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Monticello Mill Tailings Site Macroinvertebrate Sampling for 2007

A.L. Bunn
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February 2008

Prepared for the U.S. Department of Energy
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Executive Summary

In the spring of 2007, aquatic macroinvertebrates were collected from wetland 3 and the sediment pond associated with the U.S. Department of Energy's (DOE) Monticello Mill Tailings Site (MMTS), located in Monticello, Utah. Past water and sediment samples from the wetlands and sediment pond indicated that the concentration of selenium (Se) exceeded ecological risk guidelines. Results from sampling macroinvertebrates in 2005 indicated that the Se concentration in the macroinvertebrates from wetland 3 and the sediment pond exceeded ecological risk guidelines for Se in macroinvertebrate tissues. These areas were re-sampled in 2006 and 2007 using the same field sampling and analytical procedures as in 2005.

The geometric mean of the Se in macroinvertebrate samples collected with kick nets in wetland 3 and the sediment pond was above the lowest limit of the level of concern for Se but was less than the toxicity threshold, and the results from the two locations were not significantly different. There was no significant difference ($P > 0.05$) between 2005, 2006 and 2007 in the Se concentration in macroinvertebrates collected with kick nets in wetland 3 and the sediment pond.

Another sampling method was used in the sediment pond, Hester-Dendy samplers. While six samplers were deployed, late in the culturing period, the water level dropped in the pond and only two samplers remained below the water level through the time in which the samplers were retrieved. The macroinvertebrates that were collected from the two samplers that were recovered, their sample weights were too low, and had to be composited in order to be analyzed for Se. The Se concentration in the macroinvertebrate tissues from the samplers was within the level of concern for ecological risk, and similar in concentration to the geometric mean of the samples collected using kick nets in the sediment pond.

The three year comparison of Se results in macroinvertebrate tissues does not reveal any trends in the concentrations at the locations with time. While the weather and water conditions have varied each year, the tissue concentrations are not significantly different ($P > 0.05$) at each location with time from 2005 to 2007. While the weather conditions and water levels in the sampling areas at MMTS were different in 2005 compared to 2006 and 2007, there does not appear to be a correlation in the results based on those sampling conditions.

These results do not conclusively indicate that there is a risk to fish and wildlife from Se in the waters at MMTS. The Se concentrations in macroinvertebrate tissues for samples collected in Montezuma Creek in 1995 and 1996 ranged from approximately 7 to 10 mg/kg in (Peterson et al. 2002). The Se concentrations in the tissues from 2007 in wetland 3 have decreased to an average of less than 6 mg/kg. This is an indication that the Se concentration of the environment around MMTS is high. The results of the macroinvertebrate samples along with the results of the bird surveys should be considered by DOE and BTAG in determining if further investigations are warranted.

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1.0 Introduction

In the spring of 2007, aquatic macroinvertebrates were collected from wetland 3 and the sediment pond associated with the U.S. Department of Energy's (DOE) Monticello Mill Tailings Site (MMTS), located in Monticello, Utah. Past water and sediment samples from the wetlands and sediment pond indicated that the concentration of selenium (Se) exceeded ecological risk guidelines (FWS 1999). To satisfy the requirements of the Biomonitoring Plan of the Monticello Mill Tailings Site Operable Unit III Post-Record of Decision Monitoring Plan (DOE 2004), sampling was conducted in the spring of 2005 for macroinvertebrates at three constructed wetlands and a sediment pond associated with the MMTS to determine if Se concentrations exist in media that might impact fish and wildlife (DOE 2004). Results of the 2005 macroinvertebrate sampling indicated that Se concentrations were exceeding the level of concern for fish and wildlife in wetlands 1 and 2 and in the sediment pond, and the Se concentration exceeded the toxicity threshold in wetland 3 (DOE 2005). In the spring of 2006, macroinvertebrate sampling was focused on wetland 3 and the sediment pond. Results of the 2006 macroinvertebrate sampling indicated that Se concentrations were exceeding the level of concern for fish and wildlife in samples collected with kick nets in wetlands 3 and the sediment pond, and the Se concentration exceeded the toxicity threshold in samples from the sediment pond collected with Hester-Dendy samplers (Bunn et al. 2007).

Based on the 2005 sampling effort, sampling for aquatic macroinvertebrates was targeted on the regions that were of greatest concern: wetland 3 and the sediment pond. Activities in the spring of 2007 included deployment of Hester-Dendy samplers in the sediment pond, collection of macroinvertebrates with kick nets in wetland 3 and the sediment pond, and retrieval of the Hester-Dendy samplers for collection of macroinvertebrates. This work was done in accordance with Program Directive MSG 05-03 (Appendix A). Detailed procedures for collection activities are included in Appendix B. All samples were analyzed with hydride generation flow injection atomic absorption spectroscopy (HGAA-FIAS).

1.1 Selenium in the Environment

Inorganic Se occurs naturally in four oxidation states as: selenide (Se^{2-}), elemental selenium (Se^0), selenite (SeO_3^{2-}), and selenate (SeO_4^{2-}). In the -2 oxidation state, Se occurs in the gaseous state as hydrogen selenide, or as insoluble heavy metal selenides in sediment and water. Elemental Se is also insoluble and not subject to rapid redox reactions within the natural environment. Thermodynamic data indicate selenite is the favored oxidation state of Se under mildly oxidizing conditions (Figure 1-1, Geochemist's Workbench, version 6.0). Selenate is highly soluble and the most mobile form of selenium in aqueous systems. Reduction to less mobile forms such as selenite or metal selenides renders it immobile and biologically less available; however, this is strongly dependent upon the pH and redox conditions in the environment.

The complex chemistry of Se lends itself to incorporation into many geologic materials. The concentration of Se has been measured in rocks, soils, fossil fuels, volcanic gas, natural waters, and plant and animal tissues (e.g. Eisler, 1985; McNeal and Balistrieri, 1989). Se is readily abundant within the soils and sediments throughout the earth's crust. Higher Se concentrations are measured in sedimentary rocks associated with clay fractions; the greatest concentration being that of shales, ~500 mg/kg. Phosphate (1-178 mg Se/kg) and coal (1-20 mg Se/kg) formations also contain relatively high concentrations of Se. The concentration of Se in most soils lies within the range of 0.01 to 2 mg/kg.

However, certain regions including the arid Western United States and the Great Plains exhibit highly elevated concentration ranging from 38 to 1200 mg/kg (McNeal and Balistrieri, 1989). The chemical forms of Se in soils are dependent upon the redox potential and pH, but consist of any form previously discussed above (i.e. selenide, elemental, selenite, selenate, and organic selenium).

Natural waters typically have concentrations of Se < 0.01 mg/L. However, waters migrating through arid, alkaline geologic formations characteristic of the Western United States readily leach elevated concentrations of Se. The aqueous availability and mobility of Se is readily illustrated by the example regarding the effect of pH on the concentration of Se in rivers of Colorado (Scott and Voegeli, 1961). When the pH of various Colorado rivers is within the range of 6.1 to 6.9 the concentration of aqueous Se is within that of most natural water, <0.01 mg/L. When the pH of the water is elevated to values ranging between 7.8 and 8.2, the concentration of Se increases to 0.01 to 0.04 mg/L.

Leaching studies of seleniferous geologic media though the San Joaquin Valley have reported up to 4.2 mg/L Se in irrigation waters (Barnes, 1986; Sylvester, 1986; Fujii and Deverel, 1989). Resulting elevated concentrations of selenate in the Kesterson Reservoir create wildlife toxicity issues (Kilness and Simmons, 1986; Ohlendorf, 1989). Entrance into the food chain affords further biological processes that can alter the speciation and form of Se. Inorganic compounds of Se can be converted to volatile organic compounds such as dimethyl selenide or dimethyl diselenide by plants, microorganisms, and animals (Shrift, 1973; Chau et al., 1976).

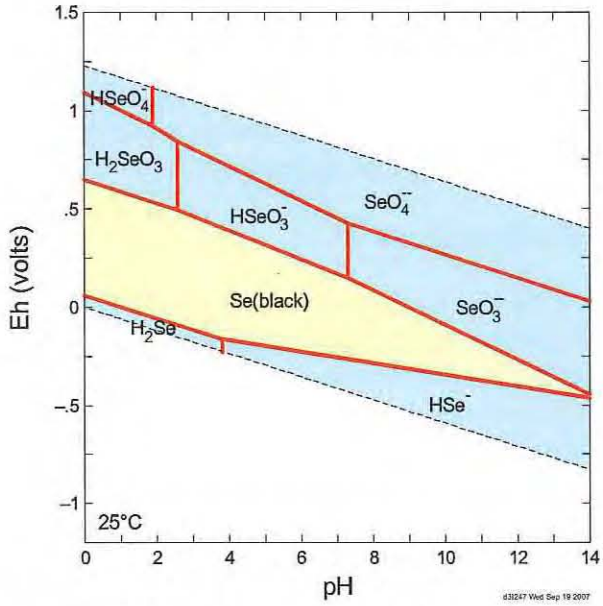


Figure 1-1. Eh-pH diagram for the Se-water system.

1.2 Selenium in the Food Chain

In the aquatic environment, Se has the ability to accumulate in organisms and the aquatic food chain. Reproductive effects have been observed in fish and wildlife (particularly avian species) that ingest macroinvertebrates with high concentrations of Se in their tissues. Guidelines for the dietary threshold for Se are based upon Se residues in macroinvertebrates. The no-effects level is 3 mg/kg Se dry weight, and

the toxic effects level is 7 mg/kg Se dry weight (Maier and Knight 1994; Lemly 1993 and 1996; Hamilton and Lemly 1999; Beckon et al. 1999; FWS 2004). Past monitoring activities within Montezuma Creek at MMTS found levels of Se in macroinvertebrates that ranged from approximately 7 to 10 mg/kg in 1995 and 1996 (Peterson et al. 2002). The ecological risk guidelines were considered when setting the benchmarks for surface water, sediment, and macroinvertebrates in the monitoring plan for MMTS (DOE 2004). Table 1-1 summarizes the ecological risk guidelines for animal tissues, water and sediment.

The Biomonitoring Plan states that if analyses of macroinvertebrate samples result in concentrations that exceed 7 mg/kg dry weight, then follow-on work should continue to determine if food chain effects are occurring (DOE 2004). The macroinvertebrate sampling has been included with the on-going surface water and sediment sampling (Program Directive MSG-04-01) as well as wildlife surveys (Program Directive MSG 05-01) from 2005 through 2007. The results of the aquatic macroinvertebrate samples were compared to the benchmarks for Se effects. These results from 2007 will be discussed by the Biological Technical Assistance Group for MMTS, and, in consultation with DOE, they will determine if macroinvertebrate sampling should continue and if other food chain effects should be monitored for evidence of Se toxicity (DOE 2004).

Table 1-1. Recommended Ecological Risk Guidelines based upon Se Residuals for Water and Sediment

Matrix	Units	No Effect*	Level of Concern*	Toxicity Thresholds*
Animal food chain (invertebrates)**	mg/kg (dry weight)	< 3	3-7	> 7
Water (total recoverable Se)	µg/L	< 2	2-5	> 5
Sediment	mg/kg (dry weight)	< 2	2-4	> 4

*Based on DOE 2004 and FWS 1999.

** The animal food chain guideline refers to hazards to birds.

1.3 Report Organization

This report summarizes the results of the 2007 macroinvertebrate sampling effort. Section 2 summarizes field sampling activities, and Section 3 discusses the analysis of Se in the macroinvertebrates tissue samples and the quality control/quality assurance issues. Section 4 summarizes Se results in comparison to ecological risk guidelines, other sampling efforts and comparison to past years sampling efforts. Section 5 includes recommendations for future activities.

2.0 Field Sampling Activities

Based on input from the Biological Technical Assistance Group, the macroinvertebrate sampling for 2007 was focused on wetland 3 and the sediment pond. Field sampling procedures were conducted in accordance with Program Directive MSG 05-03 (Appendix A). Detailed procedures were prepared from the program directive in 2005 and were updated for the reduced sampling effort in 2006 and 2007 (Appendix B).

2.1 Kick Net Sampling

Kick net collections of macroinvertebrates were conducted on May 23 and 24, 2007 in wetland 3 and the sediment pond (Figure 2-1). This method of sampling macroinvertebrates has been used in the past at MMTS (Peterson et al. 2002) and was specified in the program directive. Kick nets are a preferred method for collecting macroinvertebrates in areas where the emergent vegetation is dense and the water is shallow (Barbour et al. 1999).

The areas that were sampled with kick nets in wetland 3 and the sediment pond were dependent on the water level. In wetland 3, the inlet area was not sampled because there were only small regions of open water ($\leq$ 5 cm (2 in) in depth), and no macroinvertebrates were found in these regions. The middle region of wetland 3 (below the discharge point of "Seep 2") had water ranging in depth from 5-15 cm (2-6 in), and macroinvertebrates were collected around the emergent vegetation. The water level in the outlet area was 5-46 cm (2-18 in), and macroinvertebrates were collected around the emergent vegetation. The water level in the sediment pond was adequate for collecting macroinvertebrates at the inlet, west side and outlet areas. Sampling conditions are summarized in Table 2-1.

Two samples were collected from wetland 3 and four samples were collected from the sediment pond using kick nets. The weights of these samples in the field ranged from 2 to 20 g. After collection in the field, the samples were shipped to Richland, WA, where the composition of the macroinvertebrates was evaluated and the samples prepared for analysis in Sequim, WA. Table 2-2 summarizes the macroinvertebrate composition of the samples that were prepared for laboratory analysis in accordance with Program Directive MSG 05-03 (Appendix A). This included splitting samples (quality control) and removal of large macroinvertebrates (minimizing sample bias) from one sample collected in the inlet area of the sediment pond. The final wet weights of the samples were less than those recorded in the field because water around the macroinvertebrates was absorbed by filter paper used during observation of the composition of the organisms in the sample (see Figure 2-1 B). The process of recording the composition of the macroinvertebrates and splitting the samples in Richland, WA, during 2007 was similar to the process in 2005 and 2006 while in the field.

In wetland 3, the composition of the macroinvertebrates varied between the middle and outlet areas. Gastropods (snails) were predominant in the middle area, while *Coleoptera* (beetles) were predominant in the outlet area. The remainder of the samples consisted of *Odonata* (dragonflies and damselflies) and amphipods. In 2006, the composition of macroinvertebrates in wetland 3 was dominated by *Odonata* (dragonflies and damselflies) and four other orders of macroinvertebrates. Appendix C provides more information about the habitat, feeding styles and diets of the classes of macroinvertebrates found during the 2005 through 2007 sampling effort.

The sediment pond had greater diversity of macroinvertebrates than in wetland 3. The macroinvertebrate composition at the inlet and west side was dominated by *Odonata*, while the outlet was dominated by *Coleoptera* and *Dytisidae*. The diversity of organisms in the sediment pond in 2007 was similar to that found in past years.

