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Monticello Mill Tailings Site Macroinvertebrate Sampling for 2006

A.L. Bunn
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February 2007

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

In the spring of 2006, 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 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 between 2005 and 2006 in the Se concentration in macroinvertebrates collected with kick nets in wetland 3 and the sediment pond.

The geometric mean of the Se concentration in macroinvertebrate samples collected with Hester-Dendy artificial substrate samplers in 2006 was greater than the toxicity limit for protection of fish and wildlife. In 2006, there was a significant difference between the Se concentration in the macroinvertebrates collected with kick nets in wetland 3 and the sediment pond compared to that collected with the Hester-Dendy samplers in the sediment pond. Also, the Se results for the Hester-Dendy samples from the sediment pond in 2006 were significantly greater than the results from 2005.

The 2006 concentrations of Se in macroinvertebrate samples do not conclusively indicate that there is a risk to fish and wildlife from Se in the waters at MMTS. The macroinvertebrate results indicate that there is not a strong correlation to the Se concentration in water and sediment samples. The results of the macroinvertebrate samples along with the results of the bird surveys should be considered by DOE and the Biological Technical Assistance Group in determining if further investigations are warranted.

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1.0 Introduction

In the spring of 2006, 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).

Based on the 2005 sampling effort, aquatic macroinvertebrates were collected in the spring of 2006 from the regions that were of greatest concern in the past year: wetland 3 and the sediment pond. Activities in the spring of 2006 included deployment of artificial substrate samplers (called 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).

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 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) during 2005 and 2006. The results of the aquatic macroinvertebrate samples were compared to the benchmarks for Se effects. These results from 2006 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. 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.

This report summarizes the results of the 2006 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 and other 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 2006 was focused on wetland 3 and the sediment pond. Field sampling procedures for 2006 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 (Appendix B).

2.1 Kick Net Sampling

Kick net collections of macroinvertebrates were conducted on May 17, 2006 in wetland 3 and the sediment pond (Figure 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 conditions of wetland 3 and the sediment pond were different in 2006 than in 2005. The water level in wetland 3 during the 2006 sampling was very low, with ~20-30 cm (~8-12 in) of water in the center portion of the wetland (Table 2). In September 2005, the outlet of wetland 3 was modified to remove accumulated silt, which left much of the original wetted portion of wetland 3 without water in the spring of 2006. Much of the wetland was difficult to sample due to thick mud and dense cattails. Therefore, all kick net samples were collected near the center portion where the deepest water was found. There was a great deal more water flowing through wetland 3 during 2005, as well as through the entire watershed, due to the substantially greater snow melt run-off. The conditions in the sediment pond in 2006 were much more suitable for field collections than in 2005. The water level remained relatively stable during the spring of 2006, whereas during the sampling effort in 2005, the water level in the sediment pond was much deeper due to snow melt run-off, leaving the southern portion of the pond inaccessible for sampling.

At least four replicate samples were collected at each location, and all samples exceeded the desired mass of 3 g wet weight for Se analysis (Table 2). In wetland 3, the composition of the macroinvertebrates in each sample was primarily of the insect order *Odonata*, which includes dragonflies and damselflies (Table 3). *Odonata* composition ranged from 40 to 62% of the sample's total mass. The remainder of the mass differed for each sample and primarily comprised of aquatic insects and some gastropods (snails). Appendix C provides more information about the habitat, feeding styles and diets of the classes of macroinvertebrates found during the 2006 sampling effort.

In the sediment pond, the composition of the four replicate samples varied much more than the samples collected in wetland 3 (Table 3). Typically, the most common type of macroinvertebrate in all the samples belonged to the insect order of *Hemiptera*, which includes the predacious back swimmers. *Hemiptera* composition ranged from 10 to 20% of the sample's total mass. The kick net samples also included crustaceans (crayfish) and gastropods in addition to aquatic insects. Samples were collected along the shoreline in water depths of 0-0.75 m (0-2.5 ft), primarily along the outlet and west end of the pond where emergent vegetation was present (Table 2). A few larger crayfish (> 3 g wet weight) were collected but not included in the samples based on the field sampling procedures (Appendix 2, Attachment 2).

Figure 1. Sampling for Macroinvertebrates with Kick Net (A) and Macroinvertebrate Species Composition for Wetland 1 (B) and the Sediment Pond (C)

Table 2. Summary of 2006 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 17, 2006	Three samplers were attached to cinder blocks and placed into the sediment pond
Collected at wetland 3 using kick nets	May 17, 2006	Weather: Sunny, breezy. Samples collected 1050-1150. Water temperature = 26.5°C (79.7°F), dissolved oxygen = 7-9 mg/L, measured near east end of wetland. Comment: Wetland water level was very low with 20-30 cm (~8-12 in) of water in the center portion. The center part of wetland was hard to sample with thick mud and dense cattails. All samples were collected near the center portion where the deepest water was found.
Collected at sediment pond using kick nets	May 17, 2006	Weather: Sunny breezy. Samples collected 0800-0900. Water temperature = 15.7°C (60.3°F), dissolved oxygen = 8.6 mg/L, measured near mouth of Montezuma Creek. Comment: Samples were collected along the shoreline in water depths of 0-76 cm (0-30 in) primarily along the outlet and west end of the pond where emergent vegetation was present. A few larger crayfish were collected but not included in the samples. Checked the three Hester-Dendy samplers. The sampler located west of the inlet was not secured to the cider block and was in the sediments. The sampler was repositioned and fastened to the top of the block. While working on the sampler, there appeared to be some colonization by macroinvertebrates, but mostly by smaller dipterans.
Retrieved Hester-Dendy samplers at sediment pond	June 13-14, 2006	All 3 Hester-Dendy samplers were retrieved on June 13 according to procedure (Appendix B). Samplers were shipped, in-tact, to Richland, WA. Macroinvertebrates were collected from samplers on June 14. Empty trichoptera (caddisfly) cases were found in all samplers: 4 cases in R1 (located ~10 m west of inlet); 16 cases in R2 (north end of pond); 3 cases in R3 (near the outlet). There were five additional cases in R2 with larvae, and the cases were made partially of small grain-size substrate rather than plant material. No cases were added to samples for Se analysis.

2.2 Hester-Dendy Artificial Substrate Sampling

The Hester-Dendy artificial substrate samplers (14 plate, 7.6 cm square) were placed in the sediment pond the week of April 17, 2006. The samplers were fastened to a cinder block and placed a water depth of ~0.45 m (1.5 ft.) (Appendix B). The samplers were recovered eight weeks later on June 13-14, 2006, which was four weeks after the kick net sampling effort (Table 2). The samplers were located around the edge of the sediment pond. R1 was located ~10 m (33 ft) from the inlet on the west end of the pond; R2 was located on the north end of the pond; and R3 was located near the outlet on the east end of the pond.

