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

November 2002

Publication No. 02-03-053

printed on recycled paper

This report is available on the Department of Ecology home page on the World Wide Web at http://www.ecy.wa.gov/biblio/0203053.html

For additional copies of this publication, please contact:

Department of Ecology Publications Distributions Office
Address: PO Box 47600, Olympia WA 98504-7600
E-mail: ecypub@ecy.wa.gov
Phone: (360) 407-7472

Refer to Publication Number 02-03-053.

.

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

by
Richard Jack

Environmental Assessment Program
Olympia, Washington 98504-7710

November 2002

Waterbody Number: WA-10-1011 (Hylebos Creek Drainage)

Publication No. 02-03-053
printed on recycled paper

This page is purposely blank for duplex printing

Table of Contents

List of Figures and Tables

Abstract

The B&L Landfill, located in Milton, is composed of wood waste and slag. Adjacent to the landfill, extensive reed canary grass (*Phalaris arundinacea*) wetlands are present in an area with arsenic contaminated groundwater. This investigation was undertaken to determine the fate and transport of potential arsenic discharges and their impacts on wetland biota.

The study was conducted during late winter and spring of 2002. Initial surface water quality sampling on March 10 found one station with concentrations of 556 µg/L total arsenic, which exceeds the chronic water quality standard of 190 µg/L. Follow-up surface water sampling on May 6 determined that the bulk of arsenic in surface water was not identifiable to arsenic species, as it was likely bound to a particulate fraction.

Soil concentrations of lead, copper, and zinc were not elevated in zones closest to the landfill relative to the control locations. Soil arsenic concentrations were slightly higher in surficial soils at all study locations relative to the control location. Soil arsenic concentrations slightly exceeded the Model Toxics Control Act residential soil standard of 20 mg/Kg.

In general, pore-water metals concentrations were not elevated in areas of likely groundwater discharge relative to control stations. The exception was for total arsenic which was found at concentrations up to 397 µg/L nearest the landfill. Bioassays were conducted on soil pore waters using the Microtox bioassay. Statistically significant depression of Microtox relative light output was found throughout the study area relative to control locations.

Samples of plant root and shoot tissues demonstrated that, where arsenic concentrations are high, roots sequester significant quantities of arsenic, but less than 1% is translocated between roots and shoots. Additionally, the majority of this arsenic is in the inorganic form, and little arsenic is biotransformed by plants into less toxic organic forms.

Acknowledgements

The author of this report would like to thank the following people for their contribution to the study:

- Karin Feddersen for managing quality assurance of outside contract laboratories.
- Cliff Kirchmer, Dale Norton, and Brandee Era-Miller for their helpful comments on the study plan.
- Brandee Era-Miller, Ann Boeholt, Bob Schlemmer, and Klaus Richter for assisting with the field sample collection.
- Ann Boeholt, Dom Reale, and Klaus Richter for their thoughtful reviews of the draft report.
- Joan LeTourneau for formatting and editing the final report.

Introduction

The B&L Landfill site, located in Milton (Pierce County), was used as an industrial landfill during the 1970s and 1980s. Materials placed in the landfill include wood waste and slag from log sorting yards. Extensive wetlands surround the landfill, especially on the north side, although they have not been mapped by the National Wetlands Inventory. These wetlands moderate flood and seasonal low flows within the floodplain of Hylebos Creek. They also support salmonid and other wildlife habitat. Ditches drain west from the wetland to Hylebos Creek; elevated arsenic levels have been detected in some of these ditches. One sample from 1982 had concentrations of 10,000 µg/L total arsenic (Johnson and Norton, 1985). Because the B&L Landfill was a source of arsenic, copper, and lead to the Hylebos Creek system, cleanup actions were conducted on the landfill (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 water, and cleanup of contaminated ditch sediments. Recent monitoring in the spring of 2002 by the landfill owner/operator shows shallow groundwater contaminated with arsenic from 2 µg/L to 3.8 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. 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 wetland study location is within Puyallup Water Resource Inventory Area (WRIA) 10. The majority of the Hylebos Creek subbasin is within the City of Federal Way and is comprised of a mixture of suburban and urban development. About 400 yards to the west of the site, Interstate-5 forms the approximate western border of the wetland complex (Figure 1). Figure 1 illustrates the landfill, the mapped wetlands nearby, and Hylebos Creek. Most of the area to the north and west of the landfill is wetland, although it has not been delineated and thus is not mapped on Figure 1. All of the study area was observed with standing water throughout the winter and early spring. It has hydric soils and is dominated by facultative wetland vegetation. Thus, if a delineation were conducted, the study area would be within jurisdictional limits. Hylebos Creek parallels the western edge of the wetland along I-5. Hylebos Creek supports anadromous salmonids, including chinook, coho, and chum salmon (SASSI, 1992). To the north and east of the study area is the city of Milton.

The impacts of elevated arsenic levels on wetland systems are poorly understood, particularly at subacute exposure levels. Eisler (1988) has collected and summarized literature regarding more acute effects of arsenic on wildlife and aquatic resources. To date, no site-specific information on the impacts of metals on this wetland had been collected. This 2002 study is being conducted to gather better information on the site-specific impacts of arsenic and other metals. Results will help determine if the wetland is being impacted by landfill leachate and ensure that prior source control remediation efforts are functioning as intended.

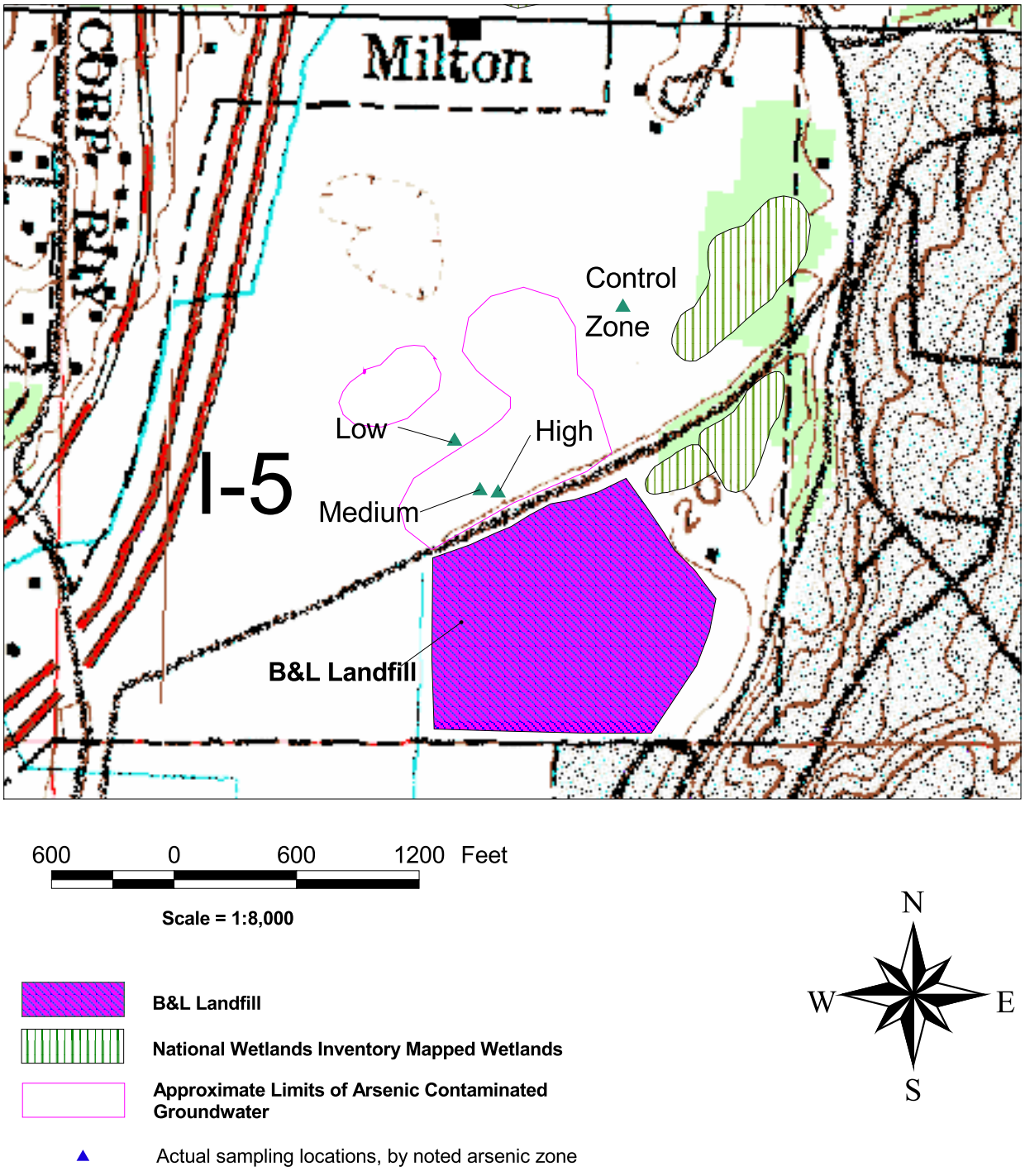

Figure 1. B&L Landfill Sampling Locations with Nearby Wetlands as Mapped by the National Wetlands Inventory.

Study Design and Goals

In the current 2002 study, levels of arsenic, copper, zinc, and lead in soil, water, and plant tissue were evaluated to determine the fate and transport of arsenic through the wetland and the magnitude of other potential confounding metals impacts. Soil bioassays were also conducted to determine the potential adverse effects of landfill leachate on wetland biota.

The project involved four components:

1) Support the in-situ investigation of the impacts of the arsenic loading on the development of selected amphibian eggs.

