

Arsenic, Mercury, and Selenium in Fish Tissue and Water from Idaho's Major Rivers: A Statewide Assessment



Prepared by Don A. Essig



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Acknowledgements

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Cover Photo: Selway River just above Selway Falls, taken by Don Essig

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This report covers the entire project from design through implementation to results, some recent related data on mercury in fish in Idaho, and discussion. These elements are presented in that order and have been arranged into six general parts.

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List of Acronyms, Abbreviations, and Symbols

$\mu\text{g/kg}$	micrograms per kilogram
μm	micrometer
As	arsenic
As(i)	inorganic arsenic
As(T)	total arsenic
ASTDR	Agency for Toxic Substances and Disease Registry
BAF	bioaccumulation factor
BCEH	Bureau of Community and Environmental Health
BCF	bioconcentration factor
CRM	certified reference material
DEQ	Idaho Department of Environmental Quality
DL	detection limit
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
Hg	mercury
Hg^{+2}	reactive mercury
IDHW	Idaho Department of Health and Welfare
IFCAP	Idaho Fish Consumption Advisory Program
Me-Hg	methylmercury
mg/kg	milligrams per kilogram
ng/g	nanograms per gram
ng/L	nanograms per liter
PQL	practical quantitation limit
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
R^2	coefficient of determination

RM	reference material
RPD	relative percent difference
Se	selenium
TMDL	total maximum daily load
USGS	U.S. Geological Service

Distribution List

Toni Hardesty, Idaho Department of Environmental Quality (DEQ) Director

Barry Burnell, DEQ Water Quality Division Administrator

Martin Bauer, DEQ Air Quality Division Administrator

Michael McIntyre, DEQ Surface Water Program Manager

Marti Bridges, DEQ Total Maximum Daily Load (TMDL) Program Lead

Don Essig, DEQ Water Quality Standards Coordinator

Mary Anne Kosterman, Ph.D., DEQ Water Quality Standards Scientist

Jason Pappani, DEQ Water Quality Monitoring and Assessment Coordinator

Jeffrey Fromm, Ph.D., DEQ Environmental Toxicologist

Carl Brown, DEQ Air Toxics Analyst

Jim Vannoy, Idaho Department of Health and Welfare Environmental Education and Assessment
Manager

Jim Werntz, US EPA Manager Idaho Operations Office

Leigh Woodruff, US EPA Idaho Operations Office

Lisa Macchio, US EPA, Region 10, Water Quality Standards Coordinator for Idaho

Bill Horton, Idaho Department of Fish and Game, State Fish Manager

Misty Kennard-Mayer, Brooks Rand LLC

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Executive Summary

The main purpose of this study was to determine the proportion of the major rivers of Idaho with an average mercury level in fish that exceeds the human health criterion for mercury (0.3 milligrams per kilogram [mg/kg] or 300 nanograms per gram [ng/g] of tissue). Arsenic and selenium in tissues were measured in addition to mercury. All three are known to bioaccumulate in fish tissue, but heretofore we have had no statewide estimate of concentration levels in fish tissue from Idaho's rivers. To better understand bioaccumulation, companion water samples were collected as well.

Major rivers are those that are normally not amenable to sampling by wading alone and require use of boats; these are rivers that most people know from highway maps. Sampling locations were determined using probabilistic choice to generate from the sample data estimates of fish tissue concentrations for all major rivers in Idaho. These statewide estimates are thus unbiased and with known precision.

In this study, a fish tissue sample is a composite of tissue from up to 10 fish of a single species from one site. The goal was to collect samples from 50 sites, obtaining multiple species where possible. Many sites did not have more than one species of game fish, and most sites did not have fish in sufficient number to get 10 fish. Ten sampled sites yielded no game fish in the time available for sampling. In the end, 76 fish tissue samples were obtained from 40 sites, representing 16 species of game fish.

For mercury, the contaminant of primary interest, it was found that:

- 8 of 40 sites sampled (20%) had fish with a mercury concentration greater than 0.3 mg/kg.
- 8 of 76 of the composite fish samples (11%) had more than 0.3 mg/kg of mercury.

From the probabilistic sample, it is estimated that 15% (95% confidence bounds of 9% to 23%) of major river miles in Idaho have game fish with mercury levels greater than the human health criterion. Because the probabilistic selection is for sites not samples, a similar estimate cannot be made for all fish that may be caught.

The data by species are very limited, and no valid extrapolations can be made. However, three of the eight samples with more than 0.3 mg/kg mercury were smallmouth bass. One was a largemouth bass, a species not usually caught from rivers. Forty-one of the samples were of mountain whitefish or trout, and all of these contained less than 0.3 mg/kg mercury.

While this study does not provide site-specific information for all Idaho rivers, or for all species that inhabit them, it does provide an overall picture of arsenic, mercury, and selenium levels in game fish caught from major rivers in Idaho.

For water, only one of 35 samples exceeded EPA's 1985 chronic aquatic life criterion for total mercury of 12 nanograms per liter (ng/L). All remaining samples had concentrations less than 2 ng/L. Upon re-sampling that one site, mercury was found in concentrations less than one-half

the criterion of 12 ng/L. High turbidity and mercury attached to suspended sediment is thought to account for the anomalously high result. Scudder et al. (2009) report the mean total mercury concentration in 352 U.S. streams to be 8.22 ng/L, with 90% of the sites having mercury concentrations less than 9 ng/L. Idaho rivers thus have less mercury than the nationwide average.

Data from this study were shared with the Idaho Department of Health and Welfare (IDHW) in 2009. In May 2009, on the advice of the interagency Idaho Fish Consumption Advisory Program (IFCAP) group, IDHW issued three new fish consumption advisories: for the Payette River (suckers), Bear River (carp), and South Fork Snake River (brown trout).

Based on the past three years of probabilistic sampling of both lakes and rivers, excess mercury in fish appears to be a widespread if not frequent problem in Idaho. No data were collected that would allow identification of sources of contamination. That is a matter for further study.

Part A. Project Management, Background, and Design

Project Organization

This project was organized and managed by the Department of Environmental Quality's (DEQ's) Surface Water Program under the direction of Michael McIntyre. Don Essig and Jason Pappani prepared the quality assurance project plan (QAPP) that guided this work.

Jason Pappani hired, trained, and supervised a seasonal field crew that performed most of the actual collection of fish and water samples, in addition to biomonitoring, as part of a broader major rivers assessment.

Brooks Rand, LLC was selected as the contract laboratory. They performed all the chemical analysis of fish tissue and quality control (QC) samples. They reported results, including associated laboratory QC summaries, to DEQ.

Xin Dai, in DEQ's Technical Services Division, was the project quality assurance officer and provided an independent evaluation of quality assurance/quality control (QA/QC) data.

Don Essig of DEQ was project manager and is the primary author of this report. He was responsible for the contract with Brooks Rand, sample tracking, receipt and management of data reports, and project budget and billing.

Mary Anne Kosterman of DEQ performed probability statistical analysis on the final data set, prepared the maps in this report, and worked with Tony Olsen of the U.S. Environmental Protection Agency (EPA) in the random selection of river sampling sites.

Background and Objectives

In this section, reasons and context for investigating possible contamination in fish from Idaho's major rivers are given.

Why Monitor Fish Tissue?

Methylmercury is a potent neurotoxin that can pass the blood-brain and placental membranes that form barriers to many other toxins (Clarkson and Maglos 2006). Mercury in fish tissue is the primary source of exposure to this toxin for most people (ASTDR 1999; EPA 2001). To address this important health risk, Idaho adopted EPA's 2001 methylmercury fish tissue criterion in 2005; the first state in the nation to do so. This action brought attention to mercury in Idaho fish and placed at least a perceived obligation on DEQ to monitor mercury in fish tissue. At that time, little was known about mercury in Idaho fish, although Idaho's first fish consumption advisory, for Salmon Falls Creek Reservoir, dates back to 2002. Since 2005, public interest in both the amount of mercury in fish tissue and the source(s) of that mercury has increased greatly. As more data have been acquired on fish tissue mercury levels from around the state, so too has the number of fish consumption advisories increased.

As of February 2009, there are thirteen lakes or reservoirs and two streams across the state of Idaho with fish consumption advisories for mercury (IFCAP 2009, Figure 1). In addition, a statewide consumption advisory for smallmouth and largemouth bass was issued in 2008 based

on the prevalence of high mercury levels in samples of those species collected in 2007 (Essig and Kosterman 2008). Older data also exist to support a fish consumption advisory for the Portneuf River (Van Every 2007). On the advice of the interagency Idaho Fish Consumption Advisory Program (IFCAP) group, the Idaho Department of Health and Welfare issued a fish consumption advisory for trout species from the Portneuf River in May 2009. Fish consumption advisories caution the public, particularly young children and pregnant women, to limit their consumption of certain kinds of fish, such as bass, and usually from specific waters, to safeguard their health. The increasing number of advisories indicates the effort in monitoring fish tissue for mercury was warranted to protect public health.

Previous Monitoring

Until 2006, monitoring of mercury in fish tissue in Idaho was directed at specific water bodies. Monitoring was sometimes targeted where mercury contamination was already known or suspected, and at other times monitoring was opportunistic—simply taking samples from fish already caught by the Idaho Department of Fish and Game for the purpose of estimating fish populations. Thus, what we knew about mercury in Idaho fish was not the result of planned sampling to answer questions about the occurrence of elevated mercury in fish tissue across the state; rather, it was haphazard, and so no general conclusions could be drawn.

This Monitoring Effort

In 2006, DEQ undertook the first effort at probabilistic statewide sampling for mercury levels in fish tissue. Sampling for mercury in fish tissue was piggybacked onto DEQ's monitoring conducted for the major rivers assessment planned under the Surface Water Ambient Monitoring Plan (Grafe 2004), with 2006 being year one of a planned two-year effort for the major rivers assessment with the second year planned for 2008. In 2007, DEQ monitored lakes and reservoirs for mercury, arsenic, and selenium in fish tissue (Essig and Kosterman 2008).

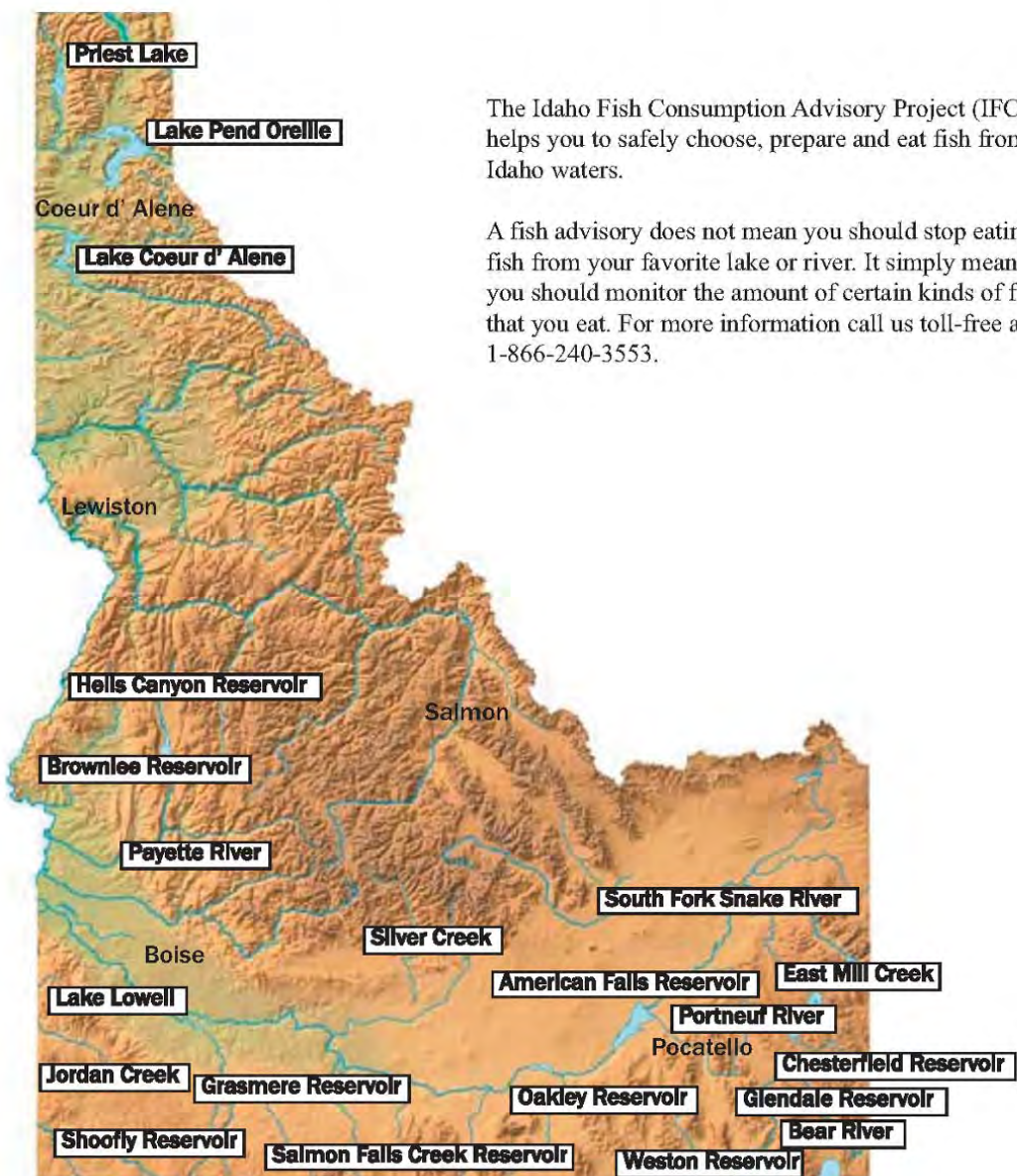
In 2008, DEQ completed its monitoring for the major rivers assessment and at the same time completed sampling for mercury in fish tissue.

Due to added funding from EPA, in 2008 DEQ was able to take advantage of the considerable effort already being invested in fish collection and have the fish also analyzed for arsenic and selenium. Analysis of arsenic and selenium analysis results also provides a statewide overview similar to that for mercury, but with fewer sites sampled than during the combined 2006/2008 effort for mercury. To provide information about bioaccumulation rates of arsenic, mercury, and selenium, DEQ also sampled river water in 2008.

Why Monitor Rivers?

To date, most of Idaho's fish consumption advisories are for lakes and reservoirs (see Figure 1). This may be because lakes and reservoirs are better places for mercury methylation and bioaccumulation, or it may be just an artifact of the available data. Rivers are also an important fishing resource for the public and a potential route of exposure to contamination in fish tissue, for those who eat local fish. Thus, it is prudent to know the prevalence of mercury contamination in Idaho's rivers as well as lakes and reservoirs. Because rivers require different site selection and sampling techniques, a separate but companion monitoring effort was required.

Idaho Fish Consumption Advisory for Selected Waters



IDAHO DEPARTMENT OF
HEALTH & WELFARE

Idaho Fish Consumption Advisory Project
450 W State St 6th Fl
Boise, ID 83702
1-866-240-3553

Figure 1. Idaho Fish Consumption Advisories as of October 2009.

Based on what is known about mercury methylation and bioaccumulation (Mason, Reinfelder, and Morel 1995; Southworth, Peterson, and Bogle 2004; Evers et al. 2007), it is reasonable to expect the frequency and magnitude of high mercury levels in fish from rivers to be less than in lakes and reservoirs. The reason for this expectation is at least twofold: 1) rivers are less likely to provide conditions that favor methylation of mercury, such as warm temperatures and anaerobic sediments; and 2) the communities of fish that inhabit rivers are different from those in lakes, with rivers having fewer of the predatory and warmwater species that tend to bioaccumulate mercury more strongly.

Despite this expectation, there are data from Idaho rivers to show they are not immune to problems of elevated mercury in fish tissue. In fact, some of the highest levels of mercury observed have come from brown trout in Silver Creek (USGS 2009) and the Portneuf River (Van Every 2007). Thus, DEQ felt it important to determine how frequent the problem of high mercury levels in fish might be in Idaho's major rivers. This study addresses that information gap from a statewide perspective.

The fish tissue data described in this report are from both 2006 and 2008. With this data, we are now able to estimate the proportion of major rivers across Idaho that have fish with mercury levels greater than the human health criterion of 0.3 mg/kg (300 micrograms per kilogram [$\mu\text{g/kg}$]).¹ This work compliments the 2007 monitoring of lakes and reservoirs.

Study Goals

The main goal of this study was to estimate the percentage of Idaho's major rivers that contain fish with methylmercury concentrations in their muscle tissue greater than 0.3 mg/kg (300 $\mu\text{g/kg}$) wet weight. Results from this study provide an overall picture of risk to the fish-eating public from mercury contamination in fish from Idaho's major rivers. This study does not provide site-specific information about each river in Idaho, nor does it provide information about risk from species not sampled.

Additional goals were to provide similar estimates for arsenic and selenium levels in fish from rivers. Even though there are no Idaho criteria for arsenic and selenium levels in fish tissue to compare to, the data allow comparison to thresholds of interest, and in the analysis (see Part D of this report), such comparisons are made. DEQ also collected concomitant water column data. In addition to being a more traditional measure of water quality, the combination of water column data and fish tissue data provides information for calculation of bioaccumulation rates in Idaho for mercury, arsenic, and selenium.

Study Design

This study used a probabilistic, or random, sample design to select major river sites for sampling. Sampling took two years, separated by a year during which lakes and reservoirs were sampled. In 2006, only fish tissue samples were collected, and these were only analyzed for total mercury. For 2008, both fish tissue and water samples were collected, and the suite of analytes expanded to include arsenic and selenium.

¹ Idaho's fish tissue criterion, which is stated in units of milligram of methylmercury per kilogram of fresh weight fish tissue, is 0.3 mg/kg. This is the same as 300 $\mu\text{g/kg}$ or 300 ng/g, the latter being the unit typically used by laboratories.

Context

To assess the condition of Idaho's waters, DEQ relies largely upon monitoring of aquatic communities, including the numbers and kinds of fish and insects present. However, at times, when needs dictate and resources allow, this biological monitoring is supplemented with other monitoring, which may include the traditional collection of water for chemical analysis. This study was a continuation of the monitoring of fish tissue for contaminant levels that DEQ conducted in 2006, 2007, and 2008. The sampling of fish tissue for mercury was precipitated by adoption of a methylmercury fish tissue criterion in 2005 and rising interest in mercury contamination in Idaho fish (DEQ 2005).

Sampling for mercury in fish tissue from major rivers is a companion to the 2007 mercury sampling in lakes and reservoirs (see Essig and Kosterman 2008). It is also part of Idaho's broader major rivers assessment, which is biological monitoring that began in 2006. (See Essig and Pappani 2008 for a description of how the monitoring for mercury in fish tissue was piggybacked onto monitoring for the major rivers assessment.) Monitoring of fish tissue (in 2006) and of fish tissue and water (in 2008) was combined with the biological monitoring efforts of the major rivers assessment to economize on the expense and effort of fielding a seasonal monitoring crew. The sampling of 50 river sites was spread across two years due to time and cost constraints. The breakdown in sampling over the two years is detailed in Part D, Sites Sampled.

The monitoring reported here of mercury levels in fish tissue from Idaho's major rivers differs from the companion 2007 lakes and reservoir monitoring in three important respects:

- 1) Fish tissue monitoring was combined with previously planned biological monitoring to make more efficient use of field crew time.
- 2) The combined efforts resulted in more time at each site, but less field time overall than two separate efforts. This, along with a shorter sampling season for rivers than for lakes, meant the effort to monitor 50 sites had to be stretched out over two separate years, 2006 and 2008.
- 3) As a result of additional EPA funding obtained in 2007, DEQ was able to expand monitoring in 2008 to add water sampling, and expand analysis of both fish and water to include arsenic and selenium in addition to mercury.

While the expansion of the effort in 2008 was a conscious decision to increase the information per unit of field effort, it also complicates data analysis and summary.

Only the results of monitoring of fish tissue and water for arsenic, mercury, and selenium are reported here. Results of the biological monitoring will be reported separately at a later date.

Probabilistic Sampling

Like the lakes and reservoirs sampling of 2007, the large rivers monitoring reported here used probabilistic site selection (see Appendix A). Also known as random sampling, this type of site selection allows use of statistics to infer or make statements about a broader population of rivers, beyond the sites actually monitored. This approach is necessary to make efficient use of limited monitoring dollars while meeting DEQ's obligation under the Clean Water Act section 305(b) to

report on the condition of all waters in the state.² Without a random selection of sites, our results would only describe conditions in the waters sampled and no others.

As described in the QAPP for this study (Essig and Pappani 2008), the choice of a sample size of 50 sites is a compromise between precision in the estimates of population proportions and the overall cost of the monitoring effort.

Target Population

For the 2006/2008 large rivers study, the population sampled was the major rivers of Idaho, based on a GIS layer of that name. (GIS layers are digital map-like layers of geographical information.)

Idaho's major rivers GIS layer is a subset of the 1:250k hydrography for the state of Idaho. It consists of mostly fifth-order and larger streams, but also includes smaller order tributaries up the mainstem to the headwaters of a named stream, and excludes some fifth-order tributaries to larger-order streams. The layer also includes the centerlines of lakes and reservoirs (but any site within a lake or reservoir was rejected for this study). Excluding named lakes and reservoirs, there are about 4,430 miles of major rivers in Idaho's major rivers layer. This compares to 96,354 miles of streams at the 1:100k scale that form the basis of Idaho's 305(b) reporting, of which 6,737 miles are fifth-order or larger.

Target Sample and Analytes

Game species were our choice for sampling, but ultimately we were limited to catching what was available the day we sampled a site and during the few hours we were able to spend in catching fish. Often we took what we could get, even though it might not have been what an angler would have kept. Prior to analysis, fish samples were composited by species at a site. That is, when multiple fish of the same species were collected, they were combined to yield one fish tissue sample of that species for that site. Compositing of fish tissue is discussed in more detail in Part C, Quality Control Results.

Fish tissue samples were analyzed for total mercury, total and inorganic arsenic (the difference being organic arsenic), total selenium, and percent solids. The latter allows translation of analytical results from a wet weight basis, as reported by the laboratory, to a calculated dry weight basis.

Water samples were analyzed for total mercury, methylmercury, total arsenic, inorganic arsenic, and total selenium. All water samples were unfiltered surface grab samples. To the extent possible, these samples were collected from a well-mixed portion of the river; eddies and other areas of slack water were avoided.

Total Mercury Rather than Methylmercury

While the criterion for mercury in fish is for the more toxic methylmercury form, fish tissue samples in this study were analyzed for their total mercury content. We assume total methylmercury concentration equals the measured total mercury. This has become standard

² Section 305(b) of the Clean Water Act requires each state to report biennially on "the water quality of all navigable waters." Once known as a 305(b) or water quality status report, this reporting has since 2002 been combined with reporting on impaired waters under section 303(d) of the act into what is known as "The Integrated Report."

practice because it has been established that the majority (typically 90% or more) of total mercury in fish tissue is in the form of methylmercury (EPA 2001; Lasorsa and Allen-Gil 1995; Bloom 1992), and because the analysis of total mercury is less expensive. This assumption allows for some cost savings in analysis while erring on the side of safety.

By determining total mercury concentration and assuming the methylmercury concentration is the same, we in fact overestimate the methylmercury concentration by a small amount. If the total mercury result is close to the criterion, a follow-up with a more costly methylmercury analysis is advisable if there are potential regulatory consequences. This was not practical for the data described in the report, for which it is necessary to have all results be on this same basis.

