its bottom.

Site 21



Flood Plot

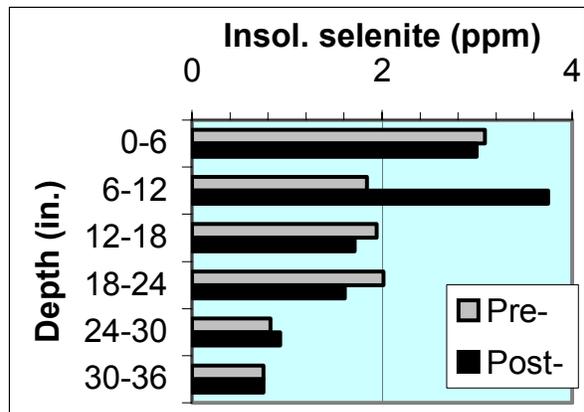
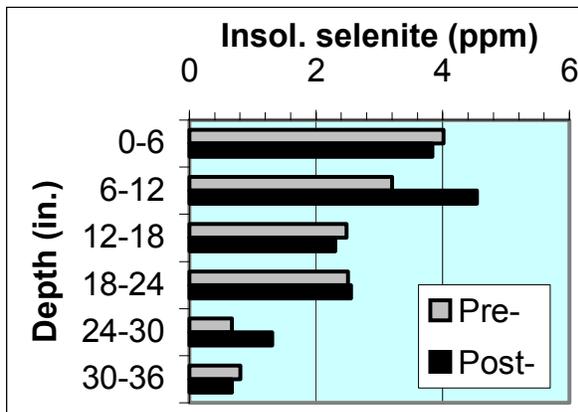
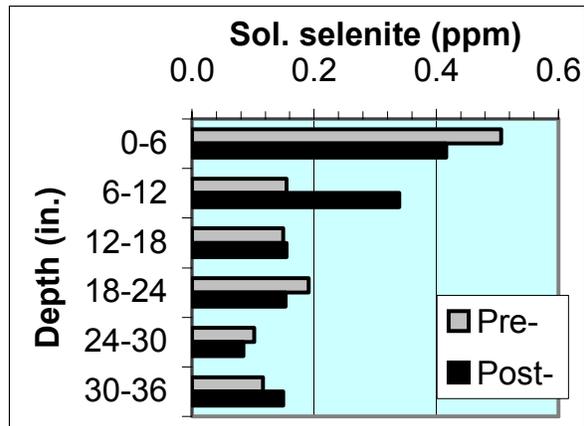
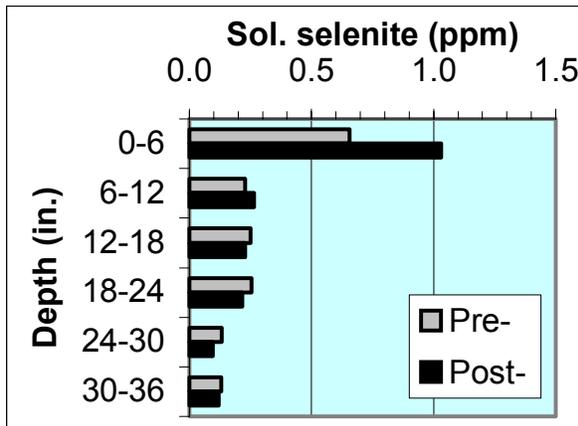
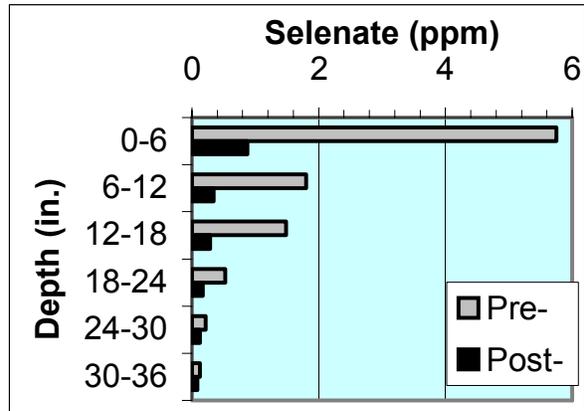
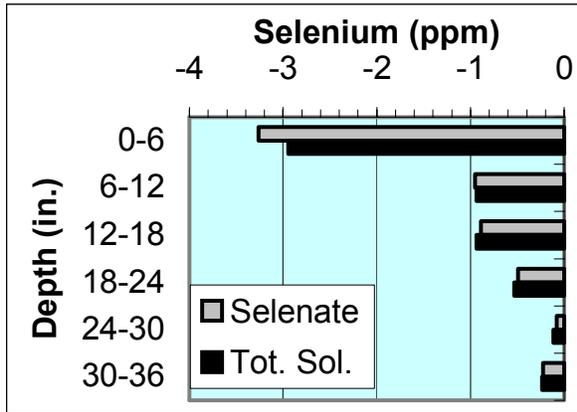


Figure 14: Pre- and Post-flood 2002 selenate and selenite concentrations at 2 sites in Stewart Lake

Site 21



Flood Plot

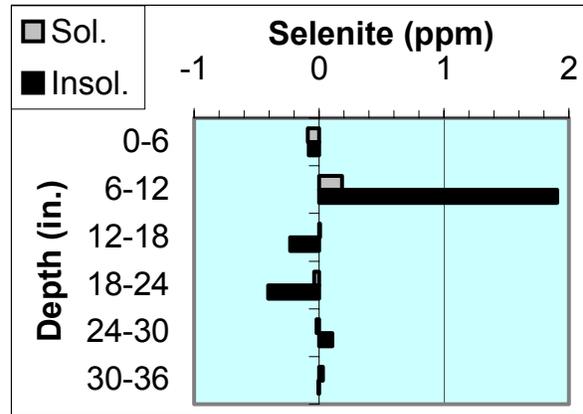
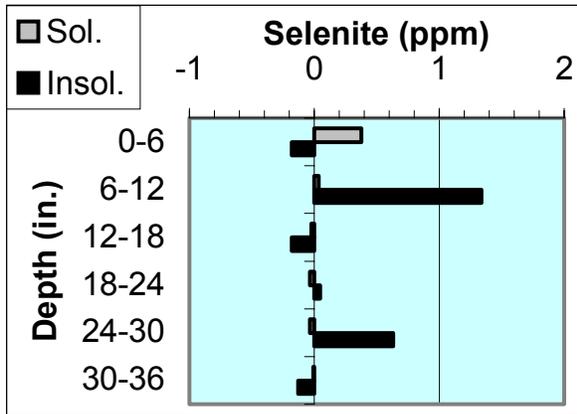
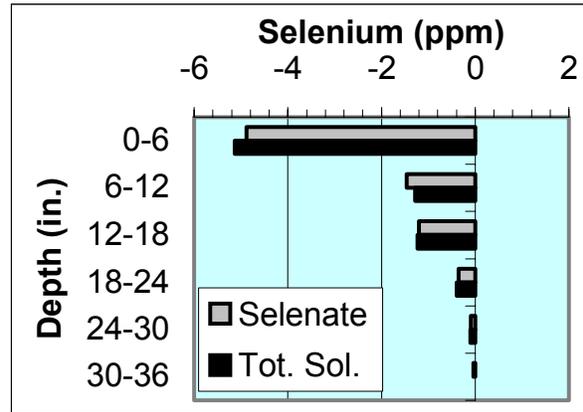


Figure 15: Changes in selenate, total soluble selenium, and selenite in profiles at 2 sites at Stewart Lake during the 2002 flood experiments

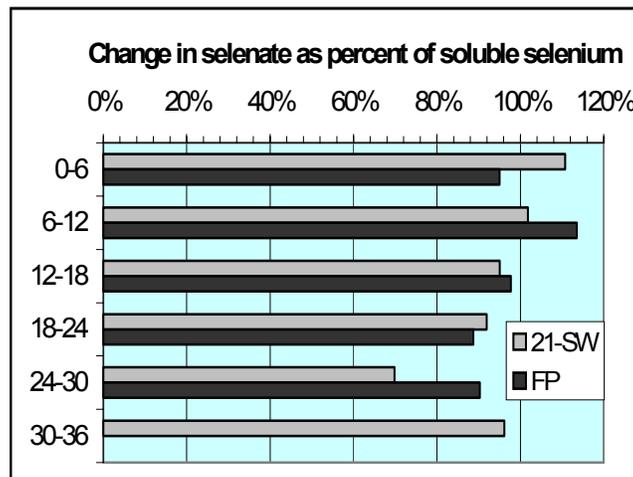


Figure 16: Percent of soluble selenium reduction due to selenate

Pre-flood soluble organic selenium concentrations are generally less than 0.2 ppm at sites FP and 21 (Figure 17). Only the surface soluble organic selenium concentrations at the 2 sites exceed 0.1 ppm. Because of the low concentrations, changes would not be expected to greatly influence changes in total soluble selenium. There were decreases in the concentrations of soluble organic selenium in the upper parts of the profiles at both sites, *i.e.* in the layers between the surface and 24 inches. However, because the changes are so small, they are difficult to see at the scale of Figure 17. There were small increases in soluble organic selenium in the deepest layers of the profile at site FP, but no change in the same layers at site 21.

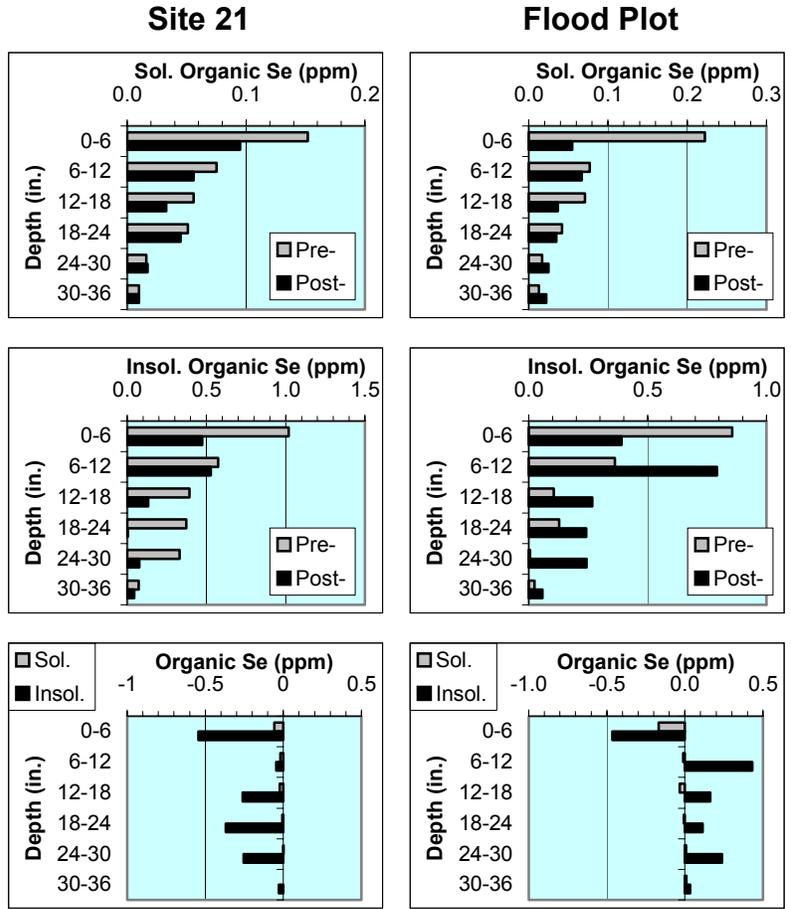


Figure 17: Pre- and post-flood concentrations and changes in organic selenium

Although pre-flood insoluble organic selenium concentrations were much higher than those of soluble organic selenium, they are still generally less than 1 ppm (Figure 17). Where changes in selenate and selenite during the flood experiment were in general agreement between sites FP and 21, the changes in insoluble organic selenium were quite different. Although there was a decrease of about 0.5 ppm of insoluble organic selenium in the surface layer of each site, responses below the surface were the exact opposite at the 2 sites (Figure 17). At site 21, insoluble organic selenium decreased in all layers below the surface. Alternatively at site FP insoluble organic selenium increased in all layers below the surface. In all cases the changes in insoluble organic selenium were much greater than those in the soluble fraction. This difference in the response in the 2 fractions is not what would be expected, but probably reflects the higher base concentration of the insoluble fraction. Based on the available data, the difference in the response of insoluble organic selenium at the 2 sites cannot be explained. However, as will be discussed later, because the organic selenium concentrations are relatively low, the differences may be due to random variation.