Four surface water samples were collected along a presumed gradient from low to high concentrations and analyzed for total arsenic. This occurred during the approximate midpoint of a winter amphibian egg mass study conducted by a University of Washington wetlands student. Prior, unpublished studies by the landfill operator had determined the arsenic concentration gradient in shallow groundwater away from the landfill. A gradient was also evident for soils and was presumed to exist for surface waters as well. The early season sampling of surface water supported the *in-situ* amphibian study and assisted in locating stations for additional, subsequent soil, water, bioassay, and plant tissue sampling. All subsequent sampling (Figure 1 and described below) occurred in four zones based on the initial surface water sampling: control, low, medium, and high arsenic zones.

2) Determine the role of the wetland in the transport of landfill arsenic.

Wetland soil/sediment, pore water, and surface water arsenic concentrations were sampled in control, high, medium, and low arsenic zones. Final sample sites were located using initial surface water data in conjunction with unpublished studies of soils and groundwater conducted by the operator.

Field reduction-oxidation potential (Eh) and pH values were also measured to help 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). As(III) is about 40 times more soluble than As(V) and is considered to be more toxic (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.

Soils data were collected from two depths, a 0”-6” surface strata and an 18”-24” subsurface strata. These depths were chosen to evaluate the potential for arsenic contamination to have been

deposited in surface soils from historic particulate runoff, or to have shallow groundwater as a source.

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

3) Determine the role of the wetland in the fate of arsenic released from the landfill.

Surface water arsenic speciation data were collected in conjunction with field Eh and pH values, as described above. The analytical methods for this project directly quantified As(III), As(V), monomethylarsenic acid (MMA), and dimethylarsenic acid (DMA). The determination of As(-3) is not practical due to its volatility. For plant tissues, total arsenic and total inorganic arsenic were determined. These data were collected to evaluate whether conditions in the wetland are conducive to arsenic mobilization, immobilization, or volatilization. The plant tissues were analyzed to evaluate whether arsenic discharges might biotransform from inorganic to organic forms. Both above and below ground tissues were collected to determine if plant harvests might be an effective bioremediation tool.

4) Determine if soil biological function are altered due to arsenic by assessing the toxicity of the sediment pore water adjacent to the landfill.

Sediment pore water from areas of high, medium, and low arsenic concentrations were collected within the wetland and the control site. Analyze pore waters for toxicity using the Microtox® bioassay (Adolphson, 2002). The Microtox bioassay uses phosphorescent bacteria which experiences reduced light output in response to toxicants. The bacteria are a measurement endpoint for soil microbial wetland functions such as decomposition and nutrient processing. The test used 100% sediment pore water as a test media without a dilution series.

To support these four objectives, additional metals were concurrently analyzed. They included lead, zinc, and copper, which may confound interpretation of arsenic impacts. Additionally, iron was 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).

A reference station was established outside of the known groundwater arsenic plume. It matched, as closely as practicable, the hydrologic regime and vegetation of the study wetland. Based on historic aerial photos, the reference station had a similar land history; therefore, potential confounding effects from agricultural arsenical pesticide/herbicide use are not anticipated.

Methods

Field Parameters

Latitude, longitude, conductivity, pH, and Eh were measured in the field. Sample locations were positioned in the field using approximate distances from well casings, soil borings, and the University of Washington student's cages used to house amphibian embryos. The actual sample locations latitude and longitude were recorded with a handheld Magellan GPS 320 (NAD, 1983). Coordinates were not differentially corrected.

Surface water pH was measured with a digital pH meter (Orion 250A) calibrated prior to sampling with pH 4 and 7 standards. Relative Eh was also measured at the approximate soil water interface. This interface was difficult to precisely locate, due to the dense vegetation and root mats. The Eh scale was calibrated to +260 mV with a proprietary Orion redox standard at the beginning of the field day. Conductivity was measured with a temperature compensated Orion 120.

Sample Collection

Water samples were collected using pre-cleaned polyethylene bottles. At the time of the sampling, standing water was present in the wetland and the soils were saturated. There was no perceptible surface water flow and water depths were approximately 25 to 75cm. Determining the exact depth of surface waters was confounded by the soft soils and extensive root mats. Water samples were collected first by wading to the station. Samples bottles were dipped to a depth of approximately 2cm into water which had not been disturbed or silted.

March 10 water samples were analyzed for total arsenic via inductively coupled plasma – mass spectrometry (ICP-MS). May 6 surface water samples were filtered in the field using pre-cleaned, disposable 0.45 µm filter units. These water samples were analyzed via Frontier Geosciences method FG-022, an ion chromatography-hydride generation-atomic fluorescence spectrometry (IC-HG-AFS) method. In this report, these filtered samples are also referred to as dissolved water concentrations. Reagent grade nitric acid was used as a preservative in samples for zinc, copper, and lead analysis, while no acid preservative was used for the arsenic speciation samples. Surface waters collected on May 6 were also separately analyzed for copper, lead, and zinc by ICP-MS.

Soil samples were collected using a steel shovel, washed with on-site water. Samples were composited from the shovel directly into precleaned glass jars. To the extent practicable, visible roots and live plant matter were removed. Because soils were to be analyzed for iron, that portion of the soil mass contacting the shovel was discarded. Soils were collected and composited from two 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 wood waste site. The 6"-18" portion of the soil column was not retained or analyzed.

Lastly, plant materials were collected from an area within about 10 feet of the soil sampling holes to avoid cross-contamination and to provide for the collection of sufficient live plants. For above-ground tissues, stainless steel scissors were used to cut stems. For below ground tissues, plants were hand pulled, roots were washed with on-site water, and forceps were used to extract roots from the soil matrix. Live (white) plant roots were preferentially selected, although distinguishing live from dead root material was not always possible. Roots were washed with on-site water to remove most adhering soil particles.

Sampling occurred from the control site to the high arsenic zone, to minimize the effects of sample contamination. Most sampling equipment was dedicated to each station. Some, like the shovel, were cleaned between stations by brushing with on-site water and rinsing with deionized water.

Pore water for chemical analyses was extracted at Ecology Headquarters within 24 hours, using a centrifuge at approximately 4500G for 30 minutes. Pore waters could not be filtered due to clogging of the 0.45 µm filter media.

Sediments for the Microtox bioassay were held unpreserved, in the dark with tightly sealed lids. Tests were initiated on May 13, five days after sample collection. While there is no established holding time for this test, most analysts consider 14 days as a reasonable holding time (USEPA, 1995).

Analytical Methods

The arsenic speciation was performed at Frontier Geosciences. Frontier Geosciences used a proprietary ion chromatography-hydride generation-atomic fluorescence (IC-HG-AFS) method for the water and tissue samples (Frontier Geosciences, 2001). Lead, copper, zinc, and iron were analyzed at Ecology's Manchester Laboratory using inductively coupled plasma (ICP) or ICP mass spectrometry methods (method 200.7 or 200.8; USEPA, 1994).

The Microtox bioassay followed Ecology's modified 100% pore-water methods (Adolphson, 2002). Pore waters were extracted from 500 mL of soil by centrifuging at 4500G for 30 minutes. Each pore water was adjusted to 20 ppt salinity with Forty Fathoms artificial sea salt. Dissolved oxygen ranged from 50 to 100% and samples did not require aeration. The pH was adjusted from 7.8 to 8.2 with NaOH or HCl as needed.

Total organic carbon was measured in site soils by Puget Sound Estuary Program (USEPA, 1997) protocols.

Data Quality Assessment

This 2002 study was conducted as a screening level investigation. Field duplicates, matrix spikes, and spike duplicates were conducted at least once on at least 75% of media-analyte combinations tested. The quality assurance (QA) measures were distributed across the various metals and matrices in an effort to evaluate whether any particular analyte-matrix combination

was critically flawed. Because of this broad distribution of QA samples, statistical calculations of particular analyte-matrix QA/QC parameters are limited.

The laboratory results of matrix spike and matrix spike duplicates recoveries were compared across the various media and analytes to evaluate whether a particular analyte or media were significantly biased. Duplicates were compared to evaluate significant differences in precision. These results are shown in Table 1. A few media and analytes did not have any QA samples associated with them.

Table 1. Quality assurance field and/or laboratory duplicates and matrix spikes.

Analyte	Units	Value	Duplicate value	Duplicate value	Matrix spike recovery	Matrix spike duplicate recovery
Hardness	mg/L	540	-	-	78.5%	86%
TOC in soils (70ºC)	%	25.7	25.1	26.4	-	-
TOC in soils (104ºC)	%	28.4	27	27.4	-	-
Total arsenic in surface water	µg/L	23	22.5	-	89.3%	-
Zinc in pore water	µg/L	60	-	-	76.2%	85.5%
Copper in pore water	µg/L	27.8	-	-	76.2%	85.5%
Lead in pore water	µg/L	62.5	-	-	102%	107%
Copper in plant roots	µg/Kg	3410	-	-	89.9%	100%
Lead in plant roots	µg/Kg	3030	-	-	85.3%	100%
Arsenic in 0-6” soils	mg/Kg	5.64	5.14	5.64	97.5%	115%
Zinc in 18-24” soils	mg/Kg	157	148	153	-	-
Copper in 0-6” soils	mg/Kg	21.8	21.7	19.8	-	-
Lead in 18-24” soils	mg/Kg	109	136	142	-	-
Iron in 18-24” soils	mg/Kg	12900	14000	-	-	-
Inorganic arsenic in plant shoots	mg/Kg	0.138	0.582	-	113.8%	85.8%
Total arsenic in plant shoots	mg/Kg	0.72	1.02	-	117.4%	-

TOC = total organic carbon

There are an insufficient number of duplicates and matrix spikes to statistically compare each matrix and analyte against the QA Project Plan goals (Jack, 2002). Additionally, some of the detected concentrations are low relative to method detection limits. When approaching the detection limit, instrument precision declines. It would be inappropriate to strictly compare such data against the QA Project Plan goals.

