Mobilization and Impacts of Arsenic Species and Selected Metals on a Wetland Adjacent the B&L Landfill, Milton, Washington

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Quality Assurance Project Plan

By
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Waterbody No. WA-10-1011
Hylebos Creek Drainage

Washington State Department of Ecology
Environmental Assessment Program
Olympia, WA 98504-7710

Approvals:

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Background and Problem Statement

The B&L Woodwaste site is located in Milton, Washington (Pierce County), and was used as an industrial landfill from the 1970s to the 1980s. The landfill was later identified as a source of arsenic, copper, and lead to the Hylebos Creek system, which prompted cleanup actions (Johnson and Norton, 1985). The remedial actions included consolidation of the landfill, capping to prevent rain-induced leaching, isolation of the landfill from off-site surface and groundwater, and cleanup of contaminated ditch sediments. Recent monitoring by the landfill owner/operator shows shallow groundwater contaminated with arsenic from 2 µg/L to 6.0 mg/L (dissolved fraction). The upper values exceed the USEPA's proposed drinking water standard of 10 µg/L (USEPA, 2001) by several orders of magnitude. Two wells/hydropunches exceed 5 mg/L, while five wells/hydropunches exceed 2 mg/L. Of approximately 20 soil/sediment samples, the highest detected arsenic concentrations are 24 and 31 mg/kg, most are non-detect at 10 mg/kg. Maps of the unpublished groundwater and soil sampling results conducted by the operator are available from the Ecology Toxics Cleanup Program lead. The landfill owner continues additional soil and water monitoring as required by the Ecology Southwest Regional Office (SWRO).

These wetlands are within the floodplain of Hylebos Creek, moderating flood and seasonal low flows. They also support salmonid and other wildlife habitat. Ditches drain west from the wetland to Hylebos Creek; some of the ditches have elevated arsenic levels (Johnson and Norton, 1985). Figure 1 illustrates the landfill, the mapped wetlands nearby, and Hylebos Creek. Extensive wetlands surround the landfill, especially on the north side, although they have not been mapped by the National Wetlands Inventory. The impacts of elevated arsenic levels on the wetland system are poorly understood. Better information on the impacts of arsenic are needed to help determine if the wetland is perturbed by landfill leachate and ensure that prior source control remediation efforts are functioning as intended.

Project Objectives

This study proposes to evaluate the levels of arsenic in soil, water, and plant tissue to determine the fate and transport of arsenic through the wetland and the magnitude of potential impacts to the ecosystem. Bioassays will also be conducted to determine the potential adverse effects of landfill leachate on wetland biota. Due to an absence of applicable plant tissue standards, tissue concentrations within the study wetland will also be compared to concentrations in a reference wetland. Soil concentrations will be principally compared to levels in the ecological literature, MTCA standards, and with concentrations found in the reference wetland.

The reference wetland will match, as closely as possible, the hydrologic regime, soil series, and vegetation of the study wetland. To the extent practicable, the reference wetland will have a similar land history to minimize confounding effects due to arsenical pesticide/herbicide use.

The project involves five components that require different expertise, and sometimes timing. The objectives and strategies in aggregate will determine the major reservoirs of arsenic in the wetland system, prominent intermedia arsenic transfers, and general wetland health. They are:

1) Support the in-situ investigation of the impacts of the arsenic loading on resident amphibian populations. During the approximate midpoint of a winter amphibian eggmass study conducted by a University of Washington wetlands student, collect three surface water samples along a presumed gradient from high to low concentration and sample for total arsenic. Prior, unpublished studies by the landfill operator have determined the arsenic concentration gradient in shallow groundwater away from the landfill. This gradient is also evident for soils and is presumed to exist for surface waters as well. The early season sampling of surface water to support the *in-situ* amphibian study will assist in locating sampling stations for additional, subsequent soil, water, bioassay, and plant tissue sampling.

All subsequent sampling (Figure 1 and described below) will occur in three zones: high, medium, and low arsenic concentrations. Prior sampling by the landfill operator suggests that a fairly sharp gradient occurs and pinpointing intermediate arsenic concentrations could be difficult. The placement of samples will allow for a determination of the relative magnitude of any observed arsenic geochemical processes. This study is not intended to determine the nature and extent of arsenic contamination, although it will help serve as confirmatory sampling of the owner/operator's investigations.

2) Determine the role of the wetland in the transport of landfill arsenic. Sample wetland soil/sediment, pore water, and surface water arsenic concentrations. Sampling will occur in high, medium, and low arsenic zones. Final sample sites will be located using initial surface water data in conjunction with unpublished studies conducted by the operator. Compare the soil and water concentrations from over the highest groundwater arsenic concentrations with soil, pore water, and surface water concentrations hydrologically downgradient. Also compare these concentrations with reference conditions, ambient water quality criteria, literature values, and Model Toxics Control Act (MTCA) cleanup standards.

Using plant tissue concentrations, with field reduction-oxidation potential (Eh) and pH values, determine prominent arsenic transport pathways in wetland soils and vegetation. Eh is a significant soil-groundwater parameter for arsenic migration. Under oxidizing conditions, arsenic remains in the As(V) valence state with limited solubility (Masscheleyn et al., 1991). During saturation, microbial decomposition of organic matter reduces co-precipitated arsenic-iron oxides and iron(hydr)oxides to ferric iron. This reaction tends to liberate arsenic, although some of this arsenic may subsequently combine to form insoluble arsenic-sulphides. Arsenic itself also serves as an electron receptor, reducing As(V) into As(III). Arsenic (III) is about 40 times more soluble than As(V) and is considered to be more toxic as well (USEPA, 1984). Under highly reducing conditions, arsenic may be reduced to As(-3), which is volatile. The pH of soils has some additional influence over arsenic mobility with lower pH soils converting As(V) to As(III) under higher Eh conditions.

Both root and stem tissues will be analyzed, as they may have a differential affinity for arsenic. These data will be used to confirm whether wetland conditions enhance or limit arsenic transport. The determination of prominent As reservoirs in soils and the speciation of soil As will utilize literature phase diagrams (sensu Masscheleyn et al., 1991).

