
# Similkameen River and Palmer Lake Investigation of Arsenic in Fish Tissue

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# Similkameen River and Palmer Lake Investigation of Arsenic in Fish Tissue

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Waterbody Numbers:
Similkameen River (WA-49-1030) and Palmer Lake (WA-49-9270)

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# Table of Contents

# List of Figures and Tables

Page

## Figures



## Tables

# Abstract

In the fall of 2006, the Department of Ecology analyzed fish from the Similkameen River and Palmer Lake for total arsenic, inorganic arsenic, monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA). This study was conducted to determine the potential of human health risk from consuming fish from the river. It was conducted as follow-up monitoring recommended by the 2005 Lower Similkameen River Arsenic Total Maximum Daily Load assessment and associated detailed implementation plan.

There were no detections of inorganic arsenic in fish tissue; inorganic arsenic is considered the most toxic form of arsenic to humans. Less than half of the samples had detections of total arsenic, MMA, and DMA. The detected arsenic results were highly variable, with detections occurring at all of the sampling locations.

Total arsenic was found mostly in suckers, and DMA was detected only in suckers and rainbow trout. MMA was found in lesser amounts in kokanee, rainbow trout, and mountain whitefish. Total arsenic was found to be slightly higher than Washington State and national average concentrations for total arsenic in freshwater fish.

The Washington State Department of Health reviewed the results of the study and concluded that there is no risk to human health based on the consumption of inorganic arsenic in fish from the lower Similkameen River and Palmer Lake.

# Acknowledgements

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- The Colville Confederated Tribes for access to the Similkameen River.
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- The Washington State Department of Health for reviewing the data and providing information on human health risks associated with fish consumption.
- Brooks Rand Laboratory for their arsenic analyses.

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# Introduction

The Similkameen River has been listed by Washington State under Section 303(d) of the federal Clean Water Act for non-attainment of the U.S. Environmental Protection Agency (EPA) human health criteria for arsenic in the water column. As a result of the listing, a Total Maximum Daily Load (TMDL) assessment was conducted for the river in 2001 (Johnson, 2002).

The TMDL and associated detailed implementation plan (Peterschmidt, 2005) established water quality targets for arsenic. The plan also recommended several monitoring actions. One of these actions was to analyze Similkameen River and Palmer Lake fish for inorganic and organic arsenic. This information was needed to assess the potential human health risk from fish consumption.

Study data were provided to the Washington State Department of Health for determination of risk to human health from consuming fish from these areas.

The study was conducted by the Washington State Department of Ecology (Ecology), Environmental Assessment Program, Toxics Studies Unit.

## Similkameen River Watershed Description

The Similkameen River originates in the Cascade Mountains along the international border between British Columbia and Washington State. It flows north out of Manning Provincial Park, and then turns south to cross the border and meet the Okanogan River at the city of Oroville (Figure 1). The Similkameen River is approximately 72 miles long, with the last 27 miles being in Washington.

The Similkameen drains 3,600 square miles, over 90% of which is in British Columbia. Peak flows normally occur in April to July as a result of snowmelt. Streamflow during the winter generally stays low due to freezing weather that maintains or contributes to the snowpack; exceptions occur when mild winter and heavy rain combine to cause flooding. The annual discharge (measured at Nighthawk, WA) is 2,300 cubic feet per second (cfs) and the average is 609 cfs (Johnson, 2002).

Downstream of the international border, the Similkameen flows through farmlands and arid sagebrush typical of north-central Washington. Six miles below the border the river meets Palmer Lake outlet, sometimes called Palmer Creek. A unique hydrologic feature of their juncture is that, during times of high flow, the Similkameen can cause Palmer Creek to reverse direction and the river flows into the lake. Other than Palmer Lake, Washington tributaries to the Similkameen are dry most of the year, except at higher elevations. Sinlahekin Creek is the major tributary to Palmer Lake. It drains into Palmer Lake from the south.

The Similkameen watershed is sparsely populated in Washington. Nighthawk, just downstream of Palmer Lake, is the largest community with approximately 26 people. Enloe Dam, about nine