When the samplers were checked in May during the kick net sampling effort, there did not appear to be many macroinvertebrates present, mostly small dipteran larvae. They were not removed at that time to allow for more macroinvertebrates to colonize the artificial substrate samplers. The sampler located west of the inlet was not secured to the cinder block and was in the sediments. It was repositioned and re-fastened to the cinder block.

Table 3. Results of Se Analyses in Macroinvertebrate Samples Collected in May 2006

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	1	3.44	6.47	5.80 (1.39)	Odonata (40%), Hemiptera (30%), Gastropoda (10%), Ephemeroptera (10%), Coleoptera (L) (10%)
	2	3.50	3.69		Odonata (60%), Corixidae (10%), Dytisidae (L) (20%), Ephemeroptera (10%)
	3	3.34	5.93		Odonata (62%), Corixidae (25%), Gastropoda (13%)
	4	3.71	7.98		Odonata (50%), Coleopteran (L) 10%, Corixidae (25%), Gastropoda (10%), Ephemeroptera (5%)
Sediment Pond, Kick Net	1	3.46	4.20	4.26 (1.19)	One small crayfish (30%), Odonata (25%) Hemiptera (10%), Gastropoda (25%), Ephemeroptera (10%)
	1 R		3.09		
	2	3.94	5.15		Ephemeroptera (50%), Hemiptera (20%), snails (20%), Trichoptera (5%), Coleoptera (A) (5%)
	3	3.24	4.74		Odonata (40%), Hemiptera (20%), Gastropoda (20%), Ephemeroptera (20%)
	3 R		4.80		
	4	10.25	3.95		Coleoptera/Dytisidae (A) (50%), Odonata (20%), Hemiptera (10%), Ephemeroptera (10%), Gastropoda (5%), Amphipoda/Chironomidae (5%)
	4 R1		2.44		
	4 R2		4.64		
Sediment Pond, Hester-Dendy	1	0.31	12.65	9.38 (1.49)	Chironomidae (70%), Coleoptera (A) 30%
	2	0.78	10.93		Trichoptera (50%), Chironomidae (40%), Amphipoda (5%), Culicidae (5%)
	3	1.09	5.97		Gastropoda (40%) , damselfly (10%), leach (40%), Chironomidae (8%), Amphipoda (2%)

NOTES: Sample numbers followed by an "R" represent the replicate redigest of the original dried sample. Sample composition information followed by an "L" are larval life stages and an "A" are adult life stages.

When the samplers were recovered in June, there were not many macroinvertebrates colonizing the substrate. All three of the samplers had less than the 3 g wet weight criteria stated in the program directive (Appendix A) and the field sampling procedures (Appendix B, Attachment 2). Each sampler had a different composition of macroinvertebrates and included types of organisms that were not collected during sampling with the kick nets (Table 3). There were numerous empty trichoptera (caddisfly) cases, indicating that the samples had been colonized by aquatic insects and the larval forms that had been in the samplers had emerged and vacated the samplers (Table 2). The caddisfly larvae that were still present on sampler R2 had cases made of fine grains of sediment rather than the plant material used for the empty cases, which indicates these were probably of a different genus of caddisfly.

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. The kick net samples were held in a freezer until the samples recovered from the Hester-Dendy samplers were available, and samples were processed on July 14 and 19, 2006 along with several types of quality control measures.

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 Teflon vessel and heated in an oven at 130°C (±10°C) for a minimum of 8 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 was collected as part of the quality control plan as stated in the program directive. The blank was prepared while collecting kick net samples. The sample was analyzed using the same methods as the tissue samples. 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 and one sample in the field was split for evaluation of quality control in the field. The field duplicate was collected in wetland 3 (sample 4). The split sample was collected in the sediment pond (sample 4). The duplicate and the split samples were analyzed in the same way as all the other macroinvertebrate samples (Table 3).

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 0.0211 mg/kg dry weight and an RL of 0.0671 mg/kg dry weight. For the field blanks, the HGAA-FIAS analysis had an MDL of 0.0633 µg/L and an RL of 0.201 µg/L. These values were the same as for the samples analyzed in 2005.

The laboratory quality control measures included a method blank, a matrix spike, a matrix spike duplicated and a laboratory control sample (standard reference material), as discussed in the program directive. These quality control measures were completed for the kick net samples and the Hester-Dendy samples. The method blank was used to determine if there was contamination associated with the laboratory storage of the samples, preparation or instrumentation. The method blank for the samples analyzed on July 14 was 0.0398 mg/kg, which was above the MDL but less than the RL. The method blank for the samples analyzed on July 19 was below the MDL and was reported at the MDL (0.0211mg/kg).

The matrix spike (MS) and matrix spike duplicate (MSD) were used to determine if there was any interference in the spike matrix and as a measure of the accuracy and precision of the analysis. For the kick net samples, the MS and MSD were 109% and 105% recovery and within the quality control requirement of 75-125% recovery. Analytical precision was measured for these samples by analyzing a duplicate sample and the MS/MSD pair. The relative percent difference (RPD) for the duplicate was 3%, which was within the quality control requirement of <20%.

Standard reference material (SRM) was also analyzed to address questions with the results for the initial batch of samples. These analyses included two laboratory control samples (LCS) and a duplicate of the second LCS (LCSD). It was thought that the spread of the results for the kick net samples from the sediment pond might have been due to incomplete acid digestion of the diversity of the macroinvertebrate in the samples. In addition, the analysis of the standard reference material would help in understanding the instrument error associated with the small sample size collected from the Hester-Dendy samplers.

A laboratory control sample (LCS) was used to determine the analytical accuracy by analyzing a standard reference material. For the first batch of samples analyzed on July 14, the percent recovery was 106%, within the quality control criterion of 80-120%. For the second batch of samples analyzed on July 19, the percent recovery was 102% (LCS) and 103% (LCSD), within the quality control criterion of 80-120%. RPD for the LCS/LCSD pair was 2% on July 19, which was within the quality control requirement of <20%.

In addition, the SRM was analyzed twice as well as a spike with the MS for the analysis of the July 19 batch of samples. The analysis of the SRM was compared to the certified or reference value, and the percent recoveries were 102% and 95%, which was within the quality control requirement of <20%. The percent recovery of the SRM with the MS was 98%, which was within the quality control requirement of <20%.

Table 3 summarizes the results by location for the macroinvertebrate samples collected with kick nets. All the samples exceeded the 3 g wet weight mass desired for analytical purposes. The field duplicate was a kick net sample from wetland 3 called sample 4. Its results are incorporated into the calculation of the mean and standard deviation for wetland 3 kick net samples.