Figure 2-1. Sampling for Macroinvertebrates with Kick Net in Wetland 3 (A) and Examples of Macroinvertebrate Species Found in Past Years (B)

Table 2-1. Summary of 2007 Field Sampling Activities by Location and Date

Field Sampling Activity by Location	Dates	Conditions and Comments
Deployed Hester-Dendy samplers at sediment pond	Week of April 16, 2007	Six samplers were deployed in the sediment pond, and positioned upright on a stake with the lower plate just at the substrate level.
Collected at wetland 3 using kick nets	May 24, 2007	Weather: Partly cloudy and cool. Samples collected 0830-1100. Water temperature = 10°C (50°F); dissolved oxygen = 5.8 mg/L in middle area, 12 mg/L at outlet "channel"; and pH = 6-7 Comment: Inlet not sampled because low water level did not allow for use of the kick net. Several small areas were located with water levels of ~ 5 cm (2 in), but no macroinvertebrates were found in the samples. Middle area sampled below the discharge point of "Seep 2", in areas with emergent vegetation (patches of cattails interspersed with patches of sedges). Water depths = 5-15 cm (2-6 in). Outlet area sampled at outlet "channel" in the sediment/water interface, along areas with moderately dense emergent vegetation (primarily cattails, sedges, and rushes). Water depths = 5-46 cm (2-18 in).
Collected at sediment pond using kick nets	May 23, 2007	Weather: Cloudy and cool. Samples collected 1600-1919. Water temperature = 13°C (55°F); dissolved oxygen = 15.3 mg/L in inlet area; and pH = 6-7. Comment: Inlet area sampled near shore in sediment/water interface in and between patches of emergent vegetation and around outside of Hester-Dendy samplers. Middle area (west side of pond) sampled near the shore in the sediment/water interface in and between patches of emergent vegetation. Outlet area sampled near shore in the sediment/water interface. Water level was below the level of most shoreline vegetation. Areas with vegetation, though sparse, were sampled as well as areas of algae and debris along the shore. A crayfish was collected along with other macroinvertebrates at inlet area. Checked all six Hester-Dendy samplers and found little to no colonization (but crayfish were present at nearly all samplers indicating that macroinvertebrates were in vicinity). Samplers were re-deployed in the same locations. Original deployment of the Hester-Dendy samplers was done with the surfaces of the samplers parallel to the water's surface. The samplers were re-deployed with the surfaces of the sampler's plates perpendicular to the water's surface.
Retrieved Hester-Dendy samplers at sediment pond	June 26, 2007	Two Hester-Dendy samplers were retrieved from north end near the inlet (based on procedure in Appendix B), and samplers were shipped, in-tact, to Richland, WA. Four Hester-Dendy samplers were exposed when water level dropped 61 cm (24 in) during the week of June 18. Macroinvertebrates were collected from samplers on June 28.

2.2 Hester-Dendy Artificial Substrate Sampling

The Hester-Dendy artificial substrate samplers (14 plates, 7.6 cm square) were deployed in the sediment pond during the week of April 16, 2007 (Table 2-1). Six samplers were deployed to try and collect more sample mass than was collected in 2005 and 2006. A different deployment method was used for the first six weeks. The samplers were fastened to a stake with their plates parallel to the water surface initially. In May, during kick net sampling, the Hester-Dendy samplers were examined and very little colonization of macroinvertebrates was observed. The samplers were re-fastened to the stakes, but the plates were oriented perpendicular to the water's surface (as was done in 2005 and 2006).

During June 2007, the water level in the sediment pond started dropping. The samplers were under water during the week of June 18, and it was thought that there was enough water going into the pond to keep the samplers in place for another week. However, the water level in the pond dropped 2 ft prior to collection on June 26, and four of the six samplers were above the water line. The two samplers that were still under water were collected from the inlet area and then were shipped to Richland, WA.

There was not enough sample weight from the macroinvertebrates collected off each Hester-Dendy samplers for analysis of Se, and the organisms had to be consolidated into one sample (Table 2-2). Chironomid larvae were the predominant colonizers of the sampler. The diversity of the macroinvertebrates on the samplers was similar to that found in past years.

Table 2-2. Results of Se Analyses in Macroinvertebrate Samples Collected in May 2007

Location, Sample Collection Technique	Sample	Sample Weight (g wet wt)	Se (mg/kg dry wt)	Geometric Mean (Geometric Standard Deviation) Se (mg/kg dry wt)	Sample Composition (based on % of total mass of sample)
Wetland 3, Kick Net	R3(outlet)	3.0	3.91	6.31 (2.78)	Coleoptera (A) (60%), Odonata (20%), Amphipoda (10%), Gastropoda (10%)
	R2/1(middle)	1.75	9.46		Odonata (L) (40%), Coleoptera (A) (40%), Amphipoda (10%), Gastropoda (10%)
	R2/2(middle)	2.21	6.80		Gastropoda (75%), Coleoptera (A) (20%), Amphipoda (5%)
Sediment Pond, Kick Net	R1(inlet)	0.52	5.10	6.26 (2.33)	Crayfish (50%), Odonata (50%)
	R1(inlet)	7.044	6.15		Odonata (50%), Coleoptera (30%), Gastropoda (10%), Ephemeroptera (10%), Hemiptera (5%)
	R2/1(west)	4.155	8.02		Odonata (75%), Coleoptera (10%), Amphipoda (10%), Notenectidae (5%)
	R2/2(west)	4.683	8.78		Odonata (75%), Coleoptera (10%), Amphipoda (10%), Notenectidae (5%)
	R3(outlet)	10.735	3.55		Coleoptera/Dytisidae (A) (40%), Odonata (40%), Hemiptera (10%), Gastropoda (10%)
Sediment Pond, Hester-Dendy	Consolidated (inlet)	1.75	5.82	---	Chironomidae (70%), Coleoptera (L) (10%), Gastropoda (10%), Oligochaeta (5%), Odonata (3%), leech (2%).

NOTES: Sample composition information followed by an "L" are larval life stages and an "A" are adult life stages. "I" designates "inlet," "W" designates "west," and "O" designated "outlet."

3.0 Analysis of Macroinvertebrates Tissue Samples

The procedures for quantifying total Se in macroinvertebrate samples were in accordance with Program Directive MSG 05-03 (Appendix A). Analyses were conducted at Battelle's Marine Science Laboratory (MSL) in Sequim, WA. The Se results of the field samples and quality assurance /quality control narratives are in Appendix D.

All macroinvertebrate tissue samples and field blanks were received at MSL in good condition (i.e. containers were not damaged and the cooler temperature was within the range of 4 ± 2 °C). The kick net samples were stored at -70 °C until the samples recovered from the Hester-Dendy samplers were available. Both kick net and Hester-Dendy samples were processed as one quality control batch on July 19, 2007 along with several types of quality control measures. The data for are summarized in Table 2-2.

The individual macroinvertebrates from the kick net samples were removed from their field sampling jars, and the tissues were freeze-dried and homogenized to determine percent dry weight prior to being analyzed for total Se. The macroinvertebrates removed from the Hester-Dendy samplers were freeze dried in their field sampling jars directly due to the small sample size, and then the tissues were further processed in the same manner as the kick net samples. The homogenized samples were digested using nitric and hydrochloric acids (aqua regia) in a sealed Teflon vessel by heating in an oven at 130°C (±10°C) for a minimum of eight hours. Digested samples were analyzed for Se using hydride generation flow injection atomic absorption spectroscopy (HGAA-FIAS) according to Battelle SOP MSL-I-030, Determination of Metals in Aqueous and Digestate Samples by HGAA-FIAS. The base method for this procedure is EPA Method 270.3 and Standard Method 3114 B (EPA 1982; APHA 1998). All results were determined and reported in units of mg/kg on a dry weight basis.

A field blank and preservation blank were collected as part of the quality control plan as stated in the program directive. The field blank was prepared while collecting kick net samples and the ethanol blank was collected from the lot of ethanol used to preserve the samples during the identification process. The blanks were analyzed using the same methods as the tissue samples; with the exception of the ethanol. Due to the volatility of the ethanol and possible interferences during the hydride generation step, the ethanol blank was diluted at a ratio of 1:10 with deionized water prior to pre-reduction and analysis. The results of the field blank and the method blank were determined and reported in units of µg/L.

In addition to field blanks, one field duplicate was also collected to evaluate invertebrate sample variability and one laboratory duplicate was prepared to evaluate analytical precision. A laboratory duplicate was defined as the splitting of a field sample in the laboratory, following homogenization, into two independent samples processed as unique samples. The field duplicate was collected on the west side of the sediment pond using kick nets (Table 2-2, R2/1 and R2/2, sample jar NFS-765). The laboratory duplicate was performed on the sample collected at the inlet of the sediment pond (Table 2-2, R1, sample jar NFJ-764) after the crayfish and large dragonfly nymph were removed. The duplicate and the split samples were analyzed in the analytical batch with all the other macroinvertebrate samples and the results are summarized in Table 2-2.

The data quality criteria for the analysis of Se include the method detection limit (MDL) and the reporting limit (RL). The reporting limit was determined as 3.18 times the MDL. For the macroinvertebrate tissues, the HGAA-FIAS analysis had an MDL of 0.0109 mg/kg dry weight and an RL of 0.035 mg/kg dry weight. For the field blanks, the HGAA-FIAS analysis had an MDL of 0.0507 µg/L and an RL of 0.16

μg/L. The MDL values are determined annually and were slightly lower than the MDLs for the 2005 and 2006 sampling events. Note that the MDL was well below the guidelines for evaluating ecological risk from Se in macroinvertebrate tissues (Table 1-1).

The laboratory quality control measures analyzed with the invertebrate and field blank samples included three method blanks, a matrix spike, a laboratory duplicate, and two laboratory control samples (standard reference materials [SRM]), as discussed in the program directive. The only variation from the program directive was the insufficient sample mass available to generate a matrix spike duplicate. There was no impact to the quality of the data as precision was determined by the laboratory and field duplicates. Three method blanks were used to determine if there was contamination associated with the laboratory storage of the invertebrate samples, preparation, and/or instrumentation. All three of the method blanks for the invertebrate tissues analyzed on July 30, 2007 were less than the RL and the average concentration was 0.0094 mg/kg, which is less than the MDL.

The matrix spike (MS) was used to determine if there was any interference in the spike matrix and as a measure of the accuracy of the analysis. Samples collected in 2005 and 2006 did not show any matrix interferences in the MS or duplicate MS samples and had good accuracy (recoveries ranging from 102% to 109%). In the 2007 sampling, the kick net sample collected from the sediment pond R3 (outlet) had sufficient sample mass to allow only one matrix spike. The matrix spike recovery for the SP-R3 sample was 127% and just outside of the quality control requirements of 75-125% recovery. The high recovery resulted from the insufficient spiking level relative to the native sample concentration. The native sample concentration was 3.55 mg/kg and the spike was 5.05 mg/kg. The entire sample was exhausted during the first analysis and reanalysis of the sample was not a viable option. However, the historical data shows no propensity for interferences with this matrix and the analytical accuracy was evaluated by the analysis of two solid matrix SRMs certified for Se and two independent lots of liquid Se certified standards. The analytical precision was evaluated by laboratory duplicates with a relative percent difference (RPD) of 2%, which was within the quality control requirement of <20% RPD.

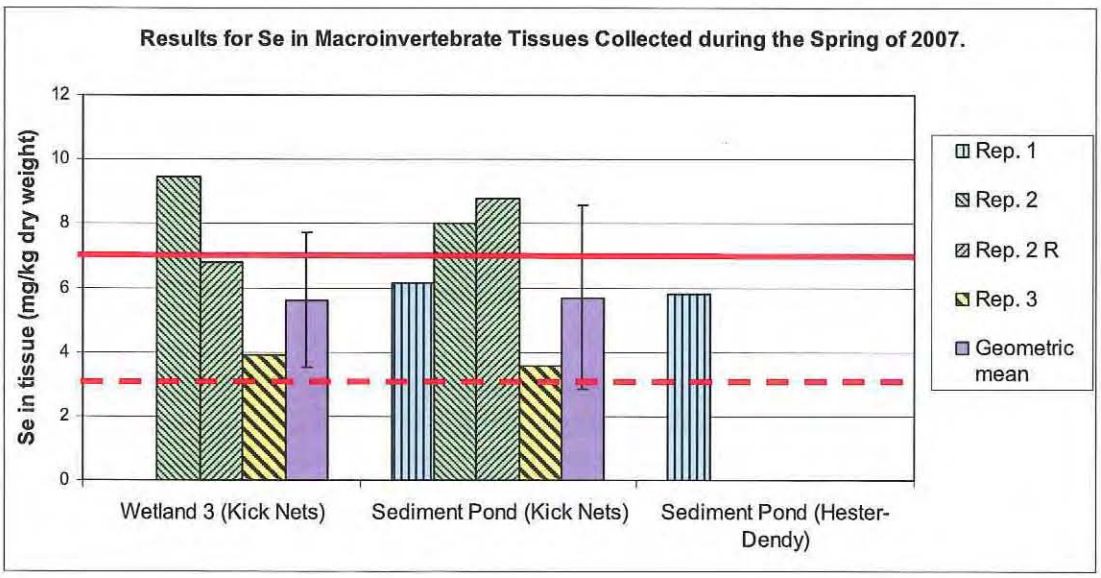
The two SRMs verified the analytical accuracy for both the digestion and analysis processes. There are no commercially available SRMs for invertebrate tissue. The two SRMs analyzed with the invertebrate samples were 1566b Oyster Tissue (95% recovery) and IAEA140 *Fucus* (102% recovery). In addition to SRMs, a laboratory control sample (LCS) or blank spike was also prepared and analyzed with the invertebrate samples. The percent recovery for the LCS sample was 100% and both the LCS and SRMs provided sound evidence of excellent analytical accuracy. Thus, the average percent recovery for this data set is 99%, resulting in an average error of only 1%. The measures of accuracy were all within the quality control criterion of 80-120% recovery.

4.0 Discussion of 2007 Macroinvertebrate Results

The purpose of biomonitoring at MMTS has been to determine if Se concentrations in the environment exceed levels that might impact fish and wildlife (DOE 2004). The recommended ecological risk guidelines for Se in macroinvertebrates, water, and sediment are listed in Table 1-1. The risk guidelines include a threshold for no effect, a range indicating a level of concern and a threshold concentration that is considered toxic to fish and wildlife that consume the macroinvertebrates.

For this discussion, the Se concentrations in macroinvertebrate tissues are presented as individual results and summarized by sample method at a location using the geometric mean (error bars represent two geometric standard deviations). The geometric mean, rather than using the arithmetic mean, was used because the Se results are similar to other environmental contamination data in that the sample results are log normally distributed. In these cases, the geometric mean is a more accurate representation of the central tendency of data with a lognormal distribution (Gilbert 1987). The geometric mean was calculated for replicates with more than one analysis, and then the geometric mean of that replicate was used in calculation of the overall geometric mean of all the replicate samples.

Figure 4-1 illustrates the Se results of the macroinvertebrate tissues collected in the spring of 2007 and summarized in Table 2-2. Samples were only collected using kick nets in wetland 3. The results for the sediment pond are shown separately for the kick net and Hester-Dendy samples. Lines on Figure 4-1 indicate the ecological risk guidelines for Se residues in macroinvertebrates.



NOTE: Geometric means are shown with error bars representing two geometric standard deviations. Lines indicate ecological risk guidelines for Se residues in macroinvertebrates: level of concern = 3-7 mg/kg dry weight Se; and toxicity threshold >7 mg/kg dry weight Se.

Figure 4-1. Analytical Results for Se in Macroinvertebrate Tissues Collected during the Spring of 2007, with Comparison to Ecological Risk Guidelines for Se Residues

In 2007, wetland 3 continued to be sampled only with kick nets. No sample was recovered in the inlet area (Table 2-1). The sample from the middle area was split upon sample receipt as a measure of quality control. The results from the middle and the outlet area are above 3 mg/kg Se in the macroinvertebrate tissues, the level of concern for ecological risk to fish and wildlife (Table 1-1). Only one of the split samples from the middle of wetland 3 near "Seep 2" had a concentration in the macroinvertebrate tissues that exceeded the 7 mg/kg Se toxicity threshold for ecological risk to fish and wildlife. The geometric mean for all the samples in wetland 3 is within the level of concern for Se in macroinvertebrate tissues.