The field and laboratory duplicate results are all acceptable, except for the field duplicate performed on the plant shoots for inorganic arsenic. These results varied significantly, probably due to heterogeneity within the sample matrix. These values, despite their variability, are three orders of magnitude below the root arsenic concentrations. Thus, they are considered appropriate for comparative purposes, despite their high relative standard deviation.

For all analytes in all matrices, percent recoveries of matrix spikes and matrix spike duplicates were within the plus or minus 25% limits provided in the respective analytical methods. Because the spikes met the method performance limits, there does not appear to be any systematic bias.

Lab and/or field blanks were conducted on many matrices. Only two of these blanks detected any analyte: zinc was detected at a concentration of 1.4 µg/L in a pore water lab blank, and iron was detected at a concentration of 5.3 mg/Kg in a soil lab blank. These results confirm that field and laboratory contamination were minimal. The detection of zinc in the lab blank resulted in a "J" for the result from the pore water equipment blank; no other samples required corrective action.

For total organic carbon (TOC), both laboratory control samples had greater than 97.1% recovery, and laboratory blanks were nondetect at 0.1%. Thus, there were no QA issues with the TOC analysis.

In summary, the duplicates detected sample heterogeneity in arsenic tissue concentrations, but all other duplicates were suitably precise. Matrix spikes and spike duplicates revealed no systematic bias in any media or analyte. Laboratory and field contamination in blanks is minimal and does not influence sample results or validity. The data appear to meet the quality control limits specified in the QA Project Plan; therefore, all analytical data are considered useable.

Results

Surface Water

Conventional Parameters

Table 2 describes the locations and some conventional surface water parameters measured at each station. Hardness was relatively low at both the control and low arsenic stations, and more than twice as high at the medium and high arsenic zones. Conductivity exhibited the same pattern, while pH did not vary substantively across the study area. Surface water electrochemical potential was positive at all sites except the medium arsenic zone.

Table 2. Conventional parameters and sampling locations, May 6.

Station	Latitude	Longitude	Surface water hardness (mg/L)	Surface water conductivity (µS/cm)	Surface water pH	Surface water relative Eh (mV)
Control	47.2472	122.3268	168	290	6.99	+172.2
Low	47.2458	122.3292	187	486	6.97	+104.7
Medium	47.2453	122.3288	548	1622	6.95	-43.2
High	47.2453	122.3285	540	1426	6.95	+56.4

All coordinates are NAD, 1983.

Initial March Surface Water

Table 3 illustrates the results from the initial water quality samples conducted on March 10, 2002. At this time, the arsenic stations/zones had not been conclusively determined and were based upon the results of 0-24" surface soil samples collected and analyzed by the landfill owner/operator. A possible control site, chosen at the discretion of the University of Washington student, was sampled with a result of 31.9 µg/L total arsenic. Because, this location was within 40 meters (130 ft) of other more contaminated stations, subsequent sampling used a more remote control station located about 200 ft north of the gravel road which bisects the wetland. Results in Table 3 use final station identifications. Table 3 also lists the acute and chronic ambient water quality criteria from Chapter 173-201A-040 WAC. These criteria are applicable to dissolved metals concentrations. Chapter 173-201A-040 WAC provides a factor of 1.0 for conversion of the dissolved criteria to total criteria, thus the ambient water quality criteria is the same for both fractions.

Table 3. March 10 arsenic surface water sampling results. All units are µg/L.

Station	Total arsenic concentration	Acute surface water quality standard	Chronic surface water quality standard
Control (initial siting)	31.9	360	190
Low	23.0	360	190
Medium	113.0	360	190
High	556.0	360	190

May Surface Water

Surface waters collected on May 6 were field filtered to remove microorganisms which might alter arsenic speciation (Table 4).

Table 4. May 6 arsenic surface water sampling results. All units are µg/L.

Station	As(III)	As(V)	MMA	DMA	Total dissolved arsenic	Estimated colloid fraction
Control	<0.1	0.8	<0.1	0.4	3.56	~2.3
Low	0.3	0.3	0.3	0.5	9.12	~7.7
Medium	1.3	0.6	0.4	3.7	16.0	~10.0
High	2.6	0.5	0.3	5.8	20.3	~11.1

MMA = monomethylarsenic acid
DMA = dimethylarsenic acid

Dissolved zinc, copper, and lead were also analyzed (Table 5). Each result has been paired with its appropriate, hardness corrected, dissolved, chronic surface water quality standard. None of the surface water samples exceeded their hardness corrected criteria.

Table 5. May 6 zinc, copper, and lead surface water sampling results. All units are µg/L

Station	Zinc	Zn chronic water quality standard	Lead	Pb chronic water quality standard	Copper	Cu chronic water quality standard
Control	7.37	162.2	0.29	4.4	0.71	17.7
Low	3.23	177.6	0.18	4.9	0.51	19.4
Medium	6.22	441.7	0.02 U	15.1	1.29	48.6
High	2.1	436.2	0.02 U	14.8	0.62	48.0

U = not detected at the detection limit shown.

Pore Water

Chemistry

Pore water samples were analyzed for copper, lead, zinc, As(III), As(V), monomethylated arsenic, dimethylated arsenic, total dissolved arsenic species, and total arsenic (Table 6). Concentrations of metals in pore water were relatively elevated at the control station for lead, and in the high arsenic zone for total arsenic but for not for dissolved arsenic.

Table 6. May 6 metals pore water sampling results.
All results are in µg/L.

Metals and Species	Station			
	Control	Low	Medium	High
Copper	273	27.8	167	178
Lead	1500	62.5	400	368
Zinc	562	60	565	431
As(III)	<0.1	<0.1	<0.1	0.3
As(V)	1.2	1.5	<0.1	1.2
MMA	<0.1	<0.1	<0.1	<0.1
DMA	<0.1	0.5	<0.2	0.3
Dissolved As	9.24	18.8	10.5	9.34
Total As	23.0	38.0	42.6	397
Estimated As Colloid Fraction	~13.8	~19.2	~32.1	~387.66

Microtox Bioassays

Microtox bioassays were conducted on 100% soil pore water from all four study locations. The mean results from the five test replicates are reported in relative light output. A laboratory control was run in addition to the field control (reference) soils. Results from these analyses are presented in Table 7. The field control station exhibited light inhibition relative to the laboratory control soil, although this reduction was not very large. All three test locations (low, medium, and high arsenic zones) displayed light inhibition after both 5- and 15-minute incubation periods.

Table 7. Mean Microtox relative light outputs by incubation time and station.

Time after incubation (minutes)	Station				
	Lab Control	Field Control	Low	Medium	High
0	91.78	79.76	**58.85**	**66.02**	**49.15**
5	76.60	67.82	**52.09**	**59.03**	**47.65**
15	62.67	58.05	**43.09**	**49.06**	**40.03**

Bold = significant toxicity $p<0.028$

All of the field stations exhibited significantly depressed light output relative to laboratory controls. P-values were all less than 0.038. All test stations also exhibited depressed light outputs relative to the field control station (AMEC Earth and Environmental, 2002), with p-values less than 0.028.

Soil

Soils were analyzed for copper, zinc, lead, iron, and arsenic in two depth ranges. Total organic carbon (TOC) was measured in surficial soils only. Table 8 illustrates the soil metals results by depth and metal from each station.

Table 8. Metals and TOC results from 0-6" and 18"-24" soil depths. Metals results are in mg/Kg; TOC is reported in percent.

Metals and Species	Station							
	Control		Low		Medium		High	
	0-6"	18-24"	0-6"	18-24"	0-6"	18-24"	0-6"	18-24"
Copper	21.8	25.4	27.1	30.3	36	31.1	30.7	31.0
Lead	142	109	71.4	79.2	98.2	5.96	62.5	15.4
Zinc	165	157	35.5	44.2	76.4	28.8	23.3	26.6
Iron	14,600	12,900	19,900	17,100	22,600	21,300	29,000	22,200
Arsenic	5.64	5.57	24	20.1	27.5	7.02	23.3	16.3
TOC (70ºC)	12	-	25.7	-	22.2	-	21.7	-
TOC (104ºC)	11.2	-	28.4	-	22.9	-	21.7	-

Soil concentrations partially reflect the variation in TOC percentages, with the control station having about one-half the organic carbon of the other stations. The control station consequently had some of the highest soil metals concentrations.

Plant Tissues

Above ground, live plant tissues (shoots) were analyzed for zinc, copper, lead, total inorganic arsenic, and total arsenic (Table 9). Root tissues were also analyzed for these same analytes (Table 10). Shoot results by analyte are very similar across all stations, whereas root concentrations vary by up to two orders of magnitude. Root concentrations of copper, lead, and zinc were highest at the control station, while both total inorganic and total arsenic increased significantly across the gradient of stations.

Table 9. Shoot metal concentrations (mg/Kg).

Metals and Species	Station			
	Control	Low	Medium	High
Copper	940	750	1720	660
Lead	100 U	100 U	100 U	100
Zinc	5,030	5,000	7,270	5,440
Arsenic, total inorganic	0.321	0.059	0.081	0.138
Arsenic, total	0.51	0.21	0.19	0.72

Table 10. Root metal concentrations (mg/Kg).

Metals and Species	Station			
	Control	Low	Medium	High
Copper	3,410	1,320	1,200	1,300
Lead	3,030	730	330	360
Zinc	25,300	6,030	5,570	7,110
Arsenic, total inorganic	4.97	1.83	23.7	169.0
Arsenic, total	3.67	3.36	56.4	247

This page is purposely blank for duplex printing

Discussion

Surface Water

Zinc, copper, and lead were detected at low levels throughout the study area. Elevated concentrations relative to the hardness-corrected, chronic surface water criteria were never found. Pre-remediation, historic surface water data are available for February 15, 1984 and August 22-24, 1983 (Johnson and Norton, 1985). Current zinc total data are similar to the historic range of 5-9 µg/L. Copper and lead were not historically analyzed. Because these elements appeared only at relatively low levels, they are not considered significant potential stressors on the wetland system. For this reason, further discussion of these metals has been limited.