Figure 18 shows the pre- and post-flood concentrations of OM-Se at sites FP and 21. As was noted above, there was a decrease of nearly 8 ppm in the surface sediments at site FP, but there was an increase of nearly 7 ppm in the 6-12 inch layer at site FP (Figure 14). There were then additional decreases of 2-3 ppm in the next 2 layers at site FP, and smaller increases near the base of the profile. The response at site 21 was somewhat different from that at site FP. There was a small increase in OM-Se at the surface at site 21, but there were decreases in all of the layers below the surface.

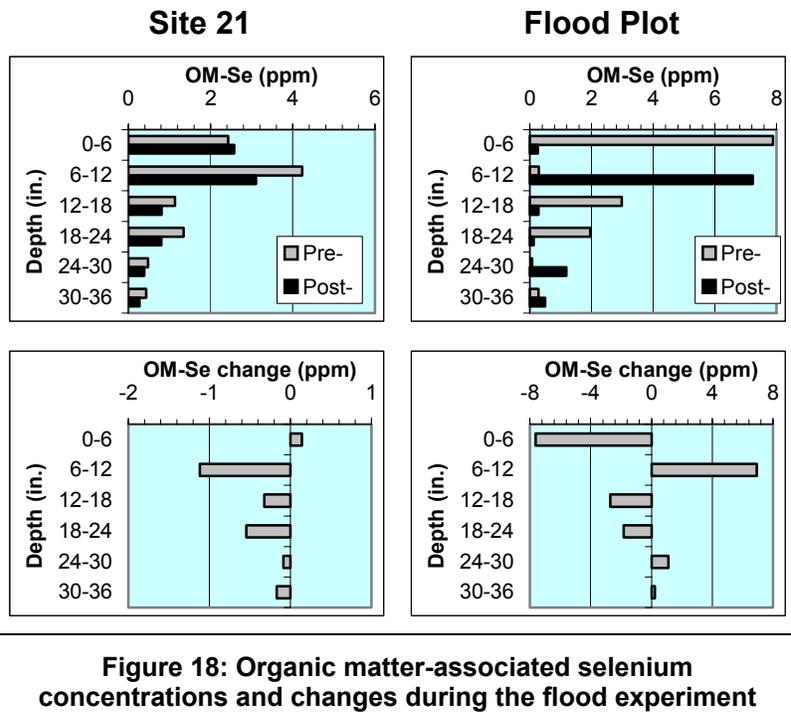
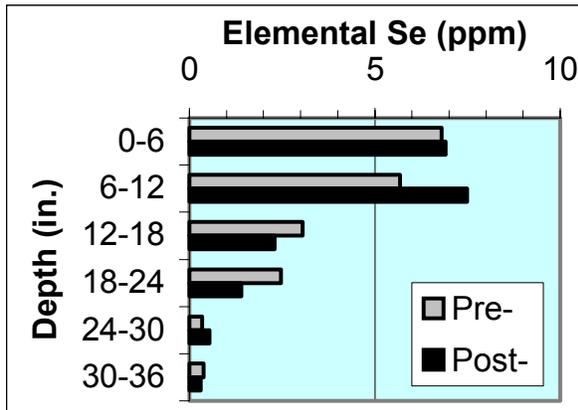


Figure 18: Organic matter-associated selenium concentrations and changes during the flood experiment

OM-Se is a difficult species to deal with in that its actual composition is unknown. OM-Se represents a significant component of the total selenium in certain samples. The OM-Se fraction is not water soluble because it is determined from the nonfiltered aliquot of the extract. Alternatively, when OM-Se appears in high concentrations in the current data, it tends to be associated with a very large change. For example, there were nearly 8 ppm of OM-Se in the pre-flood surface sediments of site FP, but it was not there in the post-flood sample (Figure 18). Alternatively, there was little in the pre-flood 6-12 inch layer of site FP, but there was over 7 ppm in the post-flood sample. These differences translate to changes of 7-8 ppm of OM-Se during the flood experiment. Since the OM-Se is not water soluble, it would not be expected to be leached from the surface, although if it were, it could be redeposited slightly deeper. Could the weight of the water be enough to compress the near-surface sediments enough that the change in layer thickness was great enough to shift the OM-Se? If that were the case, the OM-Se would be expected to rise in the profile, rather than appear to sink deeper. Without knowing the composition of the OM-Se, it is virtually impossible to hypothesize a cause for its changes, but it does raise the question as to whether the changes are real or not.

Elemental selenium is the last of the species that was present in comparatively significant amounts in the Stewart Lake sediments during the flooding experiment. Pre- and post-flood concentrations of elemental selenium are shown on Figure 19. As was noted above, there was little elemental selenium present in the surface sediments of site FP, but there was about 7 ppm present in the surface sediments of site 21. Each of the sites had about 6 ppm of elemental selenium in the 6-12 inch layer prior to the flood. The responses of elemental selenium in the layers below the surface of the 2 sites

Site 21



Flood Plot

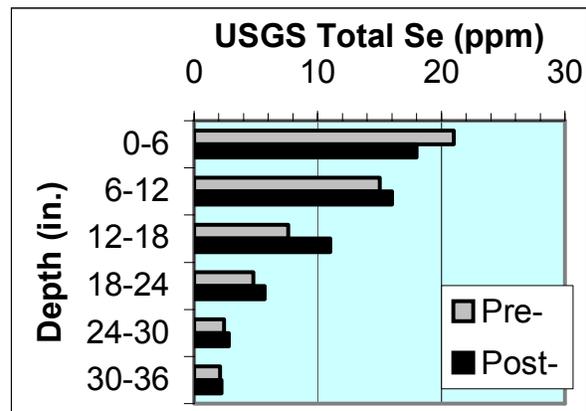
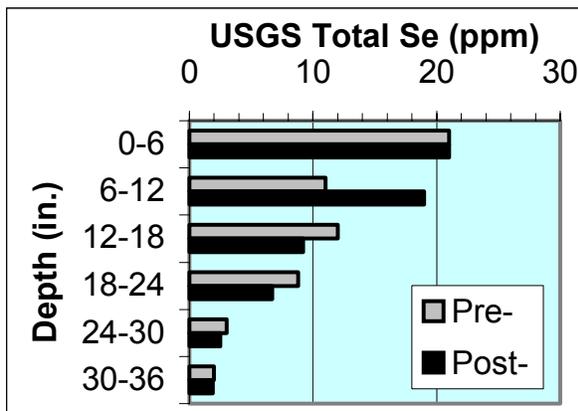
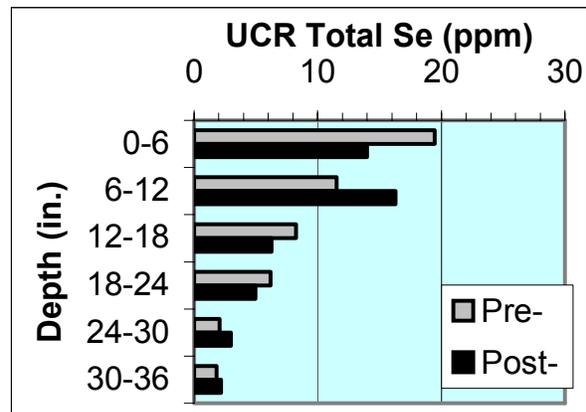
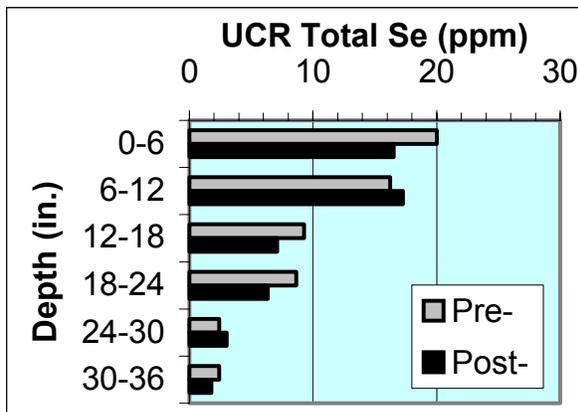
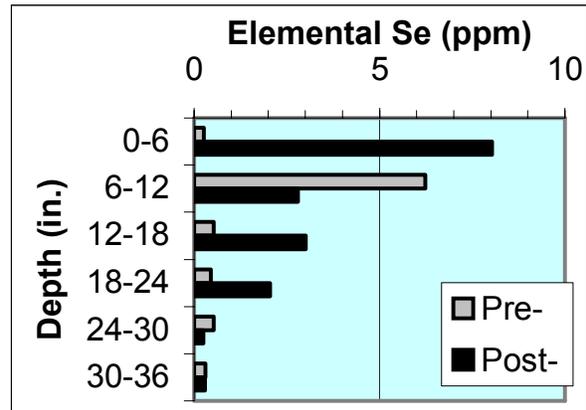
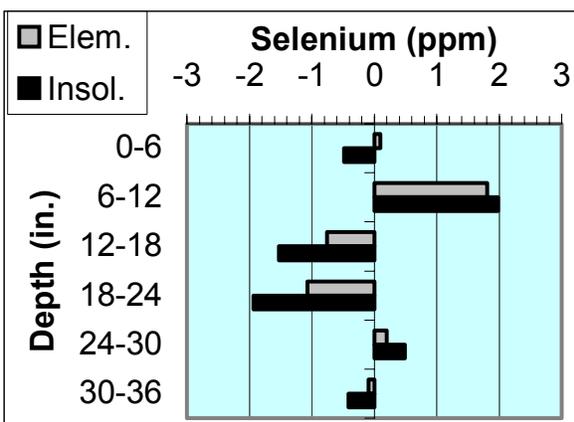


Figure 19: Pre- and post-flood concentrations of elemental and 2 measures of total selenium at 2 sites at Stewart Lake during the 2002 flooding experiment

differed somewhat (Figure 20). Both sites had an increase in elemental selenium in the surface sediment, as noted above. In the 6-12 inch layer, there was an increase of about 2 ppm at site 21, while there was a decrease of over 3 ppm at site FP. In the 2 layers between 12 and 24 inches, there was a decrease of nearly 1 ppm in each of the

Site 21



Flood Plot

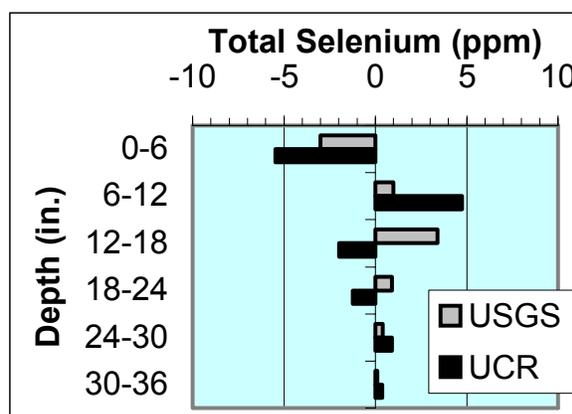
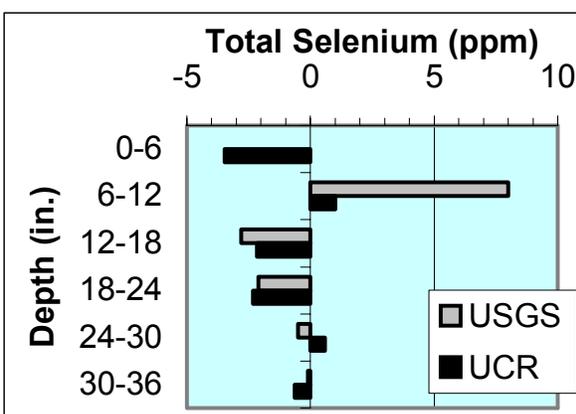
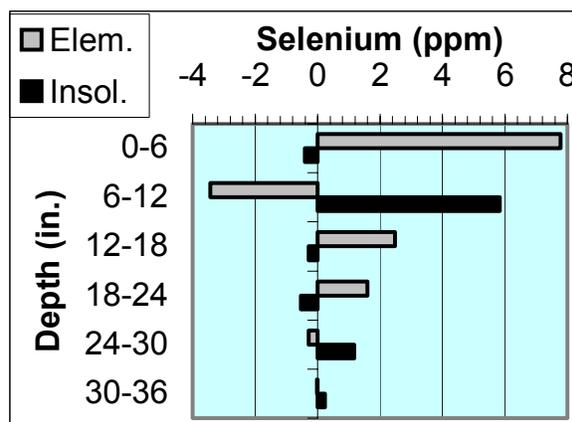


Figure 20: Changes in the concentrations of elemental, total insoluble, and 2 measures of total selenium at 2 sites during the 2002 Stewart Lake flooding experiment

layers at site 21, but an increase of about 2 ppm in those layers at site FP. In the 24-30 inch layer there was a small increase at site 21 and a small increase at site FP; even smaller, but still opposite changes in the deepest layer at the 2 sites.