There was more than one split sample prepared out of the kick net samples collected in the sediment pond because the RPDs were outside the quality control requirement of <20%. The RPD for sample 1 and the re-digest of the sample was 31%; the RPD for sample 4 and the first re-digest was 47%; and the RPD for first and second re-digest of sample 4 was 62%. However, sample 3 and the re-digest of that sample was within the quality control requirement with an RPD of 1%. Since all of the quality control samples indicated that the laboratory procedures and analytical equipment were within quality control requirements, all of the results of the kick net samples and the re-digested samples were included in the results discussed in Table 3.

Table 3 summarizes the results of the macroinvertebrates collected from the sediment pond with the Hester-Dendy samplers. While the sample size was very low from sampler R1, there was enough dried material for the analysis. There was not enough material to re-digest the samples as was done with the kick net samples from the sediment pond. Therefore, no relative percent difference could be calculated to explain the precision of the sample analyses.

4.0 Discussion of 2006 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. 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.

Figure 2 illustrates the results of the macroinvertebrates collected in the spring of 2006. Each replicate is represented by location as well as the geometric mean of all the replicates from that location (with an error bar representing two geometric standard deviations). 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.

The results for wetland 3 were collected only with kick nets. The results for the sediment pond are shown separately for the kick net and Hester-Dendy samples. Lines on Figure 2 indicate the ecological risk guidelines for Se residues in macroinvertebrates.

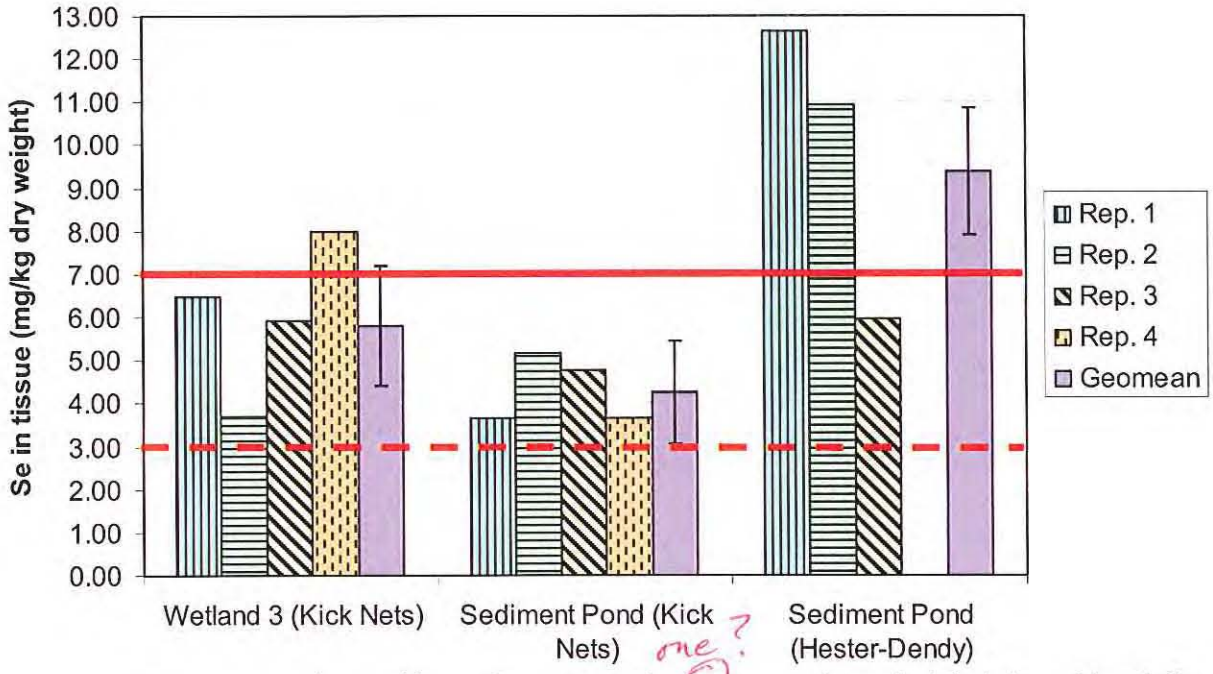
For wetland 3, the Se concentrations in the macroinvertebrates collected in kick net samples 1, 2, and 3 were within the level of concern for Se, and the Se concentration in the macroinvertebrates from sample 4 exceeded the toxicity threshold for Se. Overall, the geometric mean of the four samples was within the level of concern for Se but was less than the toxicity threshold.

For the kick net samples from the sediment pond, the Se concentration in all of the macroinvertebrates had values within the level of concern for Se. None of the results exceeded the toxicity threshold. The geometric mean of all the results from the kick net samples was within the level of concern for Se but was less than the toxicity threshold. Se results from the kick net samples collected in the sediment pond were much less variable than the kick net samples from wetland 3.

For the Hester-Dendy samples from the sediment pond, Se concentrations in the macroinvertebrates collected in samplers R1 and R2 were greater than the toxicity threshold, and the Se concentration in the macroinvertebrates from sampler R3 was within the level of concern. Overall, the geometric mean of the three samples was greater than the toxicity limit for Se concentration in macroinvertebrates.

There was no significant difference between the Se concentration in the macroinvertebrates collected with kick nets in wetland 3 and the sediment pond in 2006 (Figure 2). This is based on a comparison of the geometric standard deviations. Kick net sampling is done in a similar fashion at both locations, and that technique is likely to collect macroinvertebrates living in those locations and receiving similar exposures to the water and sediment.

There was a significant difference between the Se concentration in the macroinvertebrates collected with kick nets in wetland 3 and the sediment pond compared to the Se concentration in the macroinvertebrates collected with the Hester-Dendy samplers in 2006 ($P<0.05$) (Figure 2). This is based on a comparison of the geometric standard deviations. The two methods of sampling macroinvertebrates collect invertebrates that are living in slightly different locations within the water system and, therefore, have different exposures to the water and sediment.