Arsenic was found during the March 10, 2002 sampling event at significantly elevated concentrations. The medium zone had arsenic concentrations of 113 µg/L, while the high zone had a concentration of 556 µg/L. The high zone concentration was above both the chronic and acute water quality standards of 190 and 360 µg/L respectively. These elevated concentrations are potentially responsible for some of the impacts observed in the Microtox bioassay and other impacts measured in amphibian embryos (Schlemmer, 2002). All of the samples measured in March exceeded the drinking water maximum contaminant limit of 10 µg/L.

Historic, pre-remediation data on surface water arsenic concentrations are available for February 15, 1984. Concentrations in the "U.S. Gypsum" ditch, which is the 1984 location closest to the landfill, were 64 to 109 µg/L total arsenic. These concentrations are lower than concentrations found in this 2002 study. Other arsenic data from the "B&L Ditch at Surprise Lake Drain" were 5,400 µg/L on August 22, 1983. While these data are insufficient to draw firm conclusions, immediately adjacent surface water concentrations at the "high arsenic zone" are bracketed by these historic values.

In May 2002, surface water analysis was conducted on filtered waters to determine the fate of the more mobile metals fractions. Rising concentrations of dissolved arsenic were found across the study (low to high zones). However, the arsenic speciation analysis was unable to determine the form of most of this arsenic. Figure 2 illustrates the relative proportions of the different arsenic species measured. All samples, including the control station, exceed the arsenic regulatory criteria in the National Toxics Rule (40 CFR § 131.36) (NTR). The NTR criteria are for inorganic arsenic only and are 0.018 µg/L for the consumption of water and organisms and 0.14 µg/L for the consumption of water only. NTR criteria for arsenic are frequently exceeded in Washington rivers without known anthropogenic arsenic inputs (Johnson and Golding, 2002).

The unquantified mass of arsenic, the difference between the sum of the identified arsenic species and the total arsenic measured by ICP-MS, is believed to be associated with colloidal particles. The colloidal particles were unable to pass through the ion-chromatography separation process used on these water samples, and have not been quantified. Further evidence suggesting a significant colloidal fraction is evidenced by the rust coloration of the filtered waters,

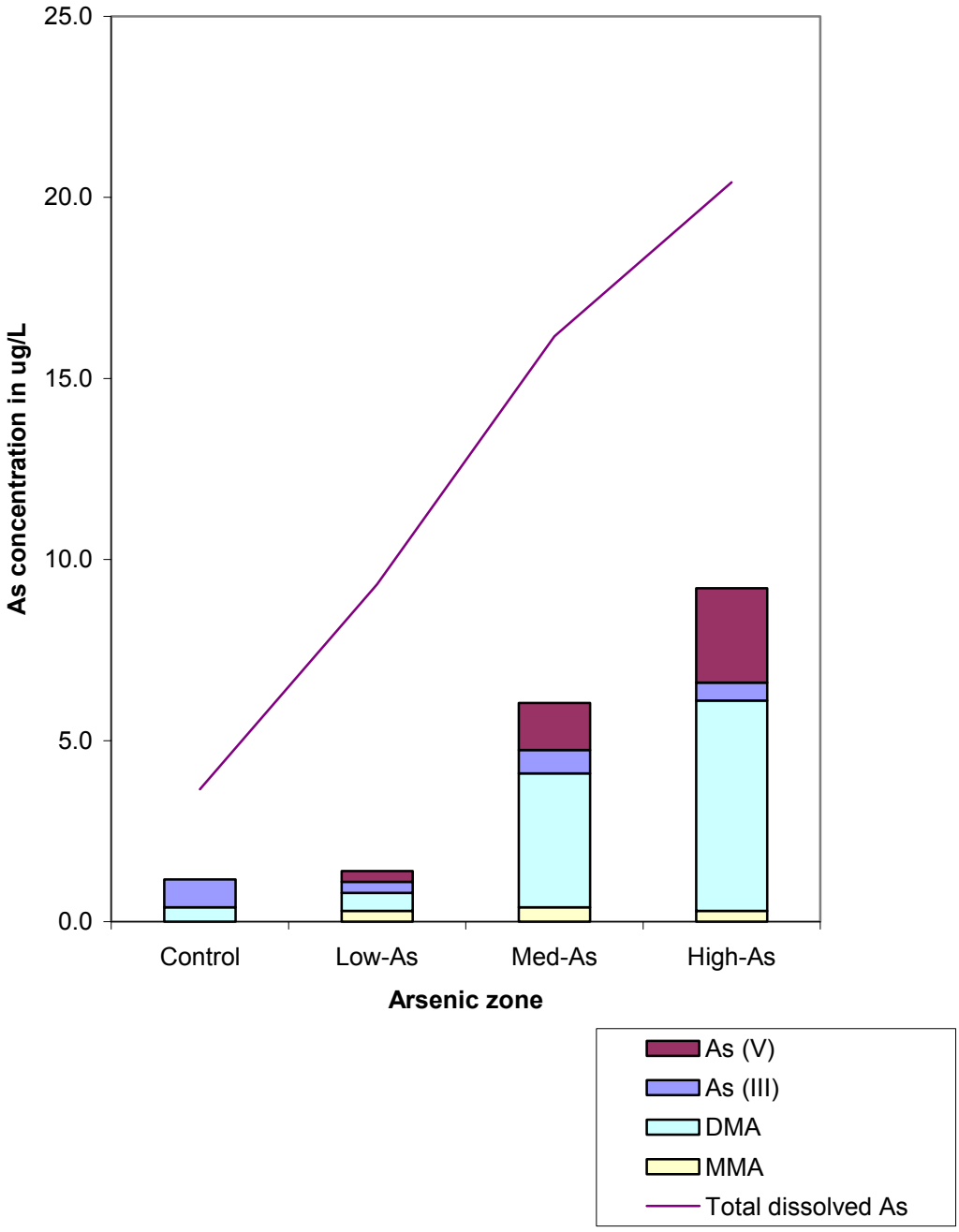

Figure 2. Surface water arsenic fractions and total dissolved arsenic by zone.

suggesting an iron precipitate was present. Lastly, large quantities of rust colored materials were observed clumped onto plant materials at all but the control station. These clumps were presumed to be iron precipitates.

These data suggest that most of the arsenic is associated with colloidal particles. The particles are clearly mobile in surface water, and because they are smaller than 0.45 µm, they are likely mobile in groundwater as well. Also, proportions of the different arsenic species did not change appreciably across the study gradient (Figure 2), suggesting little biotransformation is occurring. This is in contrast to lake oriented studies which have found organic arsenicals to be an important link in cycling of arsenic (Anderson and Bruland, 1991). Without much more refined mass balance calculations, this suggests that transformations of arsenic inputs are limited to dilution.

Figure 3 illustrates the sums of detected metals combined with bulk conductivity. While the states of major cations and anions in these solutions are not known, increasing arsenic concentrations are positively correlated with increases in conductivity. This suggests that arsenic is contributing significantly to the observed increase in conductivity noted in the higher arsenic zones (Figure 3). This elevated conductivity, in conjunction with the arsenic surface water standards exceedances, is likely responsible for any adverse impacts observed in surface waters. Historic conductivity results (Johnson and Norton, 1985) from landfill leachate were as high as 1,340 µmhos/cm, which is comparable to the values observed in surface waters in this 2002 study.

In future investigations, it may be possible to more conclusively determine the source of the elevated conductivity and hardness by tracking other parameters. Presumably, wood from log sort yards was rafted in the saline waters of Commencement Bay and may have accumulated sodium, chloride, potassium, or other marine metals at elevated concentrations relative to surrounding surface waters. By tracking these additional parameters, the source and/or pathway of elevated conductivity may become clearer.

Results from the University of Washington student investigation of amphibian embryos were inconclusive. Thus, no direct biological measure of surface water impacts has been conducted to date.

Pore Water

Pore water was centrifuged, but the supernatant was unable to be field filtered due to residual particulate concentrations. Thus, metals results partially reflect the metals contents of surrounding soils and partially reflect pore-water/shallow groundwater concentrations. For the control station, soil TOC percentages were approximately half those found at the three study sites (12% vs. 25%). The lower TOC demonstrates a high soil mineral fraction. This increased mineral fraction is reflected in the higher concentrations of zinc, copper, and lead found in the control station's pore water. Thus, concentrations of pore-water metals decline when moving from the control station to the low arsenic zone. This is probably a result of the rising TOC percentage, coupled with relatively low rates of contaminated groundwater seepage. At the