Figure 20 also shows the changes in total insoluble selenium on the plots with the changes in elemental selenium. As was noted above, elemental selenium is usually the most common insoluble selenium species. At site 21, the changes in elemental selenium track well except at the surface, where there was a small increase in elemental, but a decrease of about 0.5 ppm in insoluble selenium. Below the surface, each change in elemental selenium and total insoluble selenium are both either increases or decreases with the change in total insoluble selenium fractions of a ppm greater than those of elemental selenium (Figure 20). Alternatively, at site FP, whatever change there was in elemental selenium is accompanied by the opposite change in total insoluble selenium. Except in the very deepest layer, if one increased, the other decreased (Figure 20). Obviously insoluble selenium species other than elemental selenium are controlling the total insoluble selenium at site FP.

The changes in OM-Se are of nearly the same magnitude, but opposite the changes in elemental selenium at site FP (compare figures 18 and 20). Neither species should be easily transported. In the past there was no evidence that either species was rapidly oxidized or reduced. Because of the similarity in the magnitude of the changes in OM-Se and elemental selenium, coupled with their opposing directions, the possibility that the results were swapped on the laboratory reports has to be considered as a possible reason for the rapid changes in the 2 selenium species, although at this point there is no way to verify this.

Pre- and post-flood UCR and USGS total selenium concentrations are plotted on Figure 19 for sites FP and 21. The 2 data sets show some different results in the profiles. At site 21 the USGS data show no change in the surface sediments, while the UCR data show a decrease of nearly 4 ppm (Figure 20). At site FP both data sets show a decrease in total selenium in the surface sediments, but the UCR decrease is somewhat larger. In the 6-12 inch layer, both data sets show an increase at both sites. However, the increase in the USGS data set is larger at site 21, while the UCR data set shows the larger increase at site FP (Figure 20). The 2 layers between 12 and 24 inches show good agreement between the UCR and USGS data, but the USGS data show a decrease, while the UCR results show an increase in the 24-30 inch layer at site 21. The changes are small, and the results may reflect random error. There is reasonable agreement in the deepest layer of site 21, where there was a decrease of < 1 ppm. At site FP the USGS data set shows an increase in the 2 layers between 12 and 24 inches, but the UCR data set shows a decrease. In the deeper layers there is reasonable agreement between the 2 data sets.

Although the analytical methods are similar, there is a difference in the total selenium extractions between the UCR and USGS laboratories. The UCR total selenium determination is based on the somewhat less rigorous Environmental Protection Agency digestion using hydrogen peroxide and hydrochloric acid. The USGS method is based on a sequential digestion in 5 strong acids as well as the hydrogen peroxide digestion. The USGS method would yield higher total selenium results than the UCR method, and it does. Figure 21 shows the correlation between the 2 sets of total selenium determinations. The intercept of the regression line is essentially equal to 1, but the slope, which is an exponent, is only 0.93. The expected slope of 1 (equal line) is also shown on Figure 21. If the regression accurately represents the relationship between the 2 total selenium determinations, then they yield approximately the same result at low concentrations of total selenium, but diverge increasingly as the total selenium concentration increases. The divergence is also evident on Figure 21. For example, at total selenium concentrations of 2 ppm or less, the results are essentially the same. At a total selenium concentration of around 3 ppm, the divergence begins to be noticeable. When the UCR total selenium is around 37 ppm, the regression estimates the UCR total selenium at 29 ppm. The increasing difference in the results from the 2 methods as the total selenium concentration increases is what would be expected. The regression relationship between the 2 measures of total selenium would illustrate the different results yielded by the USGS and UCR data sets.

From the perspective of the Stewart Lake, the selenium that represents the difference between the UCR and USGS results is not important. Based on the digestion procedure that is needed to extract the additional selenium, it would be unavailable and probably would never be removed from the sediments. From that perspective, the UCR total selenium would accurately represent a cleanup level even though the results may be lower than those of the USGS digestion method.

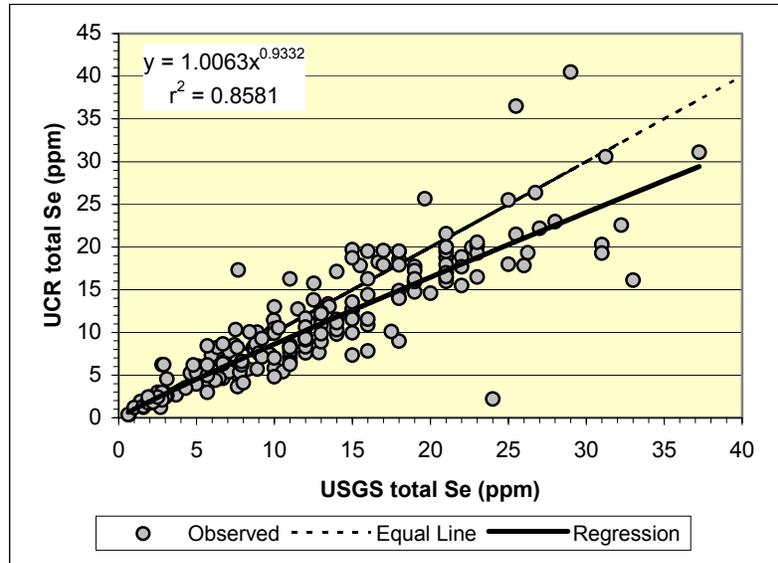


Figure 21: Relationship between UCR and USGS measures of total selenium

Selenium mass changes in the experimental flood plots

This section of the report will translate the preceding changes in sediment selenium concentrations into estimates of mass selenium movement through and out of the depth profiles at sites 21 and FP. The mass of selenium in each layer was estimated based on the following formula:

$$Se_m = Se_c * D_s * A * H,$$

where Se_m = the selenium mass in the layer, Se_c = the selenium concentration in the layer, D_s = the density of the sediment, A = the area of the plot, and H = the layer thickness. The selenium in each profile was calculated by summing the selenium in all layers in the profile. Changes in each layer in a profile were calculated by taking the difference between the pre- and post-flood selenium mass. As is noted in Appendix A, post-flood samples were collected several days after the water has seeped into the ground below each plot and the sediments were sufficiently dry to permit access for sampling. The net change in each profile was calculated by summing the differences among the layers.

Each of the plots were approximately square. The length of the sides and the area of each plot are shown in Table 4. Although profiles had been sampled in each of 4 quadrants at site 21, a pre-flood profile was only sampled in the southwest quadrant (21-SW). The changes in the profile at site 21 were adjusted to reflect ¼ of the total

Table 4. Experimental flood plot physical data				
Site	Length (ft)	Length (m)	Area (ft ²)	Area (m ²)
21- total	360	110	129,600	12,046
21-SW	180	55	32,400	3,012
FP	30	9.1	900	84

area of 21-SW, as shown in Table 4. Even though 21-SW is only a part of site 21, the area is still much larger than that of site FP. For this reason, the selenium mass values calculated at 21-SW will be much larger than those at site FP.

The density of excess samples collected in May 2001 for laboratory purposes (*i.e.*, column leaching experiments) was measured. Because the May samples were not true density samples, bulk density samples were collected in July 2001. All of the bulk sediment densities are summarized in Table 5.

The mean density of the May samples is somewhat greater than that of the July samples (Table 5). The lower density in July 2001 may reflect somewhat greater soil organic matter later in the summer. The May

Density Group (All in g/cm ³)	Mean Density	Std. Dev.	Std. Error	Confidence Interval	
				Lower	Upper
July 2001 density	0.91	0.090	0.063	0.851	0.977
May 2001 density	1.01	0.167	0.165	0.844	1.174
North end density	0.98	0.146	0.129	0.848	1.107
South end density	0.92	0.108	0.081	0.842	1.004
Grand mean density	0.95	0.122	0.070	0.876	1.016

samples had been dried and disturbed prior to the time of the density analysis. Such disturbance would affect the volume determination of the density samples. However, there is complete overlap in the confidence intervals of the 2 data sets. Due to the high degree of overlap, there is no statistically significant difference in the densities in May and July. For that reason, the 2 data sets were combined to see if there was any difference between the sediment densities in the north and south ends of Stewart Lake.

Both of the flood experimental plots are located in the north end of Stewart Lake. The north end samples were collected at sites 15 (in both May and July), 18, and 20, each of which is near the experimental flood plots (Figure 7). The samples from the south end were collected from sites 1 (in both May and July), 7, and 10. Once again, there is a high degree of overlap in the confidence intervals and no statistically significant difference in the means of the 2 data sets.

Although there was no difference in the various densities, the density as measured in the July 2001 bulk density samples were selected in estimating the selenium mass in the experimental plots. The flood experiments of 2002 were conducted after Stewart Lake had been dry for a year. If the density of the sediments was somewhat lower in the late summer of 2001 due to plant growth after the spring flood, then the later samples would be somewhat more representative of conditions at the time of the flood experiment. Although the differences in density measurements were small, even small differences would be magnified when the areas of the plots are taken into consideration.

Table 6 shows the selenium mass as calculated for each layer. The total selenium in each layer of the 2 experimental plots is shown along with its soluble and insoluble fractions. As was shown in the presentation of the profile concentrations, the soluble selenium is predominantly selenate, while the insoluble selenium is predominantly

Table 6. Summary of selenium changes in the depth profiles of the 2 experimental flood plots at Stewart Lake in Aug.-Sept. 2002

Location	Depth Interval	Total Selenium			Soluble Selenium			Insoluble Selenium		
		Total Se (grams)		Se change	Total Se (grams)		Se change	Total Se (grams)		Se change
		Pre-flood	Post-flood	(g)	Pre-flood	Post-flood	(g)	Pre-flood	Post-flood	(g)
A. Small Flood Plot	0 - 6 "	227	163	-64	76	16	-60	141	136	-5
	6 - 12 "	134	190	55	24	9	-15	102	170	68
	12 - 18 "	96	73	-23	20	6	-14	65	61	-3
	18 - 24 "	72	58	-14	9	4	-5	53	47	-6
	24 - 30 "	24	35	11	4	3	-1	17	30	14
	30 - 36 "	21	26	4	3	3	0	16	19	3
	Total	575	544	-31	135	40	-95	393	463	70
B. Site 21 - SW Quadrant	0 - 6 "	8,397	6,939	-1,458	1,985	749	-1,236	5,988	5,785	-203
	6 - 12 "	6,824	7,242	417	709	316	-393	5,741	6,573	832
	12 - 18 "	3,890	2,979	-911	632	240	-392	2,964	2,324	-640
	18 - 24 "	3,633	2,655	-978	500	276	-223	2,811	1,999	-812
	24 - 30 "	1,012	1,258	246	152	103	-49	763	968	205
	30 - 36 "	1,009	740	-269	201	102	-99	714	540	-174
	Total	24,765	21,812	-2,953	4,179	1,788	-2,391	18,981	18,189	-791

elemental selenium, although there are also significant amounts of selenite and/or organic matter selenium present in some layers.