Arsenic and Selenium

While fish tissue monitoring offers the benefit of directly assessing public health risk and integration of variability in water mercury concentrations, it is more difficult, time-consuming, and costly than water sampling. Just getting fish is a sizable monitoring investment. To make the most of that investment, arsenic and selenium were also included as analytes in this study. Arsenic and selenium were also included because they show some similarities to mercury in environmental fate and transport.

Like mercury, arsenic and selenium are contaminants of current interest. All three have complex biogeochemical cycles involving organic forms that tend to bioaccumulate. For both arsenic and mercury, fish consumption is an important route of exposure for humans. For selenium, EPA has been working for several years on a national fish tissue criterion, albeit to protect aquatic life (EPA 2004). The selenium criterion would be only the second Clean Water Act criterion based on concentrations in tissue rather than in water (mercury was the first). Selenium also influences both mercury bioaccumulation (Belzile et al. 2006) and mercury toxicity (Ralston 2008).

Arsenic is similar to mercury in being more of a human health concern than an aquatic life concern. To protect human health, EPA recommends a pair of water column criteria for arsenic (EPA 2002c). They recommend a “fish-only” criterion for locations where exposure to toxins is due solely to consuming fish; the fish-only criterion is applied to waters used for fishing.³ A companion “fish + water” criterion is based on exposure to toxins from consuming fish tissue plus drinking water from the same water body. It is applied to waters that are used for domestic water supply but which also may be fished.

While current arsenic criteria are specific to inorganic arsenic, most available data are for total arsenic, and little data is available regarding the predominant form of arsenic in Idaho waters and fish. The difference between total and inorganic arsenic is taken to be organic arsenic. Recently, important questions about the forms of arsenic (organic and inorganic), their relative toxicity, and how they differ in bioaccumulation have been raised (EPA 2003; EPRI 2003; Williams et al. 2006). Thus, it was decided to measure both total and inorganic arsenic in the samples collected for this study. Having information on the proportion of inorganic to total arsenic should help to

³ To derive a water concentration criterion, a dose of a toxin from fish consumption must be translated. A reference dose – a body burden expressed in amount of toxin per unit of body weight (e.g., µg/kg) associated with adverse health effects – is translated by accounting for the amplification that occurs in the food chain, the rate of fish consumption, a person’s body weight, and a factor that accounts for the proportion of exposure from aquatic versus other sources. For each of these factors, a default or average value is used if more specific information is not available.

better apply the recommended arsenic criteria in Idaho, translate the reference dose to water criteria, and inform future criteria development.

Wet Weight vs. Dry Weight Concentrations

The methylmercury criterion is based on fresh weight, appropriately reflecting the nature of fish destined for human consumption. In contrast, the proposed draft selenium fish tissue criterion (EPA 2004) is based on dry weight tissue concentrations, the more customary reporting basis for chemical measurements in tissue. Instead of splitting the samples and performing parallel analyses on both fresh and dried samples, fresh samples were analyzed for their metals content and for their water content. With the latter information, the reported wet weight results can be converted to a dry weight basis, thus allowing the selenium results to be compared to the draft national tissue criterion.

Extra Samples

In addition to the planned sampling described in the QAPP for this study (Essig and Pappani 2008), two sets of opportunistic sampling were conducted in 2008. In both cases, the extra sampling was accomplished through cooperative efforts, allowing DEQ to get additional information it would not have had time, money, or ability to obtain on its own.

First, water samples were obtained from six additional river sites. These were sites scheduled to be sampled for fish tissue mercury by the U.S. Geological Survey (USGS) on behalf of DEQ as part of the jointly funded Statewide Surface Water-Quality Monitoring Program. Under this joint funding agreement, USGS has matched DEQ funding to collect 52 samples of fish tissue at 31 sites since 2004 (USGS 2009). A few sites were sampled more than once, and for two sites on Silver Creek in 2007, individual fillets rather than composite samples were analyzed. The USGS sends fish tissue samples they collect to their laboratory in Middleton, Wisconsin for mercury analysis. Due to funding limitations, no sampling of water for mercury analysis accompanied the fish samples collected by the USGS for DEQ. That changed in 2008 when the USGS assisted in the present monitoring effort by collecting water samples at the six sites they sampled for fish tissue in 2008. These water samples were provided to DEQ and included with the samples for the major rivers monitoring.

Second, DEQ obtained nine samples of hatchery return Chinook salmon. DEQ was not permitted to sample any listed threatened or endangered species, so the Idaho Department of Fish and Game collected Chinook salmon samples from fish returning to state-run hatcheries, and DEQ paid for the processing and analysis of these samples. This allowed us to answer questions about mercury levels in this important Idaho species.

Results for these two sets of extra samples are reported here, but they are separate from the probabilistic sampling of major rivers and so do not factor into the reported probabilistic results.

What Constitutes a Fish Sample?

While river reaches, each anchored on an “x” spot, were the geospatial foundation of the random site selection, the fundamental sample unit for fish was a composite of tissue from several individual fish of the same species from a site. The goal was to obtain 10 fish of a given species per site. Often this goal was not met due to limited time and the difficulty of obtaining fish samples in a river while electrofishing from a raft. (Electrofishing, a common scientific technique, uses electric current to stun fish and enable collection.) Because samples were composited, there are far fewer fish samples than fish caught.

Since the focus was on Idaho's methylmercury human health criterion, we targeted game species, which are the fish that people are likely to take home and eat. We also hoped to get two species from each site. Because there may be more than one species per site, there are more fish samples than sites.

It is known that different species bioaccumulate mercury and other contaminants to different degrees (EPA 2000a; EPA 2008; Wentz 2004). Ideally, we would like to have had the same species of fish from all sites to eliminate the confounding effect of species differences in comparing sites. Because we were sampling from rivers across the state of Idaho—a large and varied geographic area—habitat conditions vary considerably and it was unrealistic to expect to obtain the same species from all sites. We were further limited by only being able to catch fish during the one day we allotted to each site for sampling. Overall, we were very limited in the fish we could catch during the single pass with the boat electrofisher.

Quality Assurance and Quality Control

Quality Assurance Project Plan

All the 2008 sampling was performed under a QAPP (Essig and Pappani 2008). Version 1.0 of the QAPP was completed and approved on June 11, 2008, before crew training began. Version 1.1 was approved and distributed June 23, 2008, before sampling began. The update (version 1.1) primarily reflected a change in plans that consisted of returning all sample coolers to Boise for centralized shipping to the laboratory. The final version of the QAPP, version 1.2, is dated October 28, 2008. Although completed after the sampling was done, the only change was to add those sites from 2006 that were sampled for fish only in 2008 to Table 2 of Appendix A, and the field crew had this knowledge all along.

Crew Training

DEQ hired and trained a dedicated seasonal crew of four to conduct sampling. The week of June 16, 2008, was spent on crew training. This training included filleting of fish, identification of fish, use of clean-hands/dirty-hands water sampling protocol, a day of electrofishing technique, whitewater rafting technique, first aid, and safety training. Don Essig went over the QAPP section by section with the crew for part of one day, emphasizing sample identification, labeling, and storage.

The field work was supervised by Jason Pappani, who completed the five-person team and was present at all sampling, as required by the fish collection permit.

Quality Control Samples

Quality control samples were taken to measure the accuracy and precision of the results we obtained and to determine if they met objectives set out in the QAPP. There were two levels of QC samples in this study: field and laboratory. The QAPP established procedures for preparation of field blanks and duplicates and data quality objectives for each.

A group of samples and an associated QC sample set is known as a “batch.” In this study, each batch consisted of not more than 10 composite fish tissue samples from the field. This maintained a frequency of not less than one QC set per 10 samples processed.

Field

Field QC samples were the responsibility of the DEQ river crew and were generated in the process of sampling. From the laboratory's perspective, field QC samples are just another sample we submit to them; they increase the batch size for the laboratory and add to our analytical costs. There are two main types of field QC samples: duplicates and blanks.

A duplicate sample is a second sample from the same site, and, in the case of fish, the same species, collected immediately after the first. Any difference in field duplicate results is a measure of the precision of the overall process of sampling and analysis and how repeatable the results are. We obtained field duplicates in this study only to provide information on precision; no QC limits were set that would have disqualified data or triggered re-sampling.

A blank is a sample that is expected to be free of the analytes of interest and is handled and processed in a manner identical to samples. Blanks provide a check for contamination that could occur via the unintentional introduction of an analyte to the sample. A measureable concentration of analyte in the blank, if it is a significant fraction of the sample analysis results, means that sample results similarly contaminated will be inaccurate by being biased high.

Water blanks were generated by taking laboratory-distilled water to the field, transferring it to sample containers in the field, holding and transporting those containers to the laboratory, and having the laboratory analyze the blank as if it were a real sample of river water.

For fish tissue, field blanks are not possible. Confidence in the lack of contamination of fish tissue introduced by monitoring activities is based on careful handling, use of gloves, cleaning of field filleting equipment, and the fact that because fish tissue is a solid matrix, only surface contamination is possible.

Laboratory

In addition to analyzing our field QC samples, the contract laboratory analyzed QC samples generated in their facilities. The laboratory used blanks and duplicates as well as matrix spikes, matrix spike duplicates, and control samples of known concentration to document the accuracy and precision of their analytical results.

Laboratory QC was performed by the contract laboratory according to the project QAPP (Essig and Pappani 2008), as required by the contract and following the laboratory's standard operating procedures. Results of laboratory QC samples associated with samples DEQ sent to the laboratory for analysis were reported with each batch of sample analysis results we received. Results not meeting data quality objectives were indicated in the laboratory reports.

Part B. Sample Collection, Sample Preparation and Handling, and Data Management

Sample Collection

Our methods for collecting fish samples and for collecting water samples are described in the following paragraphs.

Fish

Fish sampling was conducted using a 16-foot raft that was custom fitted for electrofishing (Figure 2). The raft configuration consisted of a frame-mounted generator and electrofishing control box, a pair of anodes on adjustable booms extending out over the bow, and a spring-loaded deadman foot paddle to control power to the anodes. This boat was usually manned by three people: one oarsman and two netters to net stunned fish. A second raft accompanied the electrofishing boat, both for safety and to provide the staff to perform the biological and habitat monitoring in a timely fashion. A two-boat, five-person crew arrangement was considered a minimum needed to monitor a site in a day and equates to a five-person day investment in labor just to get samples from each site.



Figure 2. Electrofishing Raft

Netted fish were usually kept in a live well on the electrofishing raft until the end of each rafting day, when the raft was taken out of the river. Fish were then weighed, measured for length, filleted, and placed in labeled bags on dry ice and kept frozen. Occasionally, the length of the sampling day dictated that whole fish be frozen immediately after capture. Whole fish would then be processed when time permitted, in the evening at camp or sometimes the next day. These fish would be minimally thawed, just enough to allow measurement and filleting, then bagged and refrozen.

Per the QAPP (Essig and Pappani 2008), the skin was left on the fillets, which were sent frozen to the laboratory for further processing.

Water

Water samples were collected using a modified clean-hands/dirty-hands protocol based on EPA method 1669 (EPA 1996). The key element of this protocol is the use of two persons to collect a sample. The clean hands person wears gloves and is the only person to touch the sample bottles. The dirty hands person assists the clean hands person in getting their gloves on and in opening and closing bags containing the sample containers. The full protocol calls for wearing a Tyvek[®] suit and facemask to guard against possible contamination of the samples. While this requirement was initially employed, it was later relaxed when a test showed we could obtain clean sample blanks with less precaution. Care was taken to minimize the time during which sample bottles were uncapped and not submerged. To the extent possible, the person collecting the sample remained downwind and downstream of the open container.

Each sample consisted of four bottles to accommodate the varying container material and preservation needs of the analytes. All samples were surface grab samples from a well-mixed portion of the river flow.

Sample Handling

In the field, fish samples were quickly frozen in a cooler with dry ice and kept frozen until they could be shipped. Water samples were stored in an iced cooler immediately after sampling and then refrigerated until they could be shipped.

Samples were shipped overnight to reach the laboratory the next morning. Fish and water samples were packaged in separate coolers. Frozen fillets were shipped on dry ice, and water samples were packed in regular ice (tap water frozen in Cubitainers[®]). All samples were sent to Brooks Rand Laboratory, LLC for analysis.

Chain of custody forms were prepared for each group of samples, put into a plastic bag, and placed in the coolers with the samples. Coolers were sealed with clear packaging tape, and a signed and dated custody seal was affixed to each cooler along with the shipping label. The laboratory was called to alert them in advance each time a shipment was ready, and, in the event of a Saturday delivery, to assure that personnel would be at the laboratory to receive the samples. The last batch of samples was sent to the laboratory on October 23, 2008.

Preliminary analytical results were obtained in PDF format by email, about 4 weeks after samples were shipped to the laboratory, and a hard copy was received a few days later by mail. The final preliminary analytical results were received by email on November 17, 2008, and in the mail on November 20, 2008.

Composite Tissue Samples

It is known that fish tissue varies in contaminant levels from fish to fish (EPA 2001; Wentz 2004). This variability can be dealt with by using the average of the results from individual analysis of several fish (10 fish are often used) to characterize the mercury in a fish sample from a site. But this magnifies the analytical costs accordingly. Alternatively, an average value can come from a single analysis of a composite sample. The latter is much more economical, though information on variability is lost.

This study used composite samples and targeted 10 fish for each sample as recommended by EPA (EPA 2000a). A composite is quite appropriate for gauging human exposure, as the dose of mercury needed to cause detriment usually comes not from consuming a single fish but from many fish over an extended period of time.

Composite samples were prepared by the laboratory using subsamples of flesh only. This is appropriate for human health concerns, as most people eat just the flesh of the fish. Also, mercury tends to concentrate most strongly in the flesh of fish (Mason, Reinfelder, and Morel 1995). So, for mercury, a flesh-only analysis also provides the most conservative result for human health of most people. Selenium concentrates most in the ovaries and exerts its effect on fish reproduction (Lemly 2002); therefore, for wildlife exposure, whole-fish analysis is more appropriate. Too little is known about tissue-specific arsenic accumulation, particularly in its different forms. In this study, for arsenic and selenium, flesh-only tissue analysis is a compromise that allows for efficiency in sampling and analysis.

Data Management

Hard copies of field forms with fish identification numbers, lengths, and weights were brought back to the DEQ State Office and are on file with Jason Pappani. Analytical results from Brooks Rand Laboratory, LLC came to Don Essig in hard copy and electronic form, the latter as both PDF image files and electronic data reports that could be processed by computer. Electronic copies of the data were distributed to Xin Dai and Mary Anne Kosterman of DEQ for QA/QC evaluation and performing of statistics, respectively.

Analytical data were entered into an Excel[®] spreadsheet for analysis and graphing. Field data on fish identification, weight, and length were entered into a separate spreadsheet. The analytical data were also imported into a database, into which field data were also directly entered for interpretative analysis and long-term storage.

The electronic reports as well as paper copies of chain of custody forms and reports will be kept by Don Essig for at least five years, through the year 2013. Copies of the QAPP, PDF laboratory reports, spreadsheet, database, and this report on CD may be obtained by contacting Don Essig of DEQ during that time.

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Part C. Quality Control Results

Xin Dai of DEQ performed an independent evaluation of the field QC samples and laboratory QC reports. Quality control objectives were largely met. Results are summarized below, and Xin Dai's report appears in Appendix G. Following is a summary of the QA/QC sampling results.

Field QC Samples

Field Blanks

Field blanks were obtained only for water samples, as a check on possible contamination of samples during collection and handling. Over the course of the summer sampling season, nine blanks were obtained. One additional blank was generated in training, and analyzed for mercury only. These results are summarized by analyte in Table 1.

Table 1. Field Blank Analysis Results

	Me-Hg ng/L	Hg ng/L	As(i) µg/L	As(T) µg/L	Se µg/L
Min	< 0.020	< 0.150	< 0.008	< 0.010	< 0.090
Max	~ 0.024	< 0.150	0.027	< 0.060	< 0.110
n	9	10	9	9	9

< denotes result less than detection limit, ~ denotes result above detection limit but below practical quantitation limit. Me-Hg = methylmercury, Hg = total mercury, As(i) = inorganic arsenic, As(T) = total arsenic, and Se = total selenium.

All except three of the field blanks had undetectable levels of analytes.

For sample batch 5, inorganic arsenic was measurable at 0.027 µg/L in a field blank that was sent for analysis on August 18, 2008. The lowest sample result in this batch, at 0.347 µg/L, was more than ten times the blank result, and so all sample analysis results for this batch were acceptable without qualification.

The blank for sample batch 7, sent for analysis on August 29, 2008, contained methylmercury in a concentration greater than detection limits (DLs) but less than quantification limits. Samples in this batch were less than 10 times the DL and may be biased high. This affects the methylmercury results for sites 031 Weiser River, 055 NF Payette River, 084 SF Salmon River, and 099 Payette River.

A second blank for batch 8, sent to the laboratory on September 8, 2008, also had detectable methylmercury. This batch contained the six extra water samples collected by the USGS, and methylmercury results for those samples may be biased high. In both cases, the potential bias is small—20% at most—and within the precision of the analysis, so all sample analysis results were used as reported by the laboratory.

Field Duplicates

Field duplicates were obtained for water and fish to provide information on overall precision in both sampling and measurement. Precision is expressed as the relative percent difference (RPD) in the duplicate analysis results.

Seven water duplicates were obtained and from these, precision was calculated. This calculation is possible only if both results in a pair of duplicates are above the DL. Complete results are in Appendix F and are summarized in Table 2.

Table 2. Precision of Field Duplicate Water Samples

	Me-Hg	Hg	As(i)	As(T)	Se
Min	0%	2%	0%	0%	5%
Max	20%	73%	39%	95%	129%
Mean	5%	34%	10%	18%	50%
n	5	7	7	7	3

Me-Hg = methylmercury, Hg = total mercury, As(i) = inorganic arsenic, As(T) = total arsenic, Se = total selenium.

Four duplicate fish samples were obtained. The results are summarized in Table 3. Results below the DL made it not possible to calculate RPD for selenium in two of the duplicates and for inorganic arsenic in all four duplicates.

Table 3. Precision of Field Duplicate Fish Samples

	Hg	As(i)	As(T)	Se
Min	9%	nc	36%	6%
Max	30%	nc	50%	41%
Mean	17%	nc	43%	17%
n	4	0	2	4

Hg = total mercury, As(i) = inorganic arsenic, As(T) = total arsenic, Se = total selenium.

nc = not calculable, results below detection limit

It proved nearly impossible to catch enough fish for duplicate samples, and so three of the four fish tissue duplicates were obtained on different dates. Ordinarily, this would invalidate the duplicates, e.g., for water. But fish tissue integrates environmental variations in exposure to contaminants and does not change rapidly. Therefore, it is felt these fish duplicate samples were taken close enough in time to when the initial samples were taken to still provide useful information about our overall precision.

Laboratory QC Samples

Laboratory QC for water samples consisted of analysis of blanks, certified reference materials (CRMs), and sample spikes to assess accuracy, and analysis of spike duplicates to assess precision. For fish tissue samples, there were also digestion blanks and digestion duplicates, the latter a preparation of two subsamples of tissue from the same composite tissue sample. Each set or batch of no more than 10 samples was accompanied by at least one set of QC samples. Over the course of the study, there were 11 batches of water samples and 10 batches of fish samples. Complete QC sample results are provided in Appendix F and summarized below.

On two occasions, problems in keeping water samples at the required preservation temperature occurred and resulted in qualification of some of the sample analysis results. (“Qualified” data is considered questionable because an associated quality control objective was not met. Such data were further evaluated to determine if they were usable.)

The set of three water samples for inorganic arsenic sent to the laboratory on July 15, 2008, were received by the laboratory the next morning at a temperature of 9.0 °C, which is 5.0 °C greater than the required preservation temperature. The analysis results from these three samples are flagged with an “H” to indicate that sample preservation requirements were not met and that the results should be considered estimates.

A sample preservation mix-up occurred in the batch of water samples received by the laboratory on August 8, 2008. Samples that needed to be shipped on ice were not, and samples that did not need to be shipped with ice, were. Consequently, some samples arrived at the laboratory the next morning at 20.0 °C instead of at the requisite temperature of less than 4.0 °C. To avoid this problem, all future sample shipments were iced regardless of requirement for chilling. The mix-up affected methylmercury results for five water samples and inorganic arsenic results for three water samples. These results are flagged with an “H” to indicate that sample preservation requirements were not met and that the results should be considered estimates. Four of the five methylmercury results were below the DL; all three inorganic arsenic results were consistent with companion total arsenic results.

All other QC criteria were met. No data were rejected as unusable.

Detection and Quantitation Limits

Measurement precision naturally worsens as analyte concentrations decline, thus defining the DL. As sample concentrations increase above the DL, analytical precision improves and we eventually reach a point at which we can reasonably tell the difference between two measurements and be confident that one is greater than another—this is the practical quantitation limit (PQL).

The DL is the lowest measured concentration at which we can be sure (99% probability) the true analyte concentration is greater than zero (in other words, the analyte is present). Concentrations less than the DL are indicated by a < sign in the tables of data in Appendices D and E. The DL is set by sampling and analytical capabilities and may not be sufficiently low to quantify contaminant levels that are environmentally relevant. This is the case with arsenic in this study. Still, useful information can be obtained in terms of the number of “detects” or “non-detects.” Conversely, just because we can detect or even quantify an analyte in a sample does not mean we have an environmental contamination problem. Our measurements need to be compared to criteria, reference concentrations, or other environmentally relevant benchmarks. An example is mercury in this study, which was detected in all fish samples but was above criteria in only a fraction of those samples.

The PQL is less well defined but in this project is taken to be three times the DL. Analyte concentrations that exceed the DL but do not exceed the PQL are considered estimated concentrations. In this range of measured concentrations, we are confident the analyte is present but cannot be sure different measurements reflect real sample concentration differences. In other words, if measurement A is greater than measurement B, it does not necessarily mean real concentrations in sample A are greater than in sample B. Estimated concentrations are indicated by a ~ symbol in the data tables.

Table 4 lists the analytical methods used in this study and typical DLs and PQLs for fish tissue analyses. Because the weight of a tissue subsample that is digested in the laboratory for analysis varies somewhat, actual DLs and PQLs also vary somewhat, depending on the ratio of weight of

the subsample to final digest volume. Note that total mercury limits are expressed in ng/g, which is a thousandfold less than mg/kg.

Table 4. Methods of Analysis and Detection Limits for Fish Tissue

Analyte	EPA Method	Detection Limit	Practical Quantitation Limit
Inorganic Arsenic	1632 (HGAA)	0.002 mg/kg	0.005 mg/kg
Total Arsenic	1638 Mod. (ICP-MS)	0.015 mg/kg	0.05 mg/kg
Total Selenium	1638 Mod. (ICP-MS)	0.04 mg/kg	0.13 mg/kg
Total Mercury	1631 (CVAF), Appendix D	0.04 ng/g	0.10 ng/g
% Solids	160.3	0.15%	0.5%

mg/kg = milligrams per kilogram, ng/g = nanograms per gram

Table 5 lists the analytical methods used in this study and typical instrumental detection and quantitation limits for water sample analyses. These limits apply to low concentration samples. Samples with high analyte concentrations require dilution, which effectively raises the detection limit for those samples, but ability to detect or quantitate the analyte is not an issue with high concentrations. Note that total mercury and methylmercury limits are expressed in ng/L, a thousandfold less than the µg/L units used for the other analytes.