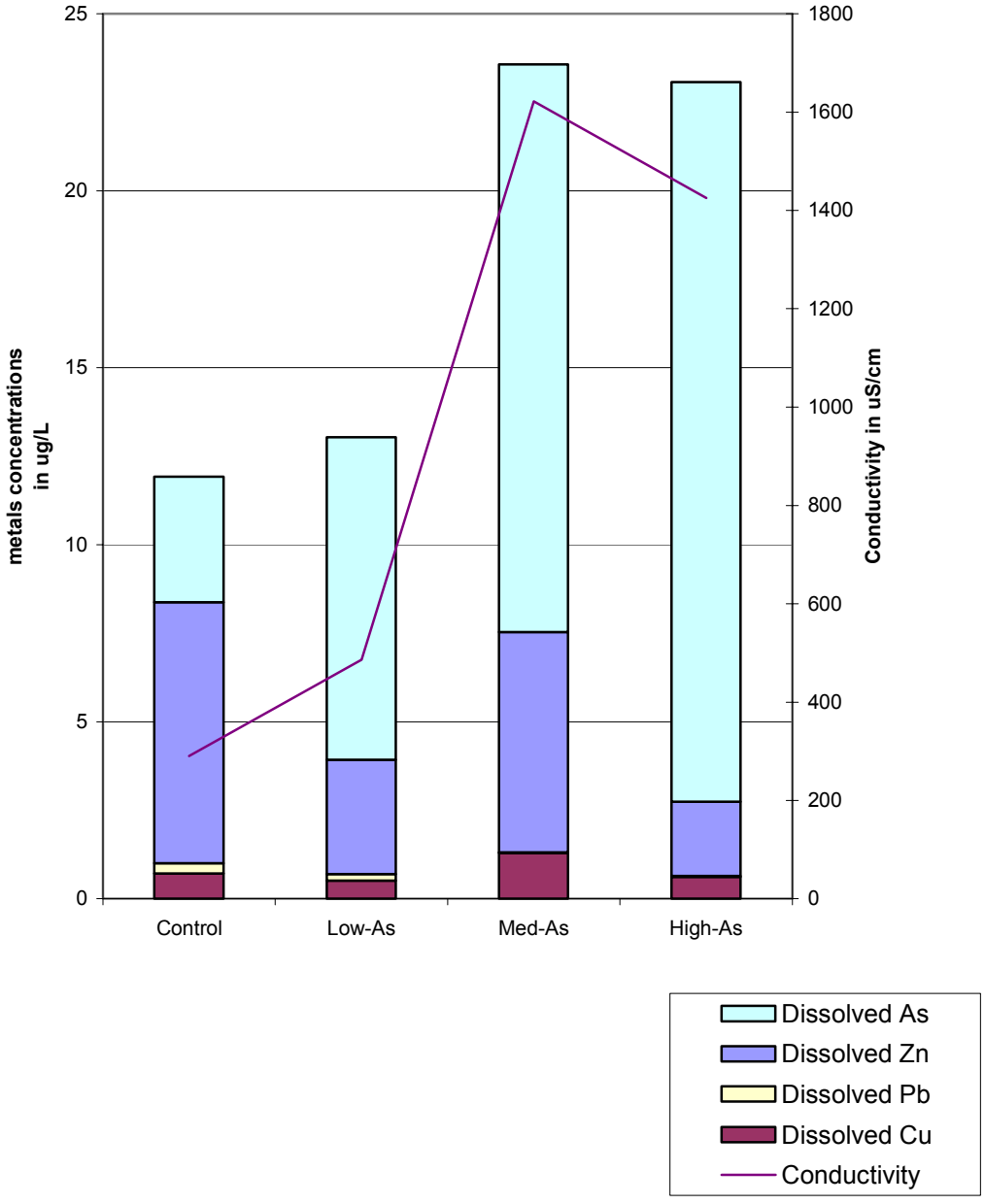

Figure 3. Dissolved metals versus conductivity.

medium and high arsenic study stations, TOC remains about the same when compared to the low station, but zinc, copper, and lead concentrations rise slightly. This is probably a reflection of a higher rate of groundwater inflow or higher groundwater metals concentrations at these locations.

For arsenic, the contract laboratory was able to filter pore waters down to 0.45 µm. Thus, both dissolved and total arsenic pore-water data are available. The speciation of arsenic in pore waters across the study gradient illustrates a relatively consistent rise in concentrations from the control site to the high arsenic zone (Table 6). Figure 4 shows that the vast majority of the total arsenic detected at the high arsenic zone was in the particulate form. There are no water quality standards for pore waters. For comparison, only the high arsenic zone total arsenic concentrations exceeded both the chronic and acute surface water standards. All other samples were below the chronic surface water standard of 190 µg/L.

Soil

In general, concentrations of zinc, copper, and lead were higher at the control site than at the study locations. This rise is believed to be due to: 1) the approximately two-fold increase from 12% to 22-25% in TOC between the control and the study stations; 2) the presence of debris. Electric fence insulators, barbed wire, and fence posts were all found in the control station soils. These materials likely led to the high zinc concentrations observed at this location, probably from fence galvanizing.

Surface soils (0-6" depths) at all three study locations were found to exceed 20 mg/Kg, the toxics cleanup program Model Toxics Control Act (MTCA) residential soil threshold. However, the exceedances were relatively small, with the medium arsenic zone having the highest arsenic surface soil concentration, with 27.5 mg/Kg. All three study location surface soil values exceed the 90th percentile statewide and Puget Sound background value of 7.0 mg/Kg arsenic established by San Juan (1994). Because the control location arsenic concentration of 5.64 mg/kg did not exceed the 90th percentile value, one can conclude that the elevated values observed in the study locations are a reflection of current or historic landfill discharges. The elevated surface soil arsenic concentrations are not due to aeolian deposition from the former smelter in Tacoma, or from prior arsenical (agricultural) pesticide usage.

A number of prior investigations have determined that iron and/or iron (hydr)oxides, coupled with Eh, are key determinants of arsenic mobility (Masscheleyn et al., 1991). In this study, iron precipitates appeared to increase from the control site to the high arsenic zone. These precipitates were found attached to plant stems above the soil-water interface.

Below the soil-water interface within the soil column itself, iron and arsenic concentrations generally increase when moving from the control towards the high arsenic zone (Figure 5). Most notable is the reduction in 18-24" soil arsenic concentrations observed at the medium arsenic zone. This is believed due to the negative Eh measured at this location (Figure 6). Eh was measured at the soil water interface, and not at specific soil depths. But, this measurement is an indication of subsurface redox potential and presumably represents relatively low Eh at depth as

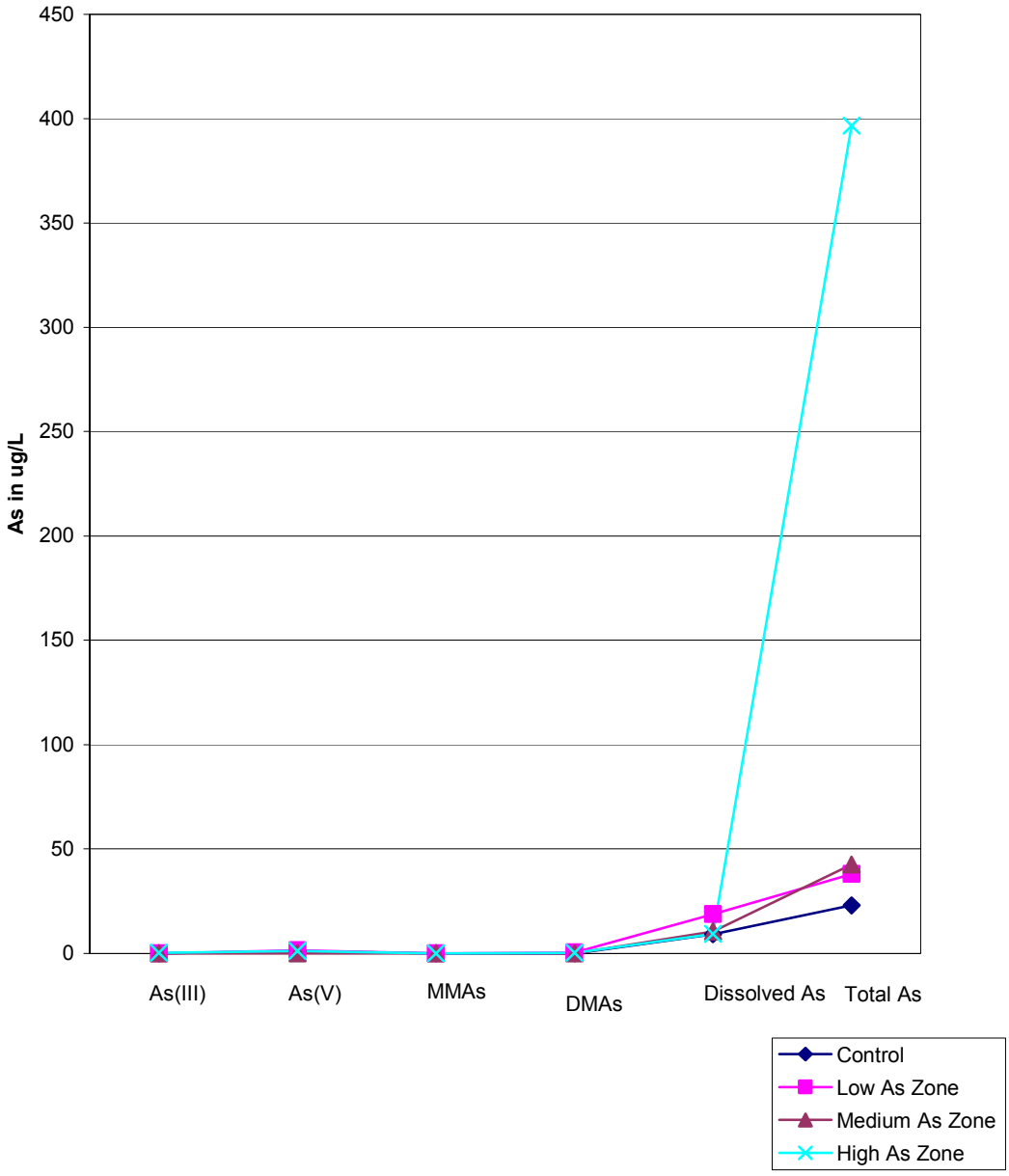

Figure 4. Pore water arsenic species concentrations by zone.