The soluble selenium increases in nearly all layers of site FP (Table 6). In most layers, the vast majority of the soluble selenium was removed, including nearly 80 percent in the top 6 inches. There was no change in soluble selenium in only the deepest layer (30-36 inches – Table 6). Although there were decreases in insoluble selenium in plot FP in several layers, there was a large increase in the 6-12 inch layer. This increase would indicate a zone of selenium deposition in the profile. There is also a zone of deposition near the base of the profile, beginning at a depth of 24 inches. Such a zone of deposition would restrict leaching of selenium to the deeper ground water. The water monitoring data collected by the USGS indicates that vertical selenium transport stopped once the water source was turned off (Personal Communication, 12/4/2003, Davis Naftz, USGS, Salt Lake City, Utah). The zones of deposition may reflect this phenomenon, combined with the short duration of the leaching experiment (*ibid.*). Despite these zones of restrictive transport, there was still a net export of selenium from site FP during the experiment. As is shown in Table 6, 31 grams of selenium were removed from the upper 36 inches of the 900 square-foot site during the flood experiment.

There was also removal of soluble selenium from all layers of 21-SW (Table 6). In addition, there was a zone of deposition in the 6-12 inch layer of 21-SW, just as there was in FP. There was also a second zone of deposition at 24-30 inches. Nevertheless, there was a net export from the upper 36 inches of 21-SW of nearly 3 Kg (Table 6).

The data for each of the plots indicate that there are zones of deposition in the profiles. In each plot there was such a zone between 6 and 12 inches. Because the zone occurred at the same depth on both sites, such a zone may be widespread throughout the Stewart Lake sediment or it may be confined to the north end of the lake in the vicinity of the experimental plots. Sediment samples to date have been collected to monitor selenium concentrations. Other factors that may have geochemical consequences for selenium transport have not been investigated. As a result, the nature of such zones of deposition are unknown.

The greatest removal of total selenium from both of the profiles during the flood experiment occurred in the surface layer (Table 6). However, the net removal from the profile at site FP was less than ½ that near the surface. Alternatively, the net removal from the profile at site 21-SW was over twice the removal that occurred near the surface. This difference in the results indicates that there are some rather large differences in selenium transport between the 2 sites.

Table 7 compares the net total selenium removal in the surface layer and that from the entire profile of each of the sites on an areal basis. Putting the removal data on a unit area basis allows for a better comparison between sites 21-SW and FP despite their large difference in size.

Table 7 indicates a high degree of variation in the results from the 2 flood plots. These differences were noted above, but Table 7 puts them into a clearer perspective. For example, the profile data indicate a net removal from the sediment profiles at each site, but the end was

Site	Selenium Form	Total Profile		Top 6 inches	
		(mg/m ²)	(mg/ft ²)	(mg/ft ²)	(mg/ft ²)
Flood Plot (FP)	Total	-371.7	-34.55	-70.86	-70.86
	Soluble	-1136.3	-105.60	-66.51	-66.51
	Insoluble	840.9	78.15	-5.19	-5.19
Site 21 (21-SW)	Total	-980.6	-91.14	-45.01	-45.01
	Soluble	-794.1	-73.80	-38.15	-38.15
	Insoluble	-262.8	-24.42	-6.27	-6.27

achieved somewhat differently. Site FP showed a net decrease in selenium despite an increase in the insoluble fraction, while 21-SW showed a net decrease in both the soluble and insoluble fractions. The overall areal decrease in total selenium in the profile was larger at site 21-SW by nearly a factor of 3. Alternatively, in the top 6 inches of each profile, there was a decrease in both the soluble and insoluble fractions at both sites. The net effect was that the decrease in total selenium at site FP was greater than that at site 21-SW. Based on these results, it appears that the surface selenium at site FP is more readily leached than that at site 21, but interactions within the deeper layers of the profile make it less likely to be leached below the 3-foot layer that was the deepest that was sampled.

Another factor that could be responsible for at least part of the variability between sites 21 and FP, as well as variability within site 21 has to do with the depth of water. Site 21 was large, and while it was leveled, the leveling was only enough to allow tilling. Consequently, the water depth varied over the site during the flooding experiment.

Water depth was measured over site 21 during the flood experiment. The depth measurements are included in the description of the flood experiment in Appendix A (see pages A-7 through A-12). Those measurements are reproduced in Table 8.

Date 2002	Time	Flood Plot	Site 21					
			SW	SE	NE	NW	Center	Average
Aug. 29	8:30	10.8	8.0	11.5	8.0	6.0	9.0	8.5
	16:00	12.0	11.0	13.0	12.0	7.0	9.0	10.4
Aug. 30	9:20	12.0	8.0	12.5	9.5	7.5	8.0	9.1
	16:05	12.0	11.5	14.0	12.0	10.5	9.5	11.5
Aug. 31	8:10	12.0	11.0	14.0	12.5	10.5	10.0	11.6
	17:30	12.0	11.0	14.0	12.0	11.0	10.0	11.6
Sept. 1	8:15	12.0	11.0	14.5	12.0	11.5	10.5	11.9
	19:20	12.0	10.5	14.0	12.0	10.0	8.0	10.9
Sept. 2	8:45	12.0	9.0	12.0	10.0	10.0	8.0	9.8

Water depths varied considerably within site 21 (Table 8). As noted in Appendix A, the depths were measured at the corners of the site. A better estimate of the depth of water within a quadrant would be the average between the corner measurement in the quadrant and the center depth. The data in Table 8 indicates that the water depths

were greater on the east side of the site, and the south end was generally deeper than the north. The data also indicate that the flood plot was deeper than the southwest quadrant, where the site 21 profile originated.

The preceding results for site 21 have focused on the sediment selenium profile from the southwest quadrant. Surface samples were collected from each of the quadrants of the site. Site 21 was originally subdivided into quadrants to evaluate variation in selenium concentrations across the site. Such a set of samples also allows further analysis of the variation, if any, in the effects of flooding on selenium leaching at the site. Net total selenium changes in each of the 4 quadrants of site along with those of the soluble and insoluble fractions are shown in Table 9.

Table 9 indicates that there is a great amount of variation in the results among the 4 quadrants. The greatest difference in total selenium among the 4 quadrants is between the 2 quarters in the north ½ of the site. The largest decrease of any occurred in the NW quarter, while there was an increase

Area	Selenium Form	West		East	
		(mg/m ²)	mg/ft ²	(mg/m ²)	(mg/ft ²)
North	Total	-759.2	-70.56	244.7	22.74
	Soluble	-192.3	-17.87	-310.7	-28.88
	Insoluble	-504.5	-46.89	465.4	43.25
South	Total	-484.3	-45.01	-420.5	-39.08
	Soluble	-410.5	-38.15	-30.4	-2.82
	Insoluble	-67.4	-6.27	-322.7	-29.99

in the NE quarter. The decrease in the soluble selenium fraction in the 2 north quarters were similar. The difference in total selenium in the 2 quadrants was entirely due to the differences in the response of the insoluble fraction to flooding. The 2 quadrants on the south end of site 21 show a similar decrease in total selenium. However, the changes in the fractions of total selenium are completely different in the quadrants in the south. In the SW quadrant, the decrease in total selenium is almost entirely, *i.e.* about 85 percent of the decrease, due to the leaching of soluble selenium, while in the SE quadrant, the vast majority of the decrease (about 80 percent) is due to a loss of insoluble selenium.

As was noted earlier, there is no mass balance between the selenium fractions and the total because the fractions do not include the residue. Although the residue should be functionally insoluble, by definition, it does not show up in either the analytically determined soluble or insoluble fractions. In other words, the residue is in reality an error term.

The above raises questions related to causes of the variability in total selenium as it relates to the changes in selenium during the flood. To further illustrate the problem, Table 10 shows the results of the total selenium changes in the 4 quadrants of site 21

Quadrant	Total Se (grams)		Se change (g)
	Pre-flood	Post-flood	
NE	7,972	7,972	0
NW	6,713	7,552	839
SE	7,133	7,552	420
SW	8,811	8,811	0
Total	30,628	31,887	1,259

as determined from the total selenium results of the USGS laboratory. Unlike the UCR results, the USGS results indicate no change in the total selenium in the NE quadrant of site 21. These latter results also indicate no change in the SW quadrant. However, the results indicate an increase in total selenium in the remaining 2 quadrants of site 21, with the result that the net change in the surface sediments of site 21 is an increase of more than 1 Kg of selenium at the site.

Selenium variation in sediment samples

There are several sources of variability in the selenium sample results. The assumption that all of the selenium variation is due to its real-world distribution in the Stewart Lake sediments may or may not be true. There is undoubtedly such variation in the sediments, but there is also variation due to sampling. In addition, there is also a certain degree of variation, *i.e.* error, in the analytical results. For example, the error associated with the pre- and post-flood total selenium results from the UCR ranged from 0.001 to 0.425 µg/g, based on the replicate laboratory results. Additional examples of the confidence intervals provided with the UCR results are included with the April data listing in Appendix B. The UCR method, including analytical error, is described in Frankenberger and Zhang (2001) and Zhang *et al.* (1999). The total selenium analysis in the UCR and USGS laboratories are based on similar methods, but the preparatory digestions are greatly different. The USGS digestion is more rigorous and yields higher total selenium concentrations at total selenium concentrations greater than 3 ppm, as was shown earlier in this report (see Figure 21).

In developing the USGS analytical method for total selenium, the standard used to evaluate its performance on soil/sediment was the NIST (National Institute of Standards and Technology) standard, SRM 2709 (Hageman and Welsch, 1996). The performance results showed a percent relative standard deviation of 7 percent and 95 percent recovery (*ibid.*). The standard, which is a sample of San Joaquin Valley, California, soil, was developed by the USGS laboratory in Denver (NIST, 2003). Before submitting the Stewart Lake samples to the USGS laboratory, standards were prepared and submitted with the samples. The analytical results of the standards analyses for the last 2 years are shown in Table 11. On several occasions, the NIST SRM 2709 standard was included with the samples. The results in Table 11 indicate that the analysis of blind SRM 2709 samples agree well with the expected results for that standard.

The Stewart Lake standard was most frequently used blind standard. The Stewart Lake standard is a composite of sediments from various sites. As shown in Table 11, the confidence interval that is used to evaluate laboratory performance has increased over time. The increase is due to additional analytical data on the standard. As of now, there have been a total of 17 analyses, and the range in acceptable laboratory performance is 6.6 ppm. Based on that level of performance, at a selenium concentration in the sediments near that of the Stewart Lake standard (28.9 ppm), any change in selenium less than 6.6 ppm should not be detectable; it would be within the range of random variation.

Table 11. Stewart Lake Recent Sediment QA/QC data						
Sample Date	USGS Lab No.	BOR Lab No.	Standard	Se ppm	Confidence Interval for Standard	
					Low C.I.	High C.I.
May 2001	C-187668	QC-3	Stewart Lake QC	28	28.4	
	C-187730	QC-6	Stewart Lake QC	28	28.4	
Jul. 2001	C-190524	QC-6	Stewart Lake Std.	30	19	35
	C-190544	QC-4	SRM 2709	1.5	1.2	2.0
	C-190564	QC-1	Stewart Lake Std.	34	26	28
	C-190584	QC-2	SRM 2709	1.6	1.49	1.65
	C-190602	QC-5	SRM 2709	1.6	1.2	2.0
Nov. 2001	C-200495	QC-2	Stewart Lake Std.	29	26.7	30.9
	C-200496	B775	N01S15VT	14	—	—
	C-200510	QC-3	Dup. B-775	12	—	—
	C-200530	QC-4	LAZ ¹	3.2	1.87	2.87
	C-200555	QC-1	SRM 2709	1.5	1.1	2.1
Apr. 2002	C-203692	SL41	SRM 2709	1.5	1.1	2.1
	C-203713	SL42	Stewart Lake Std.	39	27	31
	C-203738	SL43	Meaker Std. ²	5.5	4.7	5.1
	C-203757	SL44	SRM 2709	1.5	1.1	2.1
Aug. 2002	C-213410	C909A	Stewart Lake Std.	27	26.3	32.9
Oct. 2002	C-213719	RC-1	Stewart Lake Std.	28	26.3	32.9
¹ LAZ – Standard from Lake Andes-Wagner, South Dakota						
² Meaker – Standard from Meaker Ranch, Colorado						

Site FP is much smaller than site 21. Consequently, site FP should have less variability in selenium than site 21. The amount of potential variation within each site has the potential to affect the results of the pre- to post-flood comparison used to estimate selenium removal. Although samples were composited in each site, the number of subsamples that would need to be included in the composites from site 21 would have to be much larger than would be the case at site FP. Because the experimental control was much better at site FP, those results are probably better from an experimental perspective. However, the results at site 21 provide an idea of the potential problems involved in verifying results if the experiment were expanded to a lake-wide demonstration.