All the samples collected from the sediment pond with kick nets had Se concentrations in the macroinvertebrate tissues that exceeded the level of concern for ecological risk. Not shown in Figure 4-1, but reported in Table 2-2, are the results of the analysis of the large crayfish and dragonfly nymph that were removed from the sediment pond inlet sample during macroinvertebrate composition characterization. These individuals were removed in order to limit sample bias and in accordance with the sampling procedures (Appendix B). As shown in Table 2-2, the crayfish/nymph sample had a concentration of 5.10 mg/kg Se compared to the macroinvertebrates mixture sample that had a concentration of 6.15 mg/kg Se. Both samples exceed the level of concern for Se in macroinvertebrate tissues. The kick net sample collected from the west side of the sediment pond exceeded the toxicity limit for ecological risk. This sample was the field duplicate, and was split in the field and analyzed as two samples. The results of the field duplicate samples are similar, which indicates that the macroinvertebrates on the west side were consistently exposed to the highest level of available Se during 2007. The sediment pond outlet sample has the lowest Se concentration in the macroinvertebrate tissues collected during 2007, which is similar to the Se concentration in the wetland 3 outlet. The geometric mean for all the samples in the sediment pond are within the level of concern for Se in macroinvertebrate tissues.

The composite sample collected from two Hester-Dendy samplers in the sediment pond also exceeded the level of concern for ecological risk. The types of macroinvertebrate samples colonizing the Hester-Dendy samplers typically represent organisms that are associated with burrowing in the sediment. While the mass of the tissues collected with the samplers continued to be low for the third year in a row, the composition of the macroinvertebrates is different in the samplers compared to the kick net samples. Characterization of the Se tissue concentrations within the sediment pond is more complete using the two types of sampling techniques.

Figure 4-2 is a comparison of the macroinvertebrate sampling results from 2005 through 2007 by location and sampling method. As illustrated by the overlap in the error bars for the geometric means of the macroinvertebrate tissue Se concentration in Figure 4-2, the samples collected with kick nets in wetland 3 (A) and the sediment pond (B) are not significantly different ($P > 0.05$) from 2005 through 2007. This is based on the comparison of the standard deviations for the respective samples by location.

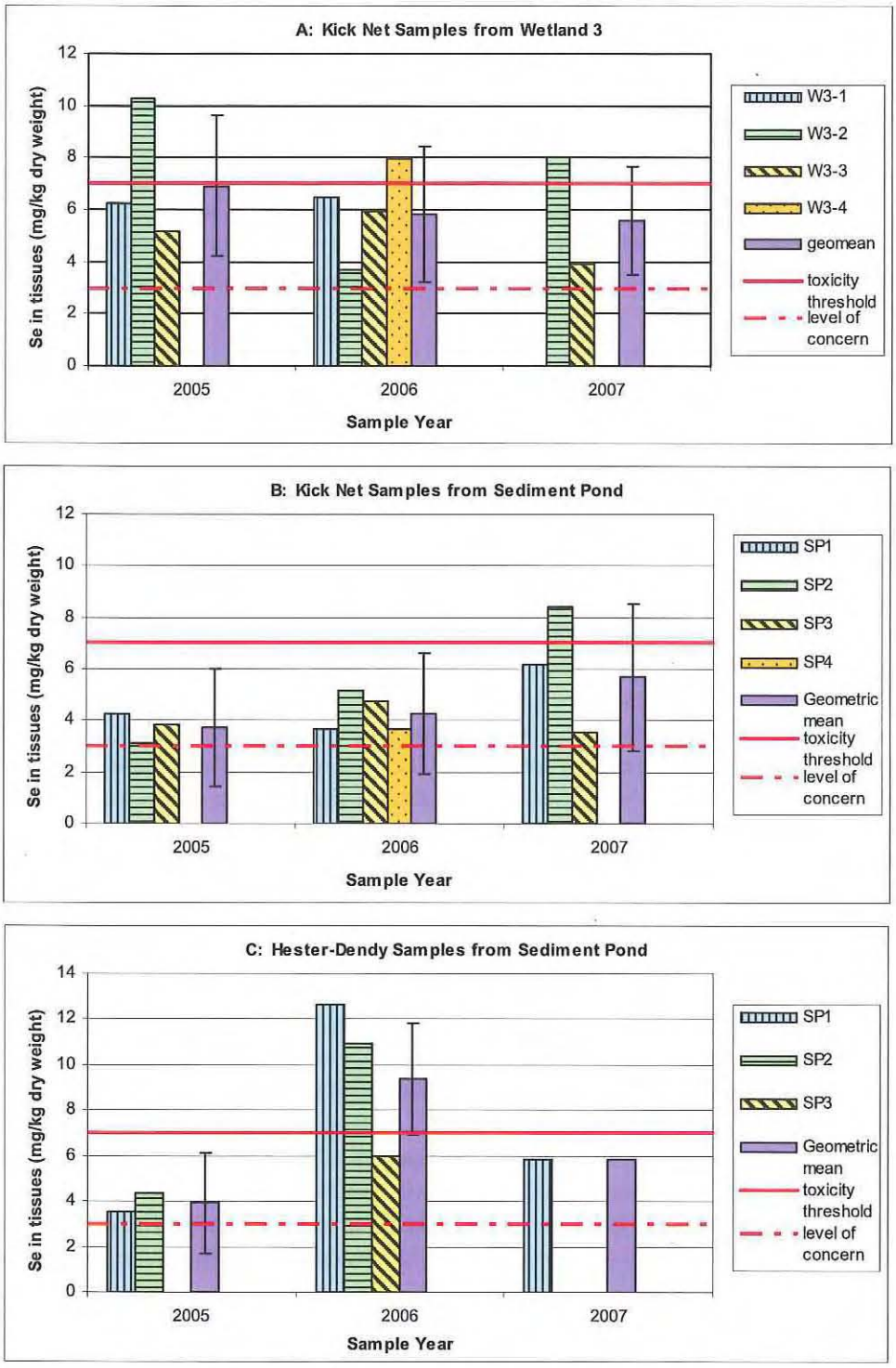


Figure 4-2. Comparison of Se Concentrations in Macroinvertebrate Tissues Collected from 2005-2007 by Location

Since only one sample from the sediment pond using the Hester-Dendy samplers was collected in 2007 (Figure 4-2, C), it is difficult to interpret if the Se concentration in those macroinvertebrates is trending with time. However, the results over time do indicate that the Se in the tissues remains to be within the level of concern for ecological risk.

Weather and water levels at MMTS have been different during the three years of sampling for macroinvertebrates. Conditions have ranged from excessive precipitation and run off in 2005 to diminished water levels in 2006 and again in 2007. The comparison of Se in macroinvertebrate tissues from the last three years does not indicate that the Se concentrations are influenced by weather and water levels.

Biomonitoring at MMTS also includes sampling the water and sediment from each wetland and the sediment pond. A comparison of these results to the macroinvertebrate results is provided to examine if the environmental media can be used as an indicator of ecological risk in the area. The ecological risk guidelines for water and sediment are different from the values for macroinvertebrate tissues (Table 1-1).

Figure 4-3 shows the Se results from unfiltered water samples from October 2004 through April 2007 collected at three established locations in wetlands 1, 2, and 3 as well as in the sediment pond. Unfiltered water samples are shown because the water best represents the exposure to the macroinvertebrates. While some water samples from wetland 1 in October 2004 and April 2005 exceeded the level of concern for ecological risk, the Se concentration has remained below the level of concern consistently since October 2005. Wetland 2 water samples have been below the level of concern for Se throughout the sampling period. Wetland 3 water samples from S1 continue to be above the level of concern, and in April 2007 the Se concentration exceeded the toxicity threshold. The Se results in sediment pond water have remained within the water quality level of concern for the last six sampling events, and while there appeared to be an upward trend in the Se concentration with time, the April 2007 results are similar to the October 2006 results. Overall, the water results support the decisions for sampling macroinvertebrates in wetland 3 and the sediment pond since 2005.

Figure 4-4 shows the Se results from sediment samples from October 2004 through April 2007 collected at three established locations in wetlands 1, 2, and 3 as well as in the sediment pond. In wetlands 1 and 2, the Se concentration in the sediment samples has always been below the level of concern for ecological risk. In wetland 3 and the sediment pond, the Se concentration in the sediment samples has exceeded the level of concern for ecological risk for some samples from 2004 through 2007. The variability of the samples during each sampling event is high in wetland 3 and the sediment pond, which may be related to the sediment loading into the area from the water shed as well as the high biological activity. The trend of the geometric means of the sediment samples from wetland 3 indicates that overall the Se concentration in the sediment is below the level of concern for ecological risk. The geometric means of the sediment samples from the sediment pond shows a downward trend to below the level of concern for ecological risk.

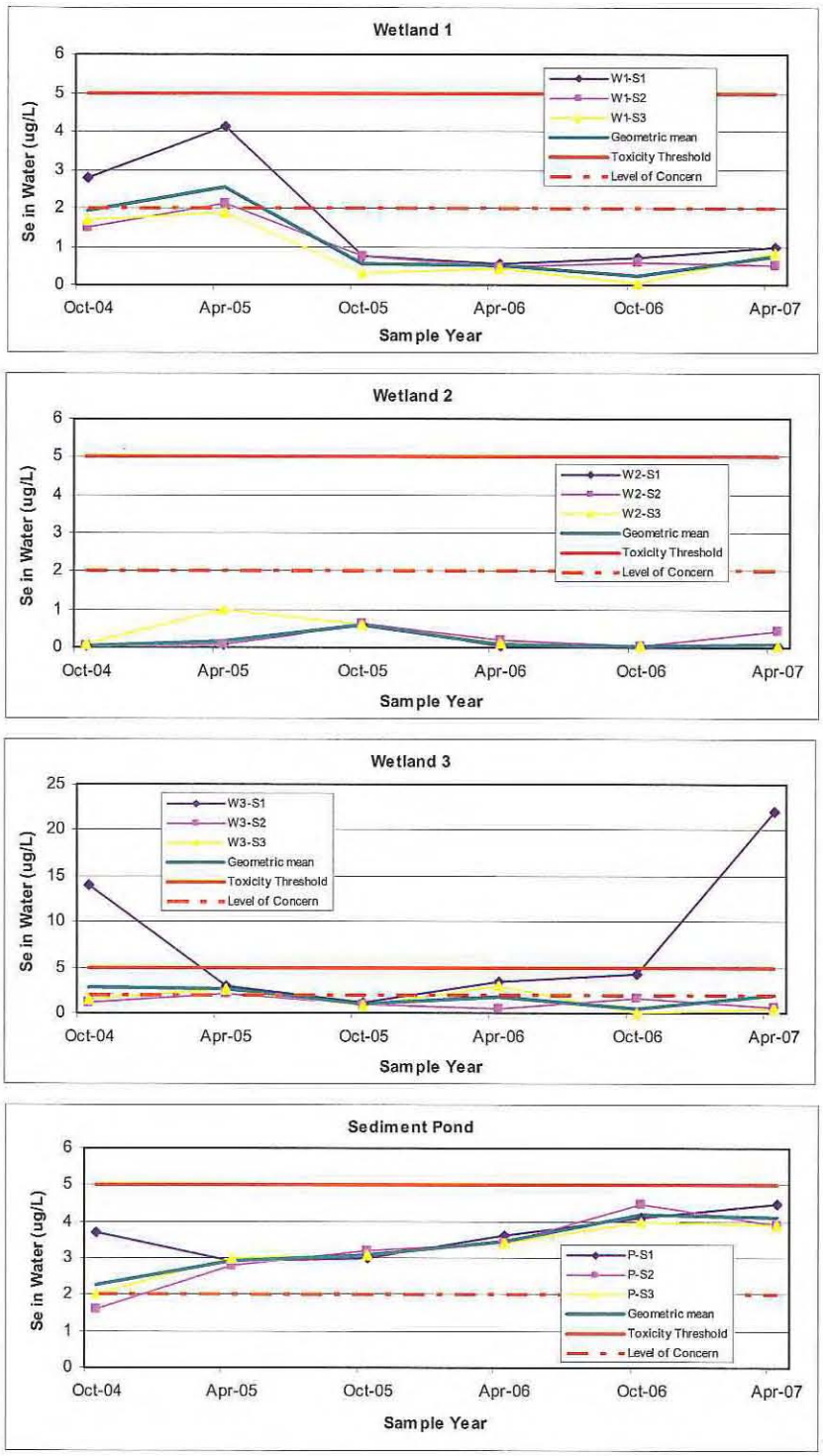


Figure 4-3. Water Sample Se Results Collected from October 2004 through April 2007 by Location

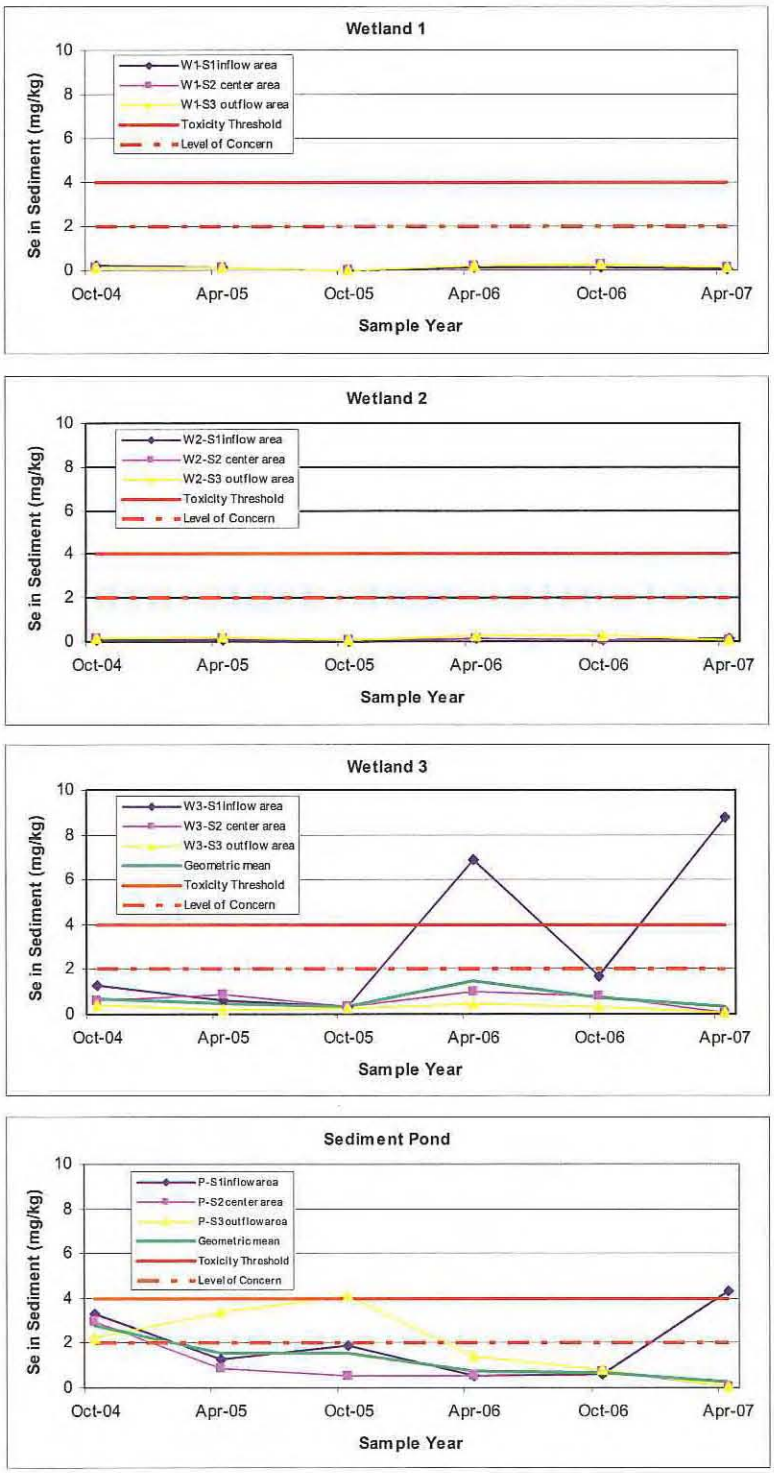


Figure 4-4. Sediment Sample Se Results Collected from October 2004 through April 2007 by Location

The large variability in the Se results from the water and sediment samples during some of the sampling events over the last few years makes it difficult to make a conclusion about the Se concentration in the environment and the Se concentration found in the macroinvertebrate tissues. Such variability is not uncommon with unfiltered water samples and with sediment samples from a pond or wetland, which have a lot of biological activity. In comparing the Se concentrations of the macroinvertebrate samples to the water and sediment samples, it appears that the water samples may be a better indicator of higher Se levels in macroinvertebrates compared to sediment samples. This may be due to the fact that the types of macroinvertebrates that were collected by the kick nets were generally organisms living in the water column or on the surfaces of submerged material rather than living in the sediment itself. Water and surface sediment concentrations represent only short periods of time with this ecosystem, are subject to loss processes, and do not account for the potential bioaccumulation of Se within the organisms. Therefore, using the Se concentration in the water and sediment to predict the Se concentration in macroinvertebrate tissues is not recommended at this time.