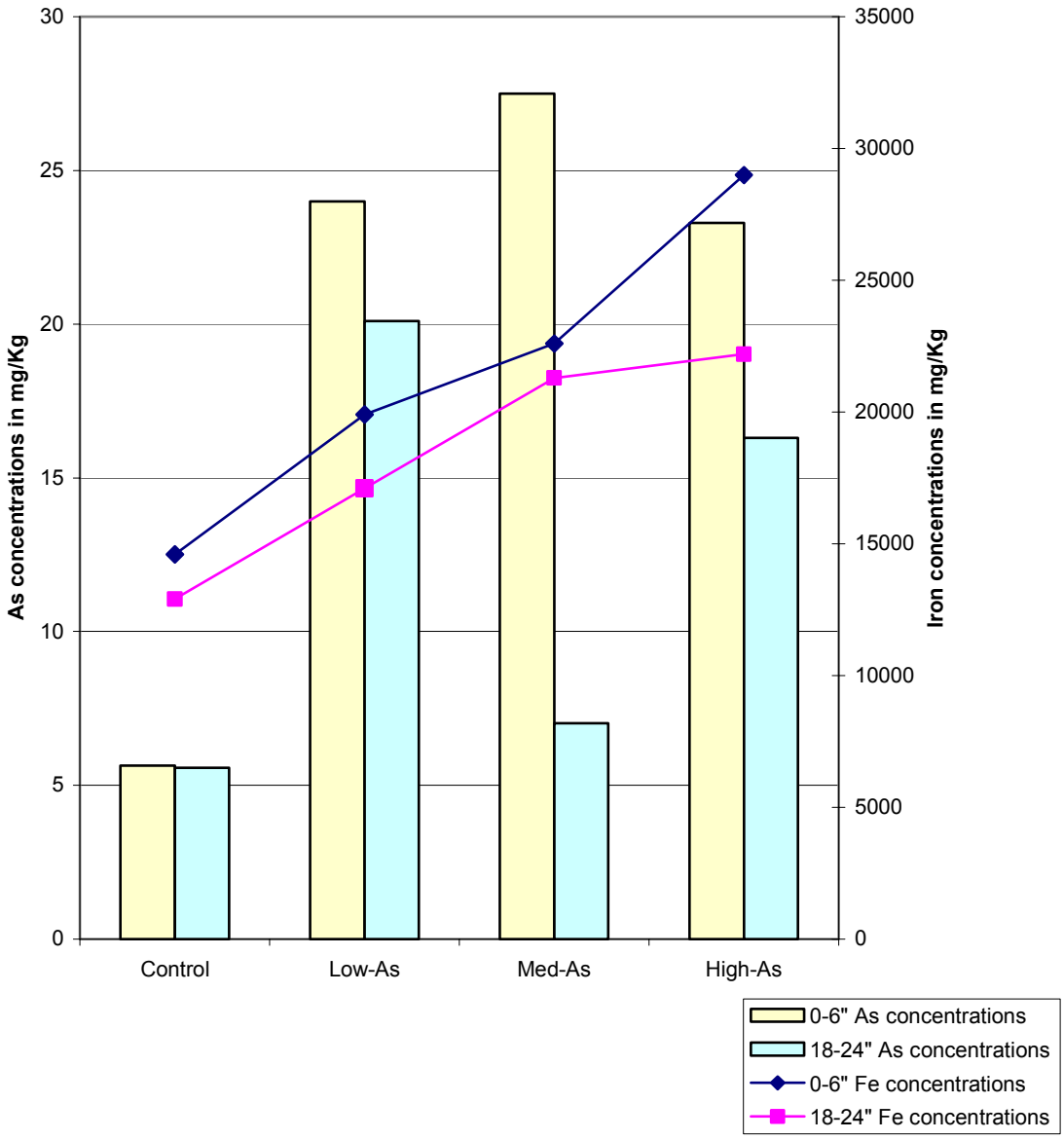

Figure 5. Arsenic soil concentrations by depth vs. iron soil concentrations.

well. Using the phase diagrams of Masscheleyn et al. (1991), the expected form of arsenic in all the study soils at pH 6.95 is H_3AsO_3. Only the medium zone, with its Eh of -43.2, should display ionic iron (Fe^{2+}) at this Eh-pH state. The control and other arsenic zones should exhibit $Fe(OH)_3$.

Iron concentrations in soil do not appear to be controlling arsenic concentrations. Regression r^2 values for 0-6" and 18-24" soil arsenic, versus soil iron, were 0.51 and 0.08 respectively. At all stations, surface soil arsenic concentrations were higher than subsurface soil concentrations. This may be due to historic, surficial deposition of arsenic in the wetland prior to landfill capping, or it might be due to increased solubility of subsurface arsenic. Figure 6 suggests that increased solubility at lower Eh probably plays a significant role in the lower concentrations of arsenic in subsurface soils, as the subsurface soil arsenic concentration is proportional to Eh at the soil water interface. Where overlying waters are well oxygenated, such as at the control station, soil concentrations do not vary with depth. The confounding variable of Eh limits our ability to determine the causative agent for the variation of arsenic with depth.

Plant Tissues

Plant tissue concentrations of zinc, copper, and lead were found to be either higher at the control station or variable across stations. Shoot metal concentrations tended to be variable across the control and study locations, while root concentrations tended to be higher at the control site when compared to study locations. The increase in root tissue concentrations of lead, copper, and zinc is attributed to the greater mineral content of the control station soils. The presence of high zinc soils led to elevated zinc concentrations in plant roots but not shoots.

The pattern of elevated root but not shoot metal concentrations was generally repeated for copper, lead, and arsenic. In the case of arsenic, shoot concentrations were relatively low across all stations. Root arsenic concentrations dramatically rose between the low station and medium stations, and again between the medium and high stations (Figure 7). Significant portions of this increased arsenic were in the inorganic state. These data provide evidence that: 1) plants are not accumulating significant quantities of arsenic in their above-ground, harvestable tissues, and 2) plants are not biotransforming significant quantities of arsenic from an inorganic to a less toxic organic state. This role of plants in arsenic cycling may be important when contemplating wetland remediation.

Microtox Bioassays

The Microtox results revealed a statistically significant drop in relative light output across the station transect. This drop was not attributable to any particular metal, to conductivity, or to hardness. This may be a reflection in some variability within the bioassay procedures or results. Unfortunately, Microtox is not suitable for a toxicity identification evaluation in this case, as the bacteria are sensitive to all of the metals sampled across the study gradient, and their cumulative effects probably led to the decline in relative light output. Nevertheless, a significant drop in bacteria functions relative to the field control station was measured when moving closer to the landfill. This drop illustrates degraded biological functions closer to the landfill.

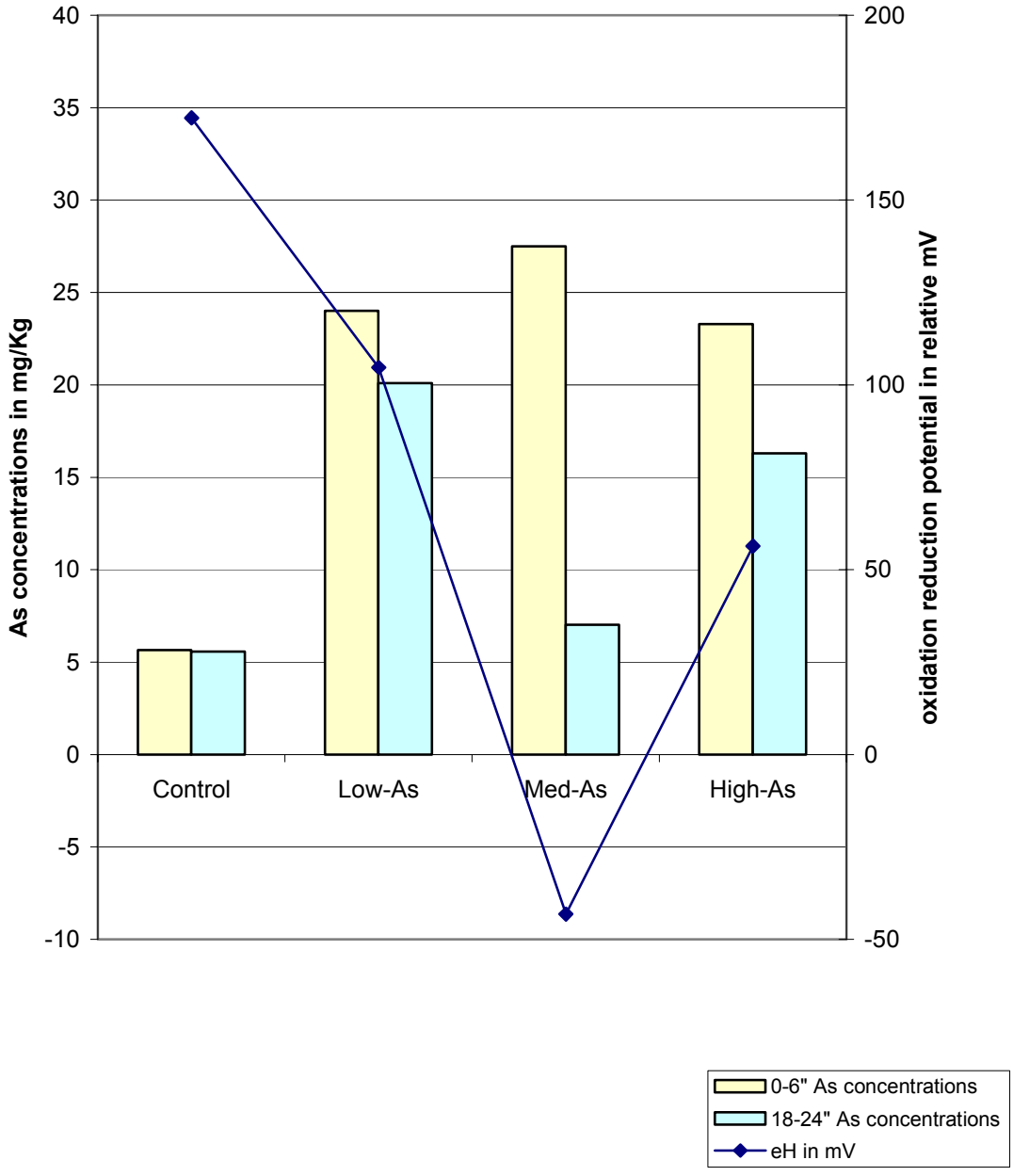

Figure 6. Arsenic soil concentrations vs. relative eH.