Table 5. Methods of Analysis and Detection Limits for Water

Analyte	EPA Method	Detection Limit	Practical Quantitation Limit
Inorganic Arsenic	1632 (HGAA)	0.008 µg/L	0.025 µg/L
Total Arsenic	1638 Mod. (ICP-MS)	0.06 µg/L	0.2 µg/L
Total Selenium	1638 Mod. (ICP-MS)	0.09 µg/L	0.3 µg/L
Total Mercury	1631 (CVAF)	0.15 ng/L	0.4 ng/L
Methylmercury	1630	0.02 ng/L	0.05 ng/L

µg/L = micrograms per liter, ng/L = nanograms per liter

The following sections provide summaries of laboratory QC results by sample type.

Laboratory Blanks

A blank is a check for possible contamination of samples. Contamination, if present, would impart a high bias to results, the effect of which would be more pronounced at lower sample concentrations. All results reported by Brooks Rand Laboratories were method blank corrected per the laboratory's standard operating procedure.

For fish tissue, there were both method blanks and digestion blanks generated by the laboratory, with analytical results below the DL for all analytes.

For water, there were only method blanks. All results for methylmercury and total arsenic were below the DL. Two of twelve batches had a method blank with detectable total mercury, but the lowest sample result was greater than five times the result from the blank. Three of eleven batches had a method blank with detectable inorganic arsenic of 0.009 µg/L; all associated samples were more than ten times higher. Three of these eleven batches also had a method blank with detectable selenium, the highest being 0.13 µg/L in batch 12. The two selenium results in this batch were 0.10 µg/L (Salmon River, site 012) and 0.12 µg/L (Payette River, site 063), and are flagged as estimated results because they are between the DL and the PQL. Many of the sample selenium results were near or below the DL.

There were no other issues with contamination of blanks that would qualify any of the sample analysis results.

Laboratory Duplicates/Precision of Measurement

Analysis of duplicates measures the reproducibility or precision of results. Precision is expressed as the RPD between two duplicate samples as described in the QAPP. Sample differences less than measured precision may be due entirely to variability introduced by processing and measurement and should not be considered real.

Laboratory precision of measurement for water samples was assessed exclusively through the use of matrix spike duplicates. All analysis results met the data quality objective (DQO) for precision of less than 25% RPD for water. Laboratory precision for water samples, expressed as RPD, is summarized in Table 6.

Table 6. Precision (as Relative Percent Difference) for Water Matrix Spike / Matrix Spike Duplicates

	MeHg	Hg	As(i)	As(T)	Se
DQO	< 25%	< 25%	< 25%	< 25%	< 25%
Min	1%	0%	1%	0%	0%
Max	11%	18%	8%	4%	17%
n	13	14	12	13	11
Mean	4%	5%	4%	2%	4%

< denotes result less than detection limit, ~ denotes result above detection limit but below practical quantitation limit.

DQO = data quality objective, Me-Hg = methylmercury, Hg = total mercury, As(i) = inorganic arsenic, As(T) = total arsenic, Se = total selenium.

For fish tissue samples, laboratory precision was assessed through both matrix spike duplicates (measuring analytical precision) and method duplicates generated by digestion of two subsamples of tissue (measuring process precision). Samples for which results are below the DL cannot be used to calculate an RPD. This was the case for all ten inorganic arsenic and three of the ten total arsenic fish tissue method duplicates. All measurable results met the DQOs for precision of less than 30% for analysis (matrix spike / matrix spike duplicate) and less than 40% for preparation and analysis of fish tissue samples (method duplicates) specified in the QAPP.

Laboratory precision for fish tissue samples is summarized in Table 7 and Table 8.

Table 7. Precision (as Relative Percent Difference) for Fish Tissue Matrix Spike / Matrix Spike Duplicates

	Hg	As(i)	As(T)	Se
DQO	< 30%	< 30%	< 30%	< 30%
Min	0%	0%	1%	1%
Max	14%	27%	12%	12%
n	9	10	10	10
Mean	6%	13%	4%	6%

< denotes result less than detection limit, ~ denotes result above detection limit but below practical quantitation limit.

DQO = data quality objective, Hg = total mercury, As(i) = inorganic arsenic, As(T) = total arsenic, Se = total selenium.

Table 8. Precision (as Relative Percent Difference) for Fish Tissue Method Duplicates

	Hg	As(i)	As(T)	Se
DQO	<40%	<40%	<40%	<40%
Min	0%	nc	0%	1%
Max	15%	nc	13%	10%
n	10	0	7	10
Mean	6%	nc	5%	5%

< denotes result less than detection limit, ~ denotes result above detection limit but below practical quantitation limit.
DQO = data quality objective, Hg = total mercury, As(i) = inorganic arsenic, As(T) = total arsenic, Se = total selenium.

Comparing the results from Table 7 and Table 8 shows that subsampling and digestion of fish tissue sample in the laboratory did not add to imprecision in the results.

Certified Reference Materials/Accuracy of Analysis

A laboratory's measurement accuracy is best judged based on its analysis of a reference material for which the true value is known.⁴ Such materials are not always available for all matrices (e.g., fish, water) and all analytes. When a reference material is not available, matrix spikes are typically used to assess laboratory accuracy of analysis. In this project, a combination of matrix spikes and reference materials was employed. The QC results are expressed as a percent recovery of the known value and are summarized in the following tables.

Table 9. Accuracy of Water Analyses, Expressed as Percent Recovery of the Known Value

	Me-Hg		Hg		As(i)		As(T)		Se	
DQO	65-135%		75-125%		65-135%		75-125%		75-125%	
	Spikes	CRM	Spikes	CRM	Spikes	CRM	Spikes	CRM	Spikes	CRM
Min	84%	75%	92%	89%	74%	na	82%	91%	76%	90%
Max	116%	111%	120%	113%	113%	na	111%	97%	117%	101%
n	26	18	28	13	24	0	24	11	24	10
Mean	103%	98%	105%	101%	94%	na	103%	93%	100%	96%

DQO = data quality objective, Me-Hg = methylmercury, Hg = total mercury, As(i) = inorganic arsenic, As(T) = total arsenic, Se = total selenium, CRM = certified reference material.

Percent recoveries for all analytes in water were within DQOs and overall show no systematic bias in the results for water samples.

⁴ Since most analytical methods of analysis are comparative, so-called "known" values in matrix materials such as fish are usually average values of round-robin analysis from several laboratories that conform to certain accreditation requirements of a certifying authority such as the National Institute of Standards and Technology.

Table 10. Accuracy of Fish Tissue Analyses, Expressed as Percent Recovery of the Known Value

	Hg		As(i)		As(T)		Se	
DQO	75-125%		75-125%		75-125%		70-130%	
	Spikes	CRM	Spikes	CRM	Spikes	CRM	Spikes	CRM
Min	92%	88%	72%	92%	92%	85%	75%	92%
Max	120%	121%	109%	123%	111%	104%	103%	114%
n	19	10	20	10	20	14	20	14
Mean	106%	112%	91%	100%	99%	93%	91%	99%

DQO = data quality objective, Hg = total mercury, As(i) = inorganic arsenic, As(T) = total arsenic, Se = total selenium, CRM = certified reference material.

Except for matrix spike recovery for inorganic arsenic in fish tissue, which had values between 70% and 75% on three occasions, percent recoveries easily met DQOs. All CRM results for inorganic arsenic met data quality objectives, and no fish tissue data were qualified as biased. Overall, the accuracy was excellent and showed no systematic bias in the fish tissue analysis results.

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Part D. Analytical Results for Water and Fish Tissue from Rivers

Sites Sampled

Figure 3 shows the river sites that were randomly sampled in 2006 and 2008. There were 100 sites in the random sample draw (Appendix A) from which we hoped to sample 50 sites. Fifty-one sites were ultimately rejected because they were not reasonably accessible or they did not qualify as river sites (e.g., a site located in an impoundment). To be reasonably accessible, there had to be put-in and take-out locations for a boat that were close enough to the target reach to make it possible to complete the sampling in one day.

Overall, 49 sites were sampled—25 in 2006 and 24 more in 2008. The 2008 effort also involved revisiting 10 of the sites first sampled in 2006. These were sites from which we obtained macroinvertebrate and periphyton samples for biologic monitoring in 2006, but failed to obtain fish for mercury analysis. In 2008, these 10 sites were therefore rescheduled for a second attempt at fish sampling. Where we re-sampled fish in 2008, water was sampled as well.

A list of river sites sampled by number and name, with information on their location, is in Appendix B.

Fish Tissue Sites

Unlike water sampling, in which planned samples are almost always obtained, sampling fish is more opportunistic, a “take what you can get” proposition.

Although 25 sites were visited in 2006, fish were obtained from only 15. The other 10 sites were added to the 2008 list of 24 sites, making 34 sites to be sampled for fish and water in 2008. We were not allowed to sample the South Fork Salmon River site in 2008 due to the presence of spawning Chinook salmon. Eight other sites yielded no fish suitable for mercury analysis.

In the end, over both years, 40 sites yielded fish tissue samples—15 in 2006, plus 25 in 2008.

Water Sites

Sampling of water was conducted in 2008 only, and 34 sites were sampled. This consists of 24 “new” sites not sampled at all in 2006, plus the 10 sites initially visited in 2006 that we revisited in 2008 to reattempt fish sampling.

Table 11 provides a breakdown of the samples obtained during our two-year sampling effort.

Table 11. Summary of Samples Obtained in 2006 and 2008

	2006	2008	Combined
Sites visited	25	34 ^a	49
Fish tissue only	15	na	15
No fish tissue or water	10	na	none
Water only	na	9	9
Fish tissue and water	na	25	25

^a Includes 10 sites from 2006 re-sampled for fish only in 2008, for a total of 49 sites visited in two years.

na = not applicable

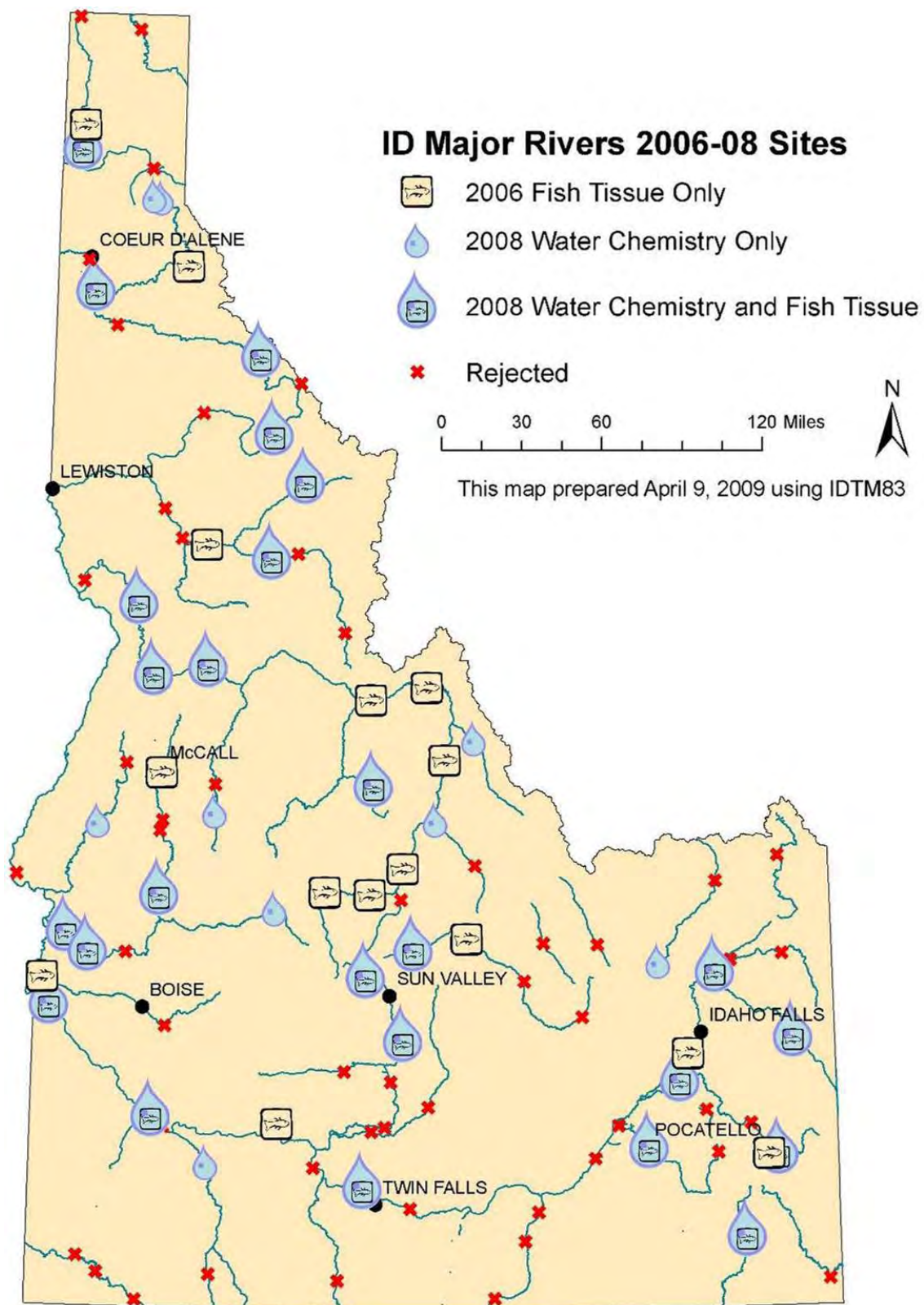


Figure 3. River Sites Sampled in 2006 and 2008

Fish Tissue Samples

Because a site may have more than one fish species, the 25 sites sampled in 2008 provided a total of 55 composite fish tissue samples, including 4 duplicate samples. Altogether, 16 species of fish were sampled. The most frequently sampled species was mountain whitefish (10 samples), followed by smallmouth bass (8 samples), and cutthroat trout and northern pikeminnow (7 samples each). The fact that different species of fish were collected confounds comparison of sites to each other because different species accumulate mercury at different rates; higher levels of mercury in fish from a particular site could be due as much or more to the species present than to greater rates of mercury loading.

Two species we caught at one river site—black crappie and largemouth bass—are typically only found in lakes. This site was on the Coeur d’Alene River as it slackens and enters Lake Coeur d’Alene. In retrospect, this site should probably not have been sampled as a river site. Table 12 summarizes the fish tissue samples by species.

Table 12. Number of Fish Tissue Samples by Species

Species	# of samples
Black crappie	1
Bridgelip sucker	2+1 duplicate
Brook trout	3
Brown trout	2
Common carp	2
Cutthroat trout	7+3 duplicates
Cutthroat x rainbow trout	1
Kokanee	1
Largemouth bass	1
Largescale sucker	5
Mountain whitefish	10
Northern pikeminnow	1
Rainbow trout	4
Smallmouth bass	8
Utah sucker	2
Yellow perch	1
Total	51+4 duplicates

Abundance of fish also varied greatly by site. This is reflected in the fact that the number of fish making up a composite sample ranged from the desired 10 fish (in only 11 of the 55 samples) to as few as one fish (in 9 samples). A composite sample of less than 10 fish is likely not as representative of average contaminant levels at a site as a composite sample of 10 fish. As few as one fish per sample was accepted, because we assumed some data were better than none. Results from all 55 samples, regardless of number of fish in the composite, are reported here.

A summary of the number of fish per species and the average weight and length per composite tissue sample is in Appendix D. Individual fish weights and lengths were recorded in a database, which is available upon request from DEQ on a data CD .

Fish size varied considerably, driven by what was available to be caught. It is known that older (larger) fish accumulate more mercury and other contaminants as well (EPA 2001). An example of this is illustrated in Figure 4 with data from a USGS project known as EMMMA

(Environmental Mercury Mapping, Modeling, and Analysis) (USGS 2008; Wentz 2004). Using fish tissue mercury levels to assess mercury contamination is further confounded by this relation of bioaccumulation to fish age (size), but this does not matter when assessing public health risk. Had we been able to afford analysis of individual fish and caught sufficient individuals of a range in size, we could regress fish size versus contaminant concentration and thus normalize tissue contaminant levels for the influence of size, at least for the species more commonly encountered. Instead, all we can say is that difference in species and fish size (age) from site to site affects the results, making observed fish tissue mercury levels a poor gauge of relative site contamination levels.

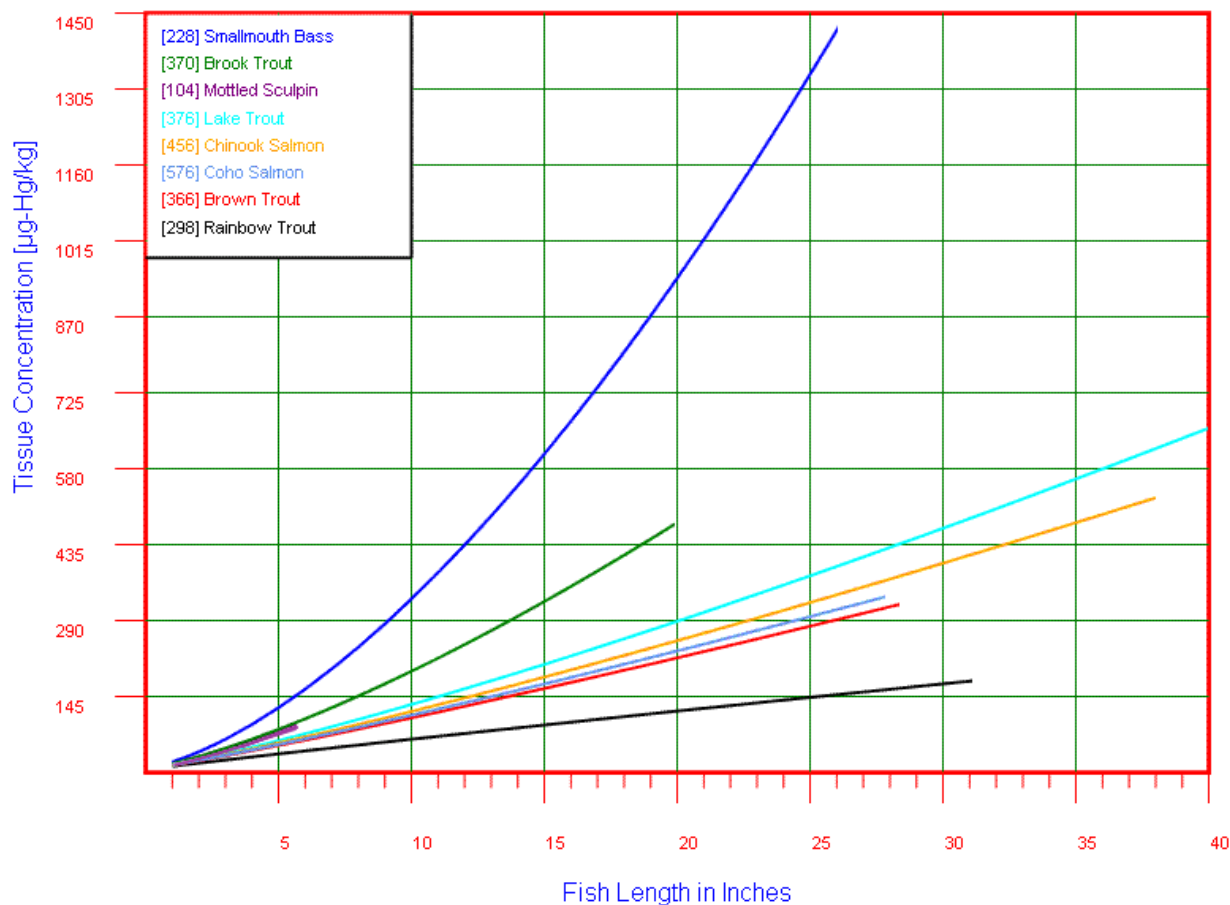


Figure 4. Example of Differences in Tissue Mercury Content by Species and Size of Fish, for Snake River at Lewiston, generated using USGS EMMMA

Mercury, Arsenic, and Selenium Levels in Fish Tissue

Table 13 summarizes results by analyte for the 55 fish tissue samples obtained in 2008.

Table 13. Frequency of Detection and Descriptive Statistics of 2008 Fish Tissue Contaminant Levels

	Hg	As(i)	As(T)	Se	% solids
# >PQL	54	0	34	41	55
# <PQL but >DL	1	1	11	13	0
# <DL	0	54	10	1	0
	Hg ng/g	As(i) mg/kg	As(T) mg/kg	Se mg/kg	
Mean	160	na	0.073 ^a	0.44 ^a	21.2
Max	674	0.006	0.309	3.08	27.9
Min	29	<0.002	<0.013	0.04	14.7
Median	123	<0.002	0.058	0.27	21.1

PQL = practical quantitation limit, DL = detection limit, Hg = total mercury, As(i) = inorganic arsenic, As(T) = total arsenic, Se = total selenium, ng/g = nanograms per gram, mg/kg = milligrams per kilogram.

^a The mean was calculated by substituting the detection limit value for each value that was below the detection limit.

The median is the concentration value at which 50% of the samples have a greater concentration and 50% have a smaller concentration. In other words, if you went to one of our target river sites and collected game fish of catchable size as we did, you would expect a fifty-fifty chance of getting a sample with a concentration greater than the median. With almost all the values below the DL for arsenic, all we can say is that the median is below the DL as well.

The mean is the arithmetic average of all samples. It is the concentration of a contaminant you would be exposed to if you were to eat equal quantities of all the fish samples that went into calculation of the mean. Concentrations less than DLs preclude calculation of an unbiased mean for all samples. There are several ways to handle this, and the author chose to calculate means by substituting the DL value for each result that was below the DL. This biases the mean high. As is typical for environmental measurements, the distribution of results is right-skewed, that is, there are a few very high results that stretch the distribution to the high side and “pull” the mean above the median. Thus, composite tissue concentrations are more likely to be less than the mean.

Results of individual composite tissue analyses are provided in Appendix E, Table E-2.

Contaminant levels are summarized by analyte in the following sections. For mercury only, results from 2008 alone are presented first and then the combined results for 2006 and 2008.

2008 Mercury

None of the 2008 mercury analysis results were below the DL, and only one sample result was below the PQL; thus, overall good quantitation of mercury levels in fish tissue was achieved. Five of the 55 river fish samples (9%) had mercury levels greater than the criterion of 300 ng/g (0.3 mg/kg). Table 14 provides a breakdown by species for those five samples.

Table 14. Fish Samples with Mercury Concentrations Greater than the Human Health Criterion^a

Species	Site name	Site Number	Hg ng/g
Northern pike minnow	Salmon River #1	040	674
Largemouth bass	Coeur d'Alene River #1	030	572
Smallmouth bass	Salmon River #2	025	548
Smallmouth bass	Salmon River #3	012	380
Largemouth bass	Snake River #3	095	318

^a The criterion is for methylmercury, even though this data reports total mercury.

ng/g = nanograms per gram

All three species represented in these five samples are piscivorous (fish-eating); the bass are also considered warmwater species. Such species are known to be better accumulators of mercury than insectivorous cold water species such as trout that inhabit many of Idaho's rivers. Of the 10 cutthroat trout, 10 mountain whitefish, and 4 rainbow trout samples also obtained, none had mercury concentrations greater than the criterion.

To calculate percentiles for sites rather than samples, it is necessary to collapse the results from sites with multiple species to one result per site. It is important to understand that this means the percentage of samples with concentrations above a threshold, e.g., the methylmercury human health criterion, will differ from the percentage of sites with results above that threshold. Due to multiple species (samples) from some sites and lack of samples from other sites, the 55 samples represent only 25 sites. Since each sample with a concentration greater than the criterion in the present data set was from a different river site, those five samples translate to 5 of 25 river sites (20%) with mercury levels in fish tissue greater than the criterion. Although it did not happen in the 2008 river monitoring, it is possible that multiple species/samples from a site could have concentrations greater than the criterion.