5.0 Recommendation for Future Activities

The MMTS macroinvertebrate sampling program was designed to test different methods for collecting the organisms for analysis of Se concentration in their tissues. Two different collection techniques were used in the sediment pond: kick nets and Hester-Dendy samplers. A sufficient mass of macroinvertebrates for analysis of Se was collected using kick nets. However, for the third year in a row, the Hester-Dendy samplers were not able to collect the desired mass for analysis of Se. In 2005, the yield of macroinvertebrates was low because the high run-off buried the samplers in sediment. In 2006, the samplers were collected after a major emergence of Trichoptera (caddisfly) larvae. In 2007, only two samplers out of six remained below the water at the time of sampling, and the mass was insufficient for multiple analyses. The results from the kick net samples and the Hester-Dendy samplers in the sediment pond indicate that the two methods are likely sampling different macroinvertebrate populations based on the composition of the communities collected. Both of these populations are likely to be grazed by predators, and, therefore, both populations are important to monitor for potential impacts to higher food chain organisms. While the effort to add more Hester-Dendy samplers to the sediment pond during 2007 did not result in greater recovery of macroinvertebrates, future sampling efforts should consider both types of sampling techniques to assess the breadth of macroinvertebrate communities and to ensure that enough sample material is available for evaluating the Se concentrations.

The three year comparison of Se results in macroinvertebrate tissues does not reveal any trends in the concentrations at the locations with time. While the weather and water conditions have varied each year, the tissue concentrations are not significantly different ($P > 0.05$) at each location with time from 2005 to 2007. While the weather conditions and water levels in the sampling areas at MMTS were different in 2005 compared to 2006 and 2007, there does not appear to be a correlation in the results based on those sampling conditions.

These results do not conclusively indicate that there is a risk to fish and wildlife from Se in the waters at MMTS. The Se concentrations in macroinvertebrate tissues for samples collected in Montezuma Creek in 1995 and 1996 ranged from approximately 7 to 10 mg/kg in (Peterson et al. 2002). The Se concentrations in the tissues from 2007 in wetland 3 have decreased to an average of less than 6 mg/kg. This is an indication that the Se concentration of the environment around MMTS is high. The results of the macroinvertebrate samples along with the results of the bird surveys should be considered by DOE and BTAG in determining if further investigations are warranted.

6.0 References

American Public Health Association (APHA). 1998. *Standard Methods for the Examination of Water and Wastewater*. 20th edition. L.S. Clesceri, A.E. Greenberg, and A.D. Eaton, eds. American Public Health Association, Washington, DC.

Barbour, M.T., J. Gerritsen, B.D. Snyder, and J.B. Stribling. 1999. *Rapid Bioassessment Protocols for Use in Streams and Wadeable Rivers: Periphyton, Benthic Macroinvertebrates and Fish*. 2nd edition. EPA 841-B-99-002, U.S. Environmental Protection Agency, Office of Water, Washington, D.C. Available at (last accessed February 23, 2007): http://www.epa.gov/owow/monitoring/rbp/download.html

Barnes, I. 1986. Sources of Selenium. In *Selenium and Agricultural Drainage: Implications for San Francisco Bay and the California Environment*. Proceedings of the Second Selenium Symposium, Berkeley, CA. 23 March 1985. The Bay Institute of San Francisco, Tiburon, CA.

Beckon, W.N., J.D. Henderson, T.C. Maurer, and S.E. Schwarzbach. 1999. *Biological Effects of the Reopening of the San Luis Drain (Grasslands Bypass Project) to Carry Subsurface Irrigation Drainwater*. Draft. U.S. Fish and Wildlife Service, Region 8, Division of Environmental Contaminants, Sacramento, CA. Available at (last accessed February 23, 2007): http://pacific.fws.gov/ecoservices/envicon/pim/reports/Sacramento/sanluirp.pdf

Bunn, A.L., R.P. Mueller, C.A. Duberstein, and J.M. Brandenberger. 2007. Monticello Mill Tailings Site Macroinvertebrate Sampling for 2006. PNWD-3802, Pacific Northwest National Laboratory, Richland, WA.

Chau, Y.K., P.T.S. Wong, B.A. Silverberg, P.L. Luxon, and G.A. Bengert. 1976. Methylation of Selenium in the Aquatic Environment. *Science* (Washington, D.C.) 192:1130-1131.

Eisler, R. 1985. Selenium Hazards to Fish, Wildlife, and Invertabrates: A Synoptic Review. U.S. Fish and Wildlife Service. *Biological Report* 85(1.5). U.S. Government Printing Office, Washington, D.C.

Fujii, R., and S.J. Deverel. 1989. Mobility and Distribution of Selenium and Salinity in Groundwater and Soil of Drained Agricultural Fields, Western San Joaquin Valley of California. In L.W. Jacobs (ed.), *Selenium in Agriculture and the Environment*. Soil Science Society of America and American Society of Agronomy, Madison, WI.

Gilbert, R.O. 1987. *Statistical Methods for Environmental Pollution Monitoring*. John Wiley & Sons Inc., New York, NY.

Hamilton, S.J., and A.D. Lemly, 1999. Commentary: Water-Sediment Controversy in Setting Environmental Standards for Selenium, *Ecotoxicology and Environmental Safety* 44:227-235.

Johnson, T.M. 2004. A review of mass-dependent fractionation of selenium isotopes and implications for other heavy stable isotopes. *Chemical Geology* 204:201-214.

Kilness, A.W., and J.L. Simmons. 1986. Toxic Effects of Selenium on Wildlife Species and Other Organisms. In *Selenium and Agricultural Drainage: Implications for San Francisco Bay and the California Environment*. Proceedings of the Second Selenium Symposium, Berkeley, CA. 23 March 1985. The Bay Institute of San Francisco, Tiburon, CA.

Lemly, A.D. 1993. Guidelines for evaluating selenium data from aquatic monitoring and assessment studies. *Environmental Monitoring and Assessment* 28:83-100.

Lemly, A.D. 1996. Selenium in aquatic organisms. In *Environmental Contaminants in Wildlife--Interpreting Tissue Concentrations*, W.N. Beyer, G.H. Heinz, and A.W. Redmon-Norwood, eds. Society of Environmental Toxicology and Chemistry Special Publication, CRC Press, Inc., Boca Raton, Florida.

McNeal, J.M., and L.S. Balistrieri. 1989. Geochemistry and Occurrence of Selenium: An Overview. In L.W. Jacobs (ed.), *Selenium in Agriculture and the Environment*. Soil Science Society of America and American Society of Agronomy, Madison, WI.

Maier, K.J., and A.W. Knight. 1994. Ecotoxicology of selenium in freshwater systems. *Review of Environmental Contamination and Toxicology* 134:31-48.

Ohlendorf, H.M. 1989. Bioaccumulation and Effects of Selenium in Wildlife. In L.W. Jacobs (ed.), *Selenium in Agriculture and the Environment*. Soil Science Society of America and American Society of Agronomy, Madison, WI.

Peterson, M.J., J.G. Smith, G.R. Southworth, M.G. Ryon and G.K. Eddlemon. 2002. Trace element contamination in benthic macroinvertebrates from a small stream near a uranium mill tailings site. *Environmental Monitoring and Assessment* 74:193-208.

Scott, R.C., and P.T. Voegeli, Sr. 1961. Radiochemical Analyses of Ground and Surface Waters in Colorado, 1954-1961. Report 7. Colorado Water Conservation Board, Denver, CO.

Shrift, A. 1973. Metabolism of Selenium by Plants and Microorganism. In D.L. Klayman and W.H.H. Gunther (eds.), *Organic Selenium Compounds: Their Chemistry and Biology*. John Wiley & Son, New York, NY.

Sylvester, M.A. 1986. Results of U.S. Geological Survey Studies Pertaining to the Agricultural Drainage Problem of the Western San Joaquin Valley, California. In *Selenium and Agricultural Drainage: Implications for San Francisco Bay and the California Environment*. Proceedings of the Second Selenium Symposium, Berkeley, CA. 23 March 1985. The Bay Institute of San Francisco, Tiburon, CA.

U.S. Department of Energy (DOE). 2004. *Monticello Mill Tailings Site Operable Unit III Post Record of Decision Monitoring Plan*. Draft-Final. DOE/LMGJ684-2004, U.S. Department of Energy, Office of Legacy Management, Grand Junction, Colorado.

U.S. Department of Energy (DOE). 2005. *Final Report: Monticello Mill Tailings Site Macroinvertebrate Sampling for 2005*. DOE-LM/GJ1021-2005. U.S. Department of Energy, Office of Legacy Management, Grand Junction, Colorado.

U.S. Environmental Protection Agency (EPA). 1982. *Methods for Chemical Analysis of Water and Wastes*. EPA-600/4-82-055, Method 270.3, U.S. Environmental Protection Agency, Washington, D.C.

U.S. Fish and Wildlife Service (FWS). 1999. *Grasslands Bypass Project Contaminants Monitoring, Data: Table 1. Recommended Ecological Risk Guidelines Based Upon Selenium Residues*. Sacramento Fish and Wildlife Office, Sacramento, California. Available at (last accessed February 23, 2007): http://www.fws.gov/sacramento/ec/GBP/table1.htm

U.S. Fish and Wildlife Service (FWS). 2004. *Grassland Bypass Project Contaminants Monitoring*, Sacramento Fish and Wildlife Office, U.S. Fish and Wildlife Service, Sacramento, California. Available at (last accessed February 23, 2007): http://sacramento.fws.gov/ec/grassland.htm

Appendix A – Program Directive MSG 05-03

Monticello Mill Tailings Site BTAG Macroinvertebrate Sampling – 2005

U.S. Department of Energy – Office of Legacy Management

Program/Project: MMTS OU III **Directive No**. MSG 05-02

Task Order No. ST05-105

Initiated By: A.L. Bunn, Environmental Compliance/Biologist

Directive Subject: Macroinvertebrate Sampling to determine if selenium concentrations are exceeding ecological risk guidelines in three wetland areas and the sedimentation pond at the Monticello Mill Tailings Site (MMTS).

Justification: The scope of this directive is limited to sampling aquatic macroinvertebrates from the three constructed wetlands and the sediment pond based on a meeting held at the site on October 5-6, 2004, with DOE, EPA Region VIII, U.S. Fish and Wildlife, and the Utah Department of Environmental Quality. No site upstream of the wetlands that can be considered a control site will be sampled. Emergent, flying macroinvertebrate samples will be collected and archived for analysis at a later date, if necessary.

Directive: Attachment 1 of this directive specifies the plan for macroinvertebrate sampling to determine if concentrations of selenium in the macroinvertebrates of the wetlands and sediment pond are exceeding ecological risk guidelines for the protection of fish and wildlife species.

Affected Documents: Monticello Mill Tailings Operable Unit III Post Record of Decision Monitoring Plan (DOE-LM/GJ684-2004) Draft Final August 2004, and Section 6.0, Biomonitoring Plan.

Review and Concurrence:

Farlie Pearl, Project Support QA — Date

Tom Kirkpatrick, Site Manager — Date

Task Order Manager Approval:

Clay Carpenter, Manager (Land Management) — Date

Effective Date: January 15, 2005 **Expiration Date**: September 30, 2005

Distribution w/Attachments:

F. Pearl – OU III Info Repository (2 copies)
Holders of Affected Document
Task Order Manager Directives Log
Record File MSG 2.7 (thru J. Glasgow)

I. Purpose

Macroinvertebrate samples will be collected in the spring of 2005 at three constructed wetlands and the sediment retention pond (Figure 1 – attached) at the Monticello Mill Tailings Site (MMTS). The collection of macroinvertebrates for selenium analyses is necessary to satisfy the requirements of Section 6.2 of the *Monticello Mill Tailings Site Operable Unit III Post-Record of Decision Monitoring Plan* (DOE 2004). The concern is that the increasing concentration of selenium in the groundwater that has been observed since completion of millsite remediation will lead to increases in selenium in surface water and sediment that can affect fish and wildlife (particularly avian species) from the consumption of selenium through the food web.

II. Sampling Scope

The Biomonitoring Plan (DOE 2004) requires that macroinvertebrate sampling will be conducted in the second year of biomonitoring and during subsequent years, as warranted. The locations and general approach for macroinvertebrate sampling was discussed October 5-6, 2004 with the Biological Technical Assistance Group (BTAG). Members at the BTAG meeting included representatives from U.S. Department of Energy (DOE), U.S. Environmental Protection Agency (EPA) Region VIII, U.S. Fish and Wildlife Service, and Utah Department of Environmental Quality. The general approach for macroinvertebrate sampling included collecting samples at three constructed wetlands and a sediment pond. Aquatic macroinvertebrate samples would be analyzed for selenium after collection. Emergent, winged macroinvertebrate samples would be collected and archived for analyses (if necessary) at a later date.

III. Background and Need for Sampling

The MMTS, located south of the town of Monticello in southeastern Utah, consisted of a former uranium and vanadium ore-processing mill. In 1989, the site was placed on the National Priorities List under the Comprehensive Environmental Response, Compensation and Liability Act. DOE, EPA Region VIII, and other Federal and state agencies have worked together for the past several years to remediate contaminated soils, surface water and ground water at the MMTS.

Following completion of remediation of Operable Unit III, groundwater, surface water and sediment were monitored for selenium to determine if concentrations may be increasing in three manmade wetlands, and a sedimentation pond (Figure 1), which is located approximately one mile east of the wetlands. The monitoring plan (DOE 2004) specifies the benchmarks for selenium of 4 mg/kg in sediments, and 5 ug/L in surface water. The surface water benchmark has been exceeded and therefore triggered macroinvertebrate sampling for 2005. The sources and concentrations of selenium in groundwater, surface water and sediment are being investigated under Program Directive MSG-04-01, and are scheduled to continue through 2006. The need for additional macroinvertebrate sampling after 2005 will be dependent on monitoring results and consultations with BTAG.