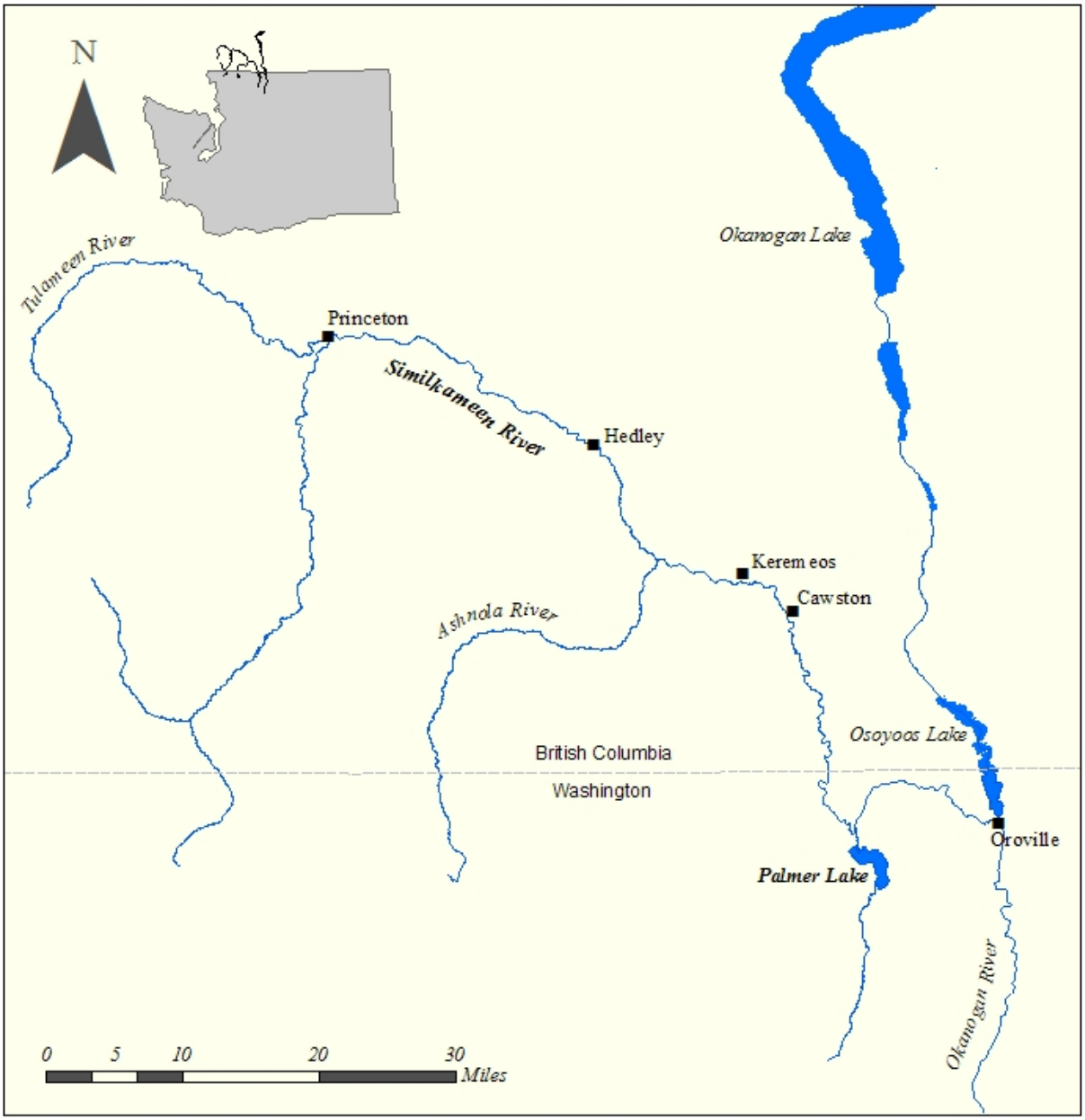


Figure 1. Similkameen River Drainage

miles below Nighthawk, was built in 1920 to generate electricity but has not been used for power since 1958. The dam blocks fish passage.

Mining, forestry, agriculture, and recreation are the major land-use activities in the Similkameen watershed. The watershed has a history of mining, although there are currently no active large-scale operations. Past mining activities in the watershed have been identified as the major source of arsenic to the river (Johnson, 2002). Notable among these are the mining operations in the vicinity of Hedley, B.C. and the Kabba, Texas mine near Nighthawk in Washington (Peterschmidt, 2005). Other arsenic sources identified in Washington were (1) Palmer Lake, likely arising from periodic flooding by the Similkameen River and perhaps inputs from the Sinlahekin Creek, and (2) resuspension of contaminated sediments (Johnson, 2002).

## Arsenic in the Environment and Human Health

Arsenic is an element that is widely distributed in the earth's crust. High concentrations of arsenic in the environment are a concern because of potential human health effects. Arsenic concentrations in the Similkameen River are unusually high when compared to other rivers in Washington.

Arsenic enters the air, water, and land from natural processes such as erosion, leaching of soil and rocks, and volcanic eruptions. Arsenic also enters the environment from human activities such as mining and smelting, coal-fired power plants, and incinerators. Inorganic arsenic compounds were once used in pesticides primarily applied to cotton fields and orchards. Some organic arsenic compounds are still used in pesticides, animal feed, metal mixtures, and lead-acid batteries (ASTDR, 2005).

Arsenic is usually found combined with other elements such as oxygen, chlorine and sulfur. These forms are called inorganic arsenic. Arsenic combined with carbon and hydrogen is referred to as organic arsenic. Inorganic forms are generally considered to be more toxic to humans than organic forms (ATSDR, 2005).

Arsenic has been recognized as a human poison for centuries. Ingestion of arsenic has been linked with skin, liver, bladder, and prostate cancer. Humans are exposed to arsenic by eating food, drinking water, and breathing air. Food is usually the largest source of arsenic.

Marine organisms, especially shellfish, are known to contain relatively high concentrations of arsenic, while arsenic concentrations in freshwater organisms are much more variable (Cullen and Reimer, 1989). Most of the arsenic in marine species is found in an organic form called arsenobetaine that is much less toxic than inorganic arsenic (ATSDR, 2005). Historically the toxic arsenic species of most concern in fish and shellfish include inorganic arsenic ($As^{+3}$ and $As^{+5}$), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA), all of which are minor constituents.

Quantitative data on inorganic arsenic in freshwater fish is sparse, and the toxicity of fish tissue containing arsenic has not been studied. This is a data gap acknowledged by the scientific community.

# Methods

## Project Description

Fish for this 2006 study were collected from various sections of the Similkameen River near the international border downstream to Enloe Dam and including Palmer Lake (Figure 2). Seven species of fish were collected including bottom-feeding fish (suckers) and predatory fish (northern pike minnow). Game fish such as largemouth bass, kokanee, mountain whitefish, and rainbow trout were collected to represent fish consumed by humans. This sampling method ensures that different contaminant exposure pathways are represented because different fish have varied life histories and feeding strategies.

Fish were analyzed for total arsenic, inorganic arsenic, MMA, DMA, and lipids. Results were provided to the Washington State Department of Health for determination of the risk to human health from fish consumption.

## Sampling Procedures

Fish were collected by several methods including boat and backpack electrofishing, gillnet, and hook and line. Fishing locations were recorded by GPS. These locations are reported in Table A-1 (Appendix A) and shown in Figure 2.

Fish selected for analysis were quickly killed with a sharp blow to the head, given an ID number, and the weight and length recorded. Fish were then individually wrapped in heavy aluminum foil and put in plastic bags, kept cold in coolers and frozen immediately upon return from the field. Biological information on the fish is included in Table A-2 (Appendix A).

### Preparation of Tissue Samples

Preparation of fish tissue samples followed *Ecology Standard Operating Procedures for Resecting Finfish Whole Body, Body Parts, or Tissue Samples* (Ecology, 2007) and took place at Ecology's Headquarters building in Lacey, Washington. Precautions were taken to minimize contamination during sample processing. Persons preparing samples wore non-talc nitrile gloves and aprons. Work surfaces were covered with heavy grade aluminum foil. Gloves, aluminum foil, and dissection tools were changed between composite samples.

All resecting instruments were washed thoroughly with Liquinox detergent and hot tap water, followed by rinses with 10% nitric acid, de-ionized water, acetone, and hexane. Instruments were then dried in a fume hood before use. The same decontamination procedure was repeated between each composite sample.

Samples were prepared by partially thawing the fish to remove the foil wrapper and rinsing in de-ionized water to remove adhering debris. Fish were de-scaled, and then the entire skin-on fillet from one or both side of each fish was removed with stainless steel knives or scalpels and homogenized by three passes through a Kitchen-Aide or Hobart commercial blender.

Composite samples were made up of equal-weight aliquots from each fish in the composite samples. Samples were then homogenized to uniform color and consistency and placed in jars, specifically-cleaned for arsenic analyses, and sent to the laboratory. The sex of each fish was recorded during processing.