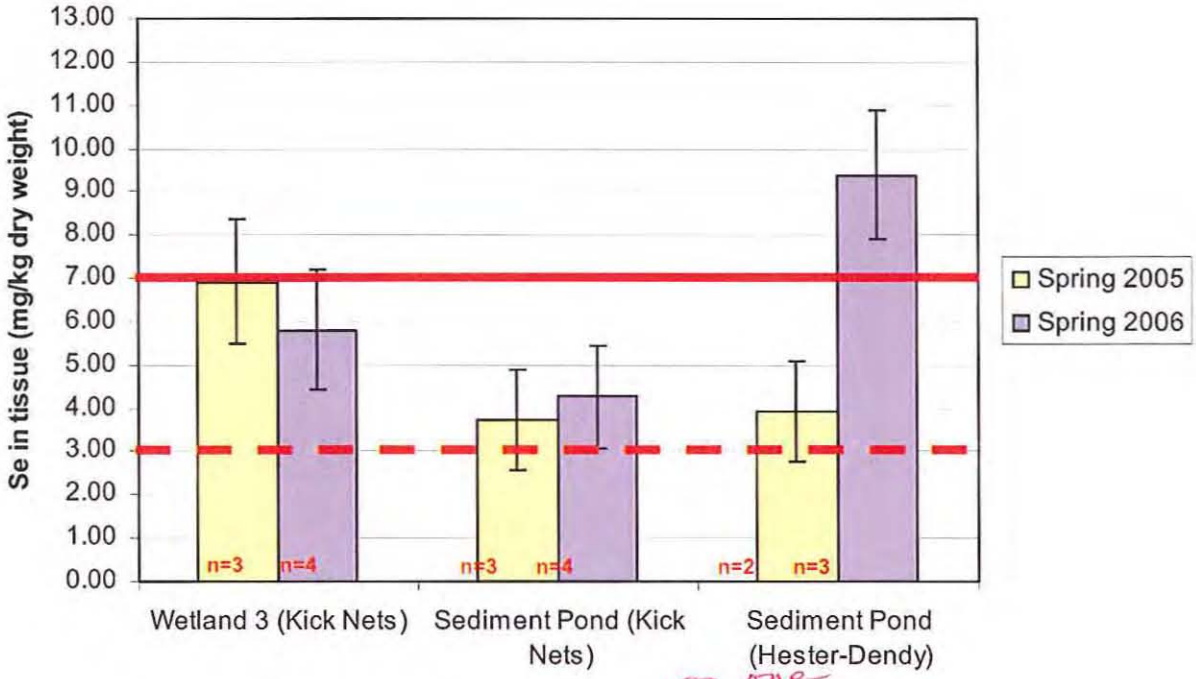


NOTE: Geometric means are shown with error bars representing two geometric standard deviations. Lines indicate ecological risk guidelines for Se residues in macroinvertebrates: level of concern = 3-7 mg/kg dry weight Se; and toxicity threshold >7 mg/kg dry weight Se.

Figure 2. Analytical Results for Se in Macroinvertebrate Tissues Collected during the Spring of 2006, with Comparison to Ecological Risk Guidelines for Se Residues

Figure 3 is a comparison of the macroinvertebrate sampling results in 2005 and 2006 by location. There is no statistical difference in the Se results for the macroinvertebrates collected with kick nets in wetland 3 and the sediment pond over the two years of sampling. This is based on the comparison of the standard deviations for the respective samples by location. However, the wetland 3 Se results in the macroinvertebrate tissues appear to be trending downward, and the 2006 results are below the toxicity threshold.

The results for Se in the macroinvertebrate tissues collected with the Hester-Dendy samplers increased significantly in 2006 compared to 2005 ($P<0.05$) (Figure 3). While the kick net and Hester-Dendy results in the sediment pond in 2005 were similar, there was a significant difference between these two collection methods in 2006. In fact, the Se results from the macroinvertebrates collected with the Hester-Dendy samplers are above the toxicity threshold in 2006. The number and composition of the macroinvertebrates collected with these samplers in 2005 and 2006 does suggest that a different population of organisms colonize the samplers compared to those collected with kick nets (Table 3 and DOE 2005). The variability between the two years of sampling may be attributed, in part, to the significant differences in the climate and water flow conditions experienced at MMTS in 2005 and 2006 (Figure 4). The geochemical species of Se in natural waters is predominately an oxyanion, which is highly soluble and behaves conservatively in the water column. This type of geochemical behavior is extremely dependant on the hydrologic conditions with evaporative concentration of Se in the water column during periods of low inflow and dilution during periods of excessive water in flows, such as in 2005 (Johnaon 2004).



NOTE: Geometric means are shown with error bars representing two one 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.

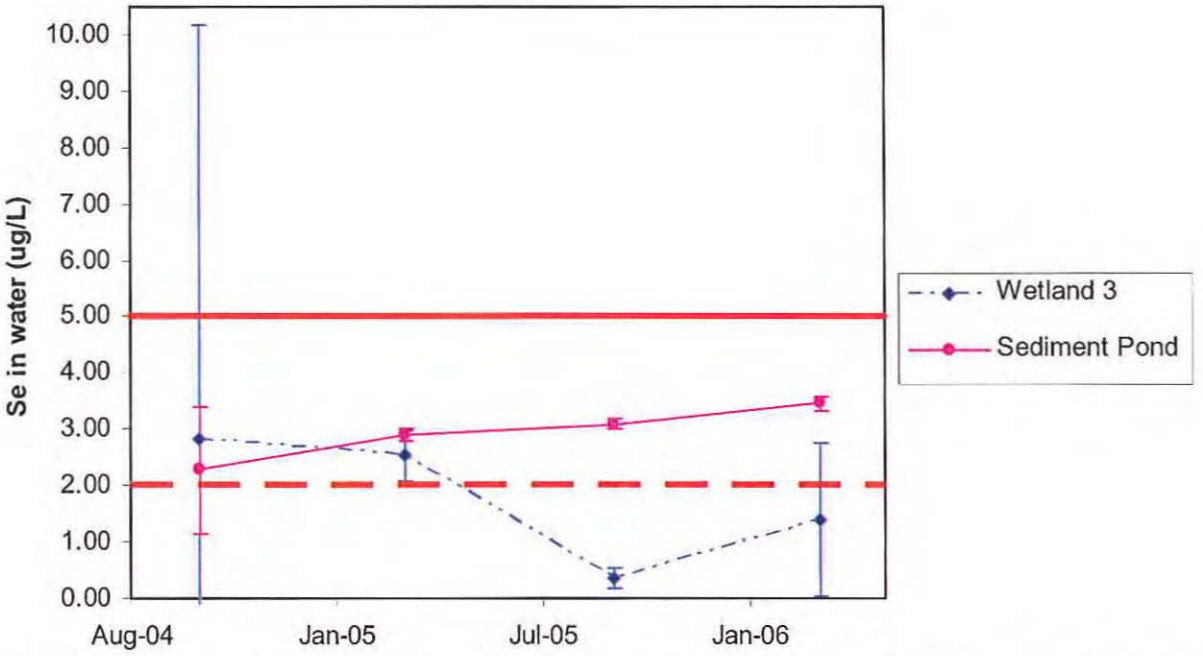
Figure 3. Comparison of Se Concentration in Macroinvertebrate Tissue for 2005 and 2006 by Location, with Comparison to Ecological Risk Guidelines for Se Residues

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).