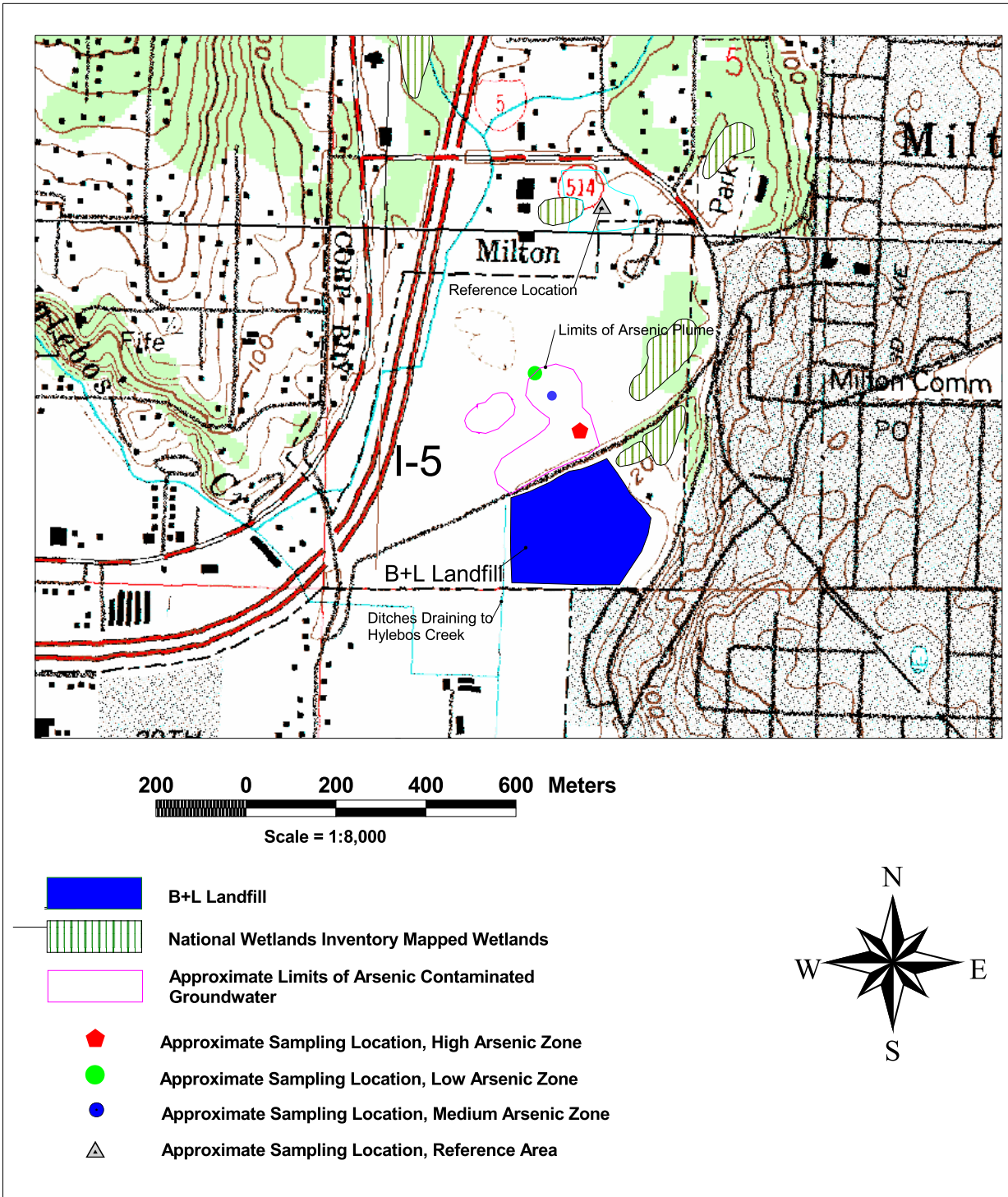

Figure 1. B+L Lanfdfill with Nearby Wetlands as Mapped by the National Wetlands Inventory.

3) Determine the role of the wetland in the fate of arsenic released from the landfill. Collect arsenic speciation data in conjunction with plant tissue concentrations, surface water, field Eh, and pH values, as described above. The methods proposed for this project will directly quantify As(III), As(V), monomethylarsenic acid (MMA), dimethylarsenic acid (DMA), and mixed arsenic-sulphides. The determination of As(-3) is not practical due to its volatility. Determine whether conditions in the wetland are conducive to arsenic mobilization, immobilization, or volatilization. Additionally, determine whether arsenic discharges convert from inorganic to organic forms or vice versa.

4) Assess the toxicity of the sediment pore water adjacent to the landfill. Collect sediment pore water from areas of high, medium, and low arsenic concentrations within the wetland and a reference site. Analyze pore waters for toxicity using the Microtox® bioassay (Adolphson, 2002). The Microtox bioassay uses a phosphorescent bacteria which experiences reduced light output in response to toxicants. The test will use 100% sediment pore water as a test media without a dilution series (Appendix B).

5) Assess the health of the wetland complex. Use data from the plant tissue analysis, the Microtox test, and the amphibian survey in conjunction with soil and surface water information and literature values to describe the overall health of the wetland complex.

This QAPP addresses the sampling and data analysis procedures for the goals described above. To support these goals, additional metals will be concurrently analyzed. These metals include lead, zinc, and copper, which may confound interpretation of arsenic impacts. Additionally, iron will be analyzed in soils, as arsenic has a high affinity for iron (hydr)oxides (McGeehan et al., 1998), and the distribution of iron may control arsenic fate and transport (Pierce and Moore, 1980; Hansel et al., 2001).

Project Organization

Richard Jack, Ecology Project Manager. Responsible for field sampling, sample preparation, and prepares draft and final Ecology report describing results of chemical and biological analyses.

Brandee Era, EAP Field and Sampling Assistance.

Jacqueline London, Project Manager, Frontier Geosciences, Inc., Seattle WA. Responsible for scheduling instrument time, preparation, and analysis of arsenic speciation samples.