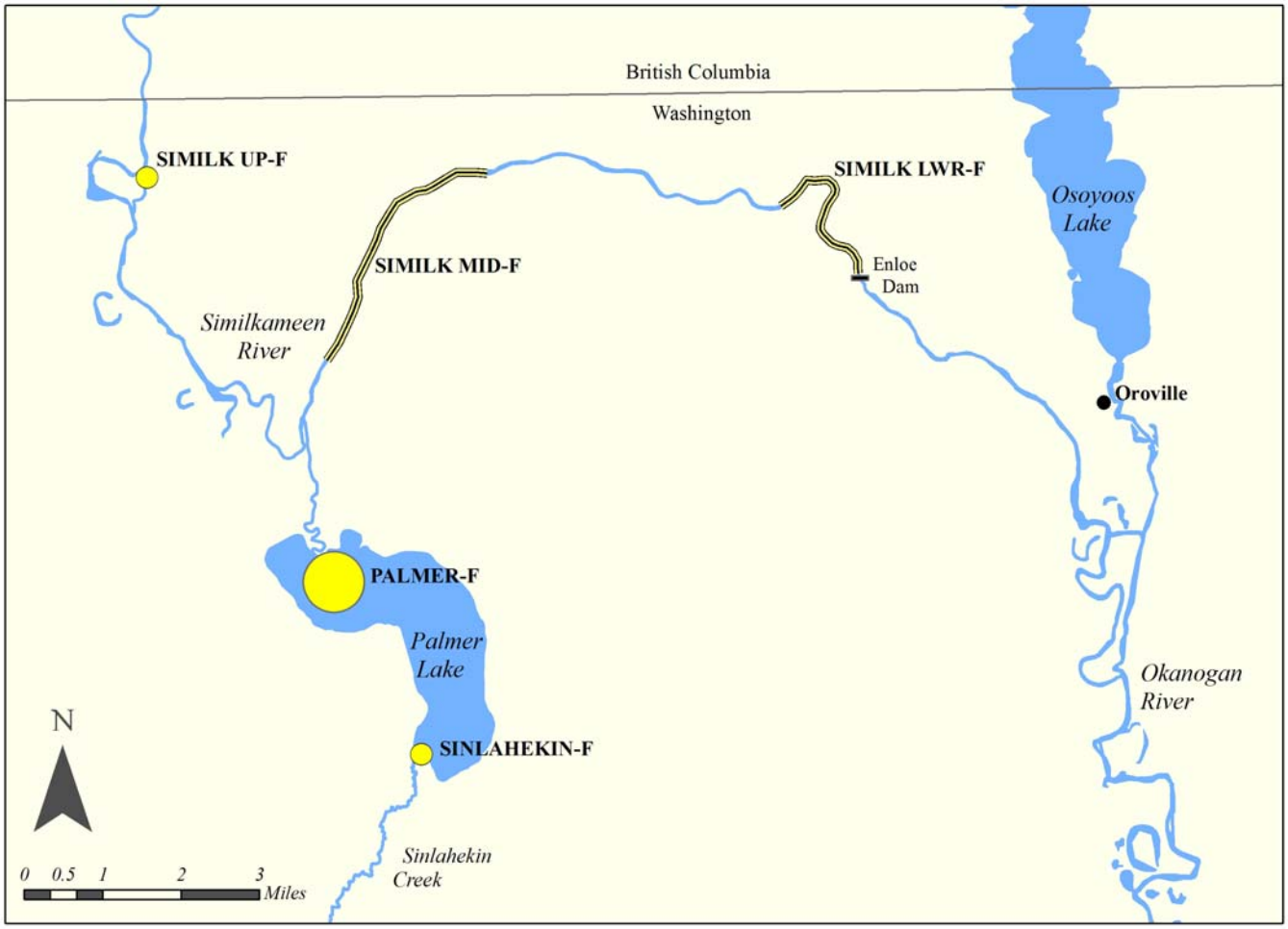


Figure 2. Simikameen River and Palmer Lake Fish Sampling Locations.

## Laboratory Analysis

Analytical methods for the study are shown in Table 1. All arsenic analyses were conducted at Brooks Rand LLC (Limited Liability Corporation) located in Seattle, Washington. Lipids analysis was done by the Ecology Manchester Environmental Laboratory (MEL) located in Manchester, Washington.

Table 1. Laboratory Methods for the Similkameen Arsenic Study

| Parameter | Laboratory Reporting Limit (ug/Kg ww) | Analytical Method | Laboratory |
|---|---|---|---|
| Lipids | n/a | Gravimetric | MEL |
| Total Arsenic | 110 | EPA 1638† | Brooks Rand |
| *Arsenic Species** | | EPA 1632 Revision A† | |
| Inorganic Arsenic | 3 | | |
| MMA | 3 | | |
| DMA | 3 | | |

* Inorganic arsenic ($As^{+3}$ + $As^{+5}$), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA)
† EPA 1996 and EPA 2001

## Data Quality

Overall, few problems were encountered in the chemical analyses, and the data are useable as qualified by MEL. A summary of the data quality follows. More detailed explanations can be found in the case narratives from MEL and Brooks Rand laboratories (Appendix B).

Low levels of inorganic arsenic were detected in method blanks. All analyte concentrations in samples with less than five times the amount in the highest blank were qualified with a "UJ" indicating that inorganic arsenic was not detected at or above the suspected laboratory contamination level.

Recoveries of arsenic in the Brooks Rand standard reference materials and certified reference materials were all acceptable at above 90%.

Precision of laboratory duplicate samples and matrix spike duplicate samples are shown in Appendix C. The relative percent differences (RPD) of these samples give a measure of analytical precision. All of the RPD values show a good level of precision (0-38%) with the exception of the laboratory duplicates for DMA (29-128%). "Process" laboratory duplicates were split during sample processing and analyzed as separate samples.

# Results

Results from the study are shown in Table 2. There were no detections of inorganic arsenic, which is considered to be the most toxic form of arsenic to humans.

Less than half of the samples had detections of total arsenic, MMA, and DMA. The detected arsenic results were highly variable, with detections occurring at all of the sampling locations. Total arsenic was most prevalent in suckers, and DMA was detected only in suckers and rainbow trout. MMA was found in lesser amounts in kokanee, rainbow trout, and mountain whitefish.

Table 2. Arsenic Results for Similkameen River Fish Fillet Samples Collected During Fall 2006 (ug/Kg, wet weight; parts per billion)