Figure 5 shows the Se results from unfiltered water samples from October 2004, April and October 2005, and April 2006 collected at three established locations in wetland 3 and the sediment pond. Unfiltered water samples are shown because the water best represents the exposure to the macroinvertebrates. The mean of the Se concentrations in the water from wetland 3 has remained near or below the water quality level of concern during the last three sampling periods. Results of the first water sample from wetland 3 in October 2004 are skewed by one of the replicate samples that exceeded the toxicity threshold (1.0, 1.5, and 14 µg/L Se). The sample from October 2004 that exceeded the toxicity threshold was collected close to a seep that is thought to be the major source of Se in wetland 3. The Se results in sediment pond water have remained within the water quality level of concern for the last four sampling events and have shown a trend of increasing Se concentration with time.

Figure 6 shows the Se results from sediment samples from October 2004, April and October 2005, and April 2006, collected at three established locations in wetland 3 and the sediment pond. The Se concentration in sediment samples from wetland 3 has remained below the level of concern. The variability during the last sampling period increased greatly because one of the replicate samples

Figure 4. Water Conditions in the Sediment Pond during Kick Net Sampling in 2005 and 2006

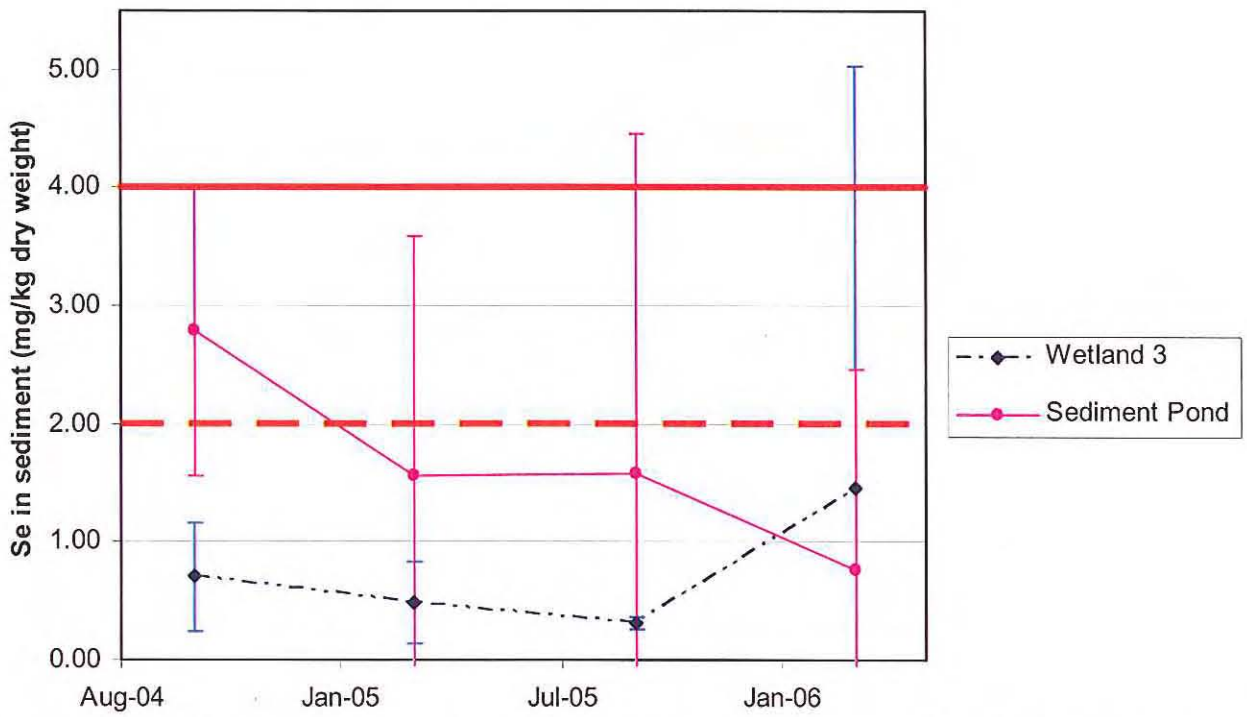


NOTE: Geometric means are shown with error bars representing two geometric standard deviations. Lines indicate ecological risk guidelines for Se residues in water: level of concern = 2-5 μg/L Se; and toxicity threshold > 5 μg/L Se.

Figure 5. Water Sample Se Results Collected in October 2004, April and October 2005, and April 2006 from Wetland 3 and Sediment Pond

exceeded the toxicity threshold (0.45, 1.0, and 6.9 mg/kg dry weight Se). Based on a comparison of the geometric standard deviations, there is no significant difference in the sediment samples collected in wetland 3 from 2004 through 2006. The geometric means of the Se results in sediment samples from the sediment pond have been below the level of concern for the last three sampling events. The variability of the samples during each sampling event is very high, which may be related to the sediment loading into the pond from the water shed as well as the high biological activity. Based on a comparison of the geometric standard deviations, there is no significant difference in the sediment samples collected in wetland 3 from 2004 through 2006.

The large variability in the Se results from the water and sediment samples during some of the sampling events over the last two 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 rather than living in the sediments 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.



NOTE: Geometric means are shown with error bars representing two geometric standard deviations. Lines indicate ecological risk guidelines for Se residues in sediment: level of concern = 2-4 mg/kg dry weight Se; and toxicity threshold > 4 mg/kg dry weight Se.

Figure 6. Sediment Sample Se Results Collected in October 2004, April and October 2005, and April 2006 from Wetland 3 and Sediment Pond

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 second 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. 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. Both of these populations are likely to be grazed by predators, and, therefore, they are important to monitor for potential impacts to higher food chain organisms. Future macroinvertebrate sampling efforts should consider both types of sampling techniques and more Hester-Dendy samplers should be placed in the sediment pond to address issues with the recovery of mass for analyses of Se.

Comparing the Se results in the macroinvertebrate tissues collected in 2005 and 2006 did not reveal a strong correlation with the concentration of Se in water or sediment samples collected from 2004-2006. While the weather conditions and water levels in the sampling areas at MMTS were different in 2005 and 2006, 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 in the waters at MMTS. 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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Appendix A – Program Directive MSG 05-03

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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).

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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

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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.