Permanent Monitoring Sites

The 20 permanent monitoring sites shown previously on Figure 1 were sampled in April and October 2002. All samples from the permanent monitoring sites have been analyzed at the USGS laboratory only in order to be consistent with earlier sample results. Speciation samples have only been collected at selected sites since 2000. The data set for the permanent monitoring sites extends back to 1995.

The April samples were collected as pre-flood samples in anticipation of the usual flooding from the Green River. However, the Green River flows were not high enough during the spring of 2002 to provide much water in Stewart Lake and the inlet gate remained closed. The data can be used to look at the overwinter change between 2001 and 2002, but there was no flood to evaluate. The October samples will be used to compare year-to-year changes since 1995 based on the post-flood/autumn samples that have been collected since remediation began.

When Stewart Lake was being flooded annually, there were sediment profiles of total selenium collected from sites 1, 10, and 15. Because site 10 was inaccessible during the spring of 2001, site 7 was substituted. In April 2002, the annual flood was still anticipated, and profile samples were collected from each of the above 4 sites. In addition profiles were collected from three 6-inch depth intervals from the 4 quadrants of site 21.

April 2002 Selenium Profiles

Samples were collected from sites 1, 7, and 10 as described in Appendix A (page A-2). The samples were submitted to the USGS laboratory only. This section of the report will address those samples, primarily as they relate to the set of samples collected in a similar manner in November 2001. The November samples were previously described in Yahnke (2002).

The total selenium profiles from the sites 1, 7, and 10 from samples collected in November 2001 and April 2002 are shown on Figure 22. During 2000 and 2001, various treatments were applied at these sites. The treatment plots were sampled separately from the control plots established during those experiments. By way of review, the treatment in 2000 consisted of tilling the treatment plots to allow greater oxidation of the selenium prior to flooding in the spring. In 2001, the treatment included the application of lime in addition to tilling. Although the treatment plots had been subdivided in 2002 to allow the application of 2 forms of lime, the plots were recombined for sampling in November 2001 and April 2002, because no difference had been seen in the effects of the 2 forms of lime.

In November of 2001 at the site 1 control plot, there was a large drop off in total selenium between the surface and the subsurface (6-12 inch layer – Figure 22). Total selenium then declined gradually from about 6 ppm to around 2 ppm at the base of the profile, with most of the decrease in the lower layers of the profile. In April 2002, there

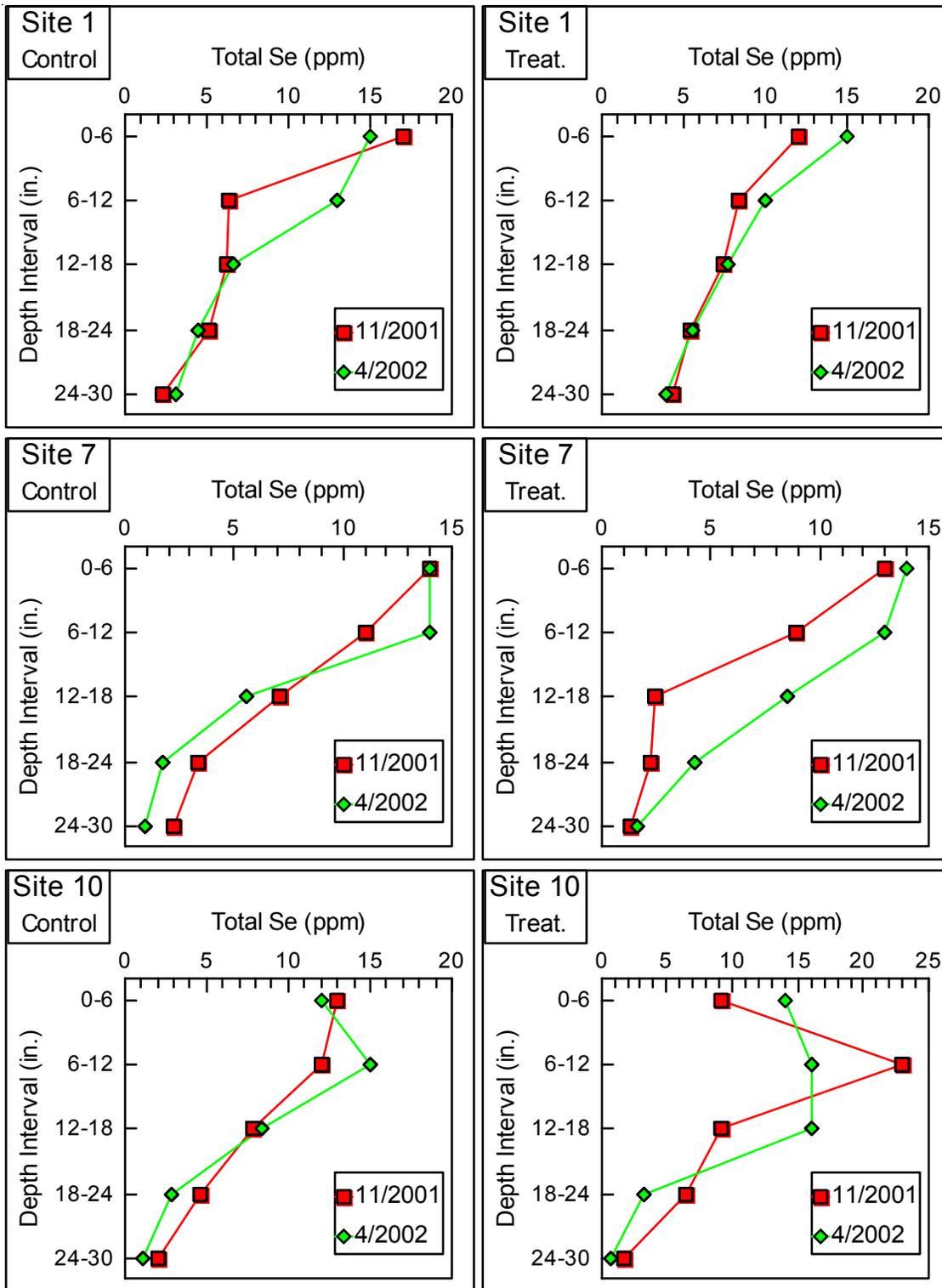


Figure 22: Total selenium profiles at sites 1, 7, and 10 in November 2001 and April 2002

was a decrease of about 2 ppm at the surface from what had been present in November. There was an even greater increase of about 7 ppm in the 6-12 inch layer that appears to be an effect of leaching from the surface. The November profiles in the treatment plot at site 1 did not show the large drop-off in selenium evident in the control plot. There was only about a 3 ppm decrease in total selenium between the top 2 layers in the treatment plot in November. The April profile showed an increase of 3 ppm in the surface sediments and a little over 1 ppm in the 6-12 inch layer. Just as was the case in the control plot, there was no change in total selenium evident below 12 inches in the treatment plot at site 1 between November and April (Figure 22).

In November 2001, there was an almost linear decrease of 3 to 4 ppm of total selenium per depth interval in the control plot at site 7 (Figure 22). That profile changed considerably in April 2002, when there was no change in total selenium between the first 2 layers, but a decrease of over 8 ppm between the 6-12 and the 12-18 inch layers, giving the profile a more stratified appearance (Figure 22). The largest change between November and April was a 3 ppm increase in the 6-12 inch layer. There was a decrease of about 1.5 ppm in each of the 3 deeper layers. In the treatment plots at site 7 in November 2001, there was a large decrease in total selenium in the upper 3 layers, but virtually no change below 18 inches (Figure 22). The large decreases in total selenium had extended to the base of the profile by April. The net effect was an increase in total selenium in all layers of the profile between November and April. The largest increase in total selenium was 6 ppm in the 12-18 inch layer, followed by an increase of 4 ppm in the 6-12 inch layer.

After a decrease of 1 ppm between the surface layers in November 2001, there was a near linear decrease in selenium of 3 to 4 ppm between the deeper layers of the profile of the control plot of site 10. The April of 2002 profile showed a 1 ppm decrease in selenium in the surface layer, followed by an increase of 3 ppm in the 6-12 inch layer, little change in the 12-18 inch layer, and small decreases below that (Figure 22). The treatment plot at site 10 showed large differences in selenium (~ 14 ppm) between the surface layers in November 2001. These differences were manifested as an anomalous peak in the profiles in the 6-12 inch layer (Figure 22). Below 18 inches, there was a more linear decrease in selenium in the profile. The anomalous peak had disappeared by April, when there was little difference in selenium between the surface and 18 inches. However, there was a large drop-off (13 ppm) in selenium below 18 inches, giving the profile a pattern of decrease from surface to bottom (Figure 22).

Profiles from site 15 were collected from much deeper profiles than those at sites 1, 7, and 10. The profile from the site control plot extended to a depth of 42 inches in both November 2001 and April 2002 (Figure 23). The site 15 profile was extended to investigate the anomalous increase in selenium that had been consistently observed in the 24-30 inch layer in previous samples. The profile from the site 15 treatment plot extended to a depth of 36 inches. The increase in selenium observed in the 24-30 inch layer of the control plot had also been observed in previous samples in the treatment plot as well, but it was not present in the November 2001 profile. However, it was present in the April 2002 profile (Figure 23).