| Reach | Location ID* | Lab ID No. | Species | No. of Fish in Sample | Lipids (%) | Total Arsenic | Total Inorganic Arsenic | MMA | DMA |
|---|---|---|---|---|---|---|---|---|---|
| Upper River | SIMILK UP-F | 014040 | LSS | 5 | 0.4 | **150 J** | 3 UJ | 3 UJ | **8 J** |
| Palmer Lake | SINLAHEKIN-F | 014041 | KOK | 5 | 1.5 | 110 UJ | 3 UJ | 3 UJ | 3 UJ |
| Palmer Lake | SINLAHEKIN-F | 014042 | KOK | 5 | 2.7 | 110 UJ | 5 UJ | **5 J** | 3 UJ |
| Palmer Lake | SINLAHEKIN-F | 014043 | KOK | 5 | 2.1 | 110 UJ | 5 UJ | **4 J** | 3 UJ |
| Palmer Lake | PALMER-F | 014034 | LMB | 5 | 0.3 | 110 UJ | 3 UJ | 3 UJ | 3 UJ |
| Palmer Lake | PALMER-F | 014035 | LMB | 5 | 0.6 | 110 UJ | 3 UJ | 3 UJ | 3 UJ |
| Palmer Lake | PALMER-F | 014036 | LMB | 5 | 0.7 | 110 UJ | 13 UJ | 3 UJ | 3 UJ |
| Palmer Lake | PALMER-F | 014037 | LSS | 5 | 1.6 | **120 J** | 3 UJ | 3 UJ | **9 J** |
| Palmer Lake | PALMER-F | 014038 | LSS | 5 | 0.9 | 110 UJ | 3 UJ | 3 UJ | 3 UJ |
| Palmer Lake | PALMER-F | 014039 | LSS | 5 | 1.9 | **120 J** | 11 UJ | 3 UJ | 3 UJ |
| Middle River | SIMILK MID-F | 014028 | BLS | 3 | 2.9 | 110 UJ | 3 UJ | 3 UJ | 3 UJ |
| Middle River | SIMILK MID-F | 014029 | BLS | 4 | 2.1 | **130 J** | 3 UJ | 3 UJ | 3 UJ |
| Middle River | SIMILK MID-F | 014030 | RBT | 1 | 1.5 | **190 J** | 3 UJ | **4 J** | **22** |
| Middle River | SIMILK MID-F | 014031 | RBT | 1 | 1.9 | **170 J** | 3 UJ | 3 UJ | **16 J** |
| Middle River | SIMILK MID-F | 014032 | RBT | 1 | 1.3 | 110 UJ | 3 UJ | 3 UJ | 3 UJ |
| Middle River | SIMILK MID-F | 014033 | RBT | 1 | 0.3 | 110 UJ | 3 UJ | 3 UJ | **5 J** |
| Lower River | SIMILK LWR-F | 014020 | LSS | 5 | 0.6 | **190 J** | 4 UJ | 3 UJ | **7 J** |
| Lower River | SIMILK LWR-F | 014021 | LSS | 5 | 0.6 | **200 J** | 3 UJ | 3 UJ | **23** |
| Lower River | SIMILK LWR-F | 014022 | LSS | 5 | 0.7 | **280 J** | 3 UJ | 3 UJ | **48** |
| Lower River | SIMILK LWR-F | 014023 | MWF | 5 | 1.8 | 110 UJ | 3 UJ | **10 J** | 3 UJ |
| Lower River | SIMILK LWR-F | 014024 | MWF | 5 | 2.7 | 110 UJ | 3 UJ | 3 UJ | 3 UJ |
| Lower River | SIMILK LWR-F | 014025 | MWF | 5 | 2.3 | 110 UJ | 5 UJ | 3 UJ | 3 UJ |
| Lower River | SIMILK LWR-F | 014026 | NPM | 1 | 0.3 | 110 UJ | 3 UJ | 3 UJ | 3 UJ |
| Lower River | SIMILK LWR-F | 014027 | NPM | 1 | 0.7 | 110 UJ | 3 UJ | 3 UJ | 3 UJ |

* EIM (Environmental Information Management database) User Location ID. EIM User Study is ID BERA0004.
MMA = monomethylarsonic acid
DMA = dimethylarsinic acid
**Bolded** results represent detections
J = The analyte was positively identified. The associated numerical result is an estimate.
UJ = The analyte was not detected at or above the reported estimated result.

BLS = Bridgelip sucker *(Catostomus columbianus)*
KOK = Kokanee *(Oncorhynchus nerka)*
LMB = Largemouth bass *(Micropterus salmoides)*
LSS = Largescale sucker *(Catostomus macrocheilus)*
MWF = Mountain whitefish *(Prosopium williamsoni)*
NPM = Northern pike minnow *(Ptychocheilus oregonensis)*
RBT = Rainbow trout *(Oncorhynchus mykiss)*

# Discussion

## Inorganic Arsenic

Detection limits for inorganic arsenic were below the National Toxics Rule (NTR) fish tissue criterion of 6.16 ug/Kg[1], with the exception of two samples (<13 ug/Kg). Ecology uses this criterion as a screening level indicator for water quality impairments. Based on comparison to the NTR criterion, inorganic arsenic concentrations in fish tissue from the Similkameen River and Palmer Lake do not appear to be of concern. Alternatively, surface water studies in the Similkameen River have shown constant exceedances of the NTR criterion for total arsenic in water (Johnson, 1997, 2002).

The Washington State Department of Health (DOH) is the agency responsible for making statements about human health risks from fish consumption in Washington State. DOH reviewed the data for this study and prepared the following statement:

> *"Ecology asked the Washington State Department of Health (DOH) to evaluate the concentrations of inorganic arsenic, monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) measured in fish tissues to determine whether there could be health concerns from eating the fish. Based on the reported concentrations of arsenic species and detection limits that were sufficiently low, DOH noted no potential arsenic-related health concerns from consuming these fish.*
>
> *Arsenic in fish tissues can be present as inorganic arsenic and as part of various organic molecules (including MMA and DMA). Inorganic arsenic has been found to be substantially more toxic than MMA and DMA. Inorganic arsenic was not detected in any of the samples and therefore, considering the low detection limits of the tests, is not a health hazard when consuming these fish. MMA was detected in 4 tissue samples and DMA was detected in 8 tissue samples, but all concentrations were too low to be of health concern, even for people who might consume the fish several times per week."*

## Total Arsenic

Total arsenic was found mostly in suckers and was detected only in suckers and rainbow trout.

This finding is supported by a recent literature review of arsenic in seafood (Chappell and Colman, 2004). The review concluded that arsenic concentrations in planktivorous fish are elevated over predatory and omnivorous fish. Arsenic does not biomagnify up the aquatic food chain as do some other chemicals. In aquatic organisms, bioconcentration of arsenic mainly occurs in algae and lower invertebrates, and the major bioaccumulation transfer occurs between water and algae.

[1] Criteria for the protection of human health are applied to the state through the EPA National Toxics Rule (NTR) [40 CFR 131.36(14)]

Suckers and rainbow trout feed primarily on food associated with the river bottom, lending them to direct exposure to arsenic-contaminated sediments and algae. Rainbow trout feed primarily on aquatic insects, worms, and fish eggs; suckers eat a variety of bottom organisms such as aquatic insect larvae, worms, detritus, and plant material (Wydoski and Whitney, 1979). The other fish species analyzed in the study, especially largemouth bass and northern pike minnow, are more predatory and spend less time feeding near the river bottom.

## Comparison to other Data

There is not much data available on inorganic arsenic, MMA, and DMA in freshwater fish tissue, but there is a fair amount of data for total arsenic. Kidwell et al. (1995) found an average total arsenic concentration for freshwater fish to be 0.16 ug/Kg wet weight (n = 2,032) based on 1984-1985 National Contaminant Biomonitoring Program data.

Figure 3 shows a comparison of the detected total arsenic results for fish from the Similkameen River and Palmer Lake to other freshwater fish in Washington State. The Similkameen River and Palmer Lake total arsenic data range from the $50^{th}$ to $90^{th}$ percentile for Washington State fish tissue studied in 1994-2006 (Figure 3). Mean total arsenic concentrations from the study (0.17 ug/Kg ww) were just above the national mean of 0.16 ug/Kg ww in fish tissue.