Selenium has the ability to accumulate in organisms and the aquatic food chain. Reproductive effects have been observed in fish and wildlife (particularly avian species) that ingest macroinvertebrates with high concentrations of selenium. Guidelines for the dietary threshold for selenium are based upon selenium residues in macroinvertebrates. The no effects level is 3 mg/kg selenium dry weight, and the toxic effects is 7 mg/kg selenium dry weight (Maier and Knight 1994; Lemly 1993 and 1996; Hamilton

and Lemly 1999; Beckon et al. 1999; FWS 2004). Past monitoring activities within Montezuma Creek at MMTS found levels of selenium in macroinvertebrates that ranged from approximately 7 to 10 mg/kg in 1995 and 1996 (Peterson et al. 2002). The ecological risk guidelines were considered when setting the benchmarks for surface water, sediment, and macroinvertebrates in the monitoring plan for MMTS (DOE 2004).

The biomonitoring plan states that if analyses of macroinvertebrate samples result in concentrations that exceed 7 mg/kg dry weight, then follow-on work should continue to determine if food chain effects are occurring (DOE 2004). The macroinvertebrate sampling will be done in conjunction with the on-going surface water and sediment sampling (Program Directive MSG-04-01) as well as wildlife surveys (Program Directive MSG 05-01). The results of the aquatic macroinvertebrate samples will be compared to the benchmarks for selenium effects. If the aquatic macroinvertebrate samples exceed 7 mg/kg dry weight benchmark and the wildlife survey indicates that there is a population of birds in the area that would consume the emergent, flying macroinvertebrates, then those samples that have been collected and archived will be analyzed for selenium concentration. In consultation with the BTAG, the results of the macroinvertebrate sampling will be used to determine if bird eggs should be sampled for evidence of toxicity (DOE 2004).

IV. Field Sampling

The purpose of the field sampling effort is to collect macroinvertebrates for selenium analysis to determine if the macroinvertebrates in wetlands 1, 2, and 3 as well as the sediment pond are at levels of concern for selenium. The wetlands will be only be sampled using kick nets (Peterson et al. 2002). Other sampling devices for macroinvertebrates are not likely to be effective because of the dense emergent vegetation and shallow waters in the wetlands. The deeper sediment pond will be sampled using both kick nets and artificial substrate samplers (Hester-Dendy samplers). Each replicate sample for selenium analysis will have a minimum mass of 3 g wet weight.

The goal for each sampling location will be to collect three replicate samples. The goal for the sediment pond will be to collect three replicate samples using kick nets and Hester-Dendy samplers. In addition to collecting aquatic macroinvertebrates, light traps at each wetland and the sediment pond will be used to collect emergent, flying macroinvertebrates during the nocturnal period. These samples will be archived for analysis at a later date.

If the goal of collecting a mass of 3 g wet weight per replicate sample cannot be achieved, then samples for a location will be composited prior to analysis. It is possible for a sample with a mass of less than 3 g wet weight to be analyzed for selenium at the detection limits necessary. Based on discussions with the analytical laboratory, it may be possible to analyze samples as small as 1 g wet weight. The compromise with a laboratory that conducts analyses on samples with a mass of less than 3 g wet weight is that not all of the laboratory quality control measures may be able to be conducted. The decision to composite the mass collected from all the replicate sampling efforts at a location due to lack of adequate mass will depend on input from the analytical laboratory. Those arrangements will be discussed prior to field sampling.

A. Sampling Wetlands 1-3

Each of the three wetlands will be sampled using the same method. Wetlands will be visually divided into three parts for the collection of replicate samples. Flagging will be used to designate the three zones. The three parts will correspond to the flow of water through the wetlands: up-gradient, middle and down-gradient of surface and groundwater flow. The areas where the sample will be collected using the kick nets will be indicated as best as possible on a map. If possible, global positioning system (GPS) measurements will be made at the flags and near the general location where samples were collected.

D-shaped aquatic kick nets with 500 um mesh netting will be used to collect macroinvertebrate samples (Peterson et al. 2002). Each net will be pre-cleaned using a non-phosphate detergent, followed by 2-5% nitric acid wash, and three rinses with laboratory-grade deionized water. The pre-cleaning process is designed to minimize contamination from field equipment prior to use. Nets will be dedicated to each wetland. The same net could be used for replicate sampling within a wetland.

The nets will be used around the perimeter of the wetland and in areas where there is open water between the emergent vegetation. The nets will be worked into the vegetation and along the water sediment interface. If macroinvertebrates are observed on the submerged vegetation, they will also be collected. Field personnel will wear Nitrile gloves during sample collection, and gloves will be changed between sample locations.

Replicate samples will represent a composite of macroinvertebrates. The field samplers will make qualitative notes during the collection of replicate samples at a location. These notes will include information about the functional feeding groups of the macroinvertebrates (Peterson et al. 2002): detritivores (e.g., Tipulidae, Limnephilidae); predators (e.g., Aeshnidae, beetles); and filter feeders (e.g., Hydropyschidae, Simuliidae). The field notes will be used to characterize the sample variability in the final report.

B. Sampling the Sediment Pond

The sediment pond will be sampled using both kick nets and Hester-Dendy Multi-Plate samplers. Due to the depth of the sediment pond, only the edges of the pond can be effectively sampled. Kick net samples will be collected using the same method as for collecting in the wetlands. The method for using the Hester-Dendy samplers is described below. Use of both techniques will ensure that sufficient sample masses are collected. In addition, comparing the results from the two sampling techniques will indicate if the preparation of the kick samples was biased by collection method.

The Hester-Dendy samplers are artificial substrate systems that allow water-column sampling of macroinvertebrates. The Hester-Dendy samplers consist of a weight with 9 to 14 plates. The plates on each sampler are spaced at varying widths and have a total surface area of 0.16 m. The samplers will be placed in the ponds for approximately 6 to 8 weeks as the length of time for maximum colonization of the samplers is not known. During the time that the samplers are in the pond, they will be colonized by periphyton, and then macroinvertebrates will colonize the spaces between the plates and consume the periphyton. Upon collection of the samplers, the macroinvertebrates can be picked off the plates with pre-cleaned, plastic forceps and placed into sample containers.

The Hester-Dendy samplers will be attached to a cinder block to hold them under water and keep the samplers from getting buried in the sediments. Three samplers will be deployed around the pond. One will be near the influent end of the pond, the other near the discharge location. The last sampler will be deployed on either side of the pond half way between the other samplers. A rope from the cinder block to the shore will be used to assist in finding the samplers later.

Three replicate kick net samples will be collected from the perimeter of the sediment pond. The pond will be divided into three parts: up-gradient, middle and down-gradient. The middle will consist of both sides of the pond, below the influent end of the pond and above the discharge point. These locations will correspond with the location of the Hester-Dendy samplers.

Replicate samples will represent a composite of macroinvertebrates. The field samplers will make qualitative notes during the collection of replicate samples for the macroinvertebrates collected on the Hester-Dendy samplers and in the kick nets. These notes will include information about the functional feeding groups of the macroinvertebrates, as mentioned above in the discussion on sampling the wetlands. The field notes will be used to characterize the sample variability in the final report.

C. Sample Preparation and Preservation

Collection of a replicate sample in a wetland will continue until a minimum mass of 3 g wet weight macroinvertebrates has been collected. If the goal of collecting a mass of 3 g wet weight per replicate sample cannot be achieved, then samples for a location may have to be composited prior to analysis.

Detritus and other plant material will be picked from the kick nets using pre-cleaned, plastic forceps. Deionized water will be used to rinse sediment from the net and the macroinvertebrates. The remaining macroinvertebrates will be transferred using pre-cleaned, plastic forceps onto a glass fiber filter (to remove excess water) and then into a labeled, pre-cleaned SPEX plastic container. The mass of the macroinvertebrate sample will be measured with a portable electronic balance (readability of 0.002g), and the weight will be recorded.

The macroinvertebrates removed from the Hester-Dendy samplers will be treated similar to the kick net samples. The organisms will be rinsed with deionized water and placed in a labeled, pre-cleaned SPEX plastic container. Sample mass will be measured with a portable electronic balance, and the weight will be recorded.

All samples will be kept at 4°C during collection and shipping in order to preserve the sample until analysis. Standard chain of custody methods and labels will be used for all collected samples. Field data forms will also be used to document all pertinent sampling information.

D. Emergent, Flying Macroinvertebrates Sampling

In addition to aquatic macroinvertebrates, emergent, flying macroinvertebrates will be collected with blacklight traps. The light traps with photoelectric switches will be set up late in the day near each wetland and the sediment pond, and the location of the trap will be recorded with GPS. The sampling surfaces of each light trap will have been pre-cleaned with hydrochloric acid. After the

lights have been in place over night, samples will be rinsed out of the light trap using deionized water, and the organisms will be collected on GF filter paper to drain off the water. A replicate sample will consist of at least 3 g wet weight. Multiple nights of collection may be necessary to collect the required mass of macroinvertebrates for each location. The samples will be collected in labeled, pre-cleaned SPEX plastic containers on ice while in the field and shipping, and then they will be frozen and archived until analyzed at a later date.

E. Quality Control of Field Sampling

To assess the quality of the field sampling technique, two types of field quality control samples will be collected:

- Field Duplicates: Field duplicates are used to assess the reproducibility of sample collection techniques. Typically, field duplicates would involve taking a separate sample at the same location. However, it is unlikely that enough organisms will be available at a location for two sampling efforts. Therefore, the field duplicate will be a split of a composite sample prepared after the determination of functional feeding groups. The split will ensure that a minimum of 3 g will be in each sample. Care will be taken to make field duplicates indistinguishable so that personnel performing analyses cannot determine which samples are duplicates. At a minimum, one field duplicate will be prepared for the Spring 2005 sampling event.

- Field Blanks: Field blanks are used to verify that the sample collection and handling process has not affected the quality of the samples. Field blanks are used to measure the cleanliness of sampling equipment. One field blank will be prepared in the field each sampling day by simulating the collection of samples for all types of media through decontaminated sampling equipment. Deionized water will be used for the field blank.

All field quality control samples are recorded as such in the field records. These quality control samples are analyzed by the laboratory to assess the quality of the sampling methodology. Field quality control samples will remain blind to the laboratory.

F. Summary of Field Sampling Efforts

The field sampling efforts will collect the following samples, if at all possible:

- 3 aquatic macroinvertebrate samples collected with kick nets in wetland 1;
- 3 aquatic macroinvertebrate samples collected with kick nets in wetland 2;
- 3 aquatic macroinvertebrate samples collected with kick nets in wetland 3;
- 3 aquatic macroinvertebrate samples collected with kick nets in sediment pond;
- 3 aquatic macroinvertebrate samples collected from Hester-Dendy samplers in sediment pond;
- 1 field duplicate from composited aquatic macroinvertebrate sample;
- 3 emergent, flying macroinvertebrate samples collected with light traps in wetland 1;
- 3 emergent, flying macroinvertebrate samples collected with light traps in wetland 2;
- 3 emergent, flying macroinvertebrate samples collected with light traps in wetland 3;

- 1 field duplicate from composited emergent, flying macroinvertebrate sample; and
- 3-4 water samples collected as field blanks (one per day) and deionized water used for any re-wetting of macroinvertebrate samples.

V. Laboratory Test Analyses

The samples collected in the field will be analyzed for selenium

A. Percent Moisture Determination

Samples collected in the field will have a wet weight, and the recommended ecological risk guidelines for macroinvertebrates are based on dry weight. To convert from wet weight to dry weight, the percent moisture in a sample must be determined. Percent moisture is determined as the percent ratio of wet to dry weight for the entire sample. Dry weights will be determined by placing the wet sample in a pre-tared, pre-cleaned sample container, lyophilizing (freeze drying) the entire sample, and then noting the change in weights. A sample of macroinvertebrates that weighs at least 3 g wet weight will be approximately 0.5 g dry weight.

B. Low-Level Trace Metals Analysis

The recommended analytical technique for analyzing selenium in marcoinvertebrates is by atomic absorption, gaseous hydride procedure for low-level trace metals analysis (EPA Method 270.3; Standard Method 3114 B) (EPA 1982; APHA 1998). Sample preparation will include lyophilizing the samples and then homogenizing them using a ball-mill prior to digestion. An aliquot of approximately 0.5 g of each dried, homogeneous sample will be combined with nitric and hydrochloric acids (aqua regia) in a Teflon vessel and heated in an oven at 130°C (±10°C) for a minimum of eight hours. After heating and cooling, deionized water will be added to the acid-digested tissue to achieve analysis volume and the digestates will be submitted for analysis.

Digested samples will be analyzed for selenium using hydride generation flow injection atomic absorption spectroscopy (HGAA-FIAS). The base method for this procedure is EPA Method 270.3 (EPA 1982). Samples that remain at 4°C or are frozen can be stored for up to a year prior to analysis. All results will be determined and reported in units of mg/kg on a dry-weight basis.

The detection limit for selenium in macroinvertebrate samples will be based on a methods detection limit (MDL) and reporting limit (RL) study to be performed by the analytical laboratory. MDLs for trace metals are typically determined annually by accredited laboratories in accordance with 40 CFR Part 136 Appendix B. MDLs for metals in tissue samples are generated by spiking tissue (e.g., cellulose or chicken breast) with low concentrations of each of the metals of interest, and processing them according to the laboratory methods. For trace metals, RL is calculated by multiplying the target analyte MDL by 3.18. The value 3.18 is based on the Student's-t value for 7 to 10 replicates, the number of replicates usually analyzed to generate the MDL. The laboratory chosen for the analysis of selenium in macroinvertebrate samples should be able to demonstrate a record of analyses for the following:

- MDL for tissues of 0.0112 mg/kg dry weight
- RL for tissues of 0.05 mg/kg dry weight

C. *Laboratory Quality Control*

Internal quality control is an important part of the measurement system to ensure that analytical results are reliable and that data integrity is maintained. Laboratory performance will be evaluated through analysis of laboratory quality control samples (in conjunction with field quality control samples, as appropriate).

Validation of the samples will evaluate the analytical performance of the laboratory by reviewing the results from analysis of the blank, matrix spike, duplicate, and quality control check samples. Evaluation will also be based upon instrumental calibration, instrument performance, adequacy of detection limits, obtained precision of replicate analyses, and comparison of the percentage of missing or undetected substances among replicate samples.

The following describes the batch preparative quality control samples that are required by the analytical method for low-level trace analysis of selenium.

- Method Blank (MB): A Method Blank consists of Type II ASTM water that is subjected to the sample preparation or extraction procedures and analyzed as a sample. It serves to measure contamination associated with laboratory storage, preparation, or instrumentation. One MB will be required for the 15 samples anticipated to be collected in Spring 2005 (typically, one sample is required for every 20 samples analyzed). If the analyte of interest is above the Reporting Limit, corrective action will be taken.

- Matrix Spike (MS): A Matrix Spike is an aliquot of sample to which known amounts of analyte have been added. It is subjected to the sample preparation or extraction procedures and analyzed as samples. The stock solutions used for spiking are purchased or prepared independently of calibration standards. One MS will be required for the 15 samples anticipated to be collected in Spring 2005 (typically, one sample is required for every 20 samples analyzed). The spike recovery measures the effects of interferences in the sample matrix and reflects the accuracy of the determination.