Bob Schlemmer, University of Washington Wetland Certificate student. Responsible for conducting the amphibian survey and selection of the initial water sampling locations to support this study.

Dom Reale, TCP Client and Project Coordinator. Responsible for review of QAPP and final reports for the project.

Ann Boeholt, Ecology Southwest Regional Office. Responsible for review of QAPP and final reports.

Schedule

Tentative

Finalize QAPP	February 2002
Amphibian Water Quality Sampling	February 2002
Collect Soils, Surface and Pore Waters, and Plant Tissues	April - May 2002
Laboratory Analysis	June 2002
Draft Report	September 2002
Final Report	November 2002

Measurement Quality Objectives

Accuracy, Bias, and Precision

This is a screening level study that will be used to define prominent media and pathways of concern and guide future investigations and/or remedial decisions. Plant tissue concentrations will be compared with levels in a reference wetland. One sample of certified reference material (peach leaves) will be analyzed for lead, copper, and zinc to estimate analytical bias in these metals. The arsenic speciation methods also include analysis of certified reference materials, although there are limited standards for arsenic species.

Table 1 summarizes the analytical accuracy, bias, and precision goals for the project, while table 2 shows the necessary reporting limits.

Table 1. Analytical Goals by Analyte/Media for the B&L Landfill Wetland Arsenic Investigation

Parameter	Accuracy (% Deviation from True Value)	Bias	Precision (RSD)
Arsenic, Total (soil and surface water)	40%	±10%	15%
Arsenic, Species (surface and pore waters)	40%	±10%	15%
Arsenic, Species (plant tissues)	70%	±20%	25%
Copper, Lead, Zinc (waters)	40%	±10%	15%
Copper, Lead, Zinc (plant tissues)	55%	±15%	20%
Total Organic Carbon	N/A[a]	N/A[a]	20%

[a]Evaluated Qualitatively
RSD = Relative Significant Deviation

Table 2. Necessary Reporting Limits for the B&L Landfill Wetland Investigation

Matrix	Analyte	Required Reporting Limit (Maximum)
Soil	Arsenic	5 mg/kg, wet
	Lead	5 mg/kg, wet
	Copper	5 mg/kg, wet
	Zinc	5 mg/kg, wet
	Total Organic Carbon	±0.5%
Surface Water	Total Arsenic	1 µg/L
	Arsenic Species	0.5 µg/L for each
	Lead	1 µg/L
	Copper	1 µg/L
	Zinc	5 µg/L
Pore Water	Arsenic Species	0.5 µg/L for each
	Lead	1 µg/L
	Copper	1 µg/L
	Zinc	1 µg/L
Plant Tissue	Arsenic Species	1 mg/kg for each
	Lead	2 mg/kg, wet
	Copper	2 mg/kg, wet
	Zinc	2 mg/kg, wet

Field blanks will be collected for surface waters. One blank will be analyzed during the initial winter surface water sampling, and one blank will be analyzed during the springtime surface water sampling. These blanks will be collected using lab supplied deionized water, transferred across any sampling equipment into sample bottles in the field.

The accuracy of bioassays is difficult to evaluate. The Microtox bioassay has been evaluated by Ecology to assess sediment toxicity (Bennett and Cubbage, 1992) and standard positive and negative controls will be utilized. Pore waters to be chemically analyzed will be extracted using the same procedures as outlined in the Microtox procedure. Additionally, pore waters from the reference wetland will be tested analytically and with the Microtox assay to establish any potential bias through the use of wetland pore waters.

Sampling Design

Three study zones will be established based upon the results of intial water sampling and prior unpublished studies by the responsible party. The high, medium, and low arsenic zone sampling locations are shown on Figure 1.

Representativeness

The objective for this study is to describe the role of the wetland in the fate and transport of arsenic from the landfill to, ultimately, Hylebos Creek. In addition to characterizing the principal arsenic pathways and geochemical transformations, these data will also be used to

describe the health of the wetland community. The exact location of the three study stations will be selected based on field access, prior soil and groundwater sampling by the landfill operator, and results of the initial wintertime water sampling. Soil from two depths, surface water, pore water, plant roots, and plant shoots will be analyzed at each location.

During the typical wintertime, the wetland is flooded with surface water predominantly originating off-site. Arsenic in these waters may or may not be in equilibrium with contaminated groundwater. The degree of equilibrium is likely dependent on prior rainfall patterns and probably fluctuates year to year. In order to represent worst-case conditions to all ecological receptors, the soil, pore water, and surface water speciation testing is scheduled to occur in late spring. In May, the wetland will still contain standing water; however, this water will have been ponded on-site for some time. The ponded waters are presumed in equilibrium with contaminated groundwater.

Comparability

Wetlands are highly site-specific environments. In addition, the geochemical conditions within the Asarco slag and woodwaste of the B&L Landfill are probably site-specific. Thus, it is unlikely that this study can be readily extrapolated to other wetlands. However, geochemical parameters such as Eh, pH, and total organic carbon (TOC) will be collected from soils and waters. With these extra parameters, some limited extrapolation to describe arsenic leaching or transport in other Puyallup River basin wetlands may be possible.

A reference location has been tentatively identified to the north of the study area (Figure 1). The reference site is mapped as containing Semiahoo muck, which is the same soil type as part of the study wetland. The remainder of the study wetland is Tisch silt, for which a reference site is not known. During a site visit on December 19, 2001, hydrologic patterns on the reference wetland appeared similar to the study wetland. Vegetation in the reference site is predominantly reed canarygrass (*Phalaris arundinacea*), which also dominates the study wetland. The reference area has some surrounding industry that may have degraded surface water quality. Otherwise, the site appears comparable to the study wetland and it is outside of the known groundwater arsenic plume. The suitability of the reference area will be conditional upon property access and observed hydrology.

Microtox test results will describe the toxicity of the pore waters in the wetland during the growing season. The results from the Microtox test should be comparable with other wetland and sediment contaminant investigations. Additional field parameters will be collected (total organic carbon, Eh and pH) to allow comparisons with other arsenic receiving waters or wetlands relative to the Microtox results.