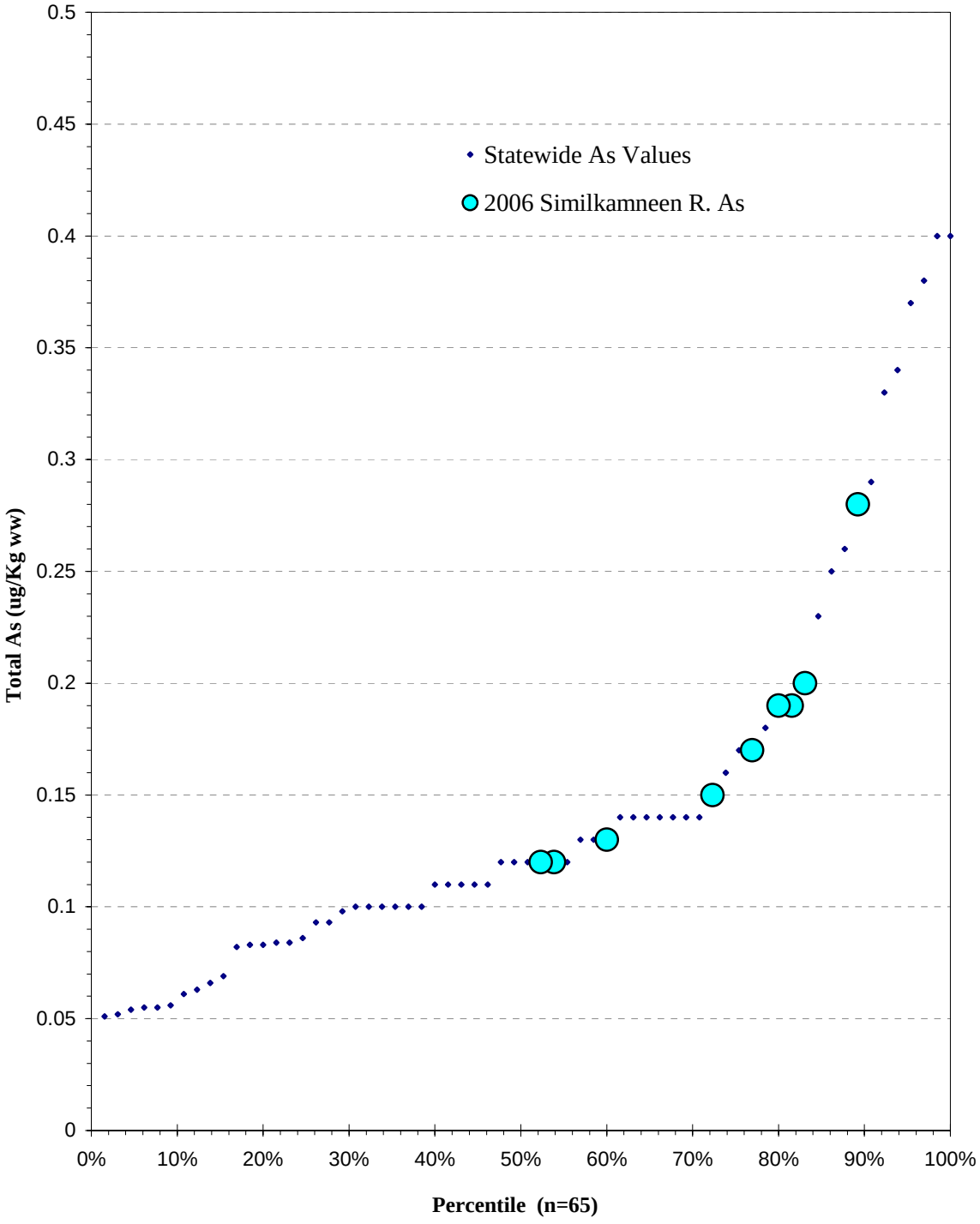


Figure 3. Cumulative Frequency Distribution of Total Arsenic in Fish Fillets (Data from Washington State 1994 - 2006).

# Conclusions and Recommendations

In this 2006 study of the Similkameen River and Palmer Lake, there were no detections of inorganic arsenic in fish tissue, which is considered to be the most toxic form of arsenic to humans. Less than half of the samples had detections of total arsenic, MMA, and DMA. The detected arsenic results were highly variable, with detections occurring at all of the sampling locations.

Total arsenic was found mostly in suckers, and DMA was detected only in suckers and rainbow trout. MMA was found in lesser amounts in kokanee, rainbow trout, and mountain whitefish. Total arsenic was found to be slightly higher than Washington State and national average concentrations for total arsenic in freshwater fish.

The Washington State Department of Health reviewed the results of the study and concluded that there is no risk to human health based on the consumption of inorganic arsenic in fish from the lower Similkameen River and Palmer Lake.

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# Appendices

# Appendix A. Location and Sample Information

Table A-1. Fish Sampling Location Descriptions

| Waterbody Name | Location ID* | Dates of Collection | Latitude North | Longitude West | Location Description |
|---|---|---|---|---|---|
| Similkameen River | SIMILK UP-F | 10/25/06 | 48° 59.185' | 119° 42.065' | Upriver backwater area near where the river bypasses the old river bend |
| | SIMILK MID-F | 10/26/06 | 48° 58.973' | 119° 37.828' | Centroid location of a 5-mile river section from the WDFW fishing access area downstream of the town of Nighthawk |
| | SIMILK LWR-F | 10/17/06 | 48° 58.741' | 119° 30.648' | Centroid of a 2-mile transect from Enloe Dam upstream to the first riffle above Shankers Bend |
| Palmer Lake | PALMER-F | 10/17 – 10/18/06 | 48° 54.456' | 119° 38.689' | North end of Palmer Lake |
| | SINLAHEKIN-F | 9/26/06 | 48° 52.712' | 119° 37.555' | At the mouth of Sinlahekin Creek near the south end of Palmer Lake |

* EIM (Environmental Information Management database) User Location ID
Datum = NAD83
WDFW = Washington Department of Fish & Wildlife

Table A-2. Fish Sample Biological Information.