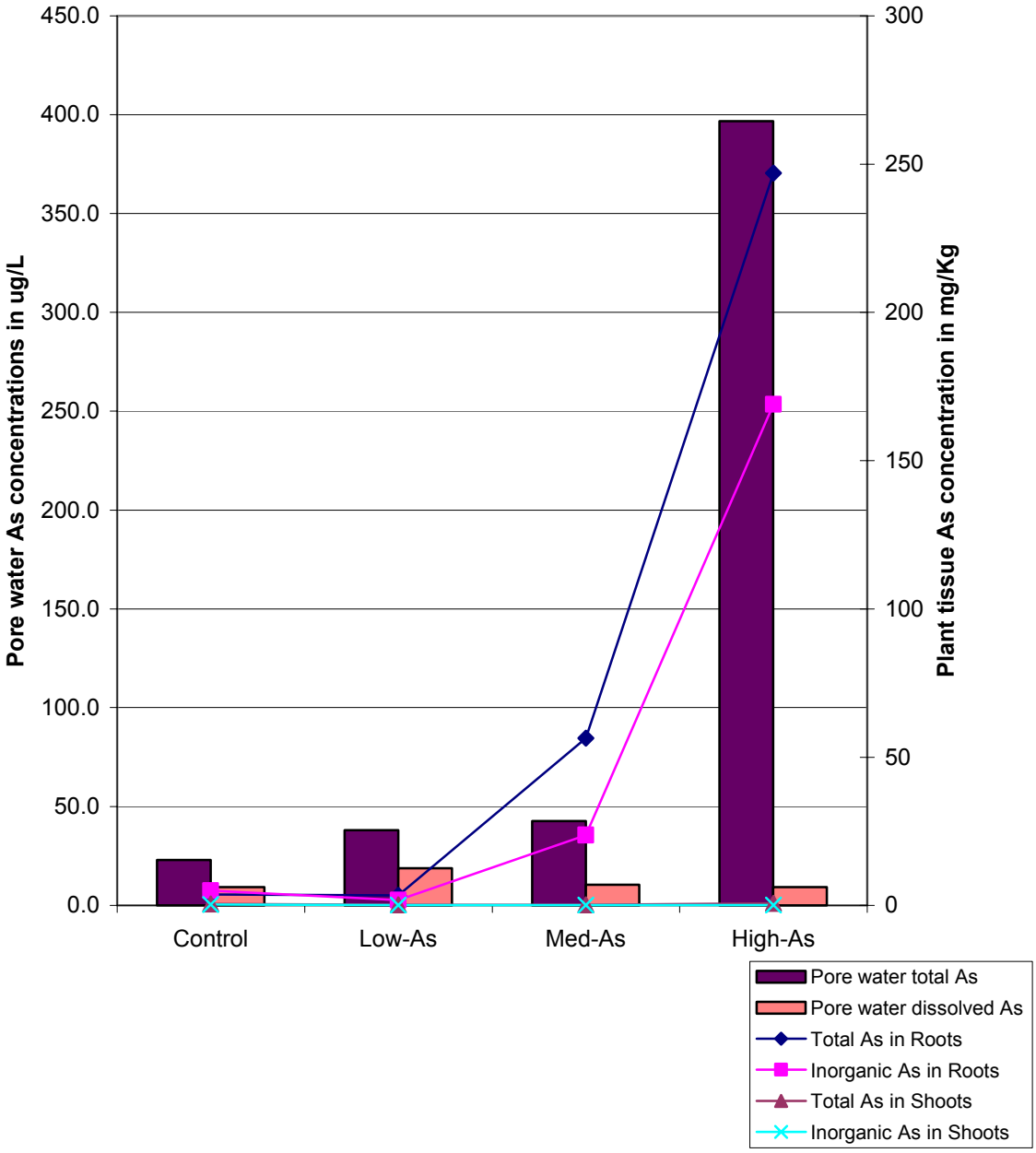

Figure 7. Pore water arsenic concentrations vs. plant arsenic concentrations.

While no one metal is conclusively responsible for the reduction in bacterial functions closer to the landfill, Figure 8 illustrates some trends. This figure uses the sum of soil metals concentrations, except iron, relative to Microtox light outputs. It appears that the soil arsenic concentrations led to some depression of Microtox outputs. Confounding this interpretation; zinc is possibly useful as a nutrient to the bacteria, and those stations with higher soil zinc concentrations also have higher Microtox light outputs. When compared to conventional variables such as Eh, pH, and conductivity, no relevant trends were observed.

In summary, Microtox bioassays showed statistically significant declines in bacteria functions closer to the landfill. Conclusively evaluating the causative agent for this reduction is not possible with the current data set.

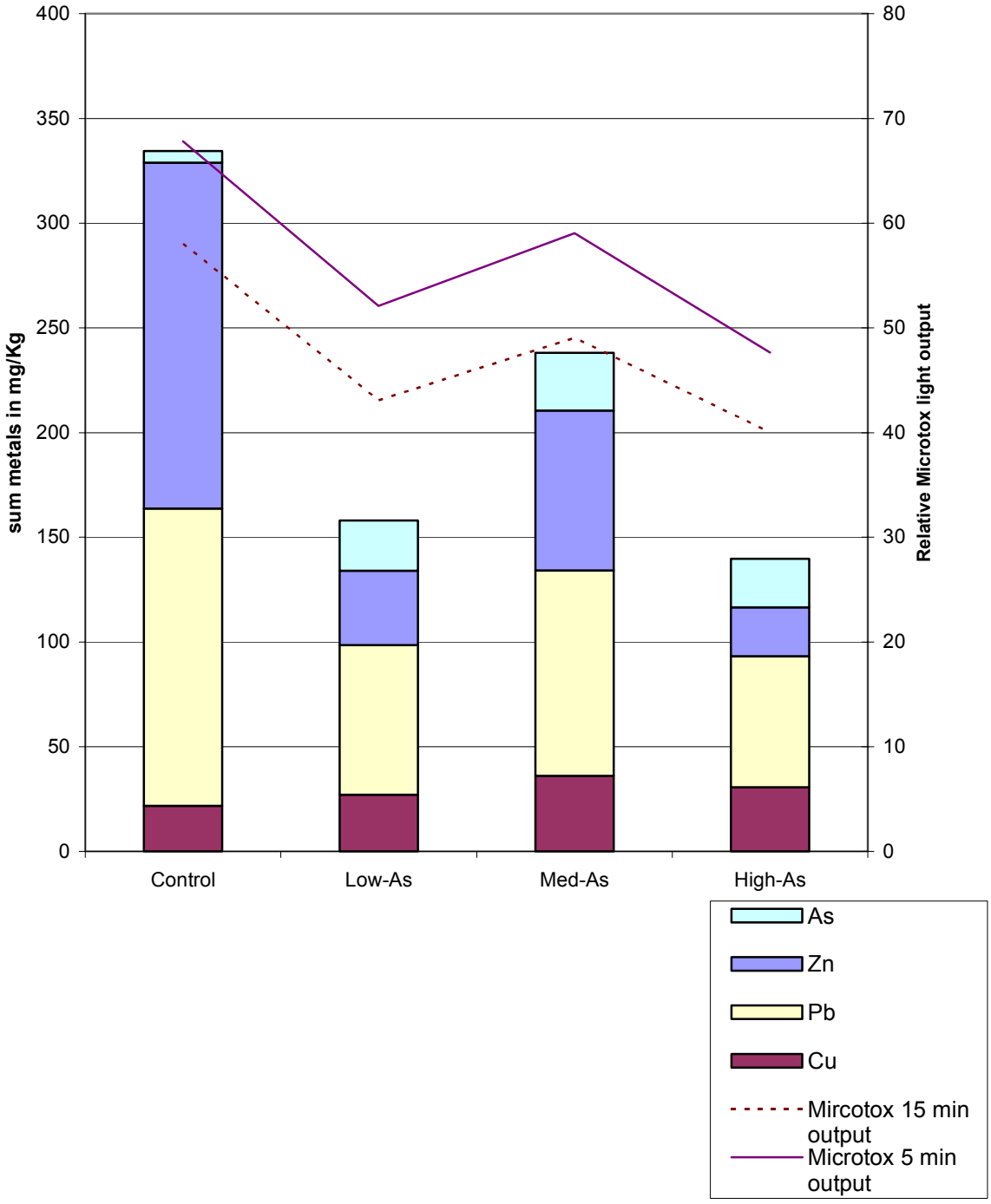

Figure 8. Sum of soil metals vs. Microtox relative light output.

Conclusions

This investigation set out to evaluate five principal issues.

1) Support the in-situ investigation of the impacts of the arsenic loading on resident amphibian populations.

- The amphibian egg mass study by the University of Washington student (Schlemmer, 2002) was inconclusive due to high mortality. The Department of Ecology supported this investigation through the collection of surface water grab samples and Ecology's analysis for total arsenic.
- Results indicate that total arsenic can significantly exceed chronic and acute surface water quality standards (Chapter 173-201A-040 WAC). The temporal and spatial extent of these exceedances is still largely unknown.

2) Determine the role of the wetland in the transport of landfill arsenic.