Sampling Methods

Water samples will be collected using pre-cleaned polyethylene bottles. At the time of the proposed sampling, standing water should be present in the wetland and the soils should be saturated. Water samples will be collected first by wading to the site from the downstream direction, taking care not to disturb sediments. For metals other than arsenic, bottles will be rinsed with on-site water and filled approximately 1 cm from the neck. The headspace will allow

the addition of acid preservatives. For arsenic, bottles will be filled without headspace to minimize potential oxidation.

Surface waters will be collected four times, once for comparison with the amphibian survey conducted in February. They will be collected concurrently again in May: once for copper, lead, and zinc analysis, and once for arsenic speciation.

Soil samples will be collected using a stainless-steel hand auger. Samples will be composited from the auger into a stainless steel bowl using stainless steel scoops. A 10x-hand lens and forceps will be used to remove all visible roots and live plant matter. Soils will be collected and composited from two different depth horizons: 0-6" and 18-24". These depths were chosen to assist in determining if arsenic is migrating up through the soil column in shallow groundwater. Alternatively, surficial soils may have been historically impacted by runoff from the woodwaste site. Previous investigations have composited soils in two foot increments.

Plant materials will be collected last. For aerial tissues, a stainless steel knife will be used to cut stems. For below ground tissues, a spade will be used to remove a plug of soil. Only roots that have not contacted the spade will be extracted from the soil matrix with a combination of washing with on-site water and forceps. Plant tissues will be scrubbed with on-site water and a brush and then rinsed with deionized water.

Sampling will occur from the reference site to the high arsenic zone, to minimize the effects of sample contamination. Sampling equipment will be cleaned by brushing with on-site water, rinsing with 10% nitric acid, and rinsing with deionized water. The various samples collected at each site and strata are shown in Table 3.

Table 3. Samples Collected by Media, Strata, and Time at the B&L Woodwaste Landfill

Sample Date		Feb. 2002	To be Sampled in April or May, 2002				To be Collected or Analyzed with Sample Media			
Media	Analyte	Amphibian Study	High As zone	Medium As zone	Low As zone	Reference Wetland	Field Blanks	Field Duplicates	Matrix Spikes	Total Field Samples
Surface Water	total As	4	1	1	1	1	1		1	10
	As species		1	1	1					3
	Pb, Cu, and Zn		1	1	1	1	1		1	5
Pore Water	As species		1	1	1	1	1	1		6
	Pb, Cu, and Zn		1	1	1	1	1		1	5
	Microtox		1	1	1	1		1		5
Soil	0-6", As, Pb, Cu, Zn, Fe, TOC		1	1	1	1			1	4
	18-24", As, Pb, Cu, Zn, Fe		1	1	1	1		1		5
Plants	Shoots, As species,		1	1	1	1		1	1	5
	Roots, As species,		1	1	1	1				4
	Shoots, Pb, Cu, Zn		1	1	1	1			1	4
	Roots, Pb, Cu, Zn		1	1	1	1		1		5

Water samples for arsenic speciation will be field filtered to remove microorganisms which might alter redox state. A 0.45µm filter-funnel with vacuum pump will be used.

Plant tissue samples require freezing to -18^0C, while ICP water samples for lead, copper, and zinc analysis require preservation with HNO_3 to pH<2. Both the freezing and acid preservation will be conducted upon return to Ecology Headquarters. Following freezing, plant tissues will be ground.

Pore water for chemical analysis will be extracted at Ecology Headquarters within 24 hours using a centrifuge at approximately 4500G for 30 minutes. Sediments for the Microtox bioassay will be held unpreserved, in the dark, as little as possible prior to test initiation.

Media will be packaged in pre-cleaned jars and bottles as specified in Table 4. Coolers will be chilled with ice and samples transported to Manchester lab via courier. Sample holding times are also shown on Table 4.

Table 4. B&L Landfill Wetland Sample Containers and Holding Times

Media	Sample Size	Container	Number of Jars	Date Collected	Holding Time
Soil-metals	100 g	4 oz. glass jar	7	May, 2002	ICP metals, 6 months
Soil-TOC	50 g	4 oz. glass jar	4	May 2002	14 days
Surface Water	1 L	1 L HDPE	10	5 in February, 2002 5 in May, 2002	ICP or ICP-MS metals, 6 months
Surface Water	1 L	1 L HDPE	3	May, 2002	As species, 2 days
Sediment to Centrifuge for Pore Water		1 gal jar	2 per sediment pore water sample	May 2002	Will be centrifuged within 24 hours
Pore Water	100 mL	1 L HDPE	6	May, 2002	As species, 2 days
Pore Water	500 mL	1 L HDPE	5	May, 2002	ICP or ICP-MS metals, 1 month
Pore Water	50 mL	1 L HDPE	5	May, 2002	Microtox,14 days
Plant Tissue	100 g	8 oz glass jar	18	May, 2002	ICP metals, 6 months As species, 2 days

Analytical Methods

Lead, copper, zinc, iron, and TOC will be analyzed at Manchester Laboratory. The arsenic speciation and Microtox will be performed at commercial laboratories contracted by Manchester. Preparation methods are shown in Table 5. Suggested analytical methods and available reporting limits are shown in Table 6. Other methods may be used at the discretion of Manchester or the contract laboratory after consulting the project lead. The arsenic speciation should be performed at Frontier Geosciences, as they have a proprietary ion chromatography-hydride generation-

atomic fluorescence (IC-HG-AFS) method well suited to this project (Frontier Geosciences 2001). Table 7 illustrates the number of samples of each media and the estimated analytical costs of the project.