- Matrix Spike Duplicate (MSD): A Matrix Spike Duplicate is an additional aliquot of sample to which known amounts of analyte have been added and subjected to the same preparation and analytical scheme as the original sample. The Relative Percent Difference (RPD) between MS and MSD measures the precision of a given analysis. One MSD will be required for the 15 samples anticipated to be collected in Spring 2005 (typically, one sample is required for every 20 samples analyzed).

- Laboratory Control Sample (LCS): Laboratory Control Sample is created from a standard reference material which is a material similar in nature to the sample being processed [traceable to the National Institute of Standards and Technology (NIST) or other agencies, to the extent possible]. A known amount of analyte is added to an aliquot of Type II ASTM water. The LCS is subjected to the sample preparation or extraction procedure and analyzed as a sample.

The stock solutions used for LCS recovery tests the function of analytical methods and instrumentation. One LCS will be required for the 15 samples anticipated to be collected in Spring 2005 (typically, one sample is required for every 20 samples analyzed).

If an adequate number of field duplicates cannot be collected for the macroinvertebrate samples, laboratory splits may be substituted. In some cases, the mass may be too small to allow use of laboratory splits. Laboratory splits are used to assess the homogenization techniques. Samples are homogenized, and then divided into two equal parts for analysis. Care is taken to make both samples representative of materials present, including heterogeneities. If possible, at least one sample will be prepared and analyzed as a split.

Based on the number of samples anticipated to be collected in the field (see Section IV F above), at least one of each laboratory quality control sample will be analyzed for the aquatic macroinvertebrates to be collected in Spring 2005. Typically, the laboratory quality control samples are prepared for every 20 samples analyzed. The goal of for the minimum mass of 3 g wet weight is so that the analytical laboratory has enough mass to perform the MS or MDS to be performed on any sample. Laboratory quality control may have to be biased towards performing the MS or MDS on only those samples that have enough mass. Arrangements with the analytical laboratory about their ability to use samples with less than 3 g wet weight will be discussed prior to field sampling.

VI. Qualifications of Field Samplers

At a minimum, two people will be needed to collect the macroinvertebrate field samples in Spring 2005. The lead field sampler must have experience with collecting macroinvertebrate samples using kick nets, Hester-Dendy samplers and black light traps. In addition, the lead field sampler must have a background in entomology and be able to segregate macroinvertebrate samples into functional feeding groups. The second field sampler must have prior field experience with environmental sampling protocol, field documentation requirements, and be physically able to assist with deploying sampling equipment, sample collection and sorting techniques, and other related tasks as directed by the lead field sampler.

Deployment of the Hester-Dendy samplers will require two people. These people must have experience with the sediment retention pond, understanding the depth and flow of water through the pond as well as knowledge of past sampling activities at the pond. They must be able to deploy the samplers and ensure that the sampler is upright in the water column and not buried in the sediments.

VII. Schedule

There are two parts scheduled for the Spring 2005: 1) deployment of Hester-Dendy samplers in the sediment pond; and 2) collection of aquatic and flying macroinvertebrates from the wetlands and sediment pond. The optimum time for the collection of macroinvertebrates would be when the water temperature has warmed to optimum growing conditions and prior to emergence of aquatic insect larvae. Based on consultation with researchers that collect macroinvertebrates in the southeastern Utah, the optimum time for collection of macroinvertebrates is likely to be late May through early June (Axford 2004). Therefore, deployment of the Hester-Dendy samplers would be 6 to 8 weeks prior, or during the first two weeks of April.

Macroinvertebrate samples will be sent to the contract laboratory within 5 days after initiation of field collection activities. Laboratory results will be available approximately 45 days after the samples have been received.

VIII. Data Report

The data report will be submitted to DOE by September 30, 2005. The report will include the following information.

- A summary of the dates, times and locations of the field sampling activities
- Any communications with federal and state agencies, and professional biologists
- Any communications or direction from DOE
- A summary of the field activities, GPS data and any maps documenting required information
- A summary of the laboratory test analyses including results, methods, detection limits, and laboratory qualifiers
- Education/qualifications of field samplers
- Comparison of results from macroinvertebrate samples to ecological risk guidelines and benchmarks
- Recommendation for follow-on activities
- References

The report will be reviewed by DOE and transmitted to EPA and UDEQ by November 1, 2005.

IX. Reference Information

The following reference information was used to develop this directive, or has been used by DOE and its contractor for other DOE sites. In many cases, it is not a complete citation because the reference was forwarded (in part) to DOE, and was not in a published format (e.g., faxed information, unpublished information).

APHA (American Public Health Association),1998. *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, Eds.: Clesceri, L.S, A.E. Greenberg, and A.D. Eaton, American Public Health Association, Washington, D.C.

Axford, D., 2004. Telephone call with Dave Axford (Field Technician/Taxonomist, Utah State University, BLM / USU National Aquatic Monitoring Center) and R. Mueller (Scientist, Battelle–Pacific Northwest Division) regarding sampling for macroinvertebrates in southeastern Utah. February.

Beckon, W.N., J.D. Henderson, T.C. Maurer, and S.E. Schwarzbach, 1999. Biological Effects of the Reopening of the San Luis Drain (Grasslands Bypass Project) to Carry Subsurface Irrigation Drainwater, Draft, U. S. Fish and Wildlife Service, Region 8, Division of Environmental Contaminants, Sacramento, CA, September. Available at (last accessed January 26, 2007): http://pacific.fws.gov/ecoservices/envicon/pim/reports/Sacramento/sanluirp.pdf

DOE (U.S. Department of Energy), 1998. *Operable Unit III Remedial Investigation,* GJO-97-6-TAR, Appendix G, *An Ecological Investigation of a Vanadium and Uranium Mill Tailings Site,* GJO-97-9-TAR, U.S. Department of Energy Grand Junction Office, Grand Junction, Colorado, January.

DOE (U.S. Department of Energy), 2004. *Monticello Mill Tailings Site Operable Unit III Post Record of Decision Monitoring Plan,* Draft-Final, DOE/LMGJ684-2004, U.S. Department of Energy, Office of Legacy Management, Grand Junction, Colorado, August.

EPA (U.S. Environmental Protection Agency), 1982. *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-82-055, Method 270.3, U.S. Environmental Protection Agency, Washington, D.C., December.

FWS (U.S. Fish and Wildlife Service), 2004. *Grassland Bypass Project Contaminants Monitoring*, Sacramento Fish and Wildlife Office, U.S. Fish and Wildlife Service, Sacramento, California. Available at (last accessed January 26, 2007): http://sacramento.fws.gov/ec/grassland.htm

Hamilton, S.J., and A.D. Lemly, 1999. Commentary: Water-Sediment Controversy in Setting Environmental Standards for Selenium, *Ecotoxicology and Environmental Safety* 44:227-235.

Lemly, A.D., 1993. Guidelines for evaluating selenium data from aquatic monitoring and assessment studies. *Environmental Monitoring and Assessment* 28:83-100.

Lemly, A.D., 1996. Selenium in aquatic organisms. In *Environmental Contaminants in Wildlife--Interpreting Tissue Concentrations*, Eds: Beyer, W.N., G.H. Heinz, and A.W. Redmon-Norwood, Society of Environmental Toxicology and Chemistry Special Publication, CRC Press, Inc., Boca Raton, Florida.

Maier, K.J., and A.W. Knight, 1994. Ecotoxicology of selenium in freshwater systems. *Review of Environmental Contamination and Toxicology* 134:31-48.

Peterson, M.J., J.G. Smith, G.R. Southworth, M.G. Ryon and G.K. Eddlemon, 2002. Trace Element Contamination in Benthic Macroinvertebrates from a Small Stream Near a Uranium Mill Tailings Site, *Environmental Monitoring and Assessment* 74:193-208.

Appendix B – Macroinvertebrate Field Sampling Procedures for May 2006

Attachment 1: Deployment Procedure for Hester-Dendy Samplers

Attachment 2: Macroinvertebrate Field Sampling Procedures for May 2006

Attachment 3: Map of the Monticello Mill Tailings Site

Attachment 4: Procedure for Acid Washing Field Equipment

Attachment 5: Sample Chain-of-Custody (COC) Form

Attachment 1: Deployment Procedure for Hester-Dendy Samplers

Purpose: Hester-Dendy (HD) samplers will be used as a secondary method of collecting macroinvertebrates from the sediment pond. The samplers will be used to acquire three replicate macroinvertebrate samples. HD samplers are artificial substrate systems that allow water-column sampling of macroinvertebrates.

Note: Field notes on the actual deployment are included at the end.

Materials (* indicates materials to be procured prior to deployment):

- 3 HD samplers
- 12 plastic cable ties
- 3 cinder blocks (6 or 8" wide blocks)*
- 24 to 30 ft rope (to be cut into 3 lengths)*
- 3 wooden stakes*

Procedure:

1. Acquire 3 cinder blocks, at least 24 ft of rope, and three wooden stakes. Rope and stakes are for marking the location of the cinder block in the sediment pond. These items do not need to be sufficient to hold the

2. Attach HD samplers to the cinder blocks as shown in Figure 1. Place the sampler in the center of an 8" cinder block. Use plastic cable ties (2 for each side) to attach the sampler to the cinder block. Place one cable tie section through the eye bolt and the other cable tie section through the last spacing on the wooded plates.

3. Divide length of rope into three pieces. Tie 6 to 10 ft rope through one end of the cinder block.

4. Determine locations for HD samplers in the sediment pond. We suggest one near the road and the other two along the east and west shoreline. Consider accessibility and safety of the individuals entering the pond in placing the samplers. Samplers preferable would be at least 3 ft apart from each other, and preferably, equidistant around the pond. Samplers need to be located beyond the vegetation growing along the shoreline and not on a deep slope.

5. Place the block in the water so that there is ~ 6 – 8 in of water covering the top of the HD sampler, ensuring that the cinder block is laying flat on the substrate. Need to push the block into the soft sediment to ensure that the block does not roll over with time and to place the samplers close enough to the sediments to encourage colonization by the macroinvertebrates. Optimally, the bottoms of the sampler will be 2 – 3 in away from the top of the sediments.

6. Tie the other end of the rope from the cinder block to a stake or fixed object on land. The rope on shore will help to identify the location of the sampler for recovery later.

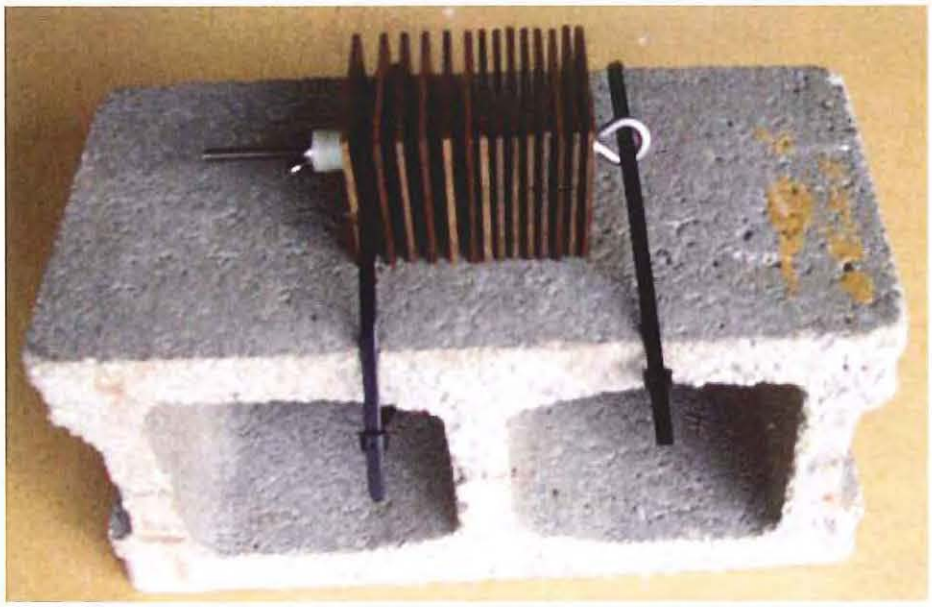


Figure 1. Hester-Dendy sampler attached to cinder block with cable ties. The cinder block shown is 10" wide.

Points of Contact for Questions:

If you have any questions about assembling or deploying the samplers, please contact:

Bob Mueller: 509-372-1344 (work)
509-539-3230 (cell)

Amoret Bunn: 509-376-6300 (work)
509-539-4548 (cell)

Field Notes:

Three Hester-Dendy samplers were placed in the sediment pond the week of April 17th, 2006. Figures 2-4 show the placement of the Hester-Dendy samplers into the sediment pond in 2005.

Figures 2-4. These pictures of the sedimentation pond (2), the influent flow into the pond (3) and the deployment of the Hester-Dendy samplers (4) were taken on April 5, 2005.

Attachment 2: Macroinvertebrate Field Sampling Procedures for May 2006

I. Purpose

Collect aquatic and terrestrial macroinvertebrates from two sites at the Monticello Mill Tailings Site to be analyzed for selenium content. The sites are three wetlands and a sediment pond. Each macroinvertebrate sample should have a wet weight of 3 g in order for the laboratory to perform and meet all quality assurance standards and desired detection limits.

The goal is to collect the following samples:

- 3 aquatic macroinvertebrate samples collected with kick nets in wetland 3;
- 3 aquatic macroinvertebrate samples collected with kick nets in sediment pond;
- 3 aquatic macroinvertebrate samples collected from Hester-Dendy samplers in sediment pond;
- 1 field duplicate from composited aquatic macroinvertebrate sample;
- 1-2 water samples collected as field blanks (one per day) and deionized water used for any re-wetting of macroinvertebrate samples.

This procedure includes:

- Materials needed in the field and for shipment to the laboratory,
- Methods for:
  - Collecting aquatic macroinvertebrates using kick-nets;
  - Collecting aquatic macroinvertebrates using Hester-Dendy samplers;
  - Preparing field blanks; and
  - Shipping samples.
- Schedule of activities.

Attachments to the procedure include:

- Map of the Monticello Mill Tailings Site;
- Procedure for acid washing the field equipment; and
- Sample of Chain-of-Custody (COC) form.

II. Materials

A. <u>Monticello Field Supplies</u>

Kick nets and handles (acid washed)
Forceps, scrapers, plastic trays (acid washed)
SPEX sample jars for macroinvertebrates
Sample bottles for field blanks
Balance, with extra AA batteries
GF filter paper
Sieve to support filter paper and allow drainage
Chest waders/Hip boots/rubber boots
Insect repellent/sunscreen
Nitrile gloves

100 m tape/flagging
GPS
Side cutters to remove Hester-Dendy (HD) samplers
Digital camera
Plastic bags/ziplocks
Clipboards
Write in rain paper
Field data sheets
Chain of Custody (COC) forms
Sharpies/pencils
Thermometer
First Aid Kit
Cell phone
Battelle Health and Safety Plan

B. Purchase in Moab
Cooler for sample shipment
Dry Ice or block ice (blue ice)
Deionized (DI) water

C. Shipping to Sequim
Cooler
Dry Ice or block ice (blue ice)
Mailing labels
COC forms
Samples (aquatic macroinvertebrates and field blank(s))

III. Methods

A. Kick net Collection of Aquatic Macroinvertebrates

1. Kick-nets will be used to collect samples at wetland 3 and the sediment pond.

2. The wetland should be visibly divided into three sections: surface water influent, middle and outlet. The sediment pond should be visibly divided into influent edge, left and right of influent edge (ending at the outlet). Flag the edges of the three parts. Note in field notebook the three parts (this information will be included in the final report). The flags and a representative point or area should be recorded with the GPS.