| Location ID* | Sample No. | Collection Date | Species | Weight (g) | Total Length (mm) | Sex |
|---|---|---|---|---|---|---|
| **Lower Similkameen River** | | | | | | |
| SIMILK LWR-F | 07014020 | 10/17/06 | LSS | 753 | 420 | ? |
| " | " | " | " | 697 | 425 | M? |
| " | " | " | " | 789 | 429 | M? |
| " | " | " | " | 752 | 435 | ? |
| " | " | " | " | 1022 | 470 | M |
| | | | **Mean** | **803** | **436** | **n/a** |
| SIMILK LWR-F | 07014021 | 10/17/06 | LSS | 984 | 471 | M |
| " | " | " | " | 1053 | 487 | F |
| " | " | " | " | 1146 | 495 | M |
| " | " | " | " | 1179 | 500 | F |
| " | " | " | " | 1369 | 522 | M |
| | | | **Mean** | **1146** | **495** | **n/a** |
| SIMILK LWR-F | 07014022 | 10/17/06 | LSS | 1387 | 523 | M |
| " | " | " | " | 1335 | 525 | F |
| " | " | " | " | 1244 | 535 | F |
| " | " | " | " | 1361 | 540 | F |
| " | " | " | " | 1366 | 540 | F |
| | | | **Mean** | **1339** | **533** | **n/a** |
| SIMILK LWR-F | 07014023 | 10/17/06 | MWF | 116 | 243 | F? |
| " | " | " | " | 119 | 246 | ? |
| " | " | " | " | 122 | 248 | ? |
| " | " | " | " | 122 | 250 | M? |
| " | " | " | " | 193 | 290 | M? |
| | | | **Mean** | **134** | **255** | **n/a** |
| SIMILK LWR-F | 07014024 | 10/17/06 | MWF | 193 | 290 | M |
| " | " | " | " | 215 | 300 | F? |
| " | " | " | " | 222 | 303 | F |
| " | " | " | " | 237 | 305 | F |
| " | " | " | " | 267 | 310 | M |
| | | | **Mean** | **227** | **302** | **n/a** |
| SIMILK LWR-F | 07014025 | 10/17/06 | MWF | 293 | 329 | M |
| " | " | " | " | 370 | 335 | F |
| " | " | " | " | 379 | 336 | F |
| " | " | " | " | 284 | 358 | F |
| " | " | " | " | 443 | 385 | F |
| | | | **Mean** | **354** | **349** | **n/a** |

| Location ID* | Sample No. | Collection Date | Species | Weight (g) | Total Length (mm) | Sex |
|---|---|---|---|---|---|---|
| **Lower Similkameen River (cont.)** | | | | | | |
| SIMILK LWR-F | 07014026 | 10/17/06 | NPM | **704** | **440** | F |
| SIMILK LWR-F | 07014027 | 10/17/06 | NPM | **715** | **445** | F |
| **Middle Similkameen River** | | | | | | |
| SIMILK MID-F | 07014028 | 10/26/06 | BLS | 810 | 430 | M |
| " | " | " | " | 959 | 444 | F |
| " | " | " | " | 882 | 447 | F |
| | | | **Mean** | **884** | **440** | **n/a** |
| SIMILK MID-F | 07014029 | 10/26/06 | BLS | 974 | 451 | F |
| " | " | " | " | 997 | 455 | F |
| " | " | " | " | 997 | 458 | F |
| " | " | " | " | 1031 | 475 | F |
| | | | **Mean** | **1000** | **460** | **n/a** |
| SIMILK MID-F | 07014030 | 10/26/06 | RBT | **381** | **362** | F |
| SIMILK MID-F | 07014031 | 10/26/06 | RBT | **276** | **324** | F |
| SIMILK MID-F | 07014032 | 10/26/06 | RBT | **303** | **330** | F |
| SIMILK MID-F | 07014033 | 10/26/06 | RBT | **231** | **299** | M |
| **Upper Similkameen River** | | | | | | |
| SIMILK UP-F | 07014040 | 10/25/06 | LSS | 82 | 204 | ? |
| " | " | " | " | 99 | 220 | ? |
| " | " | " | " | 110 | 223 | ? |
| " | " | " | " | 118 | 225 | M? |
| " | " | " | " | 295 | 312 | F? |
| | | | **Mean** | **141** | **237** | **n/a** |
| **Palmer Lake** | | | | | | |
| PALMER-F | 07014034 | 10/17/06 | LMB | 307 | 269 | F |
| " | " | " | " | 313 | 270 | F |
| " | " | " | " | 344 | 279 | M |
| " | " | " | " | 402 | 285 | M |
| " | " | " | " | 490 | 305 | M |
| | | | **Mean** | **371** | **282** | **n/a** |
| PALMER-F | 07014035 | 10/17/06 | LMB | 736 | 356 | M |
| " | " | " | " | 805 | 359 | F |
| " | " | " | " | 923 | 365 | M |
| " | " | " | " | 834 | 370 | M |
| " | " | " | " | 794 | 372 | M |
| | | | **Mean** | **818** | **364** | **n/a** |

| Location ID* | Sample No. | Collection Date | Species | Weight (g) | Total Length (mm) | Sex |
|---|---|---|---|---|---|---|
| **Palmer Lake (cont.)** | | | | | | |
| PALMER-F | 07014036 | 10/17/06 | LMB | 1197 | 397 | M |
| " | " | " | " | 1366 | 417 | M |
| " | " | " | " | 1357 | 418 | M |
| " | " | " | " | 1489 | 430 | M |
| " | " | " | " | 1486 | 439 | F |
| | | | **Mean** | **1379** | **420** | **n/a** |
| PALMER-F | 07014037 | 10/17/06 | LSS | 876 | 436 | M |
| " | " | " | " | 858 | 444 | F |
| " | " | " | " | 957 | 445 | F |
| " | " | " | " | 956 | 447 | M |
| " | " | " | " | 1073 | 449 | ? |
| | | | **Mean** | **944** | **444** | **n/a** |
| PALMER-F | 07014038 | 10/17/06 | LSS | 978 | 470 | M |
| " | " | " | " | 1216 | 474 | M |
| " | " | " | " | 912 | 475 | F |
| " | " | " | " | 1062 | 480 | F |
| " | " | " | " | 999 | 482 | M |
| | | | **Mean** | **1033** | **476** | **n/a** |
| PALMER-F | 07014039 | 10/17/06 | LSS | 1144 | 490 | F |
| " | " | " | " | 1087 | 493 | F |
| " | " | " | " | 1322 | 510 | M |
| " | " | " | " | 1408 | 520 | F |
| " | " | " | " | 1337 | 520 | F |
| | | | **Mean** | **1260** | **507** | **n/a** |
| SINLAHEKIN-F | 07014041 | 9/26/06 | KOK | n/a | 316 | F |
| " | " | " | " | n/a | 310 | F |
| " | " | " | " | n/a | 369 | F |
| " | " | " | " | n/a | 306 | F |
| " | " | " | " | n/a | 366 | F |
| | | | **Mean** | **n/a** | **333** | **n/a** |
| SINLAHEKIN-F | 07014042 | 9/26/06 | KOK | 451 | 363 | M |
| " | " | " | " | 428 | 367 | M |
| " | " | " | " | 300 | 334 | M |
| " | " | " | " | 326 | 325 | M |
| " | " | " | " | 300 | 307 | M |
| | | | **Mean** | **361** | **339** | **n/a** |

| Location ID* | Sample No. | Collection Date | Species | Weight (g) | Total Length (mm) | Sex |
|---|---|---|---|---|---|---|
| **Palmer Lake (cont.)** | | | | | | |
| SINLAHEKIN-F | 07014043 | 9/26/06 | KOK | n/a | 359 | F |
| " | " | " | " | n/a | 298 | F |
| " | " | " | " | 266 | 321 | M |
| " | " | " | " | 204 | 285 | M |
| " | " | " | " | 216 | 295 | M |
| | | | **Mean** | **n/a** | **312** | **n/a** |