Table 5. B&L Landfill Sample Preparation Methods by Media

Media	As Speciation Preparation Method	Total Metals Preparation Method	Method References
Surface Water	0.45 µm filtration, otherwise included in analytical methods	Included in analytical methods	N/A
Pore Water	4500G centrifuge for 30 minutes + 0.45 µm filtration	4500G centrifuge for 30 minutes + 0.45 µm filtration	Adolphson (2002)
Soil/Sediment	N/A	Acid Digestion	EPA Method 3050
Soils-TOC	HCl treatment to remove carbonates		USEPA (1997)
Plant Tissues	Cell disruption (Appendix C)	Acid Digestion or Microwave	EPA Method 3050 or 3051

Table 6. B&L Landfill Wetland Investigation, Analytical Methods, and Available Method Reporting Limits

Analyte	Analytical Method	Analytical Method Reference	Reporting Limit, Soils (mg/Kg, Wet)	Reporting Limit, Waters (µg/L)
Lead	ICP, EPA Method 200.7	USEPA, 1994	2	N/A
Zinc	ICP, EPA Method 200.7	USEPA, 1994	0.4	5
Copper	ICP, EPA Method 200.7	USEPA, 1994	5	0.1
Iron	ICP, EPA Method 200.7	USEPA, 1994	2	N/A
Arsenic, Total	ICP, EPA Method 200.7	USEPA, 1994	5	N/A
Arsenic	ICP-MS, EPA Method 200.8	USEPA, 1994	N/A	0.2
Lead	ICP-MS, EPA Method 200.8	USEPA, 1994	N/A	0.1
Arsenic Species	IC-HG-AFS	Frontier Geosciences, 2001	N/A	0.1 for each
Microtox	Modified Ecology 100% Pore Water	Bennett and Cubbage, 1992 (Appendix B)	N/A	N/A
TOC	PSEP combustion	USEPA, 1997	±0.02%	N/A

Table 7. Sample Numbers and Estimated Analytical Costs for the B&L Landfill Wetland Investigation

Soil/Sediments				
Analyte	Method	# Samples	Cost	Total
As	ICP	8	$14.00	$112.00
Pb	ICP	8	$14.00	$112.00
Cu	ICP	8	$14.00	$112.00
Zn	ICP	8	$14.00	$112.00
Fe	ICP	8	$14.00	$112.00
Spike	ICP	1	$70.00	$70.00
Field Duplicate	ICP	1	$70.00	$70.00
Metals Prep		10	$17.00	$170.00
TOC		4	$33.00	$132.00
Containers		13	$14.00	$182.00
			Subtotal	**$1,184.00**
Surface Water				
Analyte		# Samples	Cost	Total
As Species	Frontier	3	$312.00	$936.00
Contracting Fee		25% of	$936.00	$234.00
As	ICP-MS	4	$34.00	$136.00
Pb	ICP-MS	4	$34.00	$136.00
Cu	ICP	4	$14.00	$56.00
Zn	ICP	4	$14.00	$56.00
Spike	ICP-MS	1	$96.00	$96.00
Field Blanks	ICP-MS	1	$96.00	$96.00
Early As Sampling	ICP-MS	4	$34.00	$136.00
Spike	ICP-MS	1	$34.00	$34.00
Field Blanks	ICP-MS	1	$34.00	$34.00
Metals Prep		12	$10.00	$120.00
Bottles		12	$14.00	$168.00
			Subtotal	**$2,238.00**
Pore Water				
Analyte		# Samples	Cost	Total
As	Frontier	4	$312.00	$1,248.00
Field Blank	Frontier	1	$312.00	$312.00
Field Duplicate	Frontier	1	$313.00	$313.00
Contracting Fee		25% of	$1,560.00	$390.00
Pb	ICP-MS	4	$34.00	$136.00
Cu	ICP	4	$14.00	$56.00
Zn	ICP	4	$14.00	$56.00
Field Blanks	ICP	1	$62.00	$62.00
Spike	ICP	1	$62.00	$62.00
Metals Water Prep		6	$10.00	$60.00
Containers		11	$14.00	$154.00
			Subtotal	**$2,849.00**
Plant Roots and Shoots				
Analyte		# Samples	Cost	Total
As Species	Frontier	8	$350.00	$2,800.00
As Species, Field Dup	Frontier	1	$350.00	$350.00

Contracting Fee		25% of	$2,800.00	$700.00
Pb	ICP	8	$14.00	$112.00
Cu	ICP	8	$14.00	$112.00
Zn	ICP	8	$14.00	$112.00
Reference Peach Leaves		1	$253.00	$253.00
Reference Analysis		1	$42.00	$42.00
Field Duplicate		1	$42.00	$42.00
Prep		11	$34.00	$374.00
Containers		18	$14.00	$252.00
			Subtotal	**$5,149.00**
		# samples	Cost	Total
Microtox Bioassay	Ecology	4	$450.00	$1,800.00
Contracting Fee		25% of	$1,800.00	$450.00
			Subtotal	**$2,250.00**
Redox Standard			$63.00	**$63.00**
		Grand Total =		**$13,733.00**

Quality Control Procedures

Field Measures

The redox (ORP) probe will be field calibrated using a non-hazardous reference standard. The +260 mV redox standard is a potassium iodine solution available from ThermoOrion, Inc, Beverly, MA. The probe will be placed in the standard at the start of the day's sampling and at the end of day's sampling. Measurements from the ORP probe will be adjusted by the difference between mean of the start and ending meter readings and the known +260 mV standard.

Laboratory Measures

For soils, one matrix spike will be conducted and one field duplicate will be collected providing a 12.5% frequency for each. One of the early amphibian study surface water samples will be spiked, and one field blank will be collected, providing a 25% frequency for each.

Surface waters collected in April or May for lead, copper, zinc, and total arsenic will include one matrix spike and one field blank. The three study wetland water samples will also be analyzed for arsenic speciation, but no spiking or duplicates will be conducted for this analysis.

For the pore water analysis, one field blank and one field duplicate will be analyzed. The blank will be collected by pouring deionized water over any sampling apparatus, centrifuging, and filtering. The plant tissue samples will include one field duplicate. The Frontier Geosciences arsenic methods include a matrix duplicate, matrix spike, and matrix spike duplicate. Table 8 illustrates the frequency of quality control samples required.