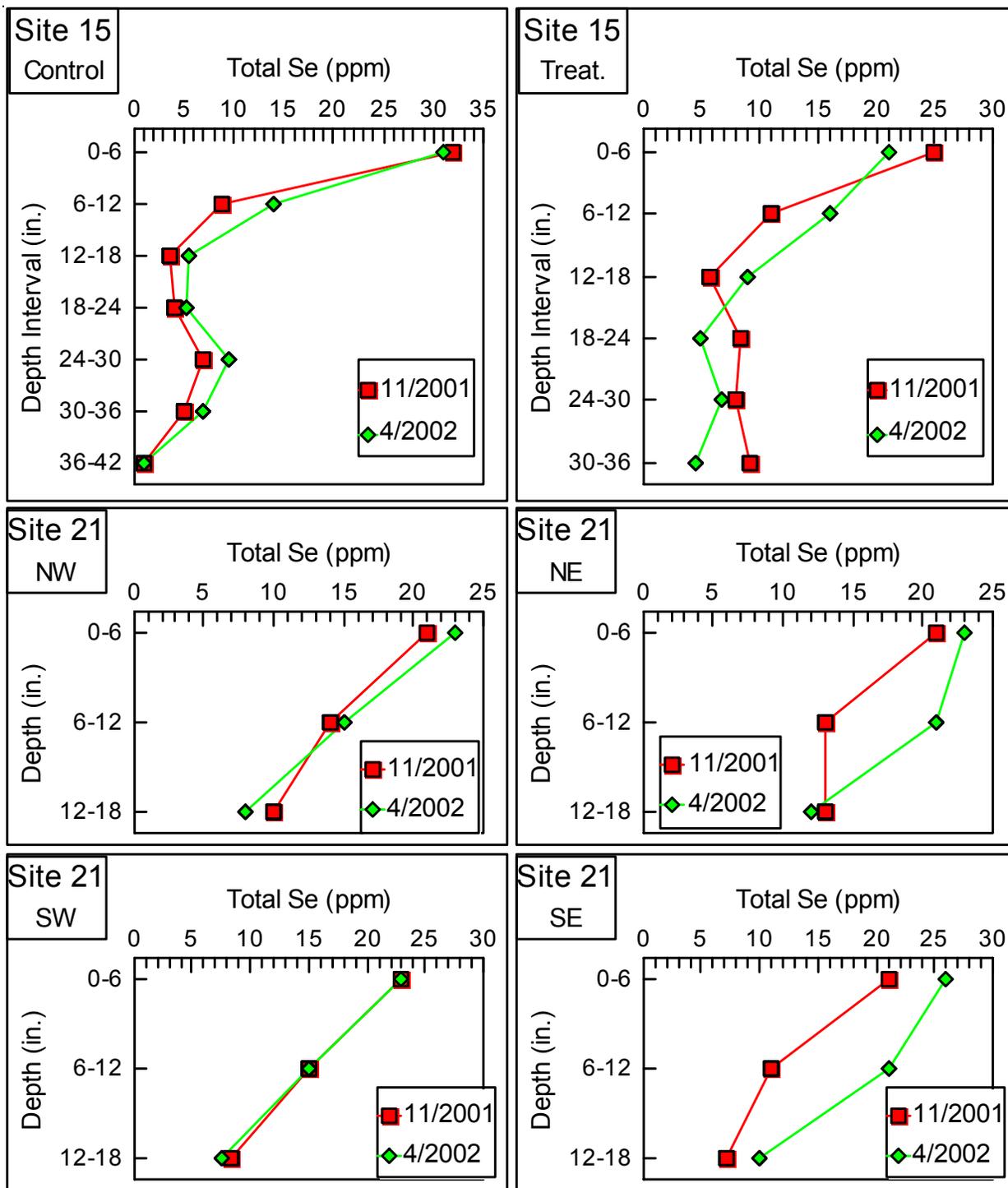


Figure 23: Total selenium profiles at sites 15 and 21 in November 2001 and April 2002

The selenium profiles from November 2001 and April 2002 at the site 15 control site are nearly identical in form (Figure 23). The April profile is offset to the right at most depths indicating an increase in selenium throughout the profile. Except for the samples from the 6-12 inch layer, which show an increase of 5 ppm, and the samples from the 36-42 inch layer, which show no change, there was an increase in selenium of between 1 and 3 ppm throughout the remainder of the profile. The selenium profiles in the site 15 treatment plot bear a somewhat confused resemblance to those in the control plot. In November, the surface layer of the treatment plot had a lower selenium concentration than the control plot by about 7 ppm. There was the same kind of large drop-off between the surface and subsurface layer in the treatment plot as shown in the control plot, but below the surface layer, all of the selenium concentrations were higher in the treatment plot than in the control plot. The surface selenium concentration decreased between November and April, but increased in the next 2 layers by 3 to 5 ppm. The result was a profile that showed a more linear decrease in selenium between the surface and 24 inches of depth. The lower part of the profile showed a decrease in selenium in each of the layers that ranged from 1.2 to 4.7 ppm.

The selenium profiles from site 21 were relatively shallow and only extended to a depth of 18 inches (Figure 23). In general the profiles from the east quadrants of site 21 showed a much greater degree of change between November and April than those to the west. In both cases the profiles to the east showed rather large increases in selenium, particularly in the 6-12 inch layer, where there were increases of 8 and 10 ppm in the northeast and southeast quadrants respectively. There were somewhat smaller increases in the surface sediments of those quadrants that amounted to 2 and 5 ppm in the northeast and southeast quadrants respectively. Alternatively, selenium in the profiles from the northwest quadrant of site 21 showed an increase of 2 ppm at the surface and a decrease of the same amount at depth. Selenium in the southwest quadrant showed virtually no change. The pattern of change in selenium in the profiles in site 21 appears to reflect the relationship of the quadrants to the remaining source of selenium, which is confined to seepage along the scarp along the north bank of Stewart Lake.

Surface Samples at the 20 Permanent Monitoring Sites

Total selenium concentrations in samples collected in April and October 2002, along with those collected in November 2001, are shown in Table 3. Change in total selenium between sampling dates are also shown in Table 12. Mean selenium concentrations are shown in Table 12. The mean selenium concentrations for the selenium concentrations at the 20 sites are geometric means, while those for the differences in selenium between samples are the arithmetic means of those differences.

Based on Table 12, total selenium increased from November 2001 to April 2002 from 14.9 ppm to 15.2 ppm. Before going farther, it should be noted that there is no statistically significant difference among the data sets. Paired comparisons of the data using the Wilcoxon signed rank test showed no significant difference between the November and April or the April and October

data sets (Table 13). The Wilcoxon signed rank test is the nonparametric equivalent of a paired t-test. In the Wilcoxon test, the differences between the individual values of the data sets are taken. The differences are then ranked. The signs of the differences are assigned to the ranks, and the positive and negative ranks are summed separately (SPSS, 2000). The smaller absolute value of the sums becomes the test statistic, Z, when divided by the square root of the sum of the squared ranks. Statistical significance of Z is based on tabular values originally developed by Wilcoxon (Snedecor and Cochran, 1967). The probabilities shown in Table 13 were calculated in SYSTAT and show no significant difference at the 0.05 α -level between consecutive samples.

Table 12. Total selenium (ppm) in surface samples collected at the 20 permanent monitoring sites from November 2001 through October 2002

Site	Nov/01	Apr/02	2001-2002 Difference	Oct/02	Apr-Oct 02 Difference
1	17.0	15.0	-2.0	15.0	0.0
2	9.3	6.7	-2.6	9.7	3.0
3	13.0	13.0	0.0	15.0	2.0
4	8.4	9.5	1.1	8.2	-1.3
5	8.1	9.5	1.4	6.6	-2.9
6	9.6	9.2	-0.4	8.1	-1.1
7	14.0	14.0	0.0	10.0	-4.0
8	8.9	9.8	0.9	11.0	1.2
9	16.0	18.0	2.0	15.0	-3.0
10	13.0	12.0	-1.0	10.0	-2.0
11	8.4	10.0	1.6	9.4	-0.6
12	16.0	17.0	1.0	17.0	0.0
13	6.3	9.5	3.2	9.1	-0.4
14	19.0	19.0	0.0	20.0	1.0
15	32.0	31.0	-1.0	21.0	-10.0
16	23.0	22.0	-1.0	22.0	0.0
17	17.0	17.0	0.0	17.0	0.0
18	22.0	20.0	-2.0	21.0	1.0
19	38.0	51.0	13.0	65.0	14.0
20	47.0	38.0	-9.0	37.0	-1.0
Mean	14.9	15.2	0.3	14.6	-0.2

Table 13. Comparison of November 2001, April 2002, and October 2002 total selenium concentrations at 20 sites at Stewart Lake

Variable 1	No. > Var. 2	Variable 2	No. > Var. 1	Z	Prob. > Z
November 2001	8	April 2002	8	0.181	0.856049
April 2002	10	October 2002	6	-0.776	0.437507

Overall, there was a small increase in total selenium from November to April and a small decrease from April to October (Table 12). In other words, there has been no

change in total selenium since the fall of 2001. However, no lake-wide remedial activity has taken place during that time either.

Long-term Selenium Monitoring: 1995-2002

Since 1995, Reclamation has monitored total selenium in the Stewart Lake sediments. The monitoring sites were not permanently established until 1998, but many of the sites that were designated as permanent had been sampled during prior years. Only those sites that ultimately were included in the permanent monitoring group are used in this analysis. Those sites include 16 of the 45 sites sampled in 1995 and 19 of the 22 sites sampled in 1997.

Table 14 shows a year by year comparison of the post-flood total selenium data collected since 1995; the current condition (October 2002) is also compared with the initial condition 1995 in the last line of the table. Where there was more than 1 data set collected in a year, only the last data set collected in the fall was used. The post-flood sampling months included in the data set range from July to as late as December. The post-flood data for 2001 and 2002 (actually, fall in 2002 since there was no flood) are the only data used in the comparison in order to be consistent with the data from the earlier years.

Line	Variable 1	No. > Var. 2	Variable 2	No. > Var. 1	Z	Prob. > Z
1	1995	14	1997	3	-2.485	0.012946
2	1997	4	1998	12	2.689	0.007170
3	1998	10	1999	8	-0.588	0.556533
4	1999	14	2000	4	-2.461	0.013871
5	2000	7	2001	12	1.070	0.284473
6	2001	11	2002	8	-0.767	0.442842
7	1995	7	2002	8	-0.085	0.932025

The results shown in Table 14 indicate that, in comparison to 1995 (variable 1 on line 1), there was a significant decrease in selenium in 1997 (variable 2 on line 1), followed by an even more significant increase in 1998 (line 2). There was no change between 1998 and 1999, but there was another significant decrease in selenium between 1999 and 2000. There was no significant change in selenium concentrations in the surface sediments between 2000 and 2001 nor between 2001 and 2002 (Table 14). What is most discouraging in the results in Table 14 (shaded line [line 7]) is that, in comparison to the baseline conditions in 1995, the current sediment selenium concentrations (2002) are no different.

Figure 19 shows plots of all of the total selenium results for each sampling date for each of the 20 permanent monitoring sites in Stewart Lake since 1995. These plots will be evaluated for trends based on the Pearson (parametric) correlations with sampling date and year presented in Table 15. The date is represented in the SYSTAT data set used

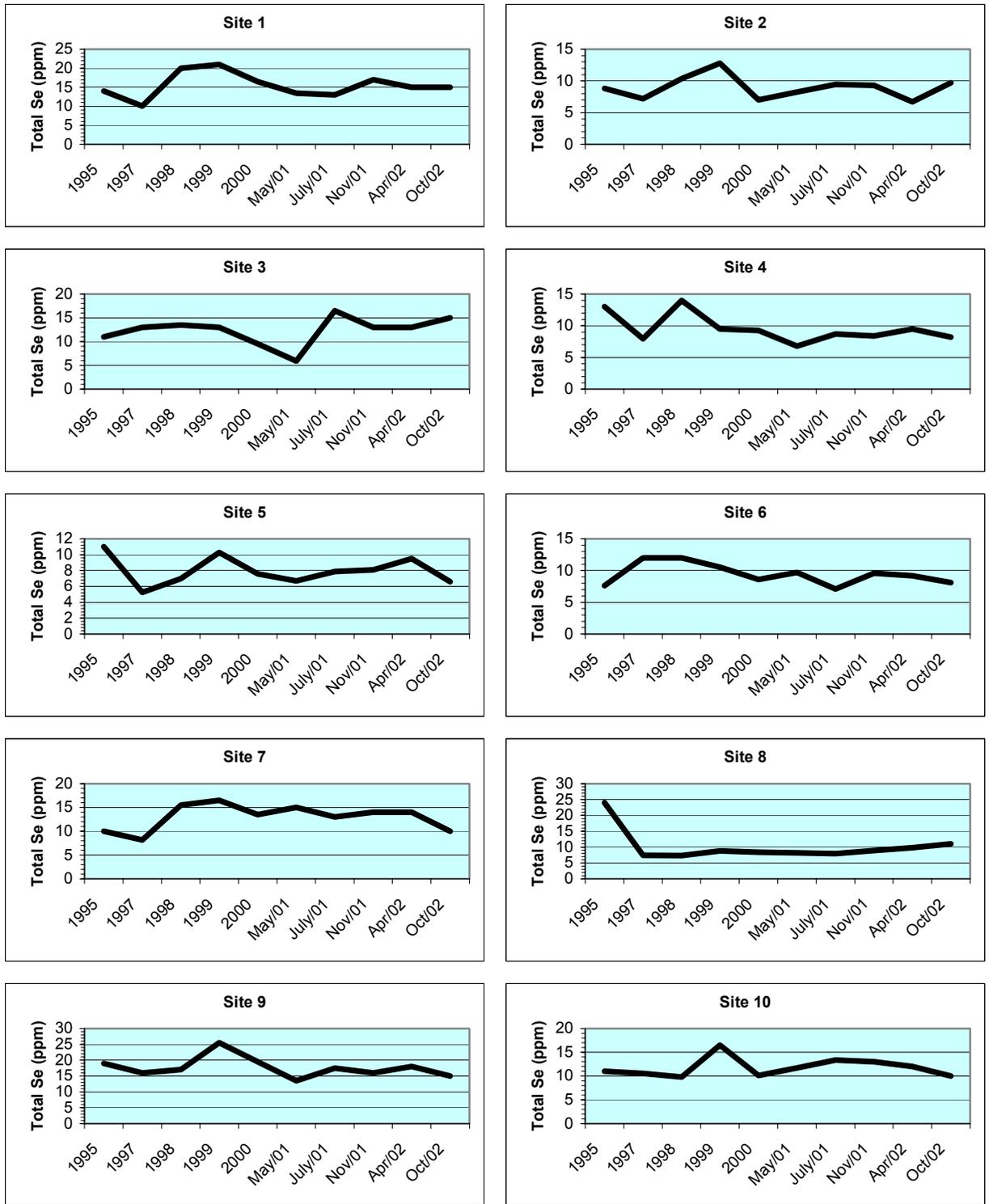


Figure 24: Total selenium concentrations by site at Stewart Lake for each sampling date since 1995