Idaho's criterion for mercury in fish tissue is based upon averaging results from multiple species at a site, using trophic level weighting. (An organism's trophic level refers to its status in the food chain.) The purpose of trophic level weighting is to account for the different fish we eat and the fact that fish from a higher trophic level typically attain higher levels of mercury by virtue of the biomagnification from prey to consumer at each trophic level. We employ trophic level generalizations—all piscivorous fish such as bass, brown trout, brook trout, and northern pikeminnow are trophic level 4; all insectivorous fish, like most trout, are trophic level 3. Kokanee, which feed primarily on plankton, are trophic level 2. These nominal trophic levels are an idealization of a species' position in a food chain or pyramid, a position that in reality is likely a blend and can shift with time and place. Bass, eating a diet of kokanee and rainbow trout, have a trophic level somewhere between 3 and 4.

Knowledge of Idaho fish consumption preferences as a whole, much less for a particular river or local population of consumers, is absent. So we also use fish consumption defaults. Of the estimated 17.5 grams per day of fish an adult in the United States is expected to eat, 3.8 grams would be fish at trophic level 2, 8.0 grams would be fish at trophic level 3, and 5.7 grams would be fish at trophic level 4. These numbers do not represent the expected fish consumption every day for every person, but an average.⁵

Putting all this together with the present fish tissue data, the trophic level weighted averages for each of the five sites with a sample concentration greater than the criterion for mercury are given in Table 15. At three of those sites, Idaho's criterion was exceeded.

Table 15. Trophic Level Weighted Average Fish Mercury for 2008 Sites with Sample Concentrations Greater than the Criterion

Site Name	Site #	Species	Hg ng/g
Salmon River #1	040	Mountain whitefish, northern pike minnow & smallmouth bass	249
Coeur d'Alene River #1	030	Largemouth bass & black crappie	401
Salmon River #2	028	Mountain whitefish & smallmouth bass	311
Salmon River #3	012	Smallmouth bass (only species)	380
Snake River #3	095	Largescale sucker & smallmouth bass	243

ng/g = nanograms per gram

⁵ This consumption rate and trophic level breakdown is the basis of EPA's 2001 methylmercury criterion and represents the 90th percentile consumption rate for the general population of the United States as a whole.

2006-2008 Mercury

In 2006, 21 fish tissue samples were obtained from 15 major river sites. These results are reported in Adams (2008) and summarized here. Three samples each from three different sites in 2006 had mercury concentrations greater than the methylmercury human health criterion of 300 ng/g. The highest mercury concentration in 2006, and over both years, was 1,110 ng/g in a sample of northern pikeminnow from the Salmon River at Deadwater below North Fork, Idaho (site 008). Suckers and mountain whitefish were also obtained from that site, and the trophic level weighted average concentration for the site is 573 ng/g. Two other 2006 samples with concentrations greater than the criterion consisted of suckers, one from the Salmon River upstream of Salmon, Idaho, at 302 ng/g (site 016, site average with mountain whitefish of 253 ng/g) and one from the Snake River near Shelley, Idaho at 317 ng/g (site 081, single species).

Fish tissue mercury concentrations for major river sites sampled in 2006 and 2008 are mapped in Figure 5. To represent sites with more than one sample we used the average level of mercury. In the combined 2006 and 2008 data, 8 out of 40 sites (20%) had at least one sample with a mercury concentration greater than the methylmercury criterion. This fraction is less than the 20 of 50 lakes (40%) with at least one species (sample) with a concentration greater than the criterion found in 2007 (Essig and Kosterman 2008). Over both years of river sampling, 8 of 76 fish samples (11%) from major rivers had concentrations greater than the criterion. This compares to the 26 of 89 (29%) of samples with concentrations greater than the criterion found in the 2007 sampling of lakes and reservoirs.

For purposes of making probabilistic statements about mercury levels in fish tissue from all major rivers in Idaho, the mercury level at each site was characterized as the average of sample concentrations for a site. It was further necessary to weight each site in our random sample by its selection weighting. This was done using the R-Statistics package. The resulting cumulative frequency distribution is shown in Appendix H, along with cumulative distribution functions for other analytes. From this distribution, it is estimated that 15% (95% confidence bounds of 7% to 24%) of the miles of major rivers in Idaho have fish with an average tissue mercury content greater than 300 ng/g. Because the basic sampling unit (the basis for random draw) was a site on the river network, not a fish sample, it would be inappropriate to similarly extrapolate results for the fish tissue samples.

In summary, mercury contamination of fish tissue in Idaho's major rivers is less common than in Idaho lakes and appears to be primarily limited to piscivorous species. While the number of sites is small and species sampled varies, the occurrence of mercury contamination of fish from major rivers appears to be most common in the Salmon River.

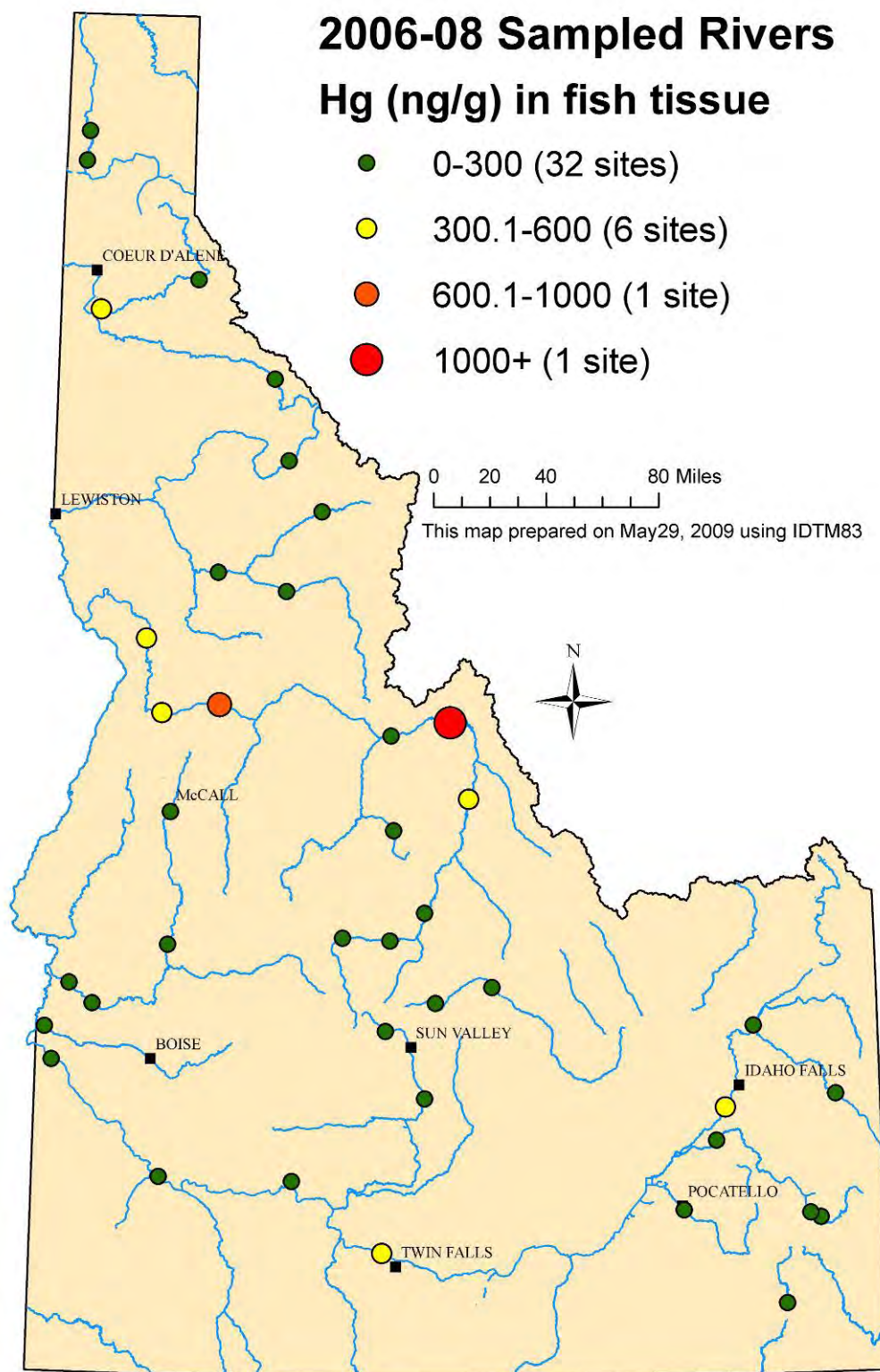


Figure 5. Mercury Concentrations in Fish Tissue, 2006 and 2008 Combined

Arsenic, Inorganic

All but one of the 55 tissue samples in this study had no detectable inorganic arsenic, even though the detection limit was very low, at 0.002 mg/kg. No descriptive statistics or probabilities of exceedance can be calculated.

So what can we say with this data about inorganic arsenic in fish tissue from Idaho rivers? While there is not a fish tissue criterion for inorganic arsenic, there is a human health criterion for inorganic arsenic in water that is based on consumption of fish tissue contaminated with inorganic arsenic. That criterion is 0.14 µg/L and it was calculated by EPA using 1) a fish consumption rate of 6.5 g/day, 2) an inorganic arsenic dose known to be associated with adverse human health effects, and 3) a bioconcentration factor (BCF) of 44 (EPA 2000b; EPA 2002b). We can use this BCF in reverse, from water to tissue, to calculate a fish tissue inorganic arsenic level of 0.006 mg/kg that would be expected to result from water containing mercury at the criterion level of 0.14 µg/L. This approach is taken by the Washington State Department of Ecology to use fish tissue monitoring to indicate compliance with water toxics criteria.

One sample in this study, for rainbow trout from site 011 on the upper Big Wood River, had inorganic arsenic that reached the level of 0.006 mg/kg. This site is near Easley Hot Springs. Since all remaining samples had concentrations that were one-third this value or less (DL = < 0.002 mg/kg), evidence is strong that there is not widespread inorganic arsenic contamination in fish from Idaho's major rivers.

Arsenic, Total

Total arsenic analysis results were also low, with 10 of the 55 fish tissue samples having a total arsenic concentration less than the DL of 0.013 mg/kg. The median concentration of total arsenic in fish was 0.058 mg/kg. The highest total arsenic concentration observed was 0.309 mg/kg for largescale suckers from site 083 on the Snake River.

Again, there is not a fish tissue criterion to compare these results to. As we did for inorganic arsenic, if we assume the BCF of 44 from the “fish only” criterion for inorganic arsenic holds as well for total arsenic, it is possible to back-calculate from fish tissue total arsenic to the equivalent total arsenic in water. Doing so, our maximum observed total arsenic in fish value equates to a water total arsenic concentration of 7 µg/L.

For comparison, the current human health criterion in Idaho is 50 µg/L inorganic arsenic, and the state has proposed to lower this to 10 µg/L in rulemaking that was announced for public comment on May 6, 2009 (Idaho Administrative Bulletin 2009). The drinking water maximum contaminant level is 10 µg/L total arsenic. Although these criteria are useful for putting the present results into perspective, comparisons should be viewed with great caution, as it is known that much of the arsenic in fish tissue is organic rather than inorganic, and that water-borne arsenic is mostly inorganic⁶ (EPA 2002a; EPA 2003). This study found that, on average, more than 96% of the arsenic in fish is organic.

The current arsenic BCF of 44 is a consumption-weighted average between a BCF of 350, for a marine oyster, and a BCF of 1, representing edible portions of all freshwater aquatic organisms,

⁶ As with mercury, evidence indicates that 85–90% of arsenic in fish tissue is organic arsenic, leaving 10–15% as inorganic (EPA 2002a; EPA 2003). In contrast to mercury, the inorganic form of arsenic is thought to be more toxic than the organic form (ASTDR 2007).

such as rainbow trout (EPA 1980). Rainbow trout does occur in Idaho; marine oysters do not. A lower BCF—the 1980 criterion document states “the BCF for arsenic is probably about 1.0 for many aquatic animals”—may be more appropriate to Idaho waters and the fish they support. A lower BCF would change the calculated equivalencies above and increase the arsenic in water criterion value.

Data from concurrent water and fish tissue sampling conducted in this study suggest a bioaccumulation factor (BAF) of 143 for total arsenic, and only 11 for inorganic arsenic. These results will be more fully discussed later.

Selenium

For selenium, all but one sample result had a concentration greater than the DL. In 13 other samples, the selenium concentration was greater than the DL but less than the PQL. This provides sufficient data to construct a cumulative frequency distribution (see appendix H), and from this we can determine that only about 8% of rivers have fish with selenium tissue concentrations of 1 mg/kg or more, on a fresh weight basis. The highest value was 3.08 mg/kg for cutthroat trout from the upper Blackfoot River (Site 037) above Blackfoot Reservoir and upstream of the Highway 34 bridge. In general, the highest fish tissue selenium levels were observed in southeast Idaho, and the lowest levels were found in fish from streams draining the batholith region of central Idaho.

As with arsenic, there are currently no fish tissue criteria for selenium. EPA is working on a selenium fish tissue criterion for protection of aquatic life, and proposed a criterion in November 2004 (EPA 2004). That proposed criterion is 7.91 mg/kg, on a dry weight basis. This was known in planning this study, but because mercury was our top priority and its criterion is expressed on a wet weight basis, and because the cost of dual analyses was beyond the budget and would have required splitting samples, the selenium results are wet weight basis. To allow post-analysis conversion of wet weight selenium results to a dry weight basis, we also had the percentage of solids in each sample (percent solids) determined. Percent solids ranged from 14.7% for rainbow trout from the North Fork Payette River to 27.9% for largescale sucker from the Snake River near Grandview, Idaho. The mean for all 55 samples was 21.2% solids. Conservatively rounding the mean down to 20% provides a “rule of thumb” factor of 5, which can be used to multiply wet weight selenium results and get equivalent dry weight results (to go the other way, divide by 5).

Looking specifically at our highest selenium result (cutthroat trout from the Blackfoot River with 21.0% percent solids), we get an equivalent dry weight selenium value of 14.7 mg/kg, nearly double EPA’s 2004 proposed selenium criterion.

The Blackfoot River drainage in the southeast corner of Idaho includes known phosphoria formations and active phosphate mining. Selenium is associated with these geologic formations and is often mobilized through mining. East Mill Creek in the upper Blackfoot watershed, upstream of site 037, is well known for its very high selenium values and has Idaho’s only fish consumption advisory for selenium (IFCAP 2009). Thus, the high selenium in fish from the Blackfoot River is no surprise and makes sense geographically. Overall, these results indicate that selenium contamination is not widespread in Idaho’s major rivers represented by this study. However, this does not mean that selenium contamination is not a concern in some locales.

Levels of Mercury, Arsenic, and Selenium in River Water

All water samples were unfiltered surface grabs from a well-mixed portion of the stream flow. Table 16 summarizes results by analyte for the 34 water samples obtained from Idaho's major rivers in 2008. Results for all samples are provided in Appendix E, Table E-1.

Table 16. Summary of Contaminant Levels in Water Samples

	Hg ng/L	Me-Hg ng/L	Me-Hg^a	As(T) µg/L	As(i) µg/L	Inorganic As^b	Se µg/L
Mean	4.00	0.071	9%	2.30	1.75	73%	0.43
Max	110	0.199	18%	17.0	12.0	100%	1.75
Min	0.17	< 0.020	0.2%	0.06	0.02	25%	< 0.09
Median	0.77	0.07	8%	1.12	0.84	76%	0.14
# @ < DL		9 @ < 0.02					14 @ < 0.09

^a Fraction of total mercury that is methylmercury. ^b Fraction of total arsenic that is inorganic.

Hg = total mercury, Me-Hg = methylmercury, As(T) = total arsenic, As(i) = inorganic arsenic, Se = total selenium, ng/L = nanograms per liter, µg/L = micrograms per liter, DL = detection limit.

The maximum total mercury result of 110 ng/L is from site 030 on the Coeur d'Alene River as it enters Lake Coeur d'Alene (site 30). If this extreme result is excluded, the mean total mercury for the remaining 33 sites drops to 0.79 ng/L, nearly the same as the median result. Site 30 was re-sampled and this is discussed below.

Total Mercury

Water total mercury concentrations for all major river sites sampled are mapped in Figure 6.

The total mercury result of 110 ng/L for site 30 (Coeur d'Alene River #1) is more than 50 times higher than any other result in this study and suggested possible contamination. However, all the associated QC samples met quality objectives, and checks with the laboratory and the field notes revealed nothing unusual. Upon further inquiry, it was learned that this sample is from an area of slackening water with bank erosion from boat wakes, and that the sample was collected on Saturday August 2, 2008, a time when boat activity would have been high. Although we have no data on turbidity at the time, the above knowledge of the site leads to the suspicion of high turbidity in the sample and mercury attached to fine particles as the cause of the anomalously high mercury level. To investigate this possibility and confirm or refute the high result, it was decided to resample water from this site and have it analyzed for both total and dissolved mercury.

Site 30 was re-sampled, in duplicate, on October 23, 2008. Total mercury in these two samples was 6.21 and 4.78 ng/L, with an average of 5.50 ng/L—still the highest among all sites but a factor of 20 lower than in the earlier August sample. By special request, an un-acidified portion of the samples was filtered at the laboratory for dissolved mercury analysis. The dissolved mercury analysis results were 0.68 and 0.53 ng/L respectively, or approximately 10% of each total mercury result, showing that nearly 90% of the total mercury in the October samples was bound to particles that would not pass through a 0.45-micrometer (µm) filter. Thus, most of the mercury was associated with suspended or re-suspended sediment. A large fraction of particulate-bound mercury likely was the case in August as well. Brigham et al. (2009) found that total mercury concentrations correlated strongly with suspended sediment and dissolved organic carbon concentration in the water. In their study of eight streams monitored across all seasons they also observed the fraction of particulate mercury to vary from 3% to 92.5%. This is important to making sense of methylmercury bioaccumulation, as only the dissolved fraction of the total mercury is readily available to bacteria for methylation.

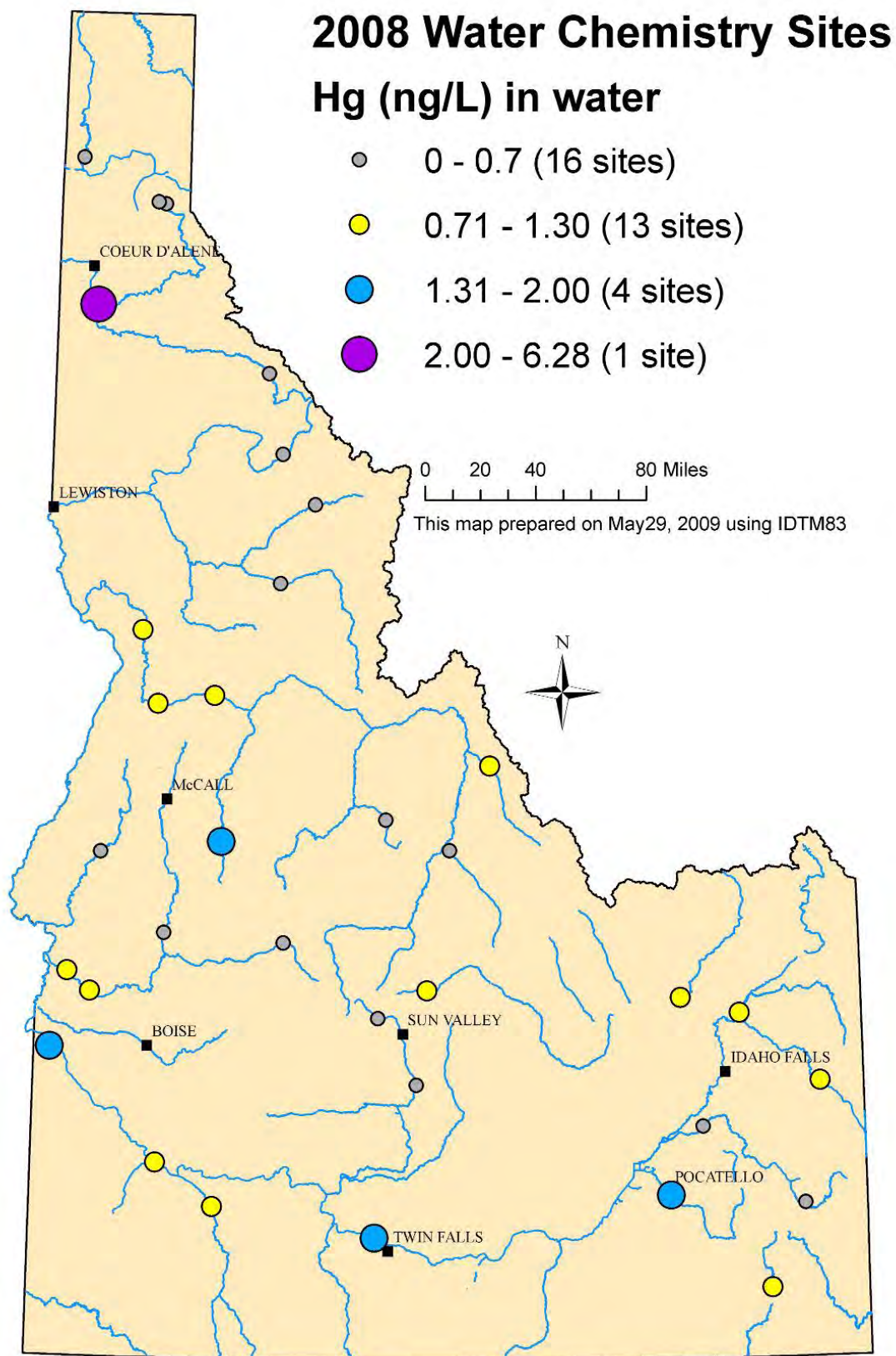


Figure 6. Map of Total Mercury in Water Concentrations

All other samples had less than 2 ng/L total mercury. The second highest result was 1.89 ng/L total mercury for the Portneuf River (site 085). For comparison, EPA's (1985) aquatic life chronic criterion for mercury currently applicable to Idaho waters is 12 ng/L as total mercury.⁷ Scudder et al. (2009) report the mean total mercury concentration in 352 streams nationwide to be 8.22 ng/L, with 90% of the sites having mercury concentrations less than 9 ng/L. Although the Scudder data are not probabilistic, it appears Idaho rivers have on average less than half the mercury than the nationwide average.

Methylmercury

Methylmercury is a more toxic form of mercury and strongly bioaccumulates in fish tissue; it is also the form of mercury that is regulated by the fish tissue criterion. There is no criterion for methylmercury applicable to water directly, but methylmercury levels in water are very important to mercury accumulation in fish. The proportion of total mercury that is methylmercury is a primary factor in explaining why sites with similar total mercury levels in water exhibit different levels of mercury in fish. It has been repeatedly observed that mercury levels in fish tissue correlate more strongly to concentrations of methylmercury in water than to concentrations of total mercury in water (Chasar et al. 2009; Scudder et al. 2009; Kelly et al. 1995). The lower variability in methylmercury versus total mercury BAFs found in this study supports this as well. Interestingly, Marvin-Dipasquale et al. (2009) reported no significant relation between methylmercury concentrations in water and those in underlying bed sediment and pore water. They concluded that upstream sources of methylmercury production, rather than local production, drive concentrations. Likely methylmercury producers are wetlands, landscape runoff, and reservoirs.