Table 8. B&L Landfill Wetland Investigation Quality Control Samples and Required Frequencies

Parameter	Check Standards	Method Blanks	Analytical Duplicates	Matrix Spike & Duplicate	Reference Materials
Lead	10% or more	1 per batch	1 per batch	1 per batch	1 per batch
Zinc	10% or more	1 per batch	1 per batch	1 per batch	1 per batch
Copper	10% or more	1 per batch	1 per batch	1 per batch	1 per batch
Total Aresenic	10% or more	1 per batch	1 per batch	1 per batch	1 per batch
Arsenic Species	10% or more	1 per batch	1 per batch	1 per batch	None
TOC	10% or more	1 per batch	1 per batch	1 per batch	1 per batch
Iron	10% or more	1 per batch	1 per batch	1 per batch	None

The Microtox bioassay includes positive and negative controls, which will be conducted at a frequency of one each per batch.

Reference Materials

Dried peach leaf certified reference material will be analyzed for copper, lead, and zinc via ICP, and total arsenic via IC-HG-AFS. The dried peach leaves are available from the National Institute of Standards and Technology, number 1547. The leaves are not certified for individual arsenic species. All three analytes shall be within the certified analytical windows.

Data Quality Assessment

The project manager will review all data and analytical narratives for completeness, bias and precision goals. The data will be verified against the data quality objectives stated above and then tabulated. Their quality will be summarized. Comparisons between measured concentrations and published values will be qualitative rather than quantitative--due to a lack of replication. Limitations of the data will be described.

Data will be tabulated and a draft report will be prepared by EAP. The report will include:

1) A map of the study area showing sample sites.
2) A map showing soil types, topography, and groundwater gradients across the study area.
3) Sample information including plant species sampled, Unified Soil Classification, and National Resource Conservation Service (NRCS) mapped soil type.
4) Photographs of site conditions during sampling activities.
5) Discussion of data quality and any significant analytical problems.
6) Summary tables of analytical data.
7) Comparisons of data with ambient surface water quality criteria, MTCA soil and groundwater standards, soil and groundwater values measured by other consultants at the site, and literature values relevant to determining impacts to the wetland ecosystem.
8) Recommendations for follow-up work including critical parameters, media, or arsenic zones as warranted.
9) An appendix of case narratives.

Project data will be entered into Environmental Information Management (EIM) prior to completion of the final report.

References

Adolphson, P. 2002. Ecology Modified Draft Final Microtox Test Procedure. January 15, 2002. See Appendix B.

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Appendix A
Frontier Geosciences Arsenic Speciation Methods

Arsenic speciation by Ion Chromatography-Hydride Generation-Atomic Fluorescence Spectrometry (IC-HG-AFS)

In this method, the four major arsenic species (As(III), As(V), MMAs, DMAs) in a water sample are separated by liquid chromatography. After separation, all species are converted on-line to their respective hydrides by reaction with sodium borohydride, purged from solution, and detected by atomic fluorescence spectrometry (AFS). In this method, AFS detection is used instead of AAS because of its higher specificity for arsenic, and because it has much better absolute detection limits, which are needed to compensate for the much smaller sample volume used for IC analyses (< 1 mL) in comparison to the batch hydride generation technique (HG-CT-GC-AAS), where up to 15 mL of sample is used.

This technique has two major advantages over the HG-CT-GC-AAS method. First, it determines all relevant arsenic species in just one analysis, and it gives a positive signal for As(V), instead of calculating it by difference, which doubles analytical uncertainty. Second, it can measure other arsenic species than the four determined by HG-CT-GC-AAS, because they give arsenic signals at different retention times than As(III), As(V), MMAs, and DMAs. This advantage is important in sulfidic ground waters, because As(III) and As(V) react with sulfide to form soluble mixed arsenic-sulfur compounds (known as thioarsenites and thioarsenates). Those compounds cannot be speciated accurately by HG-GC-CT-AAS and will yield wrong results for an apparent As(III)/As(V) distribution. Therefore, it is mandatory that an IC-based speciation method is used for measuring arsenic speciation in sulfidic waters.

This technique is internally validated, but not an official EPA approved method. It will be submitted for publication in 2001. Detection limits are around 0.1 μg/L for each arsenic species.

The method will be Washington Sate accredited prior to submission of the samples.

Appendix B
Microtox® 100 Percent Sediment Porewater Toxicity Assessment

Background

Microtox is a rapid method of assessing toxicity in aqueous media by utilizing the bioluminescent properties of the marine bacteria V*ibrio fischeri.* The test method assumes that light emitted by the bacteria can be used as an accurate assessment of the overall biological condition of the bacteria exposed to chemical compounds and mixtures. Light emitted by the bacteria exposed to potentially toxic samples is compared to light emitted to unexposed bacterial controls. Differences in luminescence are, therefore, deemed an indication of relative toxicity.

EPA has recommended Microtox for TIE/TRE applications (EPA/600/2-88/070) as well as stormwater investigations. Successful applications also include NPDES compliance and sediment evaluations in freshwater, estuarine, and marine applications. Washington State PSEP (Puget Sound Estuarine Protocols) uses both an organic and an aqueous extraction protocol to assess sediment toxicity.

Recognizing that the goal of most sediment toxicity studies is to determine if ecologically/toxicologically significant differences exist between reference and investigative site sediments, four significant differences exist between the PSEP protocol and this revised protocol. 1) Extraction procedures are 100% pore water extraction rather than complex organic and aqueous extractions; 2) No serial dilutions are performed because LC50 calculations are not required to assess sediment toxicity between reference and site sediments; 3) No MOAS (Microtox Osmotic Adjusting Solution) is utilized; and 4) Statistical procedures utilize standard Analysis of Variance (ANOVA) or t-test procedures.

Microtox Test Procedure

Porewater Extraction and Adjustment

The general Microtox procedure involves centrifugation of 500ml of both reference and test sediments at approximately 4500G in for 30 minutes resulting in approximately 50 ml of pore water**. Minimal** disturbance of the field-collected samples prior to centrifugation is (e.g. compositing of numerous subsamples followed by homogenization) is highly recommended in order to reduce volatilization of potential contaminants. After centrifugation, approximately 25mls of pore water is then pipetted into a clean glass container. The remaining porewater volume is set aside if needed for reducing salinity should the initial salinity adjustments steps outlined below result in the sample exceeding 22ppt. Samples should be adjusted and analyzed within approximately 3 hours of extraction to reduce volatilization of potential chemical contaminants.

The sample is then adjusted for salinity, dissolved oxygen and *pH* **in the following order**.