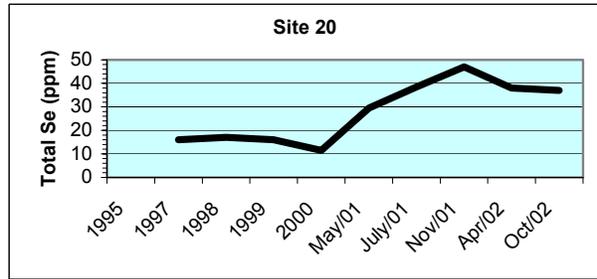
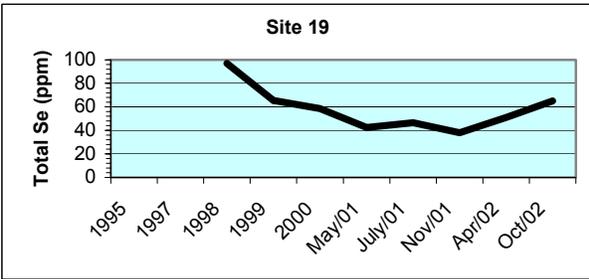
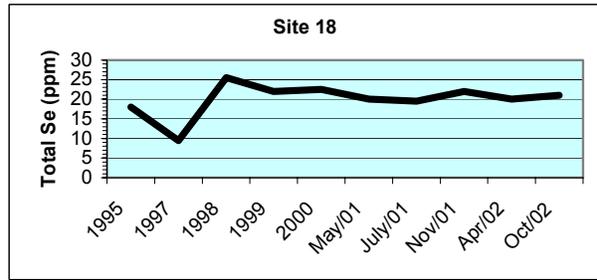
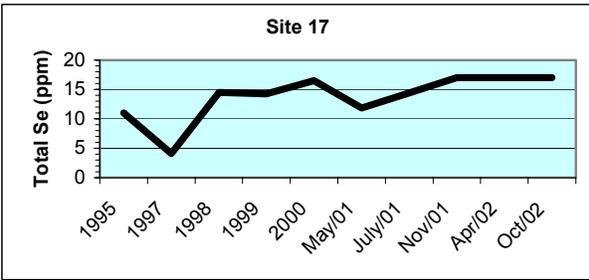
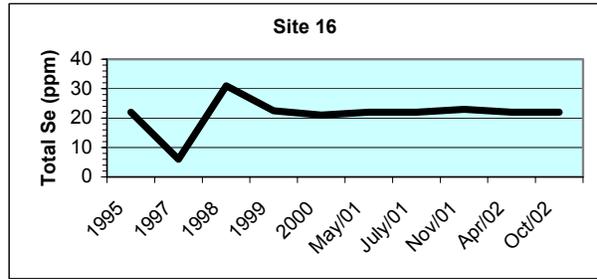
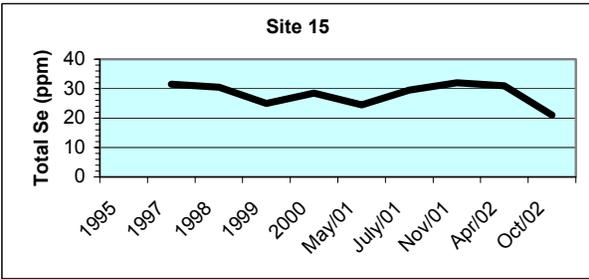
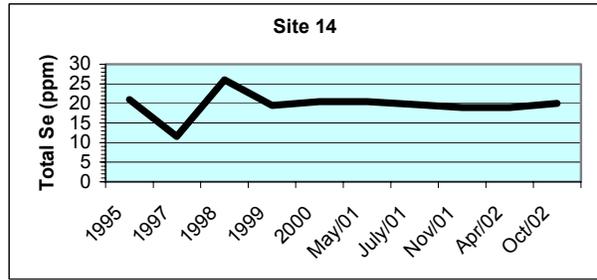
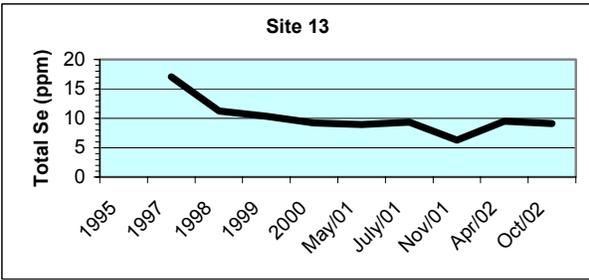
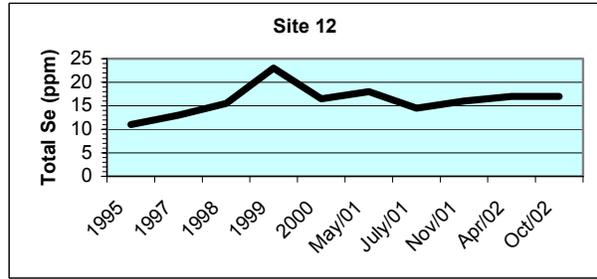
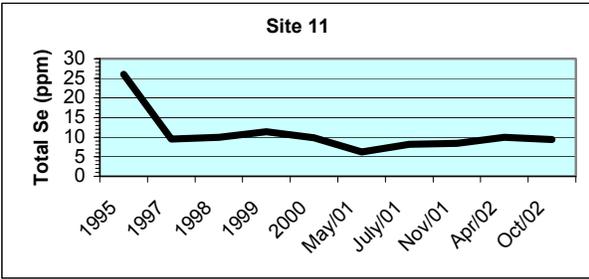


Figure 24: continued

Table 15. Pearson correlations of total selenium (USGS) with sample date and year for each of the 20 permanent monitoring sites at Stewart Lake (significant correlations [probability of $a > r < 0.05$] are highlighted)

Site		Date	Year	Site	Date	Year
S1	r	0.1181	0.0629	S11	-0.7392	-0.7413
	Prob. > r	0.7452	0.8630		0.0146	0.0141
	n	10	10		10	10
S2	r	-0.0475	-0.0911	S12	0.5229	0.4973
	Prob. > r	0.8963	0.8024		0.1210	0.1436
	n	10	10		10	10
S3	r	0.1258	0.1100	S13	-0.8294	-0.7845
	Prob. > r	0.7292	0.7623		0.0057	0.0123
	n	10	10		9	9
S4	r	-0.6031	-0.6146	S14	0.0848	0.0660
	Prob. > r	0.0649	0.0587		0.8158	0.8563
	n	10	10		10	10
S5	r	-0.2135	-0.2183	S15	-0.3746	-0.3474
	Prob. > r	0.5537	0.5445		0.3206	0.3596
	n	10	10		9	9
S6	r	-0.2768	-0.2762	S16	0.2393	0.2196
	Prob. > r	0.4389	0.4398		0.5055	0.5421
	n	10	10		10	10
S7	r	0.3636	0.3516	S17	0.7004	0.6659
	Prob. > r	0.3017	0.3191		0.0241	0.0356
	n	10	10		10	10
S8	r	-0.5684	-0.5626	S18	0.4044	0.3639
	Prob. > r	0.0865	0.0904		0.2465	0.3012
	n	10	10		10	10
S9	r	-0.2340	-0.2728	S19	-0.7121	-0.7157
	Prob. > r	0.5153	0.4458		0.0475	0.0459
	n	10	10		8	8
S10	r	0.1609	0.1518	S20	0.7384	0.7633
	Prob. > r	0.6569	0.6756		0.0231	0.0167
	n	10	10		9	9

to calculate the correlations as the cumulative number of days since January 1, 1900. On this basis, there is a distinction between multiple samples within a year. Alternatively, using the year as an independent variable essentially lumps all of the samples collected at a given site within a year as replicates. Significant correlations are represented by a probability of a greater r that is less than 0.05; these are highlighted in Table 15. The results in Table 15 represent a sort of rudimentary trend analysis.

There are no significant correlations with either sampling date or year in Table 15 at sites 1 through 10, which indicate that there are no significant trends at these sites. All of these sites are located in the more southerly part of Stewart Lake (Figure 1). The

only southern site that does show any possible change over the course of the monitoring period is at site 8, where there was a large decrease in total selenium, but all of the decrease occurred between 1995 and 1997. Since 1997, there has been what appears to be a gradual increase in total selenium (Figure 19), which probably accounts for the nonsignificance of the correlations for site 8. Alternatively, there are 5 significant correlations with both date and year for the correlations from the 10 sites numbered between 11 and 20 (Table 15).

There are inverse correlations for the total selenium data from sites 11, 13, and 19 and positive correlations for the data from sites 17 and 20. To some extent the plot of the total selenium data from site 11 resembles the plot from site 8. The main difference is in the period between 1999 and early 2001, when there was an additional decrease in total selenium at site 11. Alternatively the total selenium at site 13 shows a general decline from 1995 through the end of 2001; there was a small increase in early 2002 at the site (Figure 24). Total selenium at site 19 also shows a continual decrease from the time of the initial samples collected in 1998 until the end of 2001; total selenium began to increase in 2002 (Figure 24). At the time of its initial samples in 1998, when the selenium concentration was 100 ppm, site 19 had the highest concentration of total selenium that has been observed at any of the 20 permanent monitoring sites during the monitoring period.

The remaining significant correlations are positive correlations with both date and year at sites 17 and 20 (Table 15). Although total selenium has been fluctuating somewhat at site 17, there have been 2 periods when distinctive increases have occurred. The first was in 1998, following a typical decrease between 1995 and 1997. The second was in 2001, following another decrease between the 2000 samples and those of May 2001 (Figure 24). In both cases, the follow-up increase was greater than the preceding decline in total selenium and creates an upward trend. The other positive correlation is based on the total selenium data at site 20 (Table 15). Total selenium at site 20 was relatively constant between the time of the initial sample in 1997 until that in 2000, but began to increase in 2001. Beginning in 2002, there has been a decrease in total selenium at site 20, but it has been small relative to the preceding increase (Figure 24).

Beginning with the samples collected from the permanent monitoring sites in December 2000, a difference in the total selenium concentrations in the north and south areas of Stewart Lake was noted (see Yahnke, 2001). At that time, the line of demarcation was delineated at the latitude of the inlet channel. The reason that the difference was noted was a significant positive correlation between total selenium and site number. Since the site numbers generally increase from south to north, the correlation indicated an increasing trend in total selenium from south to north.

A plot of the coefficients for the correlations between site and total selenium for each sample date is shown on Figure 25. The plot also shows a trend line for the correlations that indicates that there has been an increasing trend since 1997. Although the trend showed a decrease from the samples in 1995 to 1997, neither of those correlations is statistically significant. All of the correlations since then are significant. The trend

toward increasing correlations coefficients ended in October 2002, when there was a small decrease in the coefficient in comparison to the April 2002 samples. The slight decrease is probably a reflection of the replacement of the maximum selenium concentration previously shown at site 20 by the one at site 19. Nevertheless, the correlation is still highly significant, *i.e.* $r = 0.61$, probability of a greater $r = 0.002$, which is down from an r of 0.71.