The fraction of water total mercury that was methylmercury in this study ranged from less than 1% for site 30, Coeur d'Alene River #1 (site of both highest total mercury and highest methylmercury in water) to 18% on the Blackfoot River. The methylmercury fraction by site in this study is shown in Figure 7. Methylmercury at site 30 declined from 0.199 ng/L in August (highest observed) to undetectable (less than 0.02 ng/L) in the October re-sample. Scudder et al. (2009) report the methyl/total mercury fraction to range from 0.02% to 41.0% with a mean of 3.24% for 352 stream sites across the United States. Food chains and total mercury being equivalent, a location with a higher percentage of total mercury as methylmercury would be expected to result in greater bioaccumulation of methylmercury in fish.

Water methylmercury analysis results for all major river sites sampled are mapped in Figure 8.

⁷ In 2005, DEQ had removed this old 1985 water criterion from its water quality standards in favor of the 2001 methylmercury fish tissue criterion. This water column criterion was reinstated by EPA disapproval action on December 12, 2008.

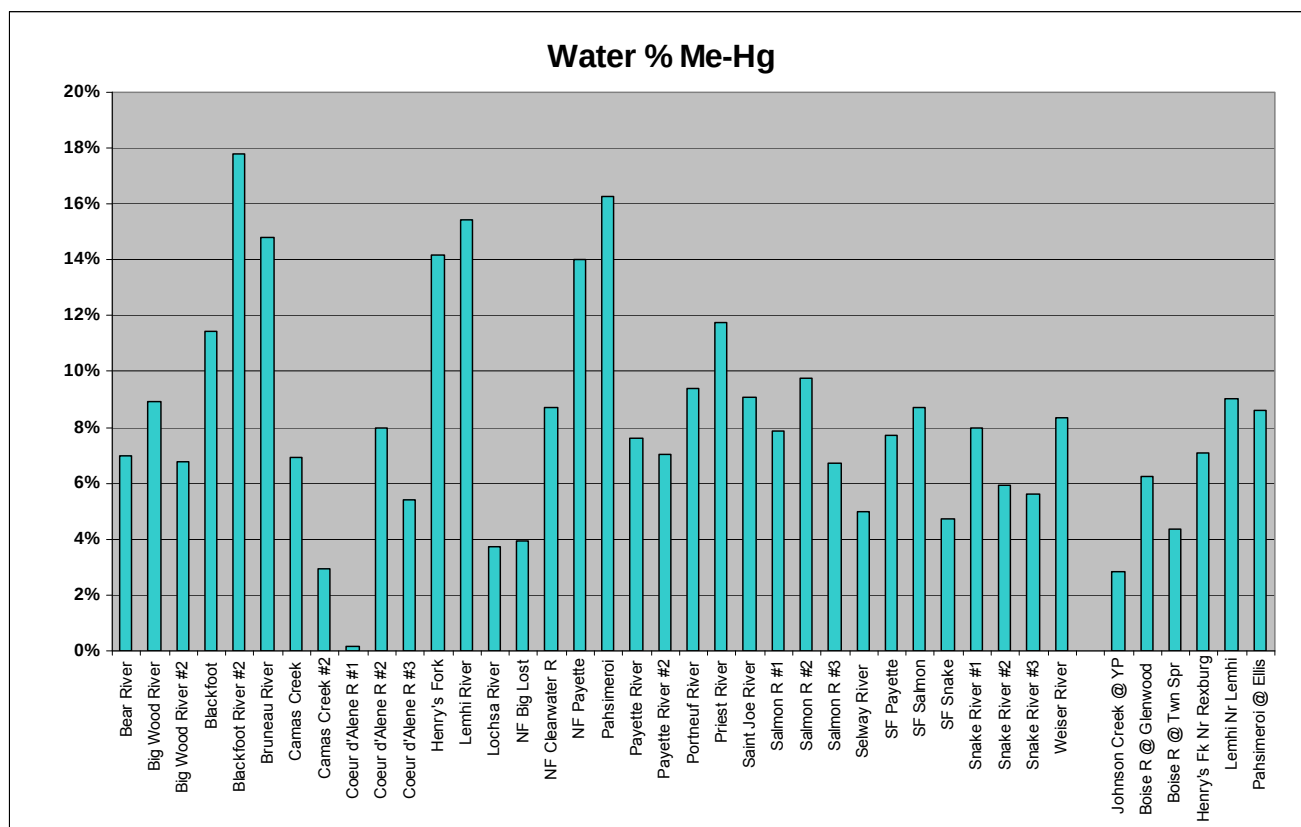


Figure 7. Fraction of Water Total Mercury that is Methylmercury (the first 34 sites shown are those that were planned for this study; the other six sites are those for which USGS provided samples)

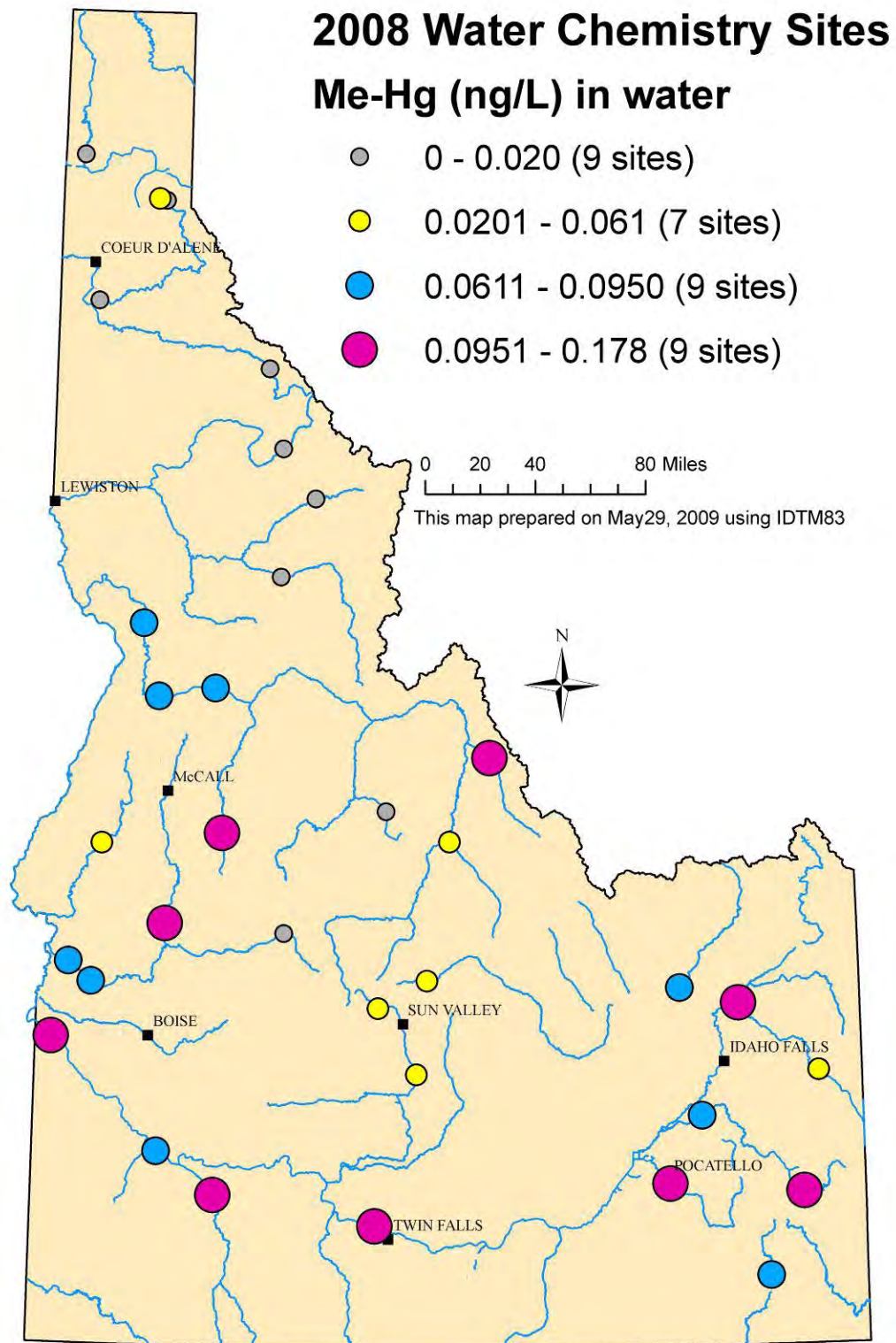


Figure 8. Map of Methylmercury in Water Concentrations

Total and Inorganic Arsenic

No sample had an arsenic concentration that exceeded Idaho's water quality criteria for arsenic (the lowest of which is 50 µg/L to protect human health). Inorganic arsenic is thought to be the more toxic form of arsenic to humans and is the form specified in Idaho's 50 µg/L human health criterion.

The highest total arsenic concentration of 17 µg/L was in the sample from the Bruneau River. The highest inorganic arsenic concentration of 12 µg/L was also in the Bruneau River sample. This was the only sample to exceed 10 µg/L, which is the drinking water maximum contaminant level and also the inorganic arsenic concentration Idaho has proposed for adoption as a surface water human health criterion.

Only two of the sites monitored had samples with concentrations less than the EPA-recommended arsenic criterion⁸ of 0.14 µg/L, which is recommended for protection of human health, applicable to cases in which the only route of exposure is the consumption of fish. No water samples had arsenic levels less than the companion criterion of 0.018 µg/L, which is recommended for cases in which exposure is both from drinking water and consuming fish from the same water body. Figure 9 shows the range in total and inorganic arsenic concentrations among sites.

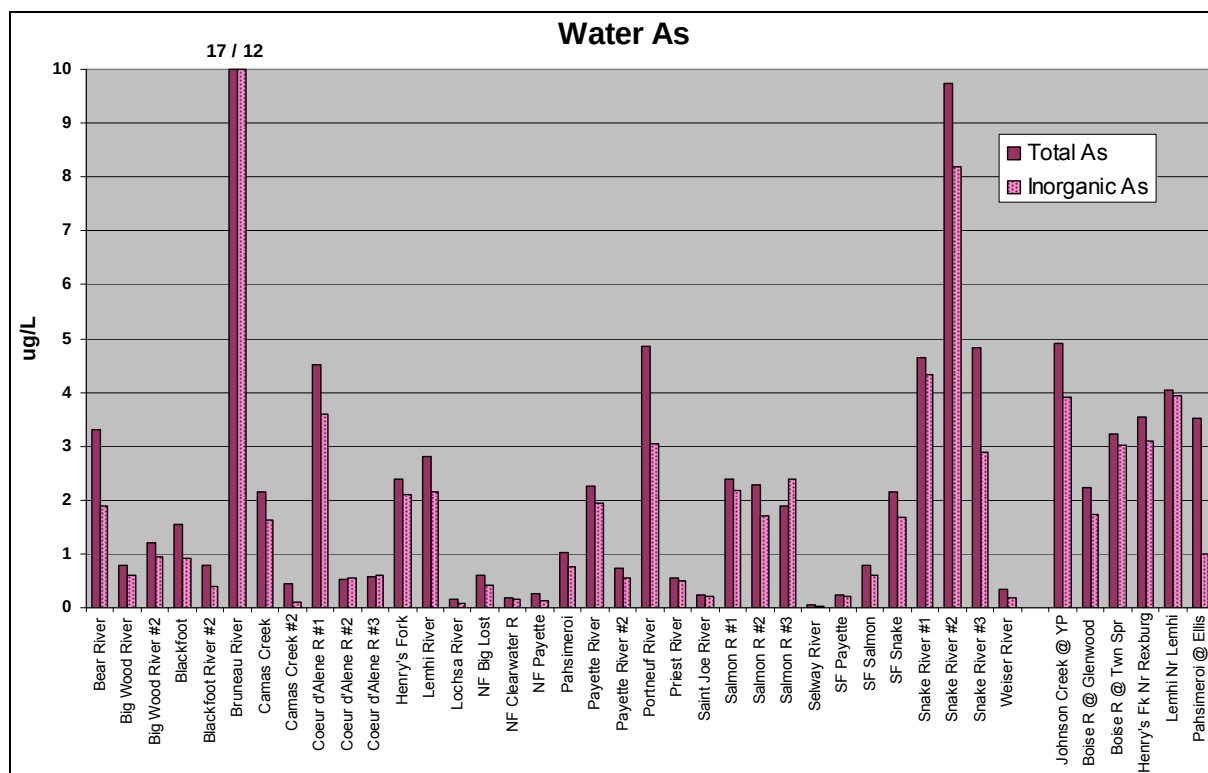


Figure 9. Total and Inorganic Arsenic (As) in Water (the first 34 sites shown are those that were planned for this study; the other six sites are those for which USGS provided samples)

⁸ See section 304(a) of the Clean Water Act. Note that the recommended criterion is for arsenic in water, not in fish, even though it relates to consumption of fish.

Although EPA's human health criteria are specific to inorganic arsenic, the form thought to be more toxic to humans, samples were analyzed for both total and inorganic arsenic to shed light on the fraction of arsenic that maybe in organic forms that perhaps do not contribute to arsenic toxicity. On average, most of the arsenic in waters sampled was in the inorganic form (73% on average). Idaho's current water quality criterion of 50 µg/L is specific to inorganic arsenic.

Selenium

No water samples had selenium concentrations that exceeded Idaho's aquatic life chronic selenium criterion of 5 µg/L. The highest total selenium result was 1.75 µg/L for a sample from the Snake River near Homedale, Idaho. The next highest was 1.57 µg/L for Blackfoot River #2, a site above Blackfoot Reservoir and close to phosphate mines. Nearly half the water samples analyzed had selenium concentrations below the detection limit (less than 0.09 µg/L) (Figure 10).

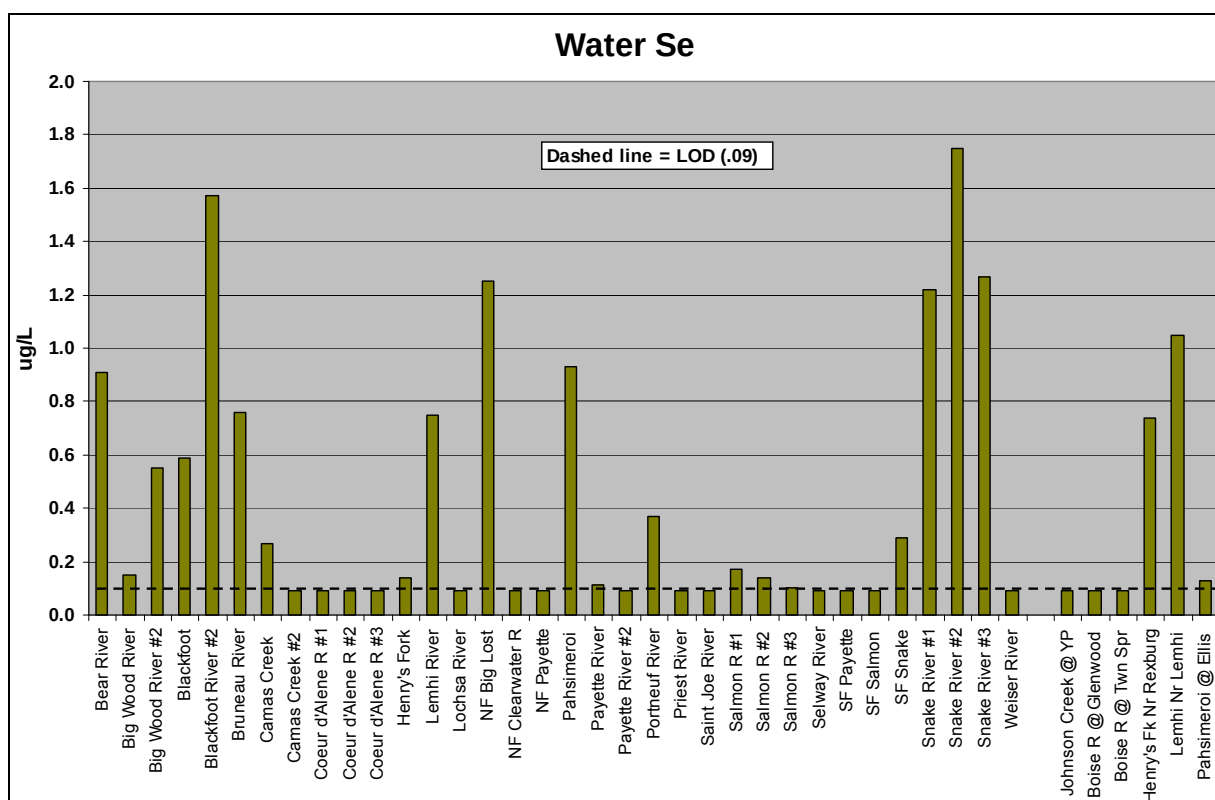


Figure 10. Total Selenium (Se) in Water (the first 34 sites shown are those that were planned for this study; the other six sites are those for which USGS provided samples) (LOD = limit of detection, also known as the detection limit)

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Part E. Analytical Results for Off-Project Monitoring

During the course of this project, two opportunities arose to obtain additional samples that were not part of the planned probabilistic monitoring. DEQ took advantage of these opportunities to augment the information provided by the planned sampling. These extra efforts and their results are presented here. Both were subject to the same QA and QC measures as the planned sampling.

Hatchery Chinook Salmon

Nine samples of Chinook salmon from five hatcheries in Idaho were provided to DEQ by the Idaho Department of Fish and Game so DEQ could assess the exposure to mercury that these stocked fish present to anglers in Idaho. Each sample consisted of three chunks of flesh from the thickest part of a fillet from each of three separate fish. All fish sampled were “3-ocean” fish—in other words, fish that had spent three years at sea before returning to Idaho to spawn. From four of the five hatcheries, we were provided separate samples of male and female fish; from the Clearwater Hatchery, only samples of female fish were received. The frozen samples were sent to DEQ’s contract laboratory, Brooks Rand LLC, for compositing and analysis in the same manner as all river project samples. Analytical results are given in Table 17.

Table 17. Hatchery Chinook Salmon Analytic Results

Hatchery	Sex	Mercury ng/g (µg/kg)	Arsenic (total) mg/kg	Arsenic (inorganic) mg/kg	Selenium mg/kg
Clearwater	F	141	0.24	< 0.002	0.16
McCall	F	151	0.17	< 0.002	0.16
McCall	M	131	0.23	< 0.002	0.17
Pahsimeroi	F	135	0.30	< 0.002	0.18
Pahsimeroi	M	138	0.27	< 0.002	0.15
Rapid River	F	134	0.18	< 0.002	0.23
Rapid River	M	158	0.41	< 0.002	0.21
Sawtooth	F	166	0.16	< 0.002	0.17
Sawtooth	M	191	0.25	< 0.002	0.15
Median →		141	0.24	< 0.002	0.17

ng/g = nanograms per gram; µg/kg = micrograms per kilogram; mg/kg = milligrams per kilogram

Chinook tissue mercury levels ranged from 131 to 191 µg/kg, with a median of 141 µg/kg, or about one-half the criterion. This mercury level is almost the same as the probabilistic median (Figure H-2) for the statewide river fish samples collected by DEQ. Median total arsenic in the Chinook samples was 0.239 mg/kg. This is greater than the 95th percentile of total arsenic in the river fish samples collected by DEQ (Figure H-1). Chinook are thus comparatively very rich in total arsenic. The median selenium in the Chinook was 0.166 mg/kg, about the 40th percentile of selenium in the statewide river fish samples (Figure H-3). Thus, Chinook are by comparison some what lower in selenium.

USGS Water Samples

The 2006/2008 probabilistic survey of mercury in fish tissue from large rivers compliments statewide trend monitoring at a fixed network of river sites that has been conducted by the USGS in cooperation with DEQ for many years under a joint funding agreement. The scope of the agreement was expanded in 2004 to include sampling of fish tissue for mercury, and since then, USGS has collected and provided DEQ with data from 52 fish tissue samples. Limited funding never allowed for accompanying analysis of mercury in water, until this study. The USGS assisted in the present study by also collecting water samples at the six sites scheduled for fish tissue sampling in 2008. Those six water samples were delivered to DEQ and sent to our contract laboratory, Brooks Rand LLC, for the same suite of analyses as samples collected for the probabilistic sampling of major rivers. The analytical results for these six samples are shown in Table 18.

Table 18. Analytic Results for Six Water Samples Collected by USGS in 2008

Site Name	Hg ng/L	Me-Hg ng/L	Me-Hg ^a	As(T) µg/L	As(i) µg/L	Inorganic As ^b	Se µg/L
Johnson Creek @ YP	0.70	< 0.020	< 3%	4.92	3.90	79%	< 0.09
Boise R @ Glenwood	0.91	0.057	6%	2.22	1.73	78%	< 0.09
Boise R @ Twn Spr	0.69	0.030	4%	3.23	3.03	94%	< 0.09
Henry's Fk Nr Rexburg	0.62	0.044	7%	3.55	3.10	87%	0.74
Lemhi Nr Lemhi	0.92	0.083	9%	4.05	3.94	97%	1.05
Pahsimeroi @ Ellis	0.51	0.044	9%	3.52	1.01	29%	0.13

^a Fraction of total mercury that is methylmercury. ^b Fraction of total arsenic that is inorganic.
ng/g = nanograms per gram; µg/kg = micrograms per kilogram.

Results for these six samples are also displayed on the right side of Figures 7, 9, and 10.

Part F. Discussion

Limitations of the Assessment

There are several limitations to the 2008 statewide assessment of contaminants in fish from Idaho's major rivers.

First, there were largely uncontrollable differences in fish species among sites sampled. Species matters greatly to the mercury concentrations we expect to find in fish tissue. It is known that methylmercury concentrations and bioaccumulation factors increase as one goes higher in the aquatic food chain (Becker and Bigham 1995). Thus, piscivorous fish (e.g., bass, pikeminnow) at the top of most aquatic food chains often contain the highest concentrations of methylmercury.

Because different fish species accumulate mercury differently, any interpretation of site-to-site differences is confounded by species differences—unless the same species (and size) of fish are sampled, it is inappropriate to compare mercury levels in fish from two sites and conclude that the site with higher mercury concentrations in fish tissue suffers from more mercury contamination. Little can be done about this limitation. Over time, with larger data sets, it may be possible to use average differences in mercury levels in different species taken from the same water body to establish interspecies correction factors that could be used to adjust or normalize results to a standard species for purposes of comparing one water body to another. This is the aim of the USGS EMMMA project and, if achieved, would allow us to better compare levels of mercury contamination among sites. These species-to-species differences do not limit the utility of this data for assessing human health risks that may result from consuming fish. People are potentially exposed to what is there and, assuming the fish caught from each site in this study are typical of what an angler would take, then consumption of fish from a site with higher mercury in fish presents a higher health risk regardless of species.

Second, there is variation in fish size. This is more controllable than species variation but is still constrained by what is caught. The sampling crew targeted “catchable size” fish and was further instructed that it was desirable that the smallest fish from a site not be less than 50% the length of the largest fish. Even with this restriction, average length and weight of fish caught varied considerably from site to site; furthermore, fish weight was found to vary more than length (see data in Appendix D). This limits our ability to compare the degree of mercury contamination, even when the species is the same. Variation in size, like species differences, does not limit the assessment of the human health risk if people are eating fish of a size within the range of the sizes of the fish sampled. Analysis of individual fish rather than composite samples would have allowed development of regression relations for fish length versus mercury concentration. With results of such regressions, it would then be possible to adjust results for fish of various lengths to a standard length for comparison. However, analysis of each fish, rather than composites, multiplies analytical cost and was beyond the budget for this project.