* EIM (Environmental Information Management database) User Location ID
? Sex is unknown

BLS = Bridgelip sucker *(Catostomus columbianus)*
KOK = Kokanee *(Oncorhynchus nerka)*
LMB = Largemouth bass *(Micropterus salmoides)*
LSS = Largescale sucker *(Catostomus macrocheilus)*
MWF = Mountain whitefish *(Prosopium williamsoni*)
NPM = Northern pike minnow *(Ptychocheilus oregonensis)*
RBT = Rainbow trout *(Oncorhynchus mykiss)*

# Appendix B. Laboratory Case Narratives

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**Manchester Environmental Laboratory**
7411 Beach Drive East, Port Orchard, Washington 98366

February 28, 2007

| | |
|---|---|
| Subject: | **Similkameen -REVISED** |
| Samples: | 07-014020 through 07-0140244 |
| Project ID: | 102507 |
| Laboratory: | Brooks Rand LLC |
| Project Officer: | Brandee Era-Miller |
| By: | Karin Feddersen |

# Arsenic Speciation

## Summary

Quality control samples are evaluated below. See Brooks Rand's narrative for more detailed information. Brooks Rand flags have been replaced with Manchester Laboratory qualifiers following EPA protocols. (E.g.: Brooks Rand's "B" qualifier, indicating a result below the PQL, has been replaced with "J") Brooks Rand typically uses a calculated MDL as the reporting limit. All non-detect results reported to the MDL have been qualified with "UJ," indicating an estimated reporting limit.

The DMA result for sample 014031 was qualified as an estimate by the laboratory due to sample loss during preparation. The lab neglected to reanalyze this sample as they were concerned about reporting the data within the specified timeframe.

All sample results were corrected for the mean of the method blanks. This practice is not described in the methods as stated in the narrative, but is part of Brooks Rand's SOPs.

## Analytical Methods

These samples were analyzed using Brooks Rand's version of EPA method 1632a.
Holding Time
Samples were analyzed within the method 1632a holding time of 2 years for frozen tissue.

## Calibration

Continuing Calibration Verification (CCV) standards and instrument blanks were analyzed every 10 samples or less. The standard recoveries were within method limits.

**Blanks**

Low levels of inorganic arsenic were detected in the method blanks.
All analyte concentrations in the samples less than 5 times the amount detected in the highest blank are considered to be likely due to laboratory contamination and not native to the sample. These sample results have been qualified with a "UJ" to indicate that this analyte was not detected at or above the suspected laboratory contamination level.

**Laboratory Control Sample**

Recoveries for arsenic in the Standard Reference Materials (SRM) 1640 and 1643e Certified Reference Materials (CRM) DOLT and DORM were all above 90%. There are no separate source standards available for Monomethyl Arsenic (MMA) or Dimethyl Arsenic (DMA). Fortified blanks were analyzed for these parameters and were within the lab's acceptance limits.

**Duplicate Samples**

Duplicate analyses were performed on samples 014020, 104030, and 014040 for Arsenic and Inorganic Arsenic. Sample 014044 was also used for MMA and DMA. The Relative Percent Differences (RPDs) were not calculated as all results were less than five times the PQL.

**Matrix Spikes**

Duplicate aliquots of samples 014020, 104030, and 014040 were spiked with Inorganic Arsenic, MMA, and DMA. Sample 014044 was also used for MMA and DMA. Recoveries and RPDs were within laboratory limits.

***Data Qualifier Codes***

| | | |
|---|---|---|
| U | - | The analyte was not detected at or above the reporting limit. |
| J | - | The analyte was positively identified. The associated numerical result is an estimate. |
| UJ | - | The analyte was not detected at or above the reported estimated reporting limit. |

# *BROOKS RAND LABS*

Report For
Washington Department of Ecology
Total Arsenic & Arsenic Speciation Analysis of Fish

Project Name: Similkameem
Brooks Rand Project #: ECY002

Report Date: February 21, 2007
Brooks Rand Tracking #: 07BR0070

**Shipping and Receiving**
Brooks Rand Labs (BRL) received twenty-five fish tissue samples at 8:30 AM on January 18, 2007. The requested analyses listed on the chain of custody (COC) form were for total arsenic (As) and arsenic speciation, contractually defined as inorganic arsenic [As(In)], monomethyl arsenic (MMA), and dimethyl arsenic (DMA). The samples were stored in a freezer in a locked BRL sample storage room until further processing. The samples were received, stored, prepared, and analyzed according to BRL standard operating procedures (SOPs) and EPA Methodology.

**Preservation and Holding Time**
All method requirements for preservation and holding time were satisfied.

**Total Arsenic by a modification of EPA Method 1638 (BRL SOP BR-00260)**
Tissue samples are hot-block digested with concentrated nitric acid ($HNO_3$) and diluted to volume with de-ionized water. Prepared samples are then analyzed by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Aliquots of sample were analyzed with a Perkin Elmer ELAN DRC II™ with $^{74}Ge$ internal standardization. This method incorporates ionization of the sample in an inductively-coupled RF plasma, with detection of the resulting ions by mass spectrometer on the basis of their mass-to-charge ratio.

*Batch # 07-0034*

*Preparation*: Samples were prepared on January 30, 2007.

*Analysis*: Samples were analyzed on February 12, 2007

*Quality Assurance*: Please refer to the Quality Assurance Summary for QA results. Results less than or equal to the method detection limit (MDL) have been qualified "U" for non-detect and have been reported at the MDL. Results above the MDL and less than or equal to the practical quantitation limit (PQL) have been qualified "B" and should be considered estimates. All QA criteria were met and no additional qualification of the data was required.

*Blank Correction*: The results have been method blank corrected as described in EPA Method 1638 mod.

**Inorganic Arsenic by EPA Draft Method 1632 (BRL SOP BR-0021)**
Biota samples are digested with 2M hydrochloric acid (HCl) and heated for approximately sixteen hours. Samples are then analyzed by hydride generation (HG) with sodium borohydride ($NaBH_4$) addition, cryogenic trap pre-collection, hydrogen/air flame quartz furnace decomposition, and detection by atomic absorption spectroscopy (AAS). All sample results for As(In) analysis are blank corrected.

*Batch # 07-0046-1*

*Preparation*: Samples were prepared on February 18, 2007.

*Analysis*: Samples were analyzed on February 19, 2007.