- Wetland soils were not found to be elevated in possible confounding elements such as lead, copper, and zinc.
- Wetland soil/sediment, pore water, and surface water arsenic concentrations were sampled. Concentrations in soil/sediment exceeded MTCA residential standards and statewide background values.
- Pore waters were found to have a significant fraction of their arsenic bound to the particulate fraction.
- Surface water concentrations were determined to be significantly associated with colloidal particles.
- The particulate fraction of both the pore water and surface water is mobile.
- Most soils were relatively oxidized, despite their flooded condition at the time of sampling. The more reducing soils were found to have lower arsenic concentrations at depth.
- Soils arsenic concentrations were higher in surface soils than at the 18"-24" depth range. This may be due to historic surficial deposition of arsenic, or due to increased solubility of arsenic at depth. Distinguishing these two rationales would require a detailed mass balance of the arsenic present in soils at multiple depths, versus the arsenic mass present in shallow ground waters at those depths.

3) Determine the role of the wetland in the fate of arsenic released from the landfill.

- Wetland plants were found to accumulate arsenic in their root tissues over the associated soil concentrations. Plants were found to not biotransform inorganic arsenic into less toxic organic forms.

- Plants do not translocate significant quantities of arsenic into their above-ground tissues. Harvest of above-ground tissues would only remove limited amounts of arsenic from the wetland.
- Because little biotransformation and/or plant uptake of arsenic is occurring, it appears that simple dilution is likely responsible for the attenuation of arsenic in surface water away from the landfill.

4) Determine if soil biological functions are altered due to arsenic by assessing the toxicity of the sediment pore water adjacent to the landfill.

- Soil bioassays revealed a statistically significant reduction in microbial function in higher arsenic zones.
- No one variable was conclusively responsible for these impacts. However, conductivity and hardness were much higher in the medium arsenic and high arsenic zones, relative to the low arsenic and control stations. The aggregate discharges of metals to the wetland are probably responsible for the declining Microtox outputs closer to the landfill. Arsenic was the single greatest contributor to the elevated metals, and probably to the elevated conductivity. Unlike the comparison to surface water standards described above, Microtox impacts were observed at all study stations relative to field control stations.
- Slightly elevated soil arsenic concentrations were observed. These concentrations were not conclusively linked with depressed soil bacterial functions as measured by Microtox bioassays. Microtox impacts were observed all across the wetland. In many ways, these results are similar to the UW student amphibian data (Schlemmer, 2002).

5) Assess the overall health of the wetland.

- The wetland has been disturbed by historic agricultural practices and by groundwater well installations. The wetland is now dominated by invasive grasses. These grasses bioaccumulate arsenic in their root tissues, but this arsenic is not translocated into, or significantly transformed by, shoot tissues.
- The wetland has elevated surface water arsenic concentrations which, in conjunction with elevated conductivities, at least seasonally impact wetland biota. Surface waters are above acute water quality standards, suggesting serious biota impacts are likely (Eisler, 1988).
- The wetland has degraded soil microbiologic functions, as measured via the Microtox soil pore-water bioassay.
- Based on the combination of impacts and measures, overall wetland health is poor to marginal.

Recommendations

The following recommendations for further investigations and future remedial designs are provided:

- The aerial and temporal extent of surface water ecological impacts should be determined prior to making conclusions about their temporal and spatial extent. Suggested monitoring should include collection of surface waters every two months, from a grid of 10 to 15 stations around the wetland, to determine the magnitude of surface water impacts. Collection of these data is suggested prior to targeting this media for remediation.

- From a human health perspective, surface waters warrant remediation, because they exceed a relevant regulatory limit (maximum contaminant limit) of 10 µg/L and relevant National Toxics Rule thresholds of 0.018 and 0.14 µg/L for inorganic arsenic.

- Plants are not significant accumulators of arsenic, and their usefulness for bioremediation is limited. Remediation designs should focus on means to remove particulate and/or colloidal surface water fractions, as these appear to be significant transport mechanisms.

- Very high conductivity and hardness were observed in stations closest to the landfill. These bulk measures probably contribute to adverse impacts in waters at the wetland. Any proposed remediation technology should try to limit the addition of materials which could elevate conductivity or hardness further. In future investigations, sodium, chloride, potassium, and other marine salts should be measured as possible leachate tracking parameters. Groundwater and/or surface water remediation technologies should be chosen to reduce conductivity and hardness measures, if possible.

- Measures of impacts to wetland biota conducted by the University of Washington student were inconclusive. One probable reason for this was fluctuating arsenic and conductivity results. Alternative bioassays using standardized laboratory conditions should be utilized if a determination of higher level biologic impacts is required. Suggested bioassays for surface waters include life cycle *Daphnia* spp. assays (ASTM, 1997) or the Fetax teratogenesis assay (ASTM, 1998). Testing to determine the causative agent should be factored into any future bioassays.

- Soils data approximately support data collected by the landfill owner and demonstrate continued small exceedances of the 20 mg/Kg soil standard. The soils concentrations observed are not strongly linked with any other media's concentration, except for some relationship with soil pore waters. However, no standards are available for pore waters. The necessity of remediation in this situation is a risk management decision.

This page is purposely blank for duplex printing

References

Adolphson, P. 2002. Ecology modified draft final Microtox test procedure. January 15, 2002.

AMEC Earth and Environmental. 2002. Toxicity Evaluation of B&L Landfill Sediments. A report prepared for the Washington Department of Ecology.

Anderson, L.C.D. and K.W. Bruland. 1991. Biogeochemistry of Arsenic in Natural Waters: The Importance of Methylated Species. Environmental Science and Technology 25:420-427.

ASTM. 1997. E1193-97 Standard Guide for Conducting *Daphnia magna* Life-Cycle Toxicity Tests. American Society of Testing a Materials, West Conshohocken, PA.

ASTM. 1998. E1439-98 Standard Guide for Conducting the Frog Embryo Teratogenesis Assay-Xenopus (Fetax). American Society of Testing a Materials, West Conshohocken, PA.

Bennett, J. and J. Cubbage. 1992. Review and Evaluation of Microtox Test for Freshwater Sediments. Washington State Department of Ecology, Pub. No. 92-e04.

Eisler, R. 1988. Arsenic Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. Contaminant Hazard Reviews Report Number 12, US Fish and Wildlife Service, Patuxent Wildlife Research Center, Laurel, MD.

Frontier Geosciences. 2001. Arsenic speciation by Ion Chromatography-Hydride Generation-Atomic Fluorescence Spectrometry. Personal Communication from Jax London, December 25, 2001. See Appendix A.

Hansel, C.M., S. Fendorf, S. Sutton, M. Newville. 2001. Characterization of Fe Plaque and Associated Metals on the Roots of Mine-Waste Impacted Aquatic Plants. Environmental Science and Technology 35:3863-3868.

Jack, R.A. 2002. Mobilization and Impacts of Arsenic Species and Selected Metals on a Wetland Adjacent the B&L Wetland, Milton, Washington. Quality Assurance Project Plan, Washington State Department of Ecology.

Johnson, A. and D. Norton. 1985. Completion Report on WQIS Project 2 for the Commencement Bay Nearshore/Tideflats Remedial investigation: Metals Concentrations in Water, Sediment, and Fish Tissue Samples from Hylebos Creek Drainage, August 1983 – September 1984. Washington State Department of Ecology, Pub. No. 85-e17.

Johnson, A. and S. Golding. 2002. Results and Recommendations from Monitoring Arsenic Levels in 303(d) Listed Rivers in Washington. Washington State Department of Ecology, Pub. No. 02-03-045.

Masscheleyn, P.H., R.D. Delaune, and W.H. Patrick, Jr. 1991. Effect of Redox Potential and pH on Arsenic Speciation and Solubility in a Contaminated Soil. Environmental Science and Technology 25:1414-1419.

McGeehan, S.L., S.E. Fendorf, and D.V. Naylor. 1998. Alteration of Arsenic Sorption in Flooded-Dried Soils. Soil Science Society of America Journal 62:828-833.

Pierce, M.L. and C.B. Moore. 1980. Adsorption of Arsenite on Amorphous Iron Hydroxide from Dilute Aqueous Solution. Environmental Science and Technology 14:214-216.

Salmonid and Steelhead Stock Inventor (SASSI). 1992. Washington Department of Fisheries, Washington Department of Wildlife, Western Washington Treaty Indian Tribes. Olympia Washington, March 1993.

Schlemmer, R. 2002. Amphibian Breeding Success in an Arsenic Contaminated Wetland. University of Washington Certificate Program in Wetland Science and Management Program.

USEPA. 1984. Health Assessment Document for Inorganic Arsenic. U.S. Environmental Protection Agency. EPA-600/8-83-021F.

USEPA. 1990a. Specifications and Guidance for Obtaining Contaminant Free Sample Containers. U.S. Environmental Protection Agency. OSWER Directive #93240.0-05.

USEPA. 1991. Methods for the Determination of Metals in Environmental Samples. U.S. Environmental Protection Agency. EPA-600/4-91-010.

USEPA. 1994. Methods for the Determination of Metals in Environmental Samples Supplement I. U.S. Environmental Protection Agency. EPA-600/R-94/111.

USEPA. 1995. Puget Sound Estuary Program (PSEP): Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments. U.S. Environmental Protection Agency, Region 10, Office of Puget Sound, Seattle WA.

USEPA. 1997. Puget Sound Estuary Program (PSEP): Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound, Recommended Guidelines for Measuring Organic Compounds in Puget Sound Water, Sediment and Tissue Samples. U.S. Environmental Protection Agency, Region 10, Office of Puget Sound, Seattle WA.

USEPA. 2001. Arsenic and Clarifications to Compliance and New Source Monitoring Rule. U.S. Environmental Protection Agency. 66 FR 6976 (January 22, 2001).