Looking at levels of mercury in fish tissue provides a direct measure of human health risk from consumption of caught fish and allows us to gauge compliance with Idaho's fish tissue criterion, but it provides no information on the origin of the mercury. Identifying sources of mercury requires much more intensive study than was done here. Even in Salmon Falls Creek Reservoir, where DEQ mounted an intensive multi-year study of mercury sources (Abbott et al. 2008; Gray and Hines 2009; Lay 2007), definitive identification, and quantification, of ultimate sources have

remained elusive—we have narrowed it down but have not “nailed it down.” On the other hand, by virtue of this study, we now have a much better picture of how widespread is the risk to human health due to accumulation of mercury in game fish in major rivers in Idaho, regardless of the source.

Summary of Comparison to Criteria

Fish Tissue

In 2008, just 5 of the 55 fish tissue samples (9%) had mercury levels greater than Idaho’s 300 ng/g (0.3 mg/kg) methylmercury criterion for protection of human health. For 2006/2008 combined, 8 of 76 (11%) fish tissue samples had levels greater than the criterion. This fraction is significantly less than the 29% of fish samples from lakes and reservoirs in 2007 that had mercury levels greater than the methylmercury criterion (Essig and Kosterman 2008).

There is no criterion for arsenic in fish tissue to which we can make direct comparisons. An equivalent fish tissue criterion of 6.2 µg/kg inorganic arsenic was calculated from EPA’s nationally-recommended water criterion of 0.14 µg/L, intended for waters where human exposure to arsenic is through consumption of fish only. All but one sample in this study had inorganic arsenic levels below the detection limit of 2 µg/kg, thus well below the calculated equivalent tissue criterion. The single sample with detectable arsenic had 6 µg/kg, which is essentially at the criterion.

For selenium, just three fish tissue samples, after correction to dry weight basis, had concentrations that exceeded EPA’s 2004 proposed 7.91 µg/g criterion for protection of aquatic life. All three of these samples were fish from the upper Blackfoot River, an area known to have selenium contamination.

Water

For mercury, just one sample, taken on August 2, 2008, from the Coeur d’Alene River (site 30), exceeded EPA’s (1985) 12 ng/L chronic aquatic life criterion, which is applicable to Idaho waters. The mercury level in the October 23, 2008, resample of this site was about one-half the criterion. Mercury levels in samples from all other sites were less than one-sixth of this criterion. There was little correspondence between sites with higher water levels of mercury, whether total mercury or methylmercury, and higher fish tissue levels of mercury. This is illustrated in Figure 11 and Figure 12. For these figures, the data from the October 23, 2008 re-sampling was used to represent site 30 (the two far right points in Figure 11), but even then these outlying points heavily influence the slope. The regressions were also run excluding this site, in which case, the value for R^2 (the coefficient of determination, which is a measure of the fraction of variation explained by the linear relation) drops from 0.23 to 0.12 for water total mercury and increases from 0.05 to 0.10 for water methylmercury (graphs not shown). These shifts in strength of regression with and without the data from site 30 also hint at the high particulate nature of the total mercury at that site, which is discussed primarily in the section on total mercury on page 33.

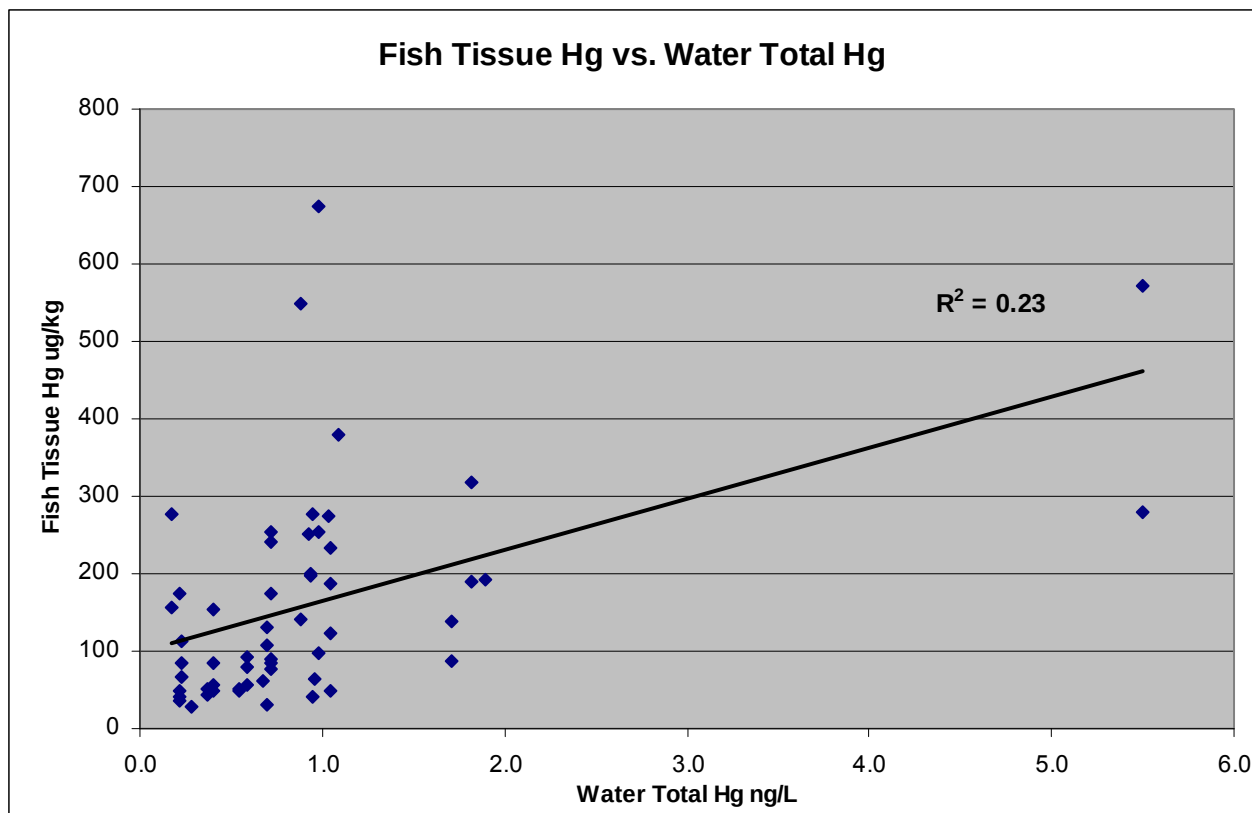


Figure 11. Relation of Fish Tissue Total Mercury to Water Total Mercury (R^2 = coefficient of determination)

We found that all waters sampled met Idaho's current arsenic criteria for aquatic life (340 $\mu\text{g/L}$ acute and 150 $\mu\text{g/L}$ chronic exposure) and for human health (50 $\mu\text{g/L}$). Humans are more sensitive to arsenic than is aquatic life, and the criterion is specific to inorganic forms of arsenic. In contrast to the comparison made with fish tissue above, only 2 of 34 sites have less arsenic than EPA's 0.14 $\mu\text{g/L}$ "fish only" human health criterion would allow. No site had less arsenic than EPA's 0.018 $\mu\text{g/L}$ "fish + water" human health criterion intended for areas where exposure may come from ingestion of water as well as fish. The latter criterion is actually less than the detection limit of 0.02 $\mu\text{g/L}$ in this study, highlighting measurement limitations and raising questions about the reasonableness of EPA's recommended criteria as a regulatory tool. This may be because the bioconcentration factor (BCF) of 44 is high for Idaho waters. Whether the BCF of 44 is inappropriately high depends as well on whether food chain enrichment is calculated for all arsenic or just inorganic arsenic, the proportion of which is greatly different in water than in fish. This will be discussed in more detail in the next section.

Idaho DEQ is currently engaged in rulemaking (Docket 58-0102-0801) to lower its arsenic human health criteria to 10 $\mu\text{g/L}$. Of the 34 sites sampled in 2008, only the Bruneau River sample had inorganic arsenic that exceeded this level

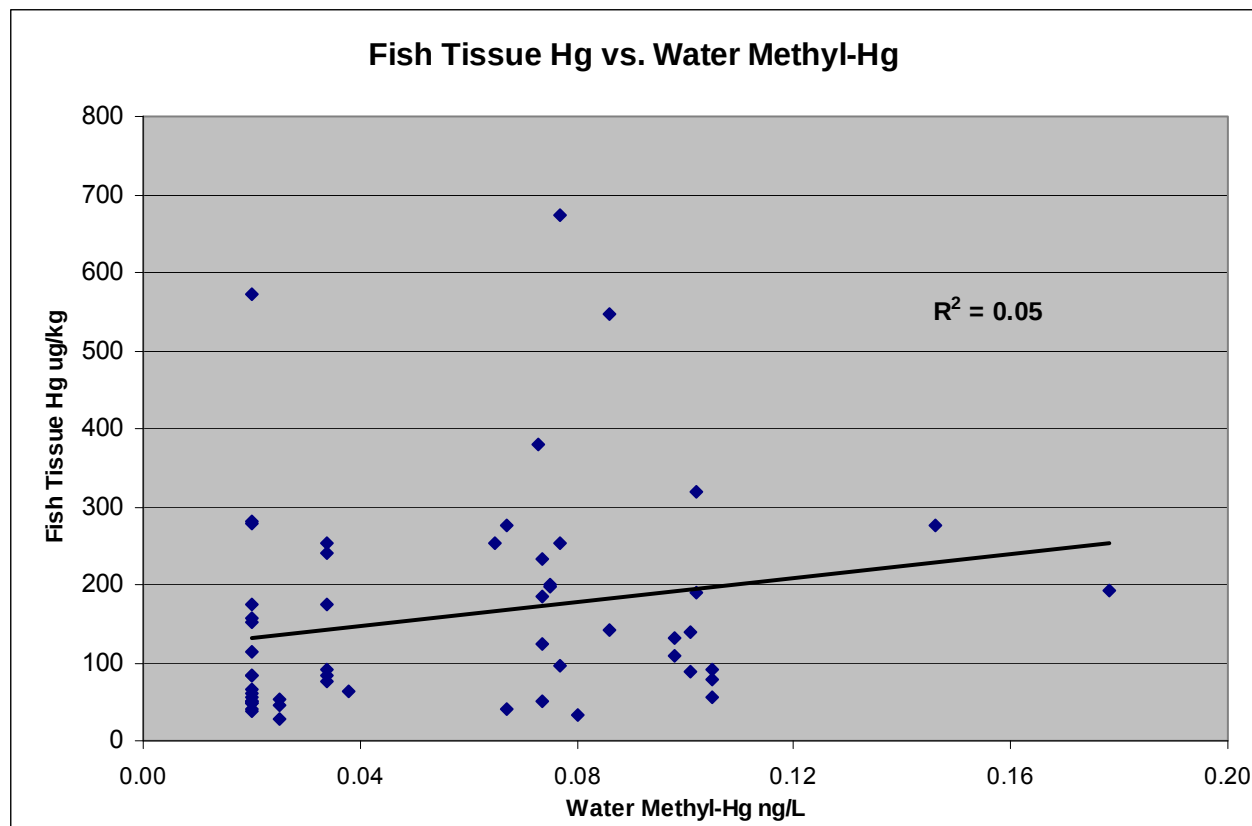


Figure 12. Relation of Fish Tissue Total Mercury to Water Methylmercury (R^2 = coefficient of determination)

Bioaccumulation Factors (BAFs)

The concurrent measurement of contaminant levels in water and fish tissue analysis allows calculation of BAFs. Recall that BAFs are ratios of contaminant concentrations in tissue to contaminant concentrations in water, expressed in units of liter per kilogram (L/kg). Even when one of the concentration levels in this study was below the DL, a BAF was still calculated by substituting the detection limit value in the calculation. For example, as was often the case with arsenic, a measurable concentration of arsenic in fish tissue was divided by a concentration, at the detection limit, of arsenic in water to provide a lower limit to the BAF (i.e., the BAF is greater than x). We calculated BAFs for each site–species combination (BAFs depend on location and species) for each of five chemical contaminants (see Table 19. Summary of Contaminant Bioaccumulation Factors). To calculate a BAF for methylmercury, it was assumed all the mercury measured in fish tissue was methylmercury. This adds a high bias to the methylmercury BAFs such that if the true concentration of methylmercury is 10% less than the total concentration of mercury, then the calculated methylmercury BAF is biased 10% high.

Table 19. Summary of Contaminant Bioaccumulation Factors

	Hg	Me-Hg	As(T)	As(i)	Se	Log ₁₀ Me-Hg
Mean	240,549	3,212,062	143	> 11	1,489	6.38
Min	2,545	400,000	> 3	> 0.2	196	5.60
Max	1,635,294	13,900,000	2,333	> 91	5,600	7.14
Max/Min	642	35	703	372	29	

Hg = mercury, Me-Hg = methylmercury, As(T) = total arsenic, As(i) = inorganic As, Se = selenium.

Note: all the As(i) BAFs are “greater than” values because all but one fish tissue sample contained As(i) below the DL; thus, the BAFs for As(i) were calculated using the detection limit, which gives a lower limit to the actual but unknown BAF. Similarly, 10 of the total arsenic fish tissue concentrations were below the DL, in which case the DL was used in the calculation, including the minimum As(T) BAF.

For a BAF to be considered representative of a site and species for which it is calculated, the contaminant concentrations in fish tissue and water must both be representative of that location. This is believed to be a fair assumption for the fish tissue data in this study, with the caveat that fish are mobile, and frequently, fewer fish than the 10 desired for a composite tissue sample were all that were available. For the water samples in this study, the assumption of representativeness could be poor simply because they represent conditions only at the time of sampling and thus do not incorporate any seasonal variation in water quality that may affect bioaccumulation. These limitations are offset by the fact that we have both fish and water data from across the state at 28 sites and from multiple species. In total, 55 BAFs were calculated per contaminant.

One measure of variability is the ratio of Max/Min, given in the last row of Table 19. By this measure, the variability in total mercury BAFs is much greater than the variability in the methylmercury BAFs, suggesting methylmercury concentrations are a more reliable predictor of differences in mercury accumulation in fish. Even though the methylmercury BAFs are biased high, it can be seen that methylmercury bioaccumulated much more strongly than total mercury. The common logarithm (log₁₀) BAFs in this study for total mercury concentrations in fish to methylmercury concentrations in water (shown in the far right column in Table 19) are very similar to those in the report of Scudder et al. (2009), who report a mean log₁₀ BAF for 274 stream sites to be 6.33 (range = 4.36 to 7.59).

Similarly, bioaccumulation of total arsenic was more variable than bioaccumulation of inorganic arsenic. Inorganic arsenic bioaccumulates less strongly than total arsenic, likely reflecting its conversion *in vivo* (inside living animals or plants) to organic forms, a known detoxification mechanism for organisms (ASTDR 2007).

The mean BAF for inorganic arsenic of greater than 11 is nominally one-fourth the BCF of 44 used by EPA in developing their currently recommended criteria.⁹ Barring a change in the cancer slope factor, fish consumption rate, or other parameters that go into calculating a human health criterion, this difference alone suggests EPA’s arsenic criteria could be higher, as much as four times higher than currently recommended, and still provide the intended level of protection.

Selenium is intermediate in its bioaccumulation rate, accumulating more strongly than arsenic, but much less so than mercury. No data were collected on the various forms and oxidation states of selenium, which could reveal differences in bioaccumulation among its chemical forms, as was evident for arsenic and mercury.

⁹ See section 304(a) of the Clean Water Act.

Arsenic Forms and Bioaccumulation

The arsenic criteria recommended by EPA are stated as being specific to inorganic arsenic (EPA 2002c, Footnote S). This is because, unlike mercury, the more toxic form of arsenic is believed to be inorganic. As with mercury, most of the arsenic in fish tissue is in organic forms, while the vast majority of the arsenic in water is inorganic. For arsenic, as for mercury, chemical form matters to toxicity – but for arsenic, it is the inorganic form, not any of the organic forms, that is more toxic.

Accepting conventional wisdom on the greater toxicity of inorganic arsenic, if we assumed the total arsenic in fish is all organic, we would completely discount the health risk. Conversely, because inorganic arsenic is the minor form in fish tissue, assuming total arsenic is all inorganic would greatly exaggerate the risk. An accurate picture of health risk due to arsenic in fish can only be had by knowing the proportions of inorganic and organic arsenic. The picture of risk that emerges is further complicated by recent research that suggests some organic forms of arsenic are also important human toxins (Kligerman et al. 2003). These risks are not accounted for by the current inorganic arsenic criteria.

Currently, EPA's nationally recommended arsenic criteria are calculated from the reference dose using a bioconcentration factor (BCF) of 44. This BCF is a consumption-weighted average for a marine oyster species and rainbow trout. Idaho has no marine waters; therefore, this BCF is obviously not appropriate to Idaho. While Idahoans may eat oysters, they are not coming from Idaho waters. Furthermore, published BCFs are typically calculated based on laboratory studies in which total arsenic accumulated in fish tissue and total arsenic in water was measured (EPA 2003). Due to the conversion of inorganic arsenic into organic forms that occurs *in vivo*, the BCF calculated for total arsenic will be greater than a BCF calculated for inorganic arsenic alone. A BCF that does not account for *in vivo* conversion of arsenic from inorganic to organic forms is inappropriate to a criterion purported to be based on toxicity of inorganic arsenic only.

EPA's current guidance on human health criteria prefers the use of BAFs to BCFs (EPA 2000b). Bioconcentration considers accumulation from water only, while bioaccumulation accounts for dietary intake as well—the added increase in concentration from prey to consumers, known as biomagnification. However, although bioaccumulation is more relevant, it is site-specific and can be measured only in field studies that are inherently difficult to conduct and fully control. Consequently, there is not much BAF data on which to base a criterion. Preference for BAFs over BCFs may be less important for arsenic than for mercury, as evidence suggests that arsenic is bio-regulated and thus does not biomagnify much (Williams et al. 2006; Luoma and Rainbow 2005).

Selenium-Mercury Interactions

The scientific literature speaks to two interactions between selenium and mercury. One is a protective effect of selenium against mercury toxicity; the other is a reduction in mercury bioaccumulation. The former has broad implications to criterion levels and assessment of human health risk (Berry and Ralston 2008; Ralston et al. 2008; Peterson et al. 2009). The latter may be important in explaining why fish from southeast Idaho waters enriched in selenium have lower tissue mercury levels than might be expected.

The physiological interaction between selenium and mercury has been studied for a long time, and a mutual antagonism between them is evident in a broad variety of animals tested (see reviews by Pelletier 1985; Cuvin-Aralar and Furness 1991; Yang et al. 2008; Khan and Wang 2009). Selenium is known to be important in brain function as an essential part of neuro-proteins containing selenocysteine (Chen and Berry 2003). It is known that selenium and mercury have a high binding affinity. It is suspected that both metals are rendered biologically inactive by being bound in an insoluble selenium-mercury compound as well as mercury seleno-protein complexes that form within brain cells.

Overall, this interaction may explain why some individuals or populations, although exposed to elevated mercury levels, suffer lesser or no ill effects. For example, there is a long-running debate on the disparate toxicological effects between studied populations of fish consumers from the Seychelles and Faroe Islands exposed to similar levels of mercury. Differing selenium exposure may offer an explanation (Raymond and Ralston 2004).

The relative proportion rather than absolute concentration of the two metals appears crucial (Ralston, Blackwell, and Raymond 2007), with an excess of selenium ($\text{Se:Hg} > 1$) being beneficial, as suggested earlier by Yoneda and Suzuki (1997). Selenium-mercury molar ratios ranged from 0.25 to 139 in the 55 fish tissue samples obtained in the 2008 river monitoring. In only three samples was this ratio less than 1.0 (greater than 1.0 is thought to be protective), and only one of these also had mercury levels greater than the criterion—largemouth bass from site 30 (the Coeur d'Alene River #1 site). Ratios greater than 50 were observed in fish from the Blackfoot River, Big Lost River, and Big Wood rivers of eastern and southern Idaho. Ratios of less than 1.0 were observed in fish from the Coeur d'Alene and Payette Rivers, in northern and western Idaho. In the 2007 lake fish data (Essig and Kosterman 2008), 13 of the 89 samples of fish tissue had both a mercury level greater than 300 $\mu\text{g/kg}$ and a selenium-mercury ratio less than 1.

While the mechanism for the protective effect of selenium has become increasingly well understood (Ralston 2008; Yang et al., 2008), it is not yet fully clear and remains controversial because of its implications for human health (Spencer Peterson, personal communication). Indeed, Mergler et al. (2007), despite the growing body of scientific study, stated “There is no human data that support a protective role for Se with respect to Hg neurotoxicity” (p.7). The question remains a fertile area of scientific research.

The second known interaction of selenium with mercury is the effect elevated selenium in the environment has on the suppression of mercury bioaccumulation. Several researchers have documented the reduction in mercury bioaccumulation caused by selenium (Paulsson and Lundbergh 1989; Southworth, Peterson, and Ryon 2000; Belzile et al. 2006). Southworth, Peterson, and Ryon (2000) postulated the effect was due to suppression of mercury methylation. Jin, Guo, and Xu (1997) directly examined the effect of selenium on methylation of mercury in laboratory experiments with samples of sediment from a eutrophic lake in which the concentrations of mercury and selenium were controlled and found mixed results depending on availability of oxygen. Microbiological methylation rates were higher in anaerobic sediments, yet aerobic sediments were observed to produce more methylmercury.

This observation of Jin, Guo, and Xu (1997) suggests a mechanism whereby the cycling of aerobic to anaerobic conditions, such as that caused by fluctuating water levels, would be particularly efficient at converting inorganic mercury to methylmercury. The effect of reservoirs on aerobic to anaerobic cycling has been empirically observed (Evers et al. 2007; Kamman et al.

2005), as has been the effect of fluctuating water levels in particular (Sorensen, Kallemeyn, and Sydor 2005). Water level fluctuation is likely an important contributing factor in the reported high levels of mercury in fish from Salmon Falls Creek Reservoir (Essig and Kosterman 2008; Lay 2007).

Other studies suggest that the mechanism by which selenium lowers mercury bioaccumulation is something other than reduced methylation. Turner and Swick (1983) found that it was selenium in the diet, not selenium in water, that suppressed mercury bioaccumulation. Belzile et al. (2006) suggest the preferential assimilation of selenium over mercury at binding sites. Another possibility is selenium interfering with bioavailability of mercury by reducing concentrations of reactive mercury (Hg^{+2}).

Clearly, the methylation of mercury is a complex process, but a reduction in methylation due to selenium is not consistent with data from this study, where the highest fraction (18%) of methylmercury was observed in the Blackfoot River in conjunction with the second highest level of selenium, while fish tissue levels of mercury were quite low. This agrees better with the observation of Turner and Swick (1983) and strongly suggests that selenium's interference with methylmercury bioaccumulation occurs once both are in the food chain. Thus, the mechanism for selenium attenuating mercury toxicity and reducing mercury bioaccumulation may be converging on the same intracellular chemical reactions.

Fish Tissue vs. Water Criteria and Protection of Aquatic Life

When Idaho adopted the methylmercury fish tissue criterion in 2005, it also removed its existing aquatic life criteria for total mercury in water from the Idaho Water Quality Standards. This was done in part to avoid competing criteria and thus simplify monitoring, but in its submittal of the rule change for approval (Essig 2004), DEQ also expressed its belief to EPA that the new fish tissue criterion (0.3 mg/kg) would also be more protective of aquatic life than the old (EPA 1985) chronic criterion regulating water concentrations of total mercury (12 ng/L). This assertion is based on known bioaccumulation rates and typical ratios of methylmercury to total mercury in water and resulting back-calculated total mercury concentrations in water. DEQ made the assertion knowing the tissue criterion was developed to protect human health, not aquatic life, but also knowing that EPA's 12 ng/L criterion was similarly translated from a fish tissue concentration—the FDA action level in fish tissue of 1.0 mg/kg—and not the result of testing mercury toxicity to aquatic life.