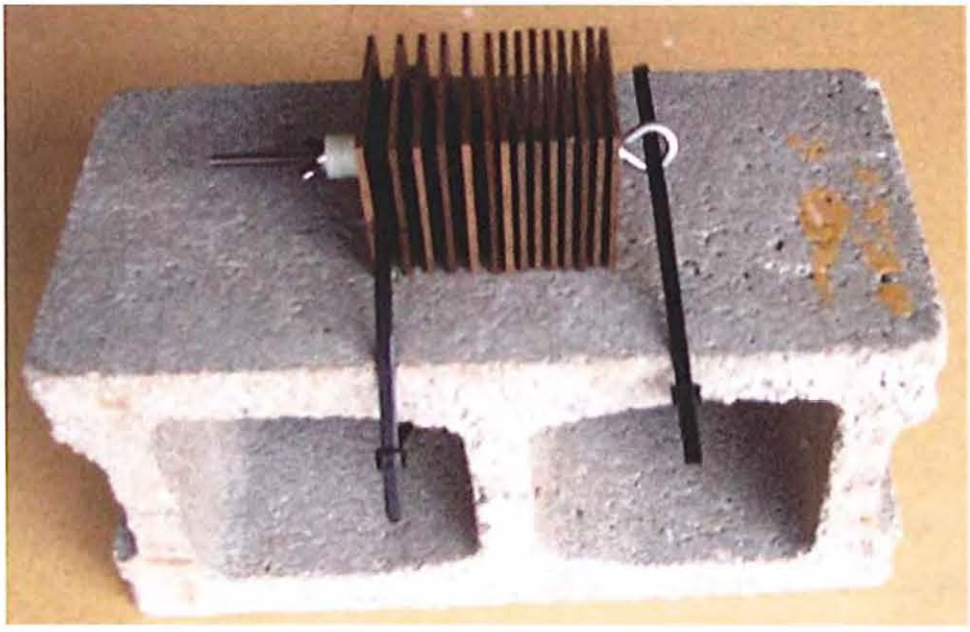


Figure 1. Hester-Dendy sampler attached to cinder block with cable ties. The cinder block shown is 10" wide.

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

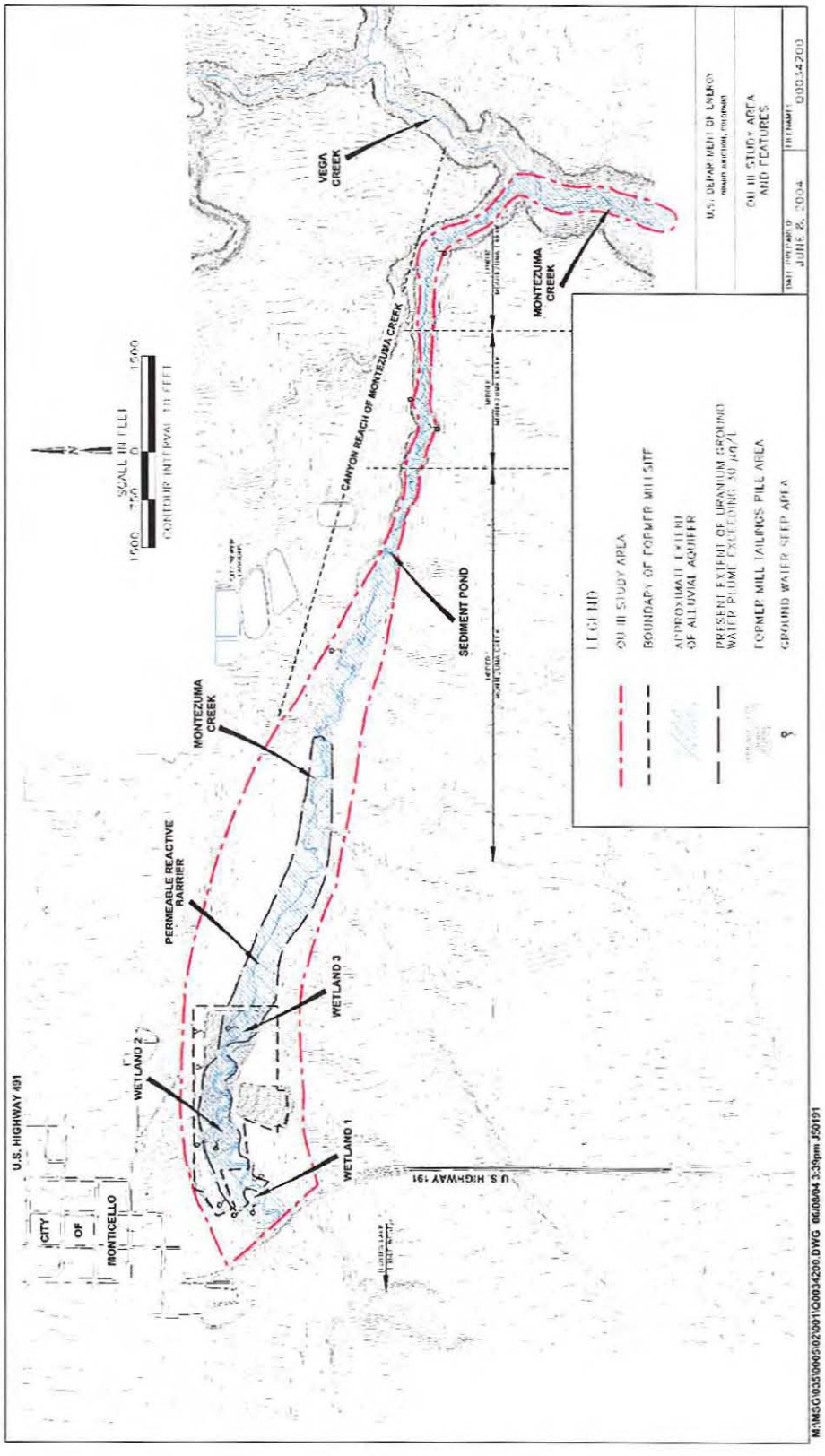
   Canyonland Copy Center
   59 S Main St
   Moab, UT 84532

IV. Schedule

Date	Activity
Thursday, May 11	Ship field equipment to Monticello Mill Tailings Site.
Monday, May 15	Arrive in Grand Junction, CO.
Tuesday, May 16	Travel to Moab and pick up supplies. Travel to Monticello site and meet with Joe Slade and Todd Moon for pre-job meeting. Start kick net collections; collect field blank; if time permits, check cultivation of Hester-Dendy samplers to determine if they can be collected.

Wednesday, May 17	AM: Collect any remaining samples (if collecting samples, prepare another field blank). Travel to Moab. FedEx collected samples to MSL and field equipment to Richland. PM: Travel to Grand Junction and return to Richland, WA.