3. Put on Nitrile gloves and appropriate footwear.

4. Open one of the pre-cleaned aquatic kick nets and use the net to collect aquatic macroinvertebrates around the edge of one section of the site (wetland or pond). Nets should also be used to collect in areas where there is open water between the emergent vegetation.

5. Place filter paper onto sieve.

6. Set up electronic balance.

7. Tare the weight of the SPEX macroinvertebrate sample jar. Container should be labeled using a permanent pen with the appropriate field ID number (see Attachment 3).

8. After collecting in a section at a site, empty contents of kick net into a pre-cleaned tray, or remove macroinvertebrates directly from the net using pre-cleaned forceps. Use DI water to rinse material out of net if needed.

9. Use pre-cleaned forceps to transfer invertebrates onto filter paper. The invertebrates should remain on the filter paper as long as needed to remove excess water from the organisms.

10. Using forceps transfer the invertebrates from the filter paper to the tared SPEX plastic container. Care should be taken to exclude any sediment or visible vegetation from the sample.

11. Collection of a replicate sample at a site will continue until a minimum mass of 3 g wet weight macroinvertebrates has been collected.

    - A single invertebrate should not exceed more than 20% of the entire 3 g replicate sample (i.e., should not exceed 0.6 g). This might happen if crayfish or large snails are collected. Large invertebrates could be segregated into a ziplock bag and may be chosen for analysis later. Bag should be labeled with site, collection technique, date, time, and initials of field sampler. The focus should be on invertebrates that can be consumed by birds.

    - If more than 3 g is collected from a single section at a site, then the invertebrates exceeding 3 g should be put into a new container. The new container will become the field duplicate (see step 18 below).

    - If less than 3 g is collected from a single section at a site, then note the weight collected for that day. On another day, try to collect more from the section at the site using kick nets and collecting with forceps aquatic invertebrate life stages found on submerged sections of the emergent vegetation. Organisms collected from a single section at a site on separate days can be consolidated into a single container and considered one replicate sample for analysis.

    - If the sample size cannot be reached by sampling a section at a site over multiple days, then sections from the same site may be consolidated to achieve the 3 g sample size.

12. Note in the field notebook the final weight of the replicate sample.

13. Note in the field notebook the types of macroinvertebrates included in the sample container. Types of invertebrates are based on the functional feeding groups: detritivores (e.g., Tipulidae, Limnephilidae); predators (e.g., Aeshnidae, beetles); and filter feeders (e.g., Hydropyschidae, Simuliidae).

14. Store sample container in cooler with ice.

15. Fill in Chain of Custody form (see Attachment 3).

16. Repeat collection of aquatic macroinvertebrates in the remaining sections of the wetland.

17. Repeat sampling in the sediment pond. A total of samples should be collected with the kick nets.

18. Prepare one field duplicate if there are excess aquatic macroinvertebrates after preparing the 3 replicates per site. A field duplicate should come from one section at a site. However, this may not be possible and the field duplicate may represent multiple sections from a single site. Field notes should describe the site and sections used to prepare the duplicate.

19. All samples should be stored at 4°C or less. Overnight storage of a container may be in a refrigerator. Sample should be cooled and maintained at a temperature of 4°C or less.

B. Hester-Dendy (HD) Collection of Aquatic Macroinvertebrates

1. HD samplers were placed only in the sediment pond. The samplers were deployed the week of April 17, 2006.

2. To find a HD sampler, locate a tee-post in the pond. The tee-posts are located just beyond the emergent vegetation and along a submerged edge in the pond. A rope from the tee-post leads to the submerged cinder block holding the HD sampler.

3. Record location of cinder block with GPS.

4. Determine if the samplers have had sufficient time to cultivate and if they are located appropriately in the water column for collection of macroinvertebrates.

5. If the samplers are to be collected, use side cutters and clip the pull tied holding the HD sampler to the cinder block. This can be done by removing the cinder block from the water with the sampler attached, or by clipping the pull ties under water.

6. Put HD sampler in pre-cleaned tray.

7. Using forceps or pre-cleaned spatulas, remove the invertebrates from the sampler and put them in DI water. This may require disassembling the sampler and picking the organisms directly from the individual plates of the sampler.

8. Place filter paper onto SS sieve.

9. Set up electronic balance.

10. Tare the weight of the SPEX plastic container. Container should be labeled using a permanent pen with the appropriate field ID number (see Attachment 3).

11. Use pre-cleaned forceps to transfer invertebrates onto filter paper. The invertebrates should remain on the filter paper as long as needed to remove excess water from the organisms.

12. Using forceps transfer the invertebrates from the filter paper to the tared SPEX plastic container. Care should be taken to exclude any sediment or visible vegetation from the sample.

13. Collection of a replicate sample from a HD sampler will continue until a minimum mass of 3 g wet weight macroinvertebrates has been collected.

    - Invertebrates from each sampler should be put in a separate container.

    - If less than 3 g is collected from a single HD sampler, then note the weight collected from that sampler. After invertebrates from all samplers have been segregated into respective containers, then the containers that have less than 3 g should have their contents consolidated. In this case, a container may have a weight greater than 3 g and this composite sample will be analyzed as one replicate sample.

    - If more than 3 g is collected from a single HD sampler, then the invertebrates exceeding 3 g should be put into a new container. The new container will become the field duplicate (see step 18 above for kick net samples).

    - A single invertebrate should not exceed more than 20% of the entire 3 g sample (i.e., should not exceed 0.6 g). This might happen if crayfish or large snails are collected. Large invertebrates could be segregated into ziplock bag and may be chosen for analysis later. Bag should be labeled with site, collection technique, date, time, and initials of field sampler. The focus should be on invertebrates that can be consumed by birds.

14. Note in the field notebook the final weight of the replicate sample.

15. Note in the field notebook the types of macroinvertebrates included in the sample container. Types of invertebrates are based on the functional feeding groups: detritivores (e.g., Tipulidae, Limnephilidae); predators (e.g., Aeshnidae, beetles); and filter feeders (e.g., Hydropyschidae, Simuliidae).

16. Store sample container in cooler with ice. Fill in Chain of Custody form (see Attachment 3).

17. Repeat collection of aquatic macroinvertebrates from the remaining HD samplers.

18. All samples should be stored at 4°C or less. Overnight storage of a container may be in a refrigerator. Sample should be cooled and maintained at a temperature of 4°C or less.

C. <u>Field Blanks</u>

1. Field blanks are used to verify that the sample collection and handling process has not affected the quality of the samples. They are used to measure the cleanliness of sampling equipment.

2. At the beginning of the day, set out a collection system. A collection system consists of a kick net, tray, and forceps, or a light trap, jar and forceps. The collection system may be unpacked from the bags used to protect the equipment after it was acid washed, or after the equipment has been used on a previous day at a site.

3. Pour 100-500 mL of DI water through a net over the forceps and into a tray. The DI water should be the same water used to rinse the kick nets or HD samplers.

4. Pour the water from the tray into a 500 mL pre-cleaned bottle.

5. Store sample bottle in cooler with ice.

6. Fill in Chain of Custody form (see Attachment 3).

7. All field blanks should be stored at 4°C or less. Overnight storage of a container may be in a refrigerator. Sample should be cooled and maintained at a temperature of 4°C or less.

D. Shipping samples to Sequim for analyses

1. Samples need to be maintained at 4°C or colder for transport to Sequim.

2. Address for shipping to Sequim is:

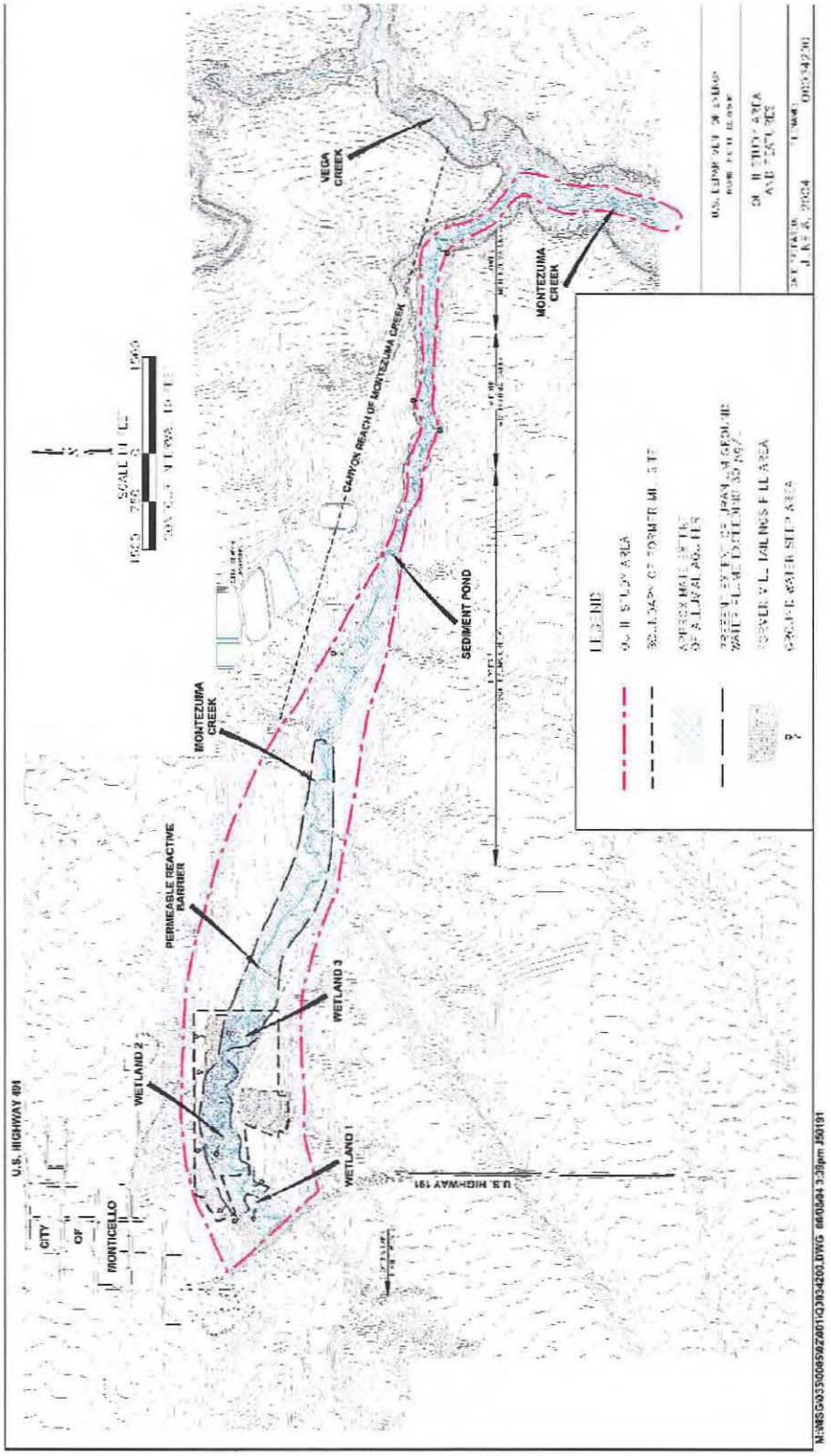
   Pacific Northwest Division
   Marine Sciences Laboratory
   1529 West Sequim Bay Road
   Sequim, Washington 98382
   Attention: Jill Brandenberger (360-681-4564)

3. FedEx in Moab is 54 miles away from Monticello on Hwy 191. Hwy 191 is Main St. in Moab. There are two locations:

   City Market
   425 S Main St
   Moab, UT 84532

   Canyonland Copy Center
   59 S Main St
   Moab, UT 84532

Attachment 3: Map of the Monticello Mill Tailings Site



Attachment 4: Procedure for Acid Washing Field Equipment

1. Wear the following protective equipment: safety glasses, blue lab coat, nitrile gloves (tyvec sleeves are optional).
2. Clean a 30 L and a 10 L plastic bin with non-phosphate lab soap.
3. Prepare a 3 L of 5% Nitric Acid (v/v) solution.
4. Pour 5% Nitric Acid solution into 30 L bin.
5. Place field equipment into bin and ensure all surfaces of equipment are submerged in nitric acid.
6. Transfer the field equipment to 10 L plastic bin.
7. Rinse equipment 3 times with MilliQ water (>18 megohm-cm)
8. Towel dry equipment and place in ziplock bags for transport to field.

Attachment 5: Sample Chain-of-Custody (COC) Form

SAMPLE CUSTODY RECORD

(SOP# MSL-A-001 & MSL-A-002)

Date _____

Battelle
... Putting Technology To Work
Pacific Northwest Division
Marine Sciences Laboratory
1529 West Sequim Bay Road
Sequim, Washington 98382

Project Name: Montrello Massachusetts
Project Manager: Anne et Burns
Phone Number: (617) 376-6500

Shipment Method: FedEx
Preservation: Ice

Line	Field Sample ID	Collection Date/Time	Matrix	No. of Containers	Test Parameters					Laboratory ID	Observations/Comments
1											
2											
3											
4											
5											
6											
7											
8											
9											
10											
11											
12											
13											
14											
15											

Relinquished By	Company	Received By	Company
Signature/Printed Name	Date/Time	Signature/Printed Name	Date/Time
Relinquished By	Company	Received By	Company
Signature/Printed Name	Date/Time	Signature/Printed Name	Date/Time

Field Sample Identification Information

The field sample ID is a 7 character code. The following describes the code recommended for use during the macroinvertebrate sampling at Monticello Mill Tailings Site.

First two characters identify the site of the sample at the Monticello Mill Tailings Site:

W3 = wetland 3
SP = sediment pond

The third and fourth characters identify the replicate number or that the sample is a field blank:

R1 = replicate 1
R2 = replicate 2
R3 = replicate 3
R4 = replicate 4, which can be analyzed as the field duplicate
FB = field blank water sample*

The fifth character identifies the type of macroinvertebrate sample:

A = aquatic macroinvertebrate

The sixth and seventh character identifies the collection technique:

KN = kick net sample
HD = Hester-Dendy sample

*The sample ID for field blanks should have characters 5-7 that describe what was tested when the water was collected. For example, if the water was collected from a kick net set-up for wetland 1, then the ID should be W1FBAKN.

Field Sample ID	Description
W3R1AKN	Wetland 3, rep 1, aquatic, kick net
W3R2AKN	Wetland 3, rep 2, aquatic, kick net
W3R3AKN	Wetland 3, rep 3, aquatic, kick net
SPR1AKN	Sediment pond, rep 1, aquatic, kick net
SPR2AKN	Sediment pond, rep 2, aquatic, kick net
SPR3AKN	Sediment pond, rep 3, aquatic, kick net
SPR1AHD	Sediment pond, rep 1, aquatic, HD
SPR2AHD	Sediment pond, rep 2, aquatic, HD
SPR3AHD	Sediment pond, rep 3, aquatic, HD
XXR4AKN	Field duplicate for the aquatic macroinvertebrates collected with the kick net. Note: "XX" should be either "W3" or "SP" depending on the location where the sample was collected.
W3R1FB	Field Blank for day 1 (Note: If the field blank was collected at the sediment pond, than the first 2 characters should be "SP". If sampling continues for a second day, the next blank should be replicate 2, "R2".