*Quality Assurance*: Please refer to the Quality Assurance Summary for QA results. Results less than or equal to the MDL have been qualified "U" for non-detect and have been reported at the MDL. Results above the MDL and less than or equal to the PQL have been qualified "B" and should be considered estimates. All QA criteria were met and no additional qualification of the data was required.

*Blank Correction*: The results have been method blank corrected as described in EPA Draft Method 1632.

**Monomethyl Arsenic by EPA Draft Method 1632 (BRL SOP #BR-0021)**
Biota samples are digested with 2M sodium hydroxide (NaOH) and heated for sixteen hours. Samples are then analyzed by hydride generation (HG) with sodium borohydride ($NaBH_4$) addition, cryogenic trap pre-collection, hydrogen/air flame quartz furnace decomposition, and detection by atomic absorption spectroscopy (AAS). All sample results for MMA analysis are blank corrected.

*Batch # 07-0045*

*Preparation*: Samples were prepared on February 15, 2007.

*Analysis*: Samples were analyzed on February 16, 2007.

*Quality Assurance*: Please refer to the Quality Assurance Summary for QA results. The vial containing the preparation of sample "07014031" (07BR0070-12) cracked during the final oven-heating step, prior to analysis. Although some of the sample preparation leaked out of the vial, sufficient volume remained to analyze the preparation. The result for this sample was a non-detect indicating that the sample was not contaminated by the vial malfunction.

Results less than or equal to the MDL have been qualified "U" for non-detect and have been reported at the MDL. Results above the MDL and less than or equal to the PQL have been qualified "B" and should be considered estimates. All QA criteria were met and no additional qualification of the data was required.

*Blank Correction*: The results have been method blank corrected as described in EPA Draft Method 1632.

*Batch # 07-0064-1*

*Preparation*: Samples were prepared on February 14, 2007.

*Analysis*: Samples were analyzed on February 15, 2007.

*Quality Assurance*: Please refer to the Quality Assurance Summary for QA results. Results less than or equal to the MDL have been qualified "U" for non-detect and have been reported at the MDL. Results above the MDL and less than or equal to the PQL have been qualified "B" and should be considered estimates. All QA criteria were met and no additional qualification of the data was required.

*Blank Correction*: The results have been method blank corrected as described in EPA Draft Method 1632.

**Dimethyl Arsenic by EPA Draft Method 1632 (BRL SOP #BR-0021)**

Biota samples are digested with 2M sodium hydroxide (NaOH) and heated for sixteen hours. Samples are then analyzed by hydride generation (HG) with sodium borohydride ($NaBH_4$) addition, cryogenic trap pre-collection, hydrogen/air flame quartz furnace decomposition, and detection by atomic absorption spectroscopy (AAS). All sample results for DMA analysis are blank corrected.

*Batch # 07-0038*

*Preparation*: Samples were prepared on February 15, 2007

*Analysis*: Samples were analyzed on February 16, 2007

*Quality Assurance*: Please refer to the Quality Assurance Summary for QA results. The vial containing the preparation of sample "07014031" (07BR0070-12) cracked during the final oven-heating step, prior to analysis. Although some of the sample preparation leaked out of the vial, sufficient volume remained to analyze the preparation. The result for this sample was greater than the PQL and has been qualified "J" as an estimate due to the potential loss of sample or contamination.

The acceptance criterion for duplicate precision [relative percent difference (RPD) < 35%] did not apply to the method duplicate (MD) analyses performed on samples "07014020" (07BR0070-01) and "07014030" (07BR0070-11) since analysis of both the native samples and the duplicates produced results that were less than the PQL and within two PQLs of each other.

Results less than or equal to the MDL have been qualified "U" for non-detect and have been reported at the MDL. Results above the MDL and less than or equal to the PQL have been qualified "B" and should be considered estimates. All QA criteria were met and no additional qualification of the data was required.

*Blank Correction*: The results have been method blank corrected as described in EPA Draft Method 1632.

*Batch # 07-0065-1*

*Preparation*: Samples were prepared on February 14, 2007.

*Analysis*: Samples were analyzed on February 15, 2007.

*Quality Assurance*: Please refer to the Quality Assurance Summary for QA results. The acceptance criterion for duplicate precision (RPD < 35%) did not apply to the MD analysis performed on sample "07014044" (07BR0070-25) since analysis of the native sample and the duplicate produced results that were less than the PQL and within two PQLs of each other.

Results less than or equal to the MDL have been qualified "U" for non-detect and have been reported at the MDL. Results above the MDL and less than or equal to the PQL have been qualified "B" and should be considered estimates. All QA criteria were met and no additional qualification of the data was required.

*Blank Correction*: The results have been method blank corrected as described in EPA Draft Method 1632

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We certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. In addition, we certify that to the best of our knowledge and belief, the data as reported are true and accurate. The Laboratory Director or her designees, as verified by the following signatures has authorized release of the data contained in this data package

Amy Durdle
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Elizabeth Madonick
Project Manager
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# Appendix C. Data Precision Table

Table C-1. Precision of Laboratory Duplicate Results (ug/Kg wet weight) and Percent Matrix Spike Recoveries.

| Parameter | Duplicate Type | Duplicates | | | Matrix Spike/ Matrix Spike Duplicate | | |
|---|---|---|---|---|---|---|---|
| | | Result | Duplicate | RPD | Spike | Duplicate | RPD |
| Lipids (%) | lab | 1.54 | 1.72 | **11%** | -- | -- | **nc** |
| | lab | 0.34 | 0.5 | **38%** | -- | -- | **nc** |
| | process | 0.62 | 0.62 | **0%** | -- | -- | **nc** |
| Total Arsenic | lab | 150 | 140 | **7%** | 92 | 92 | **0%** |
| | lab | 190 | 220 | **15%** | 90 | 90 | **0%** |
| | lab | 190 | 200 | **5%** | 89 | 96 | **8%** |
| | process | 190 | 210 | **10%** | -- | -- | **nc** |
| Total Inorganic Arsenic | lab | nd | nd | **nc** | 99 | 103 | **4%** |
| | lab | nd | nd | **nc** | 107 | 96 | **11%** |
| | lab | nd | nd | **nc** | 101 | 103 | **2%** |
| | process | nd | nd | **nc** | -- | -- | **nc** |
| MMA | lab | 4 | 4 | **0%** | 97 | 103 | **6%** |
| | lab | nd | nd | **nc** | 103 | 102 | **1%** |
| | lab | nd | nd | **nc** | 104 | 93 | **11%** |
| | process | nd | nd | **nc** | -- | -- | **nc** |
| DMA | lab | 7 | 20 | **96%** | 101 | 102 | **1%** |
| | lab | 22 | 8 | **93%** | 92 | 98 | **6%** |
| | lab | 32 | 24 | **29%** | 98 | 94 | **4%** |
| | process | 7 | 32 | **128%** | -- | -- | **nc** |

-- = not applicable
nc = not calculated
nd = not detected
RPD = relative percent difference
MMA - monomethylarsonic acid
DMA - dimethylarsinic acid