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: Monticello Macroinvertebrate
Project Manager: Annette Bunn
Phone Number: (509) 376-6300

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

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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: Quality Assurance / Quality Control Narrative for Macroinvertebrate Tissues Se Results

Attachment 3: Se Results for Equipment Blank Water

Attachment 4: Quality Assurance / Quality Control Narrative for Equipment Blank Water Se Results

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Attachment 1: Se Results for Macroinvertebrate Tissues

BATTELLE MARINE SCIENCES LABORATORIES							
Jill Brandenberger, Project Manager							
1529 West Sequim Bay Road		**Monticello Macroinvertebrates 2006**					
Sequim, Washington 98382			**Se in Tissue**				
(360) 681-4564		(Units: ug/g dry wt, data are not blank corrected)					
MSL Code	**SPONSOR CODE**	**Matrix**	**Collection Date**	**Analytical Batch**	**Percent Moisture**	**Se**	
					CAS CODE:	7782-49-2	
					Method:	HGAA-FIAS	
Laboratory Achieved Method Detection Limits (MDLs)						**0.0211**	
Reporting Limit (RL)						**0.0671**	
2567-1	SP R1 AKN	Invertebrates	05/17/2006	07/14/2006	77.7	4.20	
2567-1 Redigest	SP R1 AKN	Invertebrates	05/17/2006	07/19/2006	77.7	3.09	
2567-2	SP R2 AKN	Invertebrates	05/17/2006	07/14/2006	71.4	5.15	
2567-3	SP R3 AKN	Invertebrates	05/17/2006	07/14/2006	73.5	4.74	
2567-3 Redigest	SP R3 AKN	Invertebrates	05/17/2006	07/19/2006	73.5	4.80	
2567-4	SP R4 AKN	Invertebrates	05/17/2006	07/14/2006	74.5	3.95	
2567-4 Redigest R1	SP R4 AKN	Invertebrates	05/17/2006	07/19/2006	74.5	2.44	
2567-4 Redigest R2	SP R4 AKN	Invertebrates	05/17/2006	07/19/2006	74.5	4.64	
2567-5	W3 R1 AKN	Invertebrates	05/17/2006	07/19/2006	84.5	6.47	
2567-6	W3 R2 AKN	Invertebrates	05/17/2006	07/19/2006	79.1	3.69	
2567-7	W3 R3 AKN	Invertebrates	05/17/2006	07/19/2006	77.1	5.93	
2567-8	W3 R4 AKN	Invertebrates	05/17/2006	07/19/2006	74.3	7.98	
	Geometric Mean W3 site					*5.80*	
	Standard deviation					*1.78*	
2567-13	SPR1AHD-Inlet	Invertebrates	06/13/2006	07/14/2006	89.3	12.65	
2567-14	SPR2AHD-North	Invertebrates	06/13/2006	07/14/2006	77.7	10.93	
2567-15	SPR3AHD-Outlet	Invertebrates	06/13/2006	07/14/2006	76.7	5.97	
Procedural Blanks							
Blank071106r1	Method Blank			07/14/2006		0.0398	J
Blank 071406	Method Blank			07/19/2006		0.0211	U
Blank Spike Results							
LCS 071106r1	LCS			07/14/2006		5.28	
	Spike concentration					*5.0*	
	PERCENT RECOVERY, LCS-1					**106%**	
LCS 071406	LCS			07/19/2006		5.08	
LCSD 071406	LCSD			07/19/2006		5.16	
	Spike concentration					*5.0*	
	PERCENT RECOVERY, LCS-1					**102%**	
	PERCENT RECOVERY, LCS-2					**103%**	
	RPD					**2%**	

MSL Code	SPONSOR CODE	Matrix	Collection Date	Analytical Batch	Percent Moisture	Se	
Matrix Spike Results							
2567-4ms	MS			07/14/2006		9.41	
2567-4msd	MSD			07/14/2006		9.15	
2567-4	SP R4 AKN	Invertebrates	05/17/2006	07/14/2006	74.5	3.95	
	Spike concentration, MS					5.00	
	Spike concentration, MSD					4.93	
	PERCENT RECOVERY, MS					**109%**	
	PERCENT RECOVERY, MSD					**105%**	
	RPD					**3%**	
1566b 071406 MS	MS			07/19/2006	0.0	7.13	
1566b 071406 R1	SRM			07/19/2006	0.0	2.09	
	Spike concentration, MS					5.13	
	PERCENT RECOVERY, MS					**98%**	
Replicate analysis Results							*
2567-4 Redigest R1	SP R4 AKN	Invertebrates	05/17/2006	07/19/2006	74.5	2.44	
2567-4 Redigest R2	SP R4 AKN	Invertebrates	05/17/2006	07/19/2006	74.5	4.64	
	Mean					3.54	
	RPD					**62%**	
2567-1	SP R1 AKN	Invertebrates	05/17/2006	07/14/2006	77.7	4.20	
2567-1 Redigest	SP R1 AKN	Invertebrates	05/17/2006	07/19/2006	77.7	3.09	
	Mean					3.65	
	RPD					**31%**	
2567-3	SP R3 AKN	Invertebrates	05/17/2006	07/14/2006	73.5	4.74	
2567-3 Redigest	SP R3 AKN	Invertebrates	05/17/2006	07/19/2006	73.5	4.80	
	Mean					4.77	
	RPD					**1%**	
Standard Reference Material							
1566b 071406 R1	SRM			07/19/2006	0.0	2.09	
1566b 071406 R2	SRM			07/19/2006	0.0	1.97	
	certified or reference value					2.06	
	range					±0.15	
	percent recovery SRM 1566b-1					**102%**	
	percent recovery SRM 1566b-2					**95%**	
	RPD					**6%**	
*	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 2: Quality Assurance / Quality Control Narrative for Macroinvertebrate Tissues Se Results

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

SAMPLE CUSTODY AND PROCESSING: Fourteen tissue samples were received in two batches on 05/19/06 and 06/16/06. 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 (2567) and samples were entered into the MSL sample tracking and project management system. Samples collected from the W1 site were archived as dry tissue until further notice from the client or a maximum of 1 year.

SAMPLE PROCESSING INFORMATION:

Lab Sample IDs:	**2567*1-8 and 13-15**
Description:	Macroinvertebrates
Collection date	05/17/06 and 06/13/06
Laboratory arrival date	05/19/06 and 06/16/06
Cooler temp. on arrival	2.8°C and 2.1°C
Digestion Date (Aqua Regia, MSL-I-024)	07/11/06 and redigestion of select samples on 07/14/06
HGAA-FIAS Analysis Date (Se, MSL-I-030)	07/14/06 and 07/19/06

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.

All results were determined and reported in units of µg/g on a dry-weight basis.