1) Salinity is adjusted to 20± 2ppt using commercially available dry bulk marine aquarium reef salts (e.g. Forty Fathoms Reef®). **[Note: The salinity adjustment step is omitted for marine and estuarine sediments whose porewater exceeds 20ppt salinity.]**
2) The dissolved oxygen (DO) is then adjusted by gentle aeration or agitation until it is between 50-100% saturation.
3) The pH of the salinity and DO adjusted reference and test sediment pore water should not differ from each other by more than 0.4 pH units. The pH is adjusted to 7.9-8.2 (if necessary) using a micropipette and a dilute solution (0.5 N) NaOH or HCl. Total volume of NaOH and/or HCl should be recorded. Final concentration [compared with 100% porewater extracted] can then be calculated using these data. Final dilution should not be reduced below 90% of the pore water extract. **[Note: The control solution is prepared by using deionized or distilled water and adjusting salinity, DO and pH as described above.]**

Preparation of Bacterial Suspension and Bioassay Test Setup
A vial of freeze-dried bacteria is rehydrated with 1.0 ml of Microtox® Reconstitution solution and allowed to equilibrate for 30-90 minutes in the 4-degree Microtox Analyzer well. ***[NOTE: Mixing of the reconstituted bacteria is essential. Mix the reconstituted solution with a 1 ml pipette a minimum of 20 times by pipetting. First pipette the solution from the bottom of the cuvette and deposit the pipetted solution on the surface of the liquid remaining in the cuvette. Then pipette 1 ml of solution from the bottom of the cuvette and slowly pipette the liquid into the bottom of the cuvette.]***

One (1.0) ml of control solution is then placed in each of 5 test cuvettes and placed into the 15-degree incubation chambers. This procedure is followed for the laboratory control solution, reference sediment porewater samples, and test sediment porewater samples for up to 4 test sediments/batch (5 pseudo-replicates per site).

In each of the test, reference, and control sample cuvettes, 10 uL of rehydrated bacteria suspension are added at 30 second intervals, immediately mixed using a 1ml pipette and allowed to incubate (**Initial Incubation**) for 5 minutes. Begin the 5-minute **Initial Incubation** timer as soon as the 10ul bacterial suspension is placed into the cuvette containing the control sample at position A1. Used pipette tips are replaced with clean tips after each series of 5 pseudo-replicates (ref, control, and each test series eg: A1-A5 etc.). ***[NOTE: Extreme care must be used when pipetting these low volumes as slight residual amounts or presence of air bubbles in the pipette may cause variation due to error by as much as 100%.]***

Data Collection
At the end of the 5-minute **Initial Incubation** period, the first control vial is placed into the read chamber to **set** the instrument. At this time, start the data collection timer. This is the start of the (I_0) 5-minute analysis period. At 30-second intervals each cuvette (inclusive of A1) is placed into the read chamber for the initial reading (I_0). After 5 additional minutes, a second reading (I_5) is obtained following the above procedure. A 15-minute (I_{15}) is obtained in an additional 10 minutes.

Data Analysis
Statistical calculations are performed using a standard t-test by comparing reference with test site data. No gamma correction is required. Statistically significant differences with $\alpha = 0.05$ and the following relative differences are indications of test failure. Relative differences between reference and test results of $\geq$15% indicate SQS failure. Relative differences between reference and test results of $\geq$25% indicate CSL failure. Relative differences are calculated as follows:

RD = [100-(T/R*100)]

RD: Relative difference
T: Mean (5 pseudo-replicates) Test output results
R: Mean (5 pseudo-replicates) Reference test output results

Control output should exceed 80 percent at the 5 minute reading and 65% at the 15 minute reading.

Appendix C
Leaching of Inorganic Arsenic Species from Tissue Samples, Frontier Geosciences SOP FGS-064.3

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Originated by: Michelle L. Gauthier and Dirk Wallschläger
Revised by: Jeremy T. Nett
February 16, 2001

Effective Date: December 31, 2001

On December 31, 2001, this procedure was reviewed and validated by Michelle L. Gauthier,Laboratory Manager and acting Quality Assurance Officer.

1.0 SCOPE

1.1 Arsenic in biogenic samples may be in the form of organic or inorganic species. The organic species are assumed to be far less toxic than the inorganic, so differentiation between the two groups is required for toxicological assessments. This SOP describes the leaching of inorganic arsenic species from tissue samples. It is not an analytical procedure; therefore, the user is referred to the SOP for the corresponding analytical technique (As speciation by HG-CT-GC-AAS, FGS-022) for information on analytical methodology and QA requirements. We currently have no way of quantifying the relevant organic As species in tissues directly, but in combination with a separate oxidative total tissue digestion (FGS-058), this procedure permits the calculation of organic arsenic as total arsenic minus total inorganic arsenic.

1.2 This technique may also be used for the determination of mono- and dimethylarsenic in tissues. However, the quantitative leaching of those species from tissues has not yet been demonstrated. It is currently not possible to distinguish between As(III) and As(V) in tissues with the described technique, as As(III) is partially oxidized during the leaching process.

1.3 This method is designed for arsenic speciation in biogenic tissue (plant and animal) samples. In order to retain speciation, sample preservation is an important facet of this method.

1.4 This SOP is designed to ensure that procedures are followed and the data obtained are verifiable, reproducible, and repeatable.

1.5 The presented method was optimized on a limited number of different types of tissue. Since the leaching behavior of inorganic As species from tissues is potentially extremely matrix-dependent, the analysts performing the sample preparation and analyses are required to provide an evaluation of the method's performance to each project's manager, as well as report any unusual observations. This way, the method will be generally validated for all types of tissues, and minor adjustments will be incorporated, if necessary.

2.0 METHOD SUMMARY

2.1 In this technique, the inorganic species As(III) and As(V) are quantitatively leached from well-homogenized tissue samples with dilute hydrochloric acid. Total inorganic arsenic is determined by HG-CT-GC-AAS, as described in FGS-022. Arsenobetaine, which is assumed to be the major As species in fish tissues, has been demonstrated not to decompose to any As species measureable by HG-CT-GC-AAS under the employed extraction conditions.