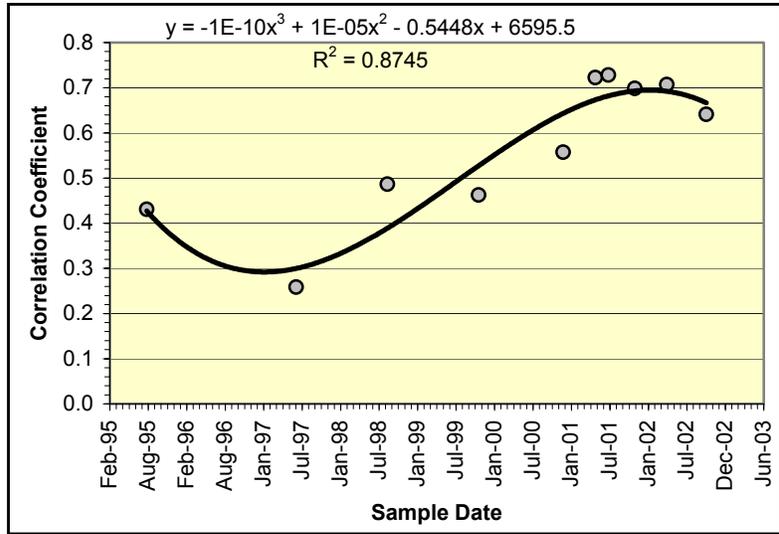


Figure 25: Correlations between selenium and site during the monitoring period 1995-2002

The south-north distribution was further explored in Yahnke (2002) using discriminant analysis. Discriminant analysis is related to both ANOVA (analysis of variance) and multiple regression (Engelman, 2000). The cases are grouped into cells as in a oneway ANOVA and the predictor variables form an equation like that in multiple regression (*ibid.*) In this case, discriminant analysis was used to see how well total selenium concentrations in the surface sediments at Stewart Lake could be used to classify the north-south grouping of sites. The discriminant analysis originally performed in Yahnke (2002) is updated based on the April and October 2002 samples in Table 16.

The breakdown of north-south sites shown in Table 16 is not strictly geographic. When the classified data from 1995 through 2001 were reviewed, it was noted that all of the site 17 observations were misclassified. As is shown on Figure 1, site 17 was located immediately south of the J1-J1A drainage channel. It was hypothesized that the channel originally conveyed the drain water away from the site, and has conveyed the remaining seepage since the drains were diverted in late 1997. However, sites 9 and 12 are located north of the extension of the conveyance channel that confines the other sites located in the north. Sites 9 and 12 are located farther south than the other sites in the north group. If the remaining

Summary Statistics	North	South	
Group Frequencies	55	135	
Group Means (ppm)	28.3	11.9	
Classification	North	South	%correct
North	40	15	73
South	5	130	96
Total	45	145	89
Statistics:			
Between groups F-matrix – df = 1,188			
F = 125.6		Prob. > F < 0.000001	
NOTE – individual classifications of each observation appear in Appendix C			

problem with selenium contamination is due to the seepage, then the seepage may not be reaching the surface sediment at sites 9 and 12. The seepage may be infiltrating into the ground water before reaching the sites, the selenium may be lost to the sediments before reaching the sites, or the seepage may be diverted from the sites by some other conveyance, possibly a natural channel.

Table 16 indicates that the groupings described above can be defined based on total selenium concentrations. The test statistic, F, which evaluates the statistical significance of the relationship has a probability of a greater F occurring by chance alone of less than 1 in a million. The difference between the groups is represented by the group mean selenium concentrations of 28 ppm in the north, as opposed to 12 ppm in the south. As is also shown in Table 16, 89 percent of the observations are correctly classified. Most of the misclassified observations are in the north (15 of 20) and are mostly due to 2 factors. First, most of the misclassified north site observations were samples collected in 1997, when the selenium concentrations were relatively uniform throughout the lake. The second set of commonly misclassified data is from site 20 before the large increase in selenium began in May 2001 (Figure 24). Neither of these factors indicate that the inclusion of the data from 2002 have shown that the division of selenium contamination of the Stewart Lake sediments has changed since that earlier data analysis in Yahnke (2001).

The split between the north and south areas of the lake based on the discriminant analysis results occurs at a selenium concentration of 20 ppm. Observations with a selenium concentration of 20 ppm or less are classified as being in the south group, while observations with more than 20 ppm of selenium are classified into the north group. Based on the misclassified observations summarized in Table 16, there are 15 observations from the north with less than 20 ppm of selenium and 5 observations in the south group that have more than 20 ppm.

Figure 26 shows a plot of the geometric mean selenium concentration in the north and south groups of sites over the course of the monitoring period. Figure 26 gives an idea of why the data for 1997 are misclassified, but it also indicates that the data from 1995 should have a large number of misclassified observations as well. Actually, only 3 of the sites in the north group were sampled in 1995, and one of those 3 was misclassified. In addition, 2 of the south sites were misclassified in 1995. Sites 8 and 11 both had selenium concentrations greater than 20 ppm at the time (Figure 24). Neither of these sites has approached 20 ppm of selenium since 1995. Figure 26 also shows that the divergence between the 2 groups of sites coincided with the significant increase in selenium in the sediments that was noted in Table 4. Figure 26 indicates that the overall increase was due to an increase in total selenium in the north group of sites, when the geometric mean selenium concentration increased from less than 10 to over 30 ppm. Table 4 indicated there was also a significant decrease in total selenium in Stewart Lake from 1999 to 2000. Although there was a relatively large decrease in the north between 1998 and 1999, that decrease coincided with an increase in the south. In the 1999 to 2000 data sets, both the north and south show a decrease. The geometric means of both groups have remained relatively constant since the decrease

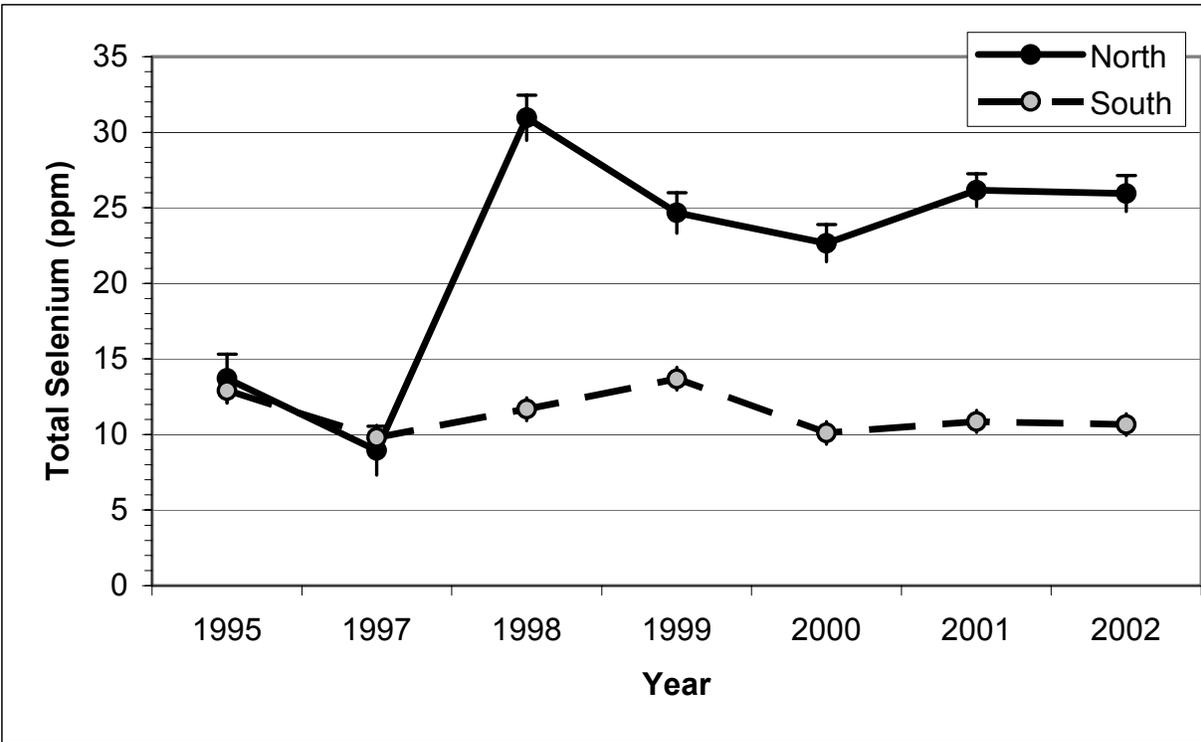


Figure 26: Annual geometric mean total selenium concentrations (USGS laboratory) in Stewart Lake surface sediments at the permanent monitoring sites as defined by the north-south site groupings

in 2000 (Figure 26). The north has had a selenium concentration of around 26 ppm, while the south has had a selenium concentration of about 11 ppm. These values are not greatly different from the overall means for the monitoring period shown in Table 16. In summary, areas in the north of the lake have a total selenium concentration in excess of 20 ppm (average 28 ppm), while areas to the south in the lake have a selenium concentration that is less than 20 ppm (average 12 ppm). The increase in selenium that occurred in Stewart Lake in 1998 was confined to its north end. As was noted in the 2002 sediment report, the initial increase in 1998 was apparently caused by the J2, J3, and J4 drains before they were diverted to the Green River. The seepage has maintained the elevated levels in the north end of the lake since then. However, there has also been no apparent change in total selenium at sites located in the south end of Stewart Lake away from the seepage (Figure 21). The sites in the south end of the lake as defined in the discriminant analysis represent 70 percent (14 of 20) of the sites and greatly affect the overall average selenium concentrations. The total selenium is much greater in the north, but those sites represent only the remaining 30 percent (6 of 20) of the sites. However, there were data for only 3 of the 6 northern sites in 1995, while there were data for 13 of the 14 southern sites. The comparison made in Table 4 indicated that there was no significant change in total selenium in Stewart Lake from 1995 though 2002. This result is biased toward the south sites, because of the missing data overall. Nevertheless, the total selenium concentration in these sites with lower total selenium in the south end of the lake remains well above the selenium cleanup goal of 4 ppm.

Conclusions

The following list of conclusions is drawn from the 2002 data. The conclusions reflect the results of the 2002 data sets collected during the flood experiment and routine monitoring samples. The routine monitoring samples relate to changes in selenium from the last samples from 2001 as well as year-to-year changes since monitoring began in 1995.

- At 5 sites sampled for selenium speciation, elemental selenium was the dominant species at 3 of the sites and selenite was the dominant species at the other 2.
- The most oxidized selenium species, selenate, increased from south to north at Stewart Lake.
- Selenate constituted 25 percent of the selenium at site 15 and less than 5 percent at site 1 near the lake outlet.
- The application of lime caused the reduction of more oxidized species of selenium, selenate and selenite, to elemental selenium.
- Flooding of 2 experimental plots when the ground water table was well below the surface effected a decrease in selenium in the upper 36 inches of Stewart Lake sediments.
- Most of the selenium decrease during the flood experiment occurred in the surface sediments (0-6 inches) where the initial selenium concentration is the greatest.
- Comparison of total selenium concentrations from analyses from laboratories at the University of California at Riverside and the U.S. Geological Survey in Denver show a concentration dependent difference, *i.e.* the difference increases as the selenium concentration increases, with the more vigorous digestion used by the Geological Survey laboratory yielding higher concentrations.
- Selenium samples from the permanent monitoring sites in 2002 showed no change from 2001.
- A statistical analysis of the late season (post-Green River flood or fall) samples from 1995 through 2002 shows that the split between selenium at sites in the north and south persists; selenium is much higher in sediments in the north end of Stewart Lake.
- Sediment selenium in Stewart Lake remains well above the cleanup goal of 4 ppm throughout Stewart Lake.

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