On December 12, 2008, EPA finally acted to disapprove Idaho's removal of its water column mercury criteria, in effect rejecting DEQ's assertion and reinstating the water-based aquatic life criteria for Clean Water Act purposes such as National Pollutant Discharge Elimination System (NPDES) permits and total maximum daily loads (TMDLs). In their disapproval, EPA insists that Idaho must have numeric aquatic life criteria for mercury. The methylmercury criterion is a numeric criterion, and DEQ has found no evidence that it is not protective of aquatic life as well as human health. The human health basis of the 0.3 mg/kg methylmercury criterion is no different than for the 12 ng/L criterion and is based on more recent information. If the basis of the 12 ng/L criterion is accepted, then the methylmercury criterion should be considered 3.33 times more protective (0.3 mg/kg versus 1.0 mg/kg). Nonetheless, EPA reinstated the 12 ng/L criterion for Idaho in December 2008. That the methylmercury criterion is likely even more than 3.33 times more protective than the 12 ng/L water column total mercury criterion is borne out by the data on concurrent water total mercury and fish tissue mercury levels from sites in Idaho.

In a previous report on fish from lakes and reservoirs, Essig and Kosterman (2008) presented data on fish and water from four sites that all showed that the fish tissue criterion was exceeded while water total mercury concentrations were far less than 12 ng/L. In one additional case, although the water concentrations exceeded 12 ng/L, estimated fish tissue levels exceeded 0.3 mg/L by a greater fraction and thus drove greater specified load reductions in a TMDL. In other words, in every situation where data existed to apply both criteria, the fish tissue criterion was more stringent. Combining data from all four sites, average fish mercury levels were more than twice the criterion, while average water total mercury levels were one-quarter the criterion, suggesting the fish tissue criterion is eight times more stringent.

With the 2008 river sampling results, we now have data from 28 more sites with both fish tissue and water data to bear on this question. Five of those sites had mercury levels in fish tissue greater than the criterion of 0.3 mg/kg. One site was the Coeur d'Alene River entering Coeur d'Alene Lake, site 30, where initial water samples showed mercury levels at 110 ng/L, far greater than the 12 ng/L criterion; however, upon re-sampling, mercury levels were less than half the criterion at 5.5 ng/L. The other four sites had less than 2 ng/L water column mercury. Looking at all 28 sites and 55 fish tissue samples, the average tissue concentration of mercury was 0.16 mg/kg, about one-half the criterion, while the average total mercury concentration in water was 0.92 ng/L, less than one-twelfth the 12 ng/L criterion. Again, the fish tissue criterion is much closer to being exceeded than is the old water column criterion, thus it is much more stringent.

Another way of examining this is to use a bioaccumulation rate and apply it to Idaho's fish tissue criterion of 0.3 mg/kg, like EPA did in deriving their 12 ng/L criterion. Using the average total mercury bioaccumulation rate of 240,549 from this study (Table 19), a fish tissue concentration of mercury equal to the criterion would give an equivalent water column concentration of 1.25 ng/L total mercury. Once more, the fish tissue criterion is much more stringent.

These data consistently show that fish tissue concentrations can exceed the human health criterion of 300 ng/g (0.3 mg/kg) methylmercury when total mercury levels in the water are far less than the old 12 ng/L chronic criterion for aquatic life. All told, there is now very strong evidence to support Idaho's assertion that the fish tissue criterion is the more protective criterion, and by a wide margin.

Fish Consumption Advisories

In Idaho, fish consumption advisories are issued by the Department of Health and Welfare Bureau of Community and Environmental Health (BCEH) under the Idaho Fish Consumption Advisory Program (IFCAP 2009). IFCAP incorporates an interagency group in which DEQ participates. While jointly discussed, the ultimate decision to issue a fish consumption advisory rests with BCEH staff. Fish consumption advisories are water body- and species-specific and generally advise limiting fish consumption, not avoiding it altogether, as it is recognized that fish are generally an important part of a healthy diet.

Idaho's fish tissue human health criterion for methylmercury is designed to protect the general population of adults. When BCEH issues a fish consumption advisory, they consider pregnant women and children as a more sensitive portion of the population. In their decision, they take into account that children weigh less than adults, and they generally use a higher fish consumption rate than the 17.5 g/day that Idaho's criterion is based on. Therefore, BCEH's

action level is 220 µg/kg of mercury in fish tissue, and they will issue fish advisories when fish tissue mercury is above that level even though it is not above Idaho's fish tissue criterion of 300 µg/kg. Discrepancies may also arise because Idaho's fish tissue criterion regulates the consumption-weighted average concentration for all species consumed, while fish consumption advisories are issued for specific fish species, e.g., bass or walleye. Fish advisories usually have specific instructions for women who are pregnant or may become pregnant and for children on the amount and frequency of fish that is safe to consume. For more information on Idaho's criterion, see the Implementation Guidance for the Idaho Mercury Water Quality Criteria (DEQ 2005). For more information on fish consumption advisories, visit the IFCAP Web site at <http://healthandwelfare.idaho.gov/Health/EnvironmentalHealth/FishAdvisories/tabid/180/default.aspx>, or contact BCEH by phone at (208) 334-0606 or 1-866-240-3553 (toll free), or by email at BCEH@idhw.idaho.gov.

Data from this report were shared with IFCAP and resulted in three new fish consumption advisories being issued in Idaho: for the Payette River (suckers), Bear River (carp), and South Fork Snake River (brown trout). In each case, mercury levels were less than the Idaho fish tissue criterion.

Source and Control of Mercury in Fish

The present study provides no direct data on sources of mercury contamination in Idaho rivers and fish. A recent study by Peterson et al. (2007) looked at fish tissue mercury data collected from rivers throughout the West and tried to correlate tissue concentrations with data on known point source discharges of mercury. Finding no correlation, the authors concluded that atmospheric transport is a key factor relative to mercury in fish across the western United States.

Air deposition of mercury is a global as well as regional issue (Abbott et al. 2008; Steding and Flegal 2002). It is known that the global air burden of mercury has increased two- to three-fold since the dawn of the industrial age (Schuster et al. 2002) and that large regional sources of air emissions of mercury have arisen more recently to the south and to the west of Idaho (EPA 2009). These sources in northern Nevada and eastern Oregon (Figure 13) are suspected to be contributing to elevated mercury concentrations in fish tissue observed in southern Idaho. In the 2006/2008 river fish data, the highest concentrations were not found in proximity to these known air sources, unlike the lake and reservoir fish sampled in 2007. It must be noted, however, that current emission patterns do not necessarily reflect historic emissions that may still be influencing fish tissue mercury levels, nor do they reflect other sources of mercury. Furthermore, rivers are fundamentally different from lakes in their environment for mercury processing and in their food chains, and this affects mercury accumulation in fish tissue.

While the chemical form of airborne mercury is important to its residence time in the atmosphere and how near its source it deposits on the landscape, mercury from at least some of the sources in neighboring states, as well as those in Idaho, is deposited in Idaho (Abbott et al. 2008). We should expect a portion of the mercury deposited in Idaho will eventually make its way into our streams and lakes and, once there, enter the food chain. If we have not yet reached a steady state with mercury loading from deposition and other sources, this added mercury will ultimately contribute to increased concentrations of mercury in fish tissue.

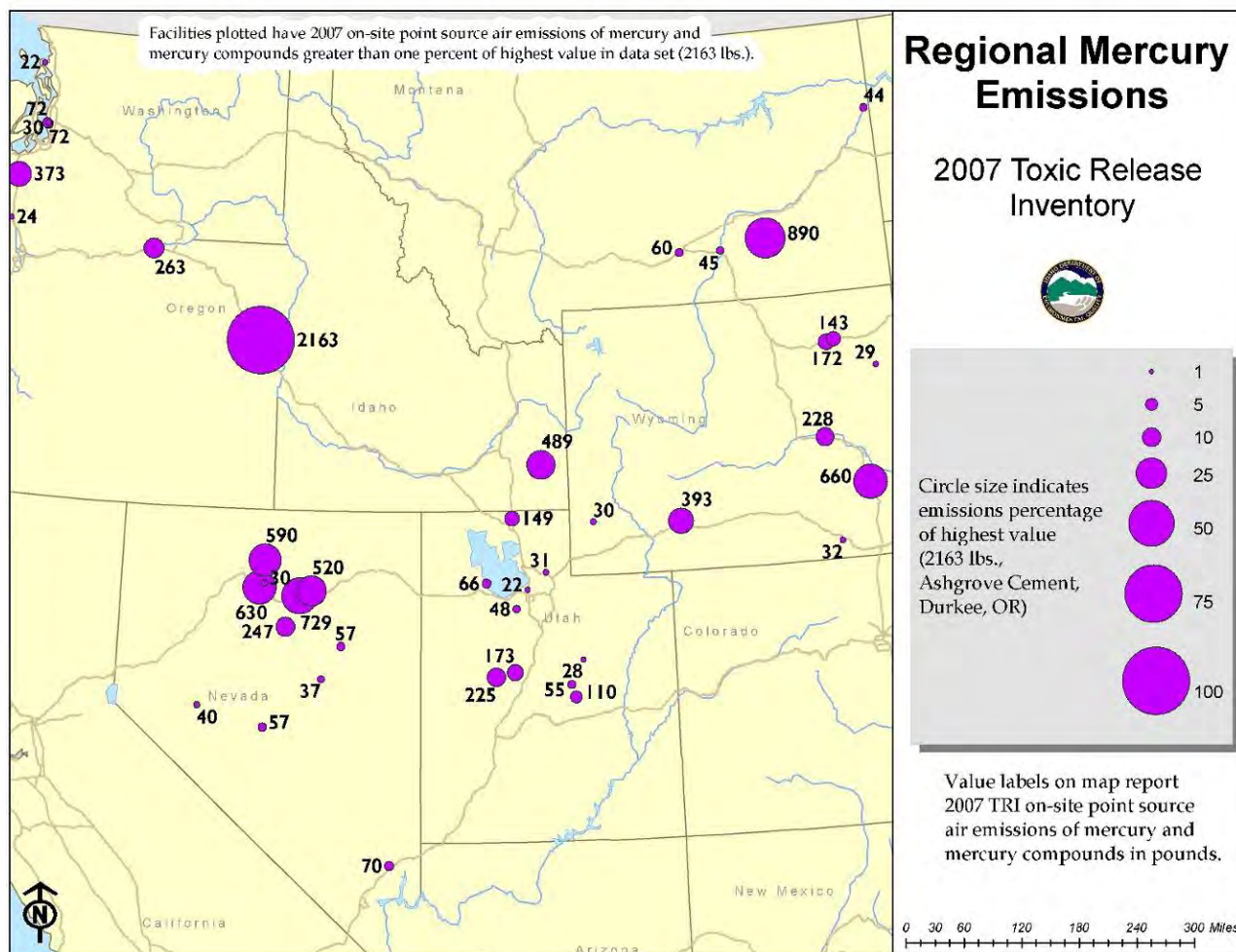


Figure 13. 2007 Regional Air Emissions of Mercury

In Minnesota, it was determined that 99.5% of the mercury in fish was from air sources. Of the airborne mercury, 30% was of natural origin and 70% was human-caused (MNPCA 2008). Of the human-caused mercury loading, it was determined that 90% was originating outside Minnesota's borders. We do not yet have adequate data to make such estimates for Idaho. Given Idaho's history of placer gold mining and common use of mercury to recover fine gold, we might expect overall a somewhat lower proportion from air here in Idaho. Still, because there are relatively few wastewater sources of mercury in Idaho, it seems likely that the predominant source of mercury causing elevated levels in fish tissue is deposition of airborne mercury; however, there are local exceptions, e.g., Jordan Creek, where legacy mining is a major source (Ingham 2007).

There is a demonstrated relationship between mercury deposition and the levels of mercury in the tissue of aquatic life in the same watershed (Evers et al. 2007; Munthe et al. 2007; Hammerschmidt and Fitzgerald 2006; Wiener et al. 2006). This is clear even though it is known that mercury bioaccumulation varies greatly among species and the food chains they occupy (Wente 2004), and, it appears now, with abiotic factors such as selenium as well. In an experiment in which added mercury was isotopically labeled, Orihel et al. (2006) found the

production of methylmercury to respond proportionally to atmospherically relevant mercury loading. Harris et al. (2007) noted a rapid rise in mercury levels in fish due to mercury deposited directly onto the water surface and concluded that availability of reactive mercury (Hg^{+2}) was the limiting factor in the biogeochemical transfer of mercury to fish. Orihel et al. (2006) documented an increase in fish tissue mercury proportional to increased inorganic mercury loading. Chasar et al. (2009) examined mercury cycling in streams and concluded that the supply of methylmercury at the base of the food chain is the strongest determinant of mercury in piscivorous fish, and that bioaccumulation thereafter is relatively similar among various ecosystems. It is becoming increasingly apparent that factors affecting the conversion of mercury to methylmercury are key in how each aquatic system responds to mercury loading.

It is also becoming clear that the response of entire watersheds to increased mercury loading is very complicated. Harris et al. (2007) found that less than 1% of mercury applied to a watershed made its way into a lake within a year, so there is likely to be a considerable lag in the transfer of landscape-deposited mercury to fish. Once deposited mercury reaches a water body, directly or indirectly, its conversion to methylmercury is affected by many site-specific factors including pH, organic matter, dissolved oxygen, and sulfide-sulfate levels (Ullrich, Tanton, and Abdrashitova 2001; Chen 2005; Brigham et al. 2009). Because of the myriad factors controlling deposition to methylation to bioaccumulation, the response of each aquatic ecosystem will be unique and the rate of mercury deposition that will lead to an unacceptable level of methylmercury bioaccumulation in aquatic life is very watershed-specific and difficult to predict. Although each aquatic system will be unique in the factors moderating methylation of mercury, unless these factors change, more mercury loading is expected to produce more methylmercury and that in turn will result in more mercury in fish. Reduced mercury loading will ultimately improve fish mercury levels, but it may take decades to centuries (Knights et al. 2009).

In summary, the chemical form of mercury matters greatly—in air transport of mercury, to mobility in runoff, in its conversion to methylmercury, and ultimately to mercury's toxicity. In addition to variation in loads and in the chemical form of airborne mercury deposited from watershed to watershed, the deposition and washoff of mercury is expected to depend on each watershed's climate, soils, and vegetation. Despite this complexity and consequent variability in the movement of mercury from air emissions to biota, over a broad area there is no scientific reason not to expect mercury air emissions to lead to increased mercury in the tissue of aquatic life. Although manipulation of factors that control rates of methylation and bioaccumulation may be feasible, ultimately it is best to address this environmental problem by reducing mercury loads at their source.

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Glossary

analyte

A chemical compound measured in laboratory testing.

arsenic

A toxic, naturally-occurring, metallic element that bioaccumulates in fish tissue.

bioaccumulation

The process of a substance accumulating inside a living organism. Arsenic, mercury, and selenium bioaccumulate in fish tissue.

bioaccumulation factor (BAF)

The ratio of a substance's concentration in a living organism to its concentration in the surrounding environment when exposure includes dietary intake. In this study, BAFs express the ratio of contaminant concentrations in fish tissue to contaminant concentrations in water, and are expressed in units of liter per kilogram. BAFs were calculated for arsenic, mercury, and selenium.

bioconcentration factor (BCF)

Calculated the same as BAF, but does not include exposure due to dietary intake. At the first step in bioaccumulation, from water to algae, BAF and BCF are the same.

biomagnification

The increase in concentration of a contaminant from one step in a food chain to the next, e.g., prey to consumer. In simple terms, bioaccumulation is the result of bioconcentration followed by biomagnification.

detection limit

The point at which concentrations of an analyte are so small that they cannot be distinguished from zero.

electrofishing

A common scientific technique that uses electric current to stun fish and enable collection.

food chain

An idealized trace of food and consumer organisms in a biological community; an accounting of who eats whom.

methylmercury

A form of mercury created in aquatic systems by the process of methylation. Methylmercury is a dangerous contaminant that can permanently damage the brain and kidneys. Developing fetuses are particularly sensitive because their brains are actively developing.

The majority of total mercury in fish tissue is in the form of methylmercury.

methylation

A process that introduces a chemical compound known as the methyl group into an element. In aquatic environments, inorganic mercury undergoes methylation to form methylmercury.

piscivorous

Describes organisms that eat fish. Fish that eat other fish are typically trophic level four.

point source

A source of pollution that comes from a discrete pipe or other clearly identifiable point.

relative percent difference (RPD)

A number that expresses the agreement between two measurements. In this study, RPD was calculated for field duplicate samples and matrix spike duplicate samples to quantify measurement precision.

selenium

A toxic, naturally-occurring, nonmetallic element that bioaccumulates in fish tissue.

total maximum daily load (TMDL)

Simply put, a TMDL is a pollutant budget. A TMDL is a calculation of the maximum amount of a pollutant that a water body can receive and still meet water quality standards. The term TMDL also refers to a written assessment by DEQ of water quality problems and contributing pollutant sources.

trophic level

A whole number that describes an organism's position in a food chain. Plants are trophic level one. Organisms that eat plants are trophic level two, and so on. Higher trophic levels provide a greater opportunity for bioaccumulation of contaminants.

turbidity

A hazy condition in water caused by suspended particles of organic matter or soil. Turbidity limits light penetration and visibility in water. Suspended particles provide binding sites for many pollutants and thus may carry much of their load in water.

Appendix A. River Site Selection

Idaho Major River Survey Design 2006-2008

Contact:

Mary Anne Kosterman
Surface Water Quality—Water Quality Standards
1410 N. Hilton
Boise, ID 83706-1255
Phone: (208) 373-0173
Fax: (208) 373-0576
Mary-Anne.Kosterman@deq.idaho.gov

Description of Sample Design

Target population: Major rivers in Idaho, as identified by Idaho.

Sample Frame: To identify the target population streams, Mary Anne Kosterman provided the GIS stream coverage. It is based on NHD with only major rivers included. Note that it appears that run-of-the-river reservoirs were included in the GIS coverage. They were included in the design.

Survey Design: A Generalized Random Tessellation Stratified (GRTS) survey design for a linear resource was used. The GRTS design includes reverse hierarchical ordering of the selected sites.

Multi-density categories: None

Stratification: None.

Panels: Two panels to be visited in two different years: Panel_2006 and Panel_2008.

Expected sample size: Expected sample size 25 sites per panel.

Over sample: 200% (100 sites).

Site Use: Within State, the base design has 50 sites. Sites are listed in SiteID order and must be used in that order. All sites that occur prior to the last site used must have been evaluated for use and then either sampled or reason documented why that site was not used. As an example, if 50 sites are to be sampled and it required that 80 sites be evaluated in order to locate 50 sampleable stream sites, then the first 80 sites in SiteID order would be used.

If the design is implemented over two years, then use the sites in siteID order within year and then continue with the next siteID in the next year. If want to identify revisit sites, use the first 5 sites in siteID order that were actually sampled in the field each year.

Sample Frame Summary

Total stream length (in km) in the sample frame is 7384.939 km.

Site Selection Summary

Number of sites in sample

mdcaty	OverSamp	Panel_2006	Panel_2008	Sum
Equal	50	25	25	100
Sum	50	25	25	100

Description of Sample Design Output:

The dbf file for the shapefile ("ID Major Rivers 2006-08 Sites") has the following variable definitions:

Variable Name	Description
SiteID	Unique site identification (character)
x	x-coordinate from map projection (see below)
y	y-coordinate from map projection (see below)
mdcaty	Multi-density categories used for unequal probability selection
weight	Weight (in km), inverse of inclusion probability, to be used in statistical analyses
stratum	Strata used in the survey design
panel	Identifies base sample by panel name and Oversample by OverSamp
EvalStatus	Site evaluation decision for site: TS: target and sampled, LD: landowner denied access, etc (see below)
EvalReason	Site evaluation text comment
auxiliary variables	Remaining columns are from the sample frame provided

Projection Information

```
PROJCS["IDTM83", GEOGCS["GCS_North_American_1983",
DATUM["D_North_American_1983", SPHEROID["GRS_1980",6378137.0,298.257222101]],
PRIMEM["Greenwich",0.0],UNIT["Degree",0.0174532925199433]],
PROJECTION["Transverse_Mercator"], PARAMETER["False_Easting",2500000.0],
PARAMETER["False_Northing",1200000.0], PARAMETER["Central_Meridian",-114.0],
PARAMETER["Scale_Factor",0.9996],
```

PARAMETER["Latitude_Of_Origin",42.0],
UNIT["Meter",1.0]]

Evaluation Process

The survey design weights that are given in the design file assume that the survey design is implemented as designed. Typically, users prefer to replace sites that can not be sampled with other sites to achieve the sample size planned. The site replacement process is described above. When sites are replaced, the survey design weights are no longer correct and must be adjusted. The weight adjustment requires knowing what happened to each site in the base design and the over sample sites. EvalStatus is initially set to "NotEval" to indicate that the site has yet to be evaluated for sampling. When a site is evaluated for sampling, then the EvalStatus for the site must be changed. Recommended codes are:

EvalStatus Code	Name	Meaning
TS	Target Sampled	site is a member of the target population and was sampled
LD	Landowner Denial	landowner denied access to the site
PB	Physical Barrier	physical barrier prevented access to the site
NT	Non-Target	site is not a member of the target population
NN	Not Needed	site is a member of the over sample and was not evaluated for sampling
Other codes		Many times useful to have other codes. For example, rather than use NT, may use specific codes indicating why the site was non-target.

Statistical Analysis

Any statistical analysis of data must incorporate information about the monitoring survey design. In particular, when estimates of characteristics for the entire target population are computed, the statistical analysis must account for any stratification or unequal probability selection in the design. Procedures for doing this are available from the Aquatic Resource Monitoring web page given in the bibliography. A statistical analysis library of functions is available from the web page to do common population estimates in the statistical software environment R.