Appendix C – Macroinvertebrate Composition by Habitat, Feeding Style and Diet

Macroinvertebrates Collected at Monticello Wetlands and Sediment Ponds 2006		
Macroinvertebrate	**Habitat**	**Feeding style and diet**
Order: *Odonata* Family: *Zygiotera* Common name: damselflies	Surface water— One to two years aquatic Dwells either crawling on surfaces under water or within the sediment	Damselfly nymphs are engulfer predators (eating whole body). They begin life eating zooplankton, and, as they grow, the size of their prey grows. Smaller invertebrates of all eating styles comprise most of their diet.
Order: *Odonata* Family: *Anisoptera* Common name: dragonflies	Surface water— Average of one year aquatic Dwells by crawling on sediment, rock or aquatic plants, or by hiding in sediment	Dragonfly nymphs are also engulfer predators, consuming the whole body of their prey. They begin eating very small prey and progress to larger prey, such as small fish, frogs and tadpoles.
Order: *Hemiptera* Family: *Notonectidae* Referred to as: notonectid Common name: back swimmers	Surface water— This species lives entire life in water column. Notonectids are free-swimming in each stage. Adults inhabit the same water as egg and larval stage as a rule. They are long-lived for insects.	Back swimmers are piercer predators—they pierce their prey, inject enzymes to liquefy the contents and suck the fluid out. They eat aquatic insects, crustaceans, and snails as well as small vertebrates such as fish fry and tadpoles.
Order: *Trichoptera* Common name: Caddisflies*	Mostly surface water— Three months to two years aquatic Mostly dwell on bottom, crawling on the underwater surfaces. A few burrow into the sediment.	Most Caddisfly larvae are true omnivores, eating plant material and other macroinvertebrates, even other caddisfly larvae. They feed on dead or decaying matter, gather or collect organisms from the water column, scrape them from the aquatic surfaces, and some either engulf or pierce prey.
Order: *Ephemeroptera* Common name: Mayflies	Surface water— Four months to two years aquatic Dwells on bottom surfaces mostly. A few burrow into sediment	Most mayflies are collector-gatherers or scrapers. This is a primary consumer role—plant-eating or micro-phyto-organisms. There is a rare species that are engulfer-predators eating mostly Chironomids—sediment dwellers.
Order: *Gastropoda* referred to as: gastropods Common name: snails	Surface water dwelling— Aquatic snails live on rocks, sand, mud, vegetation, and plant detritus for their entire life.	Most snails are scrapers—primary consumers and detritus feeders. Some gather or sieve food from the water column, some shred plant or dead material from the bottom, and some are scavengers.
Order: *Coleoptera* Common name: beetles	Surface Water— Larvae and adults share all areas in the water.	Beetles fill all the major feeding types except for shredder-detritus eater.
Order: *Amphipoda* Order:: *Malacostraca* Common name: scuds	Surface water— Scuds are totally aquatic. Scuds live on the bottom of surface water.	Scuds are omnivorous, eating mostly plant and other primary producer matter and detritus. They readily engulf dead organisms, also and have been known to capture live prey.

Macroinvertebrates Collected at Monticello Wetlands and Sediment Ponds 2006

Macroinvertebrate	Habitat	Feeding style and diet
Order: *Diptera* Family: *Chironomidae* Referred to as: diptera Common name: midges	Sediment dwellers— Aquatic for three weeks to 3 months The most common chironomid larvae lives in soft sediment and detritus.	Midge larvae eat organic components of the sediments most of them live in. They swallow everything and digest what is useful to them, expelling the indigestible sediment.
Class: *Oligochaeta* Common name: earthworms	Sediment— Aquatic earthworms are totally aquatic and are burrowers.	Most aquatic earthworms are collector-gatherers, eating mud and organics as they burrow and expelling indigestible components.
Order: *Decopoda* Common name: crayfish	Surface water— Crayfish live two to eight years and are totally aquatic.	Crayfish belong in various feeding groups depending on their family, genus and species, but their main diet is decaying plant material. They will feed on other macroinvertebrates, small fish and fish eggs.
Order: *Hemiptera* Family: *Corixidae* Common name: Water Boatman	Surface water— Water boatmen swim over the substrate.	Water Boatmen are collector-gatherers, ingesting diatoms, algae, protozoa, and other microscopic organisms living in the substrate.
Order: *Coleoptera* Family: *Dytiscidae* Common name: Predaceous diving beetle	Surface water— Predaceous diving beetles climb on aquatic plants, swim in the water, and float on the surface.	Predaceous diving beetle larvae are piercer-predators, injecting a substance that liquefies their victims and sucking out the insides. Adults are engulfer-predators, chewing and swallowing their prey in entirety.
Order: *Diptera* Family: *Culicidae* Common name: mosquitoes	Surface water— Mosquito larvae and pupae live/swim in shallow water for seven to ten days.	Mosquito larvae are collector-gatherers or collector filterers, sweeping microscopic organisms into their mouths to engulf them.
Order: *Rhynchobdellida* Family: *Glossiphoniida* Common name: leech	Surface water— Leeches skim the surface of the substrate and swim freely in the water column.	All leeches are predatory. Most are carnivorous, ingesting all of their prey.

References: Voshell, J. R. Jr., 2002. *A guide to common freshwater invertebrates of North America.* MacDonald & Woodward Publishing Company Blacksburg, VA.
EPA, 2006. Biological Indicators of Watershed Health: Leeches. U.S. Environmental Protection Agency, Washington, D.C. Available at (last accessed January 19, 2006): http://www.epa.gov/bioindicators/html/leeches.html

Appendix D – Analytical Results for 2006 Macroinvertebrate Samples

Attachment 1: Se Results for Macroinvertebrate Tissues

Attachment 2: Se Results for Equipment Blank Water

Attachment 3: Quality Assurance / Quality Control Narrative for Macroinvertebrate Tissues and Equipment Blank Water Se Results

Attachment 1: Se Results for Macroinvertebrate Tissues

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1529 West Sequim Bay Road
Sequim, Washington 98382
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Monticello Macroinvertebrates 2007
Se in Tissue
(Units: ug/g dry wt, data are not blank corrected)

MSL Code	SPONSOR CODE	Field Sample ID	Matrix	Collection Date	Analytical Batch	Percent Moisture	Se
						CAS CODE:	7782-49-2
						Method:	HGAA-FIAS
						Units:	µg/g dry wt.
Laboratory Achieved Method Detection Limits (MDLs)							**0.0109**
Reporting Limit (RL)							**0.035**
2753-1	SP-R1-AKN	NFJ-764	Crawfish	05/23/2007	F073007A	71.8	5.10
2753-2	SP-R2-AKN	NFJ-765/1	Invertebrates	05/23/2007	F073007A	83.8	8.02
2753-3	SP-R2-AKN	NFJ-765/2	Invertebrates	05/23/2007	F073007A	82.3	8.78
2753-4	SP-R3-AKN	NFJ-766	Invertebrates	05/23/2007	F073007A	81.2	3.55
2753-5	W3-R2-AKN	NFJ-768	Invertebrates	05/24/2007	F073007A	83.5	9.46
2753-6	W3-R3-AKN	NFJ-769	Invertebrates	05/24/2007	F073007A	80.8	3.91
2753-7	SP-R1-AKN	NFJ-764	Invertebrates	05/23/2007	F073007A	82.4	6.15
2753-8	W3-R2-AKN	NFJ-771	Invertebrates	05/24/2007	F073007A	70.2	6.80
2753-10	SPRI AHD	NFJ-770	Invertebrates	06/26/2007	F073007A	86.1	5.82
Procedural Blanks							
Blank R1 071907	Method Blank				F073007A		0.0109 U
Blank R2 071907	Method Blank				F073007A		0.0125 J
Blank R3 071907	Method Blank				F073007A		0.0109 U
Blank Spike Results							
LCS 07	LCS				F073007A		1.99
	Spike concentration						*2.0*
	PERCENT RECOVERY, LCS-1						**100%**
Matrix Spike Results							
2753-4 MS	MS				F073007A		9.96
2753-4	SP-R3-AKN		Invertebrates	05/23/2007	F073007A	81.2	3.55
	Spike concentration, MS						5.05
	PERCENT RECOVERY, MS						**127% N**
Replicate analysis Results							
2753-7	SP-R1-AKN		Invertebrates	05/23/2007	F073007A	82.4	6.15
2753-7 DUP	SP-R1-AKN		Invertebrates	05/23/2007	F073007A	82.4	6.01
	Mean						6.08
	RPD						**2%**
Standard Reference Material							
1566 b 071907	SRM		Oyster Tissue		F073007A		1.95
	certified value						2.06
	range						±0.15
	percent recovery SRM 1566b						**95%**
IAEA-140 071907	SRM		Fucus		F073007A		0.0808
	reference value						0.079
	range						REF
	percent recovery SRM IAEA 140						**102%**

* Duplicate analysis not within QC criterion of <20% RPD
& SRM outside QC criterion of ±20% Recovery
N Matrix spike outside QC criterion of ±25%
U Analyte not detected above the MDL, MDL reported
J Analyte detected greater than the MDL, but less than the RL
RPD Relative Percent Difference
REF Reference value for SRM

Attachment 2: Se Results for Equipment Blank Water

BATTELLE MARINE SCIENCES LABORATORIES
Jill Brandenberger, Project Manager
1529 West Sequim Bay Road
Sequim, Washington 98382
(360) 681-4564

Monticello Macroinvertebrates 2007
Equipment Blank Water

MSL Code	SPONSOR CODE	Matrix	Collection Date	Analytical Batch	Se
				CAS CODE:	7782-49-2
				Method:	HGAA-FIAS
				Units:	µg/L
Laboratory Achieved Method Detection Limits (MDLs)					**0.0507**
Reporting Limit (RL)					**0.161**
2753-9	NFS-770	EB Water	05/24/2007	F073007A	0.0567 J
2753-11	Ethanol Solution	ethanol		F073007A	1.01
Procedural Blanks					
Blank07	Method Blank			F073007A	0.0507 U

Blank Spike Results
See Tissue Table for LCS results.

Standard Reference Material
See Tissue Table for SRM results.

* Duplicate analysis not within QC criterion of <20% RPD
& SRM outside QC criterion of ±20% Recovery
N Matrix spike outside QC criterion of ±25%
U Analyte not detected above the MDL, MDL reported
J Analyte detected greater than the MDL, but less than the RL
RPD Relative Percent Difference

Attachment 3: Quality Assurance / Quality Control Narrative for Macroinvertebrate Tissues and Equipment Blank Water Se Results

PROJECT: Monticello Invertebrates
PARAMETER: Selenium (Se)
LABORATORY: Battelle Marine Sciences Laboratory (MSL), Sequim, Washington
MATRIX: Macroinvertebrates and equipment blank water

SAMPLE CUSTODY AND PROCESSING: Nine tissue samples and two equipment blank samples were received in two batches on 06/01/07 and 06/29/07. All samples were received in good condition (i.e., no sample containers were broken or leaking). The project was assigned a Battelle central file (CF) identification number (2753) and samples were entered into the MSL sample tracking and project management system.

SAMPLE PROCESSING INFORMATION:

Lab Sample IDs:	**2753*1-8, 10 (tissue) and 2753*9, 11 (equipment blank)**
Description:	Macroinvertebrates and equipment blank samples
Collection date	05/23/07, 05/24/07, 06/26/07
Laboratory arrival date	06/01/07 and 06/29/07
Cooler temp. on arrival	2.6°C and 2.7°C
Digestion Date (Aqua Regia, MSL-I-024)	07/19/07
HGAA-FIAS Analysis Date (Se, MSL-I-030)	07/30/07

METHODS: All tissue samples were freeze-dried and homogenized using a ball-mill prior to digestion according to Battelle SOP MSL-C-003, Percent Dry Weight and Homogenizing Dry Sediment, Soil and Tissue. Tissue samples were digested according to Battelle SOP MSL-I-024, Mixed Acid Tissue Digestion. An approximately 500-mg aliquot of each dried, homogeneous sample was combined with nitric and hydrochloric acids (aqua regia) in a Teflon vessel and heated in an oven at 130°C (±10°C) for a minimum of eight hours. After heating and cooling, deionized water was added to the acid-digested tissue to achieve analysis volume. Digested samples were analyzed for Se using hydride generation flow injection atomic absorption spectroscopy (HGAA-FIAS) according to Battelle SOP MSL-I-030, Determination of Metals in Aqueous and Digestate Samples by HGAA-FIAS. The base method for this procedure is EPA Method 270.3. Tissue results were determined and reported in units of µg/g on a dry-weight basis.

Equipment blank samples consisted of a deionized water blank (sample 2753*9) and an ethanol blank (2753*11). The ethanol was diluted 1:10 with deionized water and both samples were pre-reduced for total Se prior to analysis by hydride generation flow injection atomic absorption spectroscopy (HGAA-FIAS) according to Battelle SOP MSL-I-030, Determination of Metals in Aqueous and Digestate Samples by HGAA-FIAS. The base method for this procedure is EPA Method 270.3. Liquid equipment blank samples results were determined and reported in units of µg/L.

HOLDING TIMES: The project specific holding time is one year for all metals in tissue and six months for water samples. Holding times were achieved for both matrices.

DATA QUALITY CRITERIA (DQC):

Analyte	Analytical Method	Range of MS/MSD Recovery	Replicate Precisions (RPD)	SRM Accuracy (PR)	Matrix	MDL	Reporting Limit
Se	HGAA-FIAS	75-125%	±20%	80%-120%	Tissue	0.0109 µg/g dry wt.	0.035 µg/g dry wt.
					EB samples	0.0507 µg/L	0.161 µg/L

RPD = Relative Percent Difference
PR = Percent Recovery
EB = Equipment Blanks

DETECTION LIMITS: Analytical results were reported to the laboratory achieved method detection limits (MDL) as determined from the annual MDL study. The MDL study is determined annually according to 40 CFR Part 136 Appendix B and defined as seven replicates of cellulose or chicken breast for tissue (tissue matrices with metals low enough to performing an acceptable MDL study) and spiked deionized water. MDLs are determined using the same methodology as the samples. The reporting limit (RL) is determined as 3.18 times the achieved MDL. Data are evaluated and flagged in accordance with the following criteria:

U The analyte was not above the MDL, MDL was reported.

J The value is less than the achieved reporting limit, but greater than the MDL.

N Matrix spiked sample was outside the QC criterion of 75-125% recovery.

& SRM was outside the QC criterion of 80-120% recovery.

* Duplicate analysis outside QC criterion of ±20% relative percent difference.

METHOD BLANKS: Three method blanks were prepared with the tissue samples and one for the equipment blank samples. Se was not detected at a level greater than the RL.

LABORATORY CONTROL SAMPLE (LCS) ACCURACY: One laboratory control sample (LCS) was analyzed with these samples. The percent recovery was within the QC criterion of 75-125% recovery.

MATRIX SPIKE (MS/MSD) ACCURACY: There was sufficient material to analyze one matrix spike with the tissue samples. The matrix spike sample recovered at 127% and was just outside the QC criterion of 75-125% recovery. The high recovery was attributed to the insufficient spiking level relative to the native sample concentration. Acceptable accuracy was demonstrated by the LCS sample and both SRMs.

REPLICATE PRECISION: Analytical precision was determined by the digestion and analysis of sample in duplicate. Analytical precision of replicate analyses was expressed as the relative percent difference (RPD) between the replicate results. The laboratory duplicates were within the QC criterion of <20% RPD.

STANDARD REFERENCE MATERIAL ACCURACY: Analytical accuracy was expressed as the percent recovery of the measured value relative to the certified value for two separate standard reference materials (SRM). One SRM was 1566b Oyster tissue and the other was IAEA 140 Fucus. The percent recoveries were within the QC criterion of 80-120% recovery.