2.2 Total arsenic is determined by ICP-MS (FGS-054) on a separate tissue sample after complete acid digestion (concentrated HNO_3), as described in FGS-058. The difference between the total arsenic concentration and the inorganic fraction is believed to be organic forms of arsenic.

2.3 Typical estimated method detection limits are on the order of 1 µg/kg TIAs, based on tissue wet weight, for TIAs determined by HG-CT-GC-AAS.

3.0 INTERFERENCES

3.1 Please refer to the SOP for the analytical methods to be used for specific interference related to the detection system being used. Typically samples will be analyzed by HG-CT-GC-AAS following FGS-022 for inorganic arsenic.

4.0 SAFETY

4.1 Personnel will don appropriate laboratory attire according to the Chemical Hygiene Plan. This includes, but is not limited to, laboratory coat, safety goggles, and latex gloves under clean gloves.

4.2 The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. All laboratory personnel should refer to the MSDS for each chemical they are working with.

4.3 The cell disrupter is only to be used mounted on a stand, and the analyst performing the sample extraction should always wear protective gloves during this step to minimize the risk of injury due to breakage from the glass vial. In addition, safety glasses must always be worn to prevent eye injuries from HCl spraying out of the vial during the leaching process. Refer to Frontier's CHP for proper handling of and risk associated with the involved chemicals.

5.0 EQUIPMENT

5.1 Borosilicate glass vials (40 mL).

5.2 Equipment for tissue pre-homogenization, such as a cleaned cutting board, knives, razorblades, food processor, etc.. Equipment is cleaned first by scrubbing with an alkaline detergent (e.g., 409) to remove lipids and tissue particles, then rinsed successively with dilute hydrochloric acid and reagent water, and finally wiped dry with disposable paper towels.

5.3 Laboratory centrifuge, capable of generating 3,000 rpm and holding the 40 mL extraction vials.

5.4 Cell disrupter: Polytron PT-MR 2100 with generator PT-DA 2112-EC (Kinematica, Switzerland).

5.5 Pipettors: plastic pneumatic variable pipettors in the range of 5.0 µL to 5 mL.

5.6 Analytical Balance capable of weighing accurately to 0.001 grams.

6.0 REAGENTS

6.1 Deionized reagent Water - 18 MΩ ultra pure deionized water starting from a prepurified (distilled, R.O., etc.) source. To remove any remaining trace metals and organics an activated carbon cartridge is placed between the final ion exchange bed and the 0.2-μm filter.

6.2 Arsenate (As(V)) Spiking Solution - Refer to FGS-022 for instruction for the preparation of an As(V) standard.

6.3 Hydrochloric Acid - A.C.S. grade. Make 2 M HCl by appropriate dilution of concentrated HCl in reagent water. Use the same batch of HCl that is used for the TIAs analysis to ensure minimal blank results.

6.4 Anti-foaming agent ("Antifoam"), Baker.

7.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 Samples must be collected in accordance with established ultraclean sampling techniques (see e.g. FGS-008). Samples may be placed in plastic zip type bags (double bagged) or wide-mouth jars with Teflon lined lids. Maintain sample at <5 ^{o}C until it can be frozen (within 24 hours). Keep samples frozen until day prior to analysis.

7.2 Just prior to extraction, samples are thawed and, if necessary, minced or homogenized in a cleaned food processor. The sample is well mixed to ensure the most representative sample possible.

8.0 PROCEDURES

8.1 Approximately 1.0 g wet tissue, accurately weighed, is placed in a 40-mL borosilicate glass vial with 20 mL of 2 M HCl.

8.2 The sample within the vial is emulsified with the cell disrupter until all solids are destroyed. The proper way to utilize the cell disrupter is to keep its bottom away from the vial bottom to allow free circulation of the solution under the cell disrupter rod ("generator"). Adjust the rotation speed so that the liquid level is between the lower and upper outlet hole of the generator. Optimal homogenization is achieved if a proper vortex is generated that sucks the tissue up into the generator. Typically, the tissue is homogenized in a few seconds. Ensure that no small pieces of tissue get stuck at the tip of the cell disrupter.

8.3 The digestate is diluted up to the 40-mL mark with reagent water.

8.4 The vial is centrifuged for 15 min at 3,000 rpm, until the solids are completely settled. The sample is now ready for analysis via HG-CT-GC-AAS (FGS-022), but may be left standing overnight prior to analysis.

8.5 Tissue extracts may foam strongly during the hydride generation step of the analysis. Use Antifoam as necessary, to suppress the foaming (try using approximately three drops of antifoam (≈ 50µL) per 5 mL of tissue extract as a rule of thumb).

9.0 QUALITY CONTROL

9.1 For every batch of 20 samples, two pre-extraction spikes (one matrix spike and one separate matrix spike duplicate) and one analytical duplicate are analyzed. The pre-extraction spike should be spiked with As(V). If total As concentration levels for the tissues are already measured, the spike target concentration should be 10-25 % of the total arsenic concentration. If the total As concentration of the sample is unknown, the target spiking level is 20-50 µg/kg. The spike and all results are calculated on a wet weight basis. Even though no reference material is currently certified for inorganic As, extract one appropriate tissue SRM with every sample batch as a secondary laboratory control sample. In addition, if pre-homogenization of the tissues is performed (e.g. with a food processor), then three separate blanks for this procedure are generated by putting 15 mL of deionized water through that procedure before subjecting it to the extraction step.

9.2 Before measuring samples, re-demonstrate that the antifoam is free of TIAs (blank) and does not impair the recovery of TIAs (blank spike).

9.3 All other analytical batch QC specified in the determination SOP must also be followed. This includes requirements for the calibration curve, ICV, ICB, CCVs, and CCBs

9.4 Matrix spike recoveries should range between 75 and 125%. The total preparation blank should not exceed 5 µg/kg (ww). Detection limits are supposed to be below 1µg/kg (ww).

10.0 CORRECTIVE ACTIONS

10.1 This is a sample preparation SOP; therefore, corrective actions are not required. Corrective actions are listed in the analytical SOP.