HOLDING TIMES: The project specific holding time is one year for all metals in tissue. All samples were freeze dried and either archived or analyzed within in one year.

DATA QUALITY CRITERIA (DQC):

Analyte	Analytical Method	Range of MS/MSD Recovery	Replicate Precisions (RPD)	SRM Accuracy (PR)	MDL (µg/g dry wt.)	Reporting Limit (µg/g dry wt.)
Se	HGAA-FIAS	75-125%	±20%	80%-120%	0.0211	0.0671

RPD = Relative Percent Difference
PR = Percent Recovery

DETECTION LIMITS: Analytical results were reported to the laboratory achieved method detection limits (MDL) as determined from the annual tissue 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 (tissue matrices with metals low enough to performing an acceptable MDL study). MDLs are determined on a dry weight basis identical to the sample processing methodology. The reporting limit (RL) was determined as 3.18 times the achieved MDL. Data were 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.

ANALYTICAL NOTE: The samples were originally digested as a single batch. The laboratory duplicates were outside the QC criterion and samples with remaining mass were digested a second time to evaluate sample heterogeneity. See discussion in replicate precision for more information.

METHOD BLANKS: Two method blanks were analyzed with these samples. Se was not detected in the method blanks above the RL.

LABORATORY CONTROL SAMPLE (LCS) ACCURACY: Three LCS samples were analyzed with these samples. The percent recoveries were within the QC criterion of 75-125% recovery.

MATRIX SPIKE (MS/MSD) ACCURACY: One sample was selected for a matrix spike/matrix spike duplicate. There was insufficient material available for a matrix spike in the second batch; therefore, the SRM was analyzed an unspiked and then two replicates were analyzed with a spike. The percent recoveries for the MS/MSD samples were within the QC criterion of 75-125% recovery.

REPLICATE PRECISION: Three measures of analytical precision were conducted with this set of samples. Laboratory duplicates, LCS duplicates, and a MS/MSD pairs were digested and analyzed with this set of samples. Analytical precision of replicate analyses was expressed as the relative percent difference (RPD) between the replicate results. Two of the three RPD values for the laboratory duplicates were outside the QC criterion of <20% difference. The samples were redigested if there was sufficient material and indicate the poor reproducibility was attributed to sample heterogeneity. Precision was evaluated using other measures of laboratory precision including duplicate LCS samples and SRM samples. The RPD values for these samples were all within the QC criterion.

STANDARD REFERENCE MATERIAL ACCURACY: Analytical accuracy was expressed as the percent recovery of the measured value relative to the certified value for a standard reference material (SRM). Two replicates of SRM 1566b were digested and analyzed with this batch of samples. The percent recoveries were within the QC criterion of 80-120% recovery.

Attachment 3: Se Results for Equipment Blank Water

BATTELLE MARINE SCIENCES LABORATORIES						
Jill Brandenberger, Project Manager						
1529 West Sequim Bay Road		**Monticello Macroinvertebrates 2006**				
Sequim, Washington 98382		**Equipment Blank Water**				
(360) 681-4564			Units: µg/L			
MSL Code	**SPONSOR CODE**	**Matrix**	**Collection Date**	**Analytical Batch**	**Se**	
					7782-49-2	
					HGAA-FIAS	
Laboratory Achieved Method Detection Limits (MDLs)					**0.0633**	
Reporting Limit (RL)					**0.201**	
2567-12	W1 R1 FB	EB Water	05/17/2006	07/19/2006	0.0633	U
Procedural Blanks						
Blank071406	Method Blank		07/19/2006	07/19/2006	0.0633	U
Blank Spike Results						
LCS 071406	LCS			07/19/2006	5.08	
LCSD 071406	LCSD			07/19/2006	5.16	
	Spike concentration				*5.0*	
	PERCENT RECOVERY, LCS-1				**102%**	
	PERCENT RECOVERY, LCS-2				**103%**	
	RPD				**2%**	
Standard Reference Material						
See Tissue Table for SRM 1566b analyzed in the analytical batch.						
*	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 4: Quality Assurance / Quality Control Narrative for Equipment Blank Water Se Results

PROJECT: Monticello Invertebrates
PARAMETER: Selenium (Se)
LABORATORY: Battelle Marine Sciences Laboratory (MSL), Sequim, Washington
MATRIX: Equipment Blank (EB) Water

SAMPLE CUSTODY AND PROCESSING: One EB water samples was received on 05/19/06. The sample was received in good condition (i.e., no sample containers were broken or leaking). The project was assigned a Battelle Central File (CF) identification number (2567) and sample information was entered into the MSL sample tracking and project management system. The samples were acidified at the laboratory to a pH<2.0 with double distilled nitric acid.

SAMPLE PROCESSING INFORMATION:

Lab Sample IDs:	**2567*12**
Description:	Equipment Blank water
Collection date	05/17/06
Laboratory arrival date	05/19/06
Cooler temp. on arrival	2.8°C
HGAA-FIAS Analysis Date (Se, MSL-I-030)	07/19/06

METHODS: EB water 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.

All results were determined and reported in units of µg/L.

HOLDING TIMES: The suggested holding time for Se in water of six months from sample collection was achieved for all samples.

DATA QUALITY CRITERIA (DQC):

Analyte	Analytical Method	Range of MS/MSD Recovery	Replicate Precisions (RPD)	SRM Accuracy (PR)	MDL (µg/L)	Reporting Limit (µg/L)
Se	HGAA-FIAS	75-125%	±20%	80%-120%	0.0633	0.201

RPD = Relative Percent Difference
PR = Percent Recovery

DETECTION LIMITS: Analytical results were reported to the laboratory achieved method detection limits (MDL) as determined from the annual water MDL study. The MDL study is determined annually according to 40 CFR Part 136 Appendix B and defined as seven replicates of deionized water spiked at an appropriate level. The reporting limit (RL) was determined as 3.18 times the achieved MDL. Data were 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: One method blank was analyzed with these samples. Se was not detected in the method blank above the MDL.

LABORATORY CONTROL SAMPLE (LCS) ACCURACY: Two LCS samples were analyzed with these samples. The percent recovery were within the QC criterion of 75-125% recovery.

MATRIX SPIKE (MS) ACCURACY: The sample matrix is DI water; therefore a matrix spike is not applicable. See the blank spike or LCS for accuracy and precision.

STANDARD REFERENCE MATERIAL ACCURACY: Analytical accuracy was expressed as the percent recovery of the measured value relative to the certified value for a standard reference material (SRM). The water sample was analyzed with the digested macroinvertebrates and the SRM is reported on the tissue table. The percent recoveries were within the QC criterion of 80-120% recovery.

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