For further information, contact

Anthony (Tony) R. Olsen USEPA NHEERL Western Ecology Division 200 S.W. 35th Street
Corvallis, OR 97333 Voice: (541) 754-4790 Fax: (541) 754-4716 email: Olsen.Tony@epa.gov

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Web Page: <http://www.epa.gov/nheerl/arm>

Appendix B. River Sites Actually Sampled

Table B-1. River Sites Sampled

	SITE #	Site_ID	SITE_NAME	Latitude	Longitude	Panel	Year Sampled
*	005	IDR06615-005	Blackfoot River	43 12 29.64	-112 12 14.48	Panel_2006	2006 & 2008
	008	IDR06615-008	Salmon River	45 22 30.75	-114 05 06.47	Panel_2006	2006
*	011	IDR06615-011	Big Wood River	43 46 50.84	-114 32 32.02	Panel_2006	2006 & 2008
*	012	IDR06615-012	Salmon River #3	45 24 24.35	-116 11 30.71	Panel_2006	2006 & 2008
	013	IDR06615-013	Big Lost River	44 00 35.01	-113 47 07.70	Panel_2006	2006
	016	IDR06615-016	Salmon River	44 58 51.81	-113 57 02.52	Panel_2006	2006
*	017	IDR06615-017	Bear River	42 21 37.33	-111 44 11.78	Panel_2006	2006 & 2008
	022	IDR06615-022	Coeur d'Alene River	47 38 38.25	-116 00 01.51	Panel_2006	2006
	023	IDR06615-023	Snake River	43 00 06.90	-115 11 45.44	Panel_2006	2006
	026	IDR06615-026	North Fork Clearwater River	46 43 12.73	-115 17 30.34	Panel_2008	2008
	027	IDR06615-027	North Fork Big Lost River	43 55 37.76	-114 11 16.07	Panel_2008	2008
	028	IDR06615-028	Salmon River #2	45 47 22.75	-116 19 12.21	Panel_2008	2008
	029	IDR06615-029	Teton River	43 52 54.25	-111 48 40.36	Panel_2008	2008
	030	IDR06615-030	Coeur d'Alene River #1	47 28 42.30	-116 44 08.72	Panel_2008	2008
	031	IDR06615-031	Weiser River	44 37 45.08	-116 35 09.18	Panel_2008	2008
	037	IDR06615-037	Blackfoot River #2	42 48 04.03	-111 29 06.54	Panel_2008	2008
	038	IDR06615-038	Coeur d'Alene River #2	48 00 47.07	-116 14 05.85	Panel_2008	2008
	040	IDR06615-040	Salmon River #1	45 27 18.08	-115 46 20.41	Panel_2008	2008
	044	IDR06615-044	Pahsimeroi River	44 39 31.90	-114 01 25.82	Panel_2008	2008
	047	IDR06615-047	Snake River #2	43 36 23.55	-116 54 39.16	Panel_2008	2008
	050	IDR06615-050	Priest River	48 14 31.27	-116 53 01.92	Panel_2008	2008
*	051	IDR06615-051	Bruneau River	42 47 22.47	-115 43 03.60	OverSamp	2006 & 2008
	054	IDR06615-054	Coeur d'Alene River #3	48 01 20.89	-116 17 35.23	OverSamp	2008
*	055	IDR06615-055	NF Payette River	44 12 49.08	-116 6 23.63	OverSamp	2006 & 2008
	056	IDR06615-056	Middle Fork Clearwater River	46 08 17.28	-115 48 11.37	OverSamp	2006
	059	IDR06615-059	Salmon River	44 15 40.83	-114 51 18.96	OverSamp	2006
	060	IDR06615-060	Salmon River	45 18 18.40	-114 30 53.00	OverSamp	2006
*	061	IDR06615-061	Camas Creek	43 52 54.36	-112 21 05.86	OverSamp	2006 & 2008
*	063	IDR06615-063	Payette River	44 00 12.85	-116 48 12.48	OverSamp	2006 & 2008
	068	IDR06615-068	Camas Creek #2	44 49 03.30	-114 29 33.64	OverSamp	2008
	069	IDR06615-069	Blackfoot River	42 49 34.41	-111 33 18.25	OverSamp	2006

Appendix B. River Sites Actually Sampled

SITE #	Site_ID	SITE_NAME	Latitude	Longitude	Panel	Year Sampled
072	IDR06615-072	North Fork Payette River	44 53 54.56	-116 06 40.73	OverSamp	2006
* 074	IDR06615-074	Lochsa River	46 27 31.49	-115 02 25.34	OverSamp	2006 & 2008
075	IDR06615-075	Salmon River	44 14 54.28	-114 30 54.94	OverSamp	2006
076	IDR06615-076	Salmon River	44 23 31.56	-114 15 59.40	OverSamp	2006
* 077	IDR06615-077	Henry's Fork	43 47 49.49	-111 55 37.70	OverSamp	2006 & 2008
081	IDR06615-081	Snake River	43 22 42.93	-112 08 18.27	OverSamp	2006
082	IDR06615-082	Priest River	48 23 39.93	-116 52 05.75	OverSamp	2006
083	IDR06615-083	Snake River #1	43 00 52.52	-116 07 54.48	OverSamp	2008
084	IDR06615-084	South Fork Salmon River	44 41 42.04	-115 42 05.63	OverSamp	2008
085	IDR06615-085	Portneuf River	42 51 02.50	-112 26 30.37	OverSamp	2008
086	IDR06615-086	Saint Joe River	47 08 23.09	-115 24 29.02	OverSamp	2008
087	IDR06615-087	South Fork Payette River	44 10 17.03	-115 14 04.57	OverSamp	2008
088	IDR06615-088	Selway River	46 02 44.38	-115 17 47.04	OverSamp	2008
091	IDR06615-091	Big Wood River #2	43 26 03.52	-114 15 44.92	OverSamp	2008
094	IDR06615-094	Lemhi River	45 06 01.90	-113 43 36.48	OverSamp	2008
095	IDR06615-095	Snake River #3	42 38 07.66	-114 33 28.82	OverSamp	2008
097	IDR06615-097	SF Snake River	43 26 08.74	-111 21 27.49	OverSamp	2008
099	IDR06615-099	Payette River #2	43 54 02.98	-116 37 59.82	OverSamp	2008

* INDICATES SITES FROM 2006 RE-FISHED IN 2008

Appendix C. Fish Species Code List

Table C-1. Fish Species Codes and Trophic Levels

Species code	Common name	Scientific name	Trophic Level
8*	kokanee	<i>Oncorhynchus nerka</i>	2
9*	chinook salmon	<i>Oncorhynchus tshawytscha</i>	3
10*	rainbow trout	<i>Oncorhynchus mykiss</i>	3
11	cutthroat trout	<i>Oncorhynchus clarki</i>	3
16*	mountain whitefish	<i>Prosopium williamsoni</i>	3
19*	brown trout	<i>Salmo trutta</i>	4
21*	brook trout	<i>Salvelinus fontinalis</i>	4
22	bull trout	<i>Salvelinus confluentus</i>	4
24	Arctic grayling	<i>Thymallus arcticus</i>	3
27	chiselmouth	<i>Acrocheilus alutaceus</i>	3
30*	common carp	<i>Cyprinus carpio</i>	3
36*	northern pikeminnow	<i>Ptychocheilus oregonensis</i>	4
42*	Utah sucker	<i>Catostomus ardens</i>	3
43	longnose sucker	<i>Catostomus catostomus</i>	3
44*	bridgelip sucker	<i>Catostomus columbianus</i>	3
45	bluehead sucker	<i>Catostomus discobolus</i>	3
46*	largescale sucker	<i>Catostomus macrocheilus</i>	3
47	mountain sucker	<i>Catostomus platyrhynchus</i>	3
48	black bullhead	<i>Ameiurus melas</i>	3
49	brown bullhead	<i>Ameiurus nebulosus</i>	3
50	channel catfish	<i>Ictalurus punctatus</i>	3
52	flathead catfish	<i>Pylodictis olivaris</i>	3
61*	smallmouth bass	<i>Micropterus dolomieu</i>	4
62*	largemouth bass	<i>Micropterus salmoides</i>	4
64*	black crappie	<i>Pomoxis nigromaculatus</i>	3
65*	yellow perch	<i>Perca flavescens</i>	3
66	walleye	<i>Sander vitreus</i>	4
77	whitefish	<i>Coregonus sp.</i>	3
78	Pacific salmon/trout (Oncorhynchus sp.)	<i>Oncorhynchus sp.</i>	3
77	whitefish	<i>Prosopium sp.</i>	
80	Atlantic salmon/trout (Salmo sp.)	<i>Salmo sp.</i>	3
84	chub (Couesius sp.)	<i>Couesius sp.</i>	3
85	chub (Gila sp.)	<i>Gila sp.</i>	3
86	squawfish	<i>Ptychocheilus sp.</i>	3
89	sucker	<i>Catostomus sp.</i>	3
79	whitefish	<i>Prosopium sp.</i>	3
90	catfish	<i>Ictalurus sp.</i>	3
91	trout-perch	<i>Percopsis sp.</i>	3
93	bass	<i>Micropterus sp.</i>	4
95	perch	<i>Perca sp.</i>	3
116	yellow bullhead	<i>Ameiurus natalis</i>	3
501	cutthroat X rainbow trout	<i>Oncorhynchus clarki</i> X <i>O. mykiss</i>	3

Bold = Target species

* = species caught

Appendix C. Fish Species Code List

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Appendix D. Summary of Fish Lengths and Weights

Table D-1. Summary of Lengths and Weights for Sampled Fish

Site_ID	Species Code	American Fisheries Society Common Name	Number Caught	Ave ¹ Length (cm)	StDev ² Length (cm)	RSD ³ Length	Ave ¹ Weight (g)	StDev ² Weight (g)	RSD ³ Weight
IDR06615-005	42	Utah sucker	2	44	1.4	3%	1050	70.7	7%
IDR06615-011	10	rainbow trout	5	28	5.2	19%	239	150.5	63%
IDR06615-012	61	smallmouth bass	2	29	1.4	5%	353	3.5	1%
IDR06615-017	30	common carp	10	57	4.1	7%	2370	446.7	19%
IDR06615-026	8	kokanee	6	32	1.3	4%	278	30.6	11%
IDR06615-026	16	mountain whitefish	10	35	3.4	10%	406	88.7	22%
IDR06615-026	11	cutthroat trout	1	34			380		
IDR06615-027	21	brook trout	5	25	3.6	14%	170	95.4	56%
IDR06615-028	61	smallmouth bass	9	30	3.5	12%	300	106.1	35%
IDR06615-028	16	mountain whitefish	1	33			400		
IDR06615-030	62	largemouth bass	1	50			1500		
IDR06615-030	64	black crappie	1	25			220		
IDR06615-037	11	cutthroat trout	2	30	2.1	7%	250	35.4	14%
IDR06615-037	42	Utah sucker	10	44	8.7	20%	970	447.3	46%
IDR06615-040	36	northern squawfish	5	33	3.1	9%	299	72.5	24%
IDR06615-040	61	smallmouth bass	1	27			300		
IDR06615-040	16	mountain whitefish	1	32			300		
IDR06615-047	30	common carp	10	61	4.6	8%	4040	1071.0	27%
IDR06615-047	61	smallmouth bass	1	33			550		
IDR06615-050	46	largescale sucker	4	41	4.3	11%	705	285.8	41%
IDR06615-050	61	smallmouth bass	8	26	5.0	19%	244	114.8	47%
IDR06615-055	65	yellow perch	2	23	1.4	6%	138	3.5	3%
IDR06615-055	10	rainbow trout	1	38			500		
IDR06615-063	16	mountain whitefish	1	32			250		
IDR06615-063	44	bridgelip sucker	9	55	2.6	5%	1650	206.2	12%
IDR06615-063	46	largescale sucker	8	51	2.0	4%	1525	148.8	10%
IDR06615-063	61	smallmouth bass	6	29	2.1	7%	363	91.9	25%
IDR06615-068	16	mountain whitefish	10	31	3.5	11%	296	122.1	41%
IDR06615-074	16	mountain whitefish	10	35	2.7	8%	373	87.5	23%
IDR06615-074	11	cutthroat trout	8	30	5.3	18%	278	144.1	52%
IDR06615-077	11	cutthroat trout	2	53	7.1	13%	1600	848.5	53%
IDR06615-083	61	smallmouth bass	5	35	4.5	13%	665	318.3	48%
IDR06615-083	46	largescale sucker	10	55	4.0	7%	1870	424.4	23%
IDR06615-085	42	Utah sucker	6	38	5.7	15%	518	85.9	17%
IDR06615-086	11	cutthroat trout	3	23	1.4	6%	130	56.6	44%
IDR06615-086	16	mountain whitefish	3	32	3.5	11%	318	103.7	33%
IDR06615-086	21	brook trout	2	43	11.3	26%	728	526.8	72%
IDR06615-086	11	cutthroat trout	6	28	3.8	14%	213	98.3	46%
IDR06615-088	16	mountain whitefish	3	31	3.1	10%	267	102.1	38%
IDR06615-088	11	cutthroat trout	8	32	6.3	20%	232	133.4	58%
IDR06615-088	21	brook trout	1	40			500		
IDR06615-091	10	rainbow trout	10	33	2.3	7%	295	67.5	23%

Appendix D. Fish Lengths and Weights

Site_ID	Species Code	American Fisheries Society Common Name	Number Caught	Ave ¹ Length (cm)	StDev ² Length (cm)	RSD ³ Length	Ave ¹ Weight (g)	StDev ² Weight (g)	RSD ³ Weight
IDR06615-091	19	brown trout	1	36			500		
IDR06615-095	46	largescale sucker	10	45	4.0	9%	1025	237.2	23%
IDR06615-095	61	smallmouth bass	1	40			1000		
IDR06615-097	16	mountain whitefish	10	36	2.8	8%	396	64.1	16%
IDR06615-097	11	cutthroat trout	4	38	4.9	13%	588	154.8	26%
IDR06615-097	19	brown trout	10	45	5.2	11%	875	318.2	36%
IDR06615-097	10	rainbow trout	2	42	2.8	7%	550	0.0	0%
IDR06615-097		cutthroat trout x	1	46			700		
	501	rainbow trout							
IDR06615-099	46	largescale sucker	10	54	3.8	7%	1680	265.8	16%
IDR06615-099	16	mountain whitefish	7	28	3.9	14%	231	117.8	51%

1. Ave.—average

2. St. Dev.—standard deviation

3. RSD—relative standard deviation

Appendix E. Analytical Results

Table E-1. Water Samples Results by Site

Site #	Site Name	Date	Hg(T) ^a ng/L	Me-Hg ^b ng/L	% MeHg	As(T) ^c μg/L	As(i) ^d μg/L	% Org As ^e	Se(T) ^f μg/L	% As(i)	Hg(D) ^g ng/L
017	Bear River	8/13/2008	0.93	0.065	7%	3.30	1.90	42%	0.91	58%	
011	Big Wood River	7/9/2008	~ ^h 0.28	~ 0.025	~ 9%	0.80	0.60	25%	~ 0.15	75%	
091	Big Wood River #2	7/10/2008	~ 0.37	~ 0.025	~ 7%	1.21	0.94	22%	0.55	78%	
005	Blackfoot	7/19/2008	0.70	0.080	11%	1.54	0.92	40%	0.59	60%	
037	Blackfoot River #2	8/12/2008	0.59	0.105	18%	0.80	0.39	51%	1.57	49%	
051	Bruneau River	8/14/2008	0.81	0.120	15%	17.0	12.0	29%	0.76	71%	
061	Camas Creek	7/16/2008	0.95	0.066	7%	2.15	1.62	25%	~ 0.27	75%	
068	Camas Creek #2	9/4/2008	0.68	< 0.020	< ⁱ 3%	0.45	0.11	75%	< 0.09	25%	
030	Coeur d'Alene R #1	8/2/2008	110	0.199	0.2%	4.52	3.60	20%	< 0.09	80%	
038	Coeur d'Alene R #2	7/31/2008	~ 0.25	< 0.020	< 8%	0.53	0.54	< 1%	< 0.09	100%	
054	Coeur d'Alene R #3	8/1/2008	0.39	< 0.021	< 5%	0.59	0.59	< 1%	< 0.09	100%	
077	Henry's Fork	7/17/2008	1.03	0.146	14%	2.40	2.09	13%	~ 0.14	87%	
094	Lemhi River	9/3/2008	1.10	0.170	15%	2.82	2.14	24%	0.75	76%	
074	Lochsa River	9/17/2008	0.54	< 0.020	4%	~ 0.16	0.08	52%	< 0.09	48%	
027	NF Big Lost	7/15/2008	0.96	~ 0.038	~ 4%	0.61	0.41	32%	1.25	68%	
026	NF Clearwater R	9/16/2008	~ 0.23	< 0.020	9%	~ 0.19	0.15	24%	< 0.09	76%	
055	NF Payette	8/28/2008	0.70	0.098	14%	0.26	0.14	47%	< 0.09	53%	
044	Pahsimeroi	9/5/2008	~ 0.35	0.057	~ 16%	1.03	0.76	26%	0.93	74%	
063	Payette River	8/21/2008	1.08	0.082	8%	2.25	1.93	14%	~ 0.11	86%	
099	Payette River #2	8/25/2008	0.95	0.067	7%	0.74	0.56	25%	< 0.09	75%	
085	Portneuf River	7/20/2008	1.89	0.178	9%	4.86	3.04	37%	0.37	63%	
050	Priest River	7/30/2008	~ 0.17	< 0.020	< 12%	0.54	0.50	9%	< 0.09	91%	
086	Saint Joe River	8/3/2008	~ 0.22	< 0.020	< 9%	0.24	0.21	12%	< 0.09	88%	
040	Salmon R #1	9/9/2008	0.98	0.077	8%	2.39	2.17	9%	~ 0.17	91%	
028	Salmon R #2	9/10/2008	0.88	0.086	10%	2.29	1.71	25%	~ 0.14	75%	
012	Salmon R #3	9/29/2008	1.09	0.073	7%	1.90	2.40	< 1%	~ 0.10	100%	
088	Selway River	9/18/2008	0.40	< 0.020	5%	~ 0.06	~ 0.02	63%	< 0.09	37%	
087	SF Payette	9/2/2008	~ 0.26	< 0.020	< 8%	0.24	0.20	15%	< 0.09	85%	
084	SF Salmon	8/27/2008	1.41	0.123	9%	0.78	0.61	22%	< 0.09	78%	
097	SF Snake	7/18/2008	0.72	~ 0.034	~ 5%	2.14	1.68	21%	~ 0.29	79%	
083	Snake River #1	8/18/2008	0.94	0.075	8%	4.64	4.33	7%	1.22	93%	

Appendix E. Analytical Results

Site #	Site Name	Date	Hg(T) ^a ng/L	Me-Hg ^b ng/L	% MeHg	As(T) ^c µg/L	As(i) ^d µg/L	% Org As ^e	Se(T) ^f µg/L	% As(i)	Hg(D) ^g ng/L
047	Snake River #2	8/19/2008	1.71	0.101	6%	9.74	8.19	16%	1.75	84%	
095	Snake River #3	8/20/2008	1.82	0.102	6%	4.83	2.89	40%	1.27	60%	
031	Weiser River	8/26/2008	0.54	~ 0.045	~ 8%	0.33	0.19	42%	< 0.09	58%	
13313000	Johnson Creek @ YP	9/2/2008	0.70	< 0.020	< 3%	4.92	3.90	21%	< 0.09	79%	
13206000	Boise R @ Glenwood	9/4/2008	0.91	0.057	6%	2.22	1.73	22%	< 0.09	78%	
13185000	Boise R @ Twn Spr	9/5/2008	0.69	~ 0.030	~ 4%	3.23	3.03	6%	< 0.09	94%	
13056500	Henry's Fk Nr Rexburg	9/9/2008	0.62	~ 0.044	~ 7%	3.55	3.10	13%	0.74	87%	
13305000	Lemhi Nr Lemhi	9/10/2008	0.92	0.083	9%	4.05	3.94	3%	1.05	97%	
13302005	Pahsimeroi @ Ellis	9/11/2008	0.51	~ 0.044	~ 9%	3.52	1.01	71%	~ 0.13	29%	
Summary statistics for 34 probabilistic sites		Mean	4.00	0.071	9%	2.30	1.75	27%	0.43	73%	
		Max	110	0.199	18%	17	12	75%	1.75	100%	
		Min	0.17	< 0.020	0.2%	0.06	0.02	1%	< 0.09	25%	
			1 > 12	9 < 0.02		1 > 10	1 > 10		14 < 0.09		
		Median	0.77	0.07	8%	1.12	0.84	24%	0.14	76%	
		Mean*	0.79	*Excluding high value of 110							
Summary statistics for all 40 sites sampled in 2008, DEQ & USGS		Mean	3.51	0.067	8%	2.50	1.91	26%	0.42	74%	
		Max	110	0.199	18%	17	12	75%	1.75	100%	
		Min	0.17	< 0.020	0.2%	0.06	~ 0.02	1%	< 0.09	25%	
				10 < 0.02		1 > 10	1 > 10		17 < 0.09		
		Median	0.71	0.06	0.08	2.02	1.32	0.23	0.14		
x99	Boise R. Ann Morrison	6/13/2008	1.33								
063	Payette R, Dup	9/25/2008	1.01	0.065	6%	2.98	3.30	< 1%	~ 0.12	100%	
030	Coeur d'Alene R #1	10/23/2008	6.21	< 0.02	< 1%	1.10	1.04	5%	< 0.11	95%	0.68
030	" " dup	10/23/2008	4.78	< 0.019	< 1%	1.12	1.04	7%	< 0.11	93%	0.53
		Mean	5.50							94%	0.61

^a Hg(T) = total mercury; ng/L = nanograms per liter

^b Me-Hg = methylmercury

^c As(T) = total arsenic; µg/L = micrograms per liter

^d As(i) = inorganic arsenic

^e Org As = organic arsenic

^f Se(T) = total selenium

^g Hg(D) = dissolved mercury

^h ~ = between detection limit & practical quantitation limit

ⁱ < = less than detection limit

Appendix E. Analytical Results

Table E-2. Fish Tissue Results by Species

Site #	Site Name	Date	Species	# of Fish	Hg μg/kg ^a	As mg/kg ^b	As(i) ^c mg/kg	%Org As ^d	Se ^e mg/kg	% Solids	Se mg/kg dry wt ^f
026	NF Clearwater R	9/16/2008	8	6	113	< ^g 0.015	< 0.002	> 87%	~ ^h 0.080	16.4	0.49
011	Big Wood R, U	9/22/2008	10	5	29	0.070	0.006	91%	0.813	22.1	3.67
055	NF Payette R	8/28/2008	10	1	132	0.060	< 0.002	> 97%	~ 0.040	14.7	0.27
091	Big Wood R, L	9/22/2008	10	10	44	< 0.013	< 0.002	> 85%	0.875	22.2	3.94
097	SF Snake R	9/24/2008	10	2	175	< 0.014	< 0.002	> 86%	0.269	16.0	1.68
026	NF Clearwater R	9/16/2008	11	1	66	< 0.015	< 0.002	> 87%	~ 0.075	20.4	0.37
037	Blackfoot R-2	8/12/2008	11	2	56	0.059	< 0.002	> 97%	3.08	21.0	14.69
074	Lochsa R	9/17/2008	11	8	48	< 0.013	< 0.002	> 85%	~ 0.065	23.9	0.27
077	Henry's Fork R	7/17/2008	11	2	275	0.064	< 0.002	> 97%	0.405	21.3	1.90
086	Saint Joe R	8/3/2008	11	3	37	0.063	< 0.002	> 97%	0.257	20.0	1.28
086	Saint Joe R, Dup	9/30/2008	11	5	50	0.091	< 0.002	> 98%	0.169	21.7	0.78
088	Selway R	9/18/2008	11	3	49	< 0.013	< 0.002	> 85%	~ 0.073	22.1	0.33
088	Selway R, Dup	9/29/2008	11	5	57	~ 0.020	< 0.002	> 90%	~ 0.079	22.3	0.35
097	SF Snake R	7/18/2008	11	2	84	~ 0.025	< 0.002	> 92%	0.454	21.1	2.15
097	SF Snake R, Dup	9/24/2008	11	2	77	< 0.013	< 0.002	> 85%	0.399	22.1	1.80
026	NF Clearwater R	9/16/2008	16	10	85	0.057	< 0.002	> 96%	~ 0.076	25.2	0.30
028	Salmon R-2	9/10/2008	16	1	142	~ 0.021	< 0.002	> 90%	0.389	20.4	1.90
040	Salmon R-1	9/9/2008	16	1	97	0.060	< 0.002	> 97%	0.300	21.3	1.41
063	Payette R	9/25/2008	16	1	50	0.056	< 0.002	> 96%	~ 0.103	20.3	0.51
068	Camas Cr-2	9/4/2008	16	10	61	0.065	< 0.002	> 97%	0.275	24.7	1.12
074	Lochsa R	9/17/2008	16	10	52	0.058	< 0.002	> 97%	~ 0.058	26.9	0.22
086	Saint Joe R	8/3/2008	16	3	40	0.096	< 0.002	> 98%	0.185	24.4	0.76
088	Selway R	9/18/2008	16	3	83	< 0.014	< 0.002	> 86%	~ 0.050	21.7	0.23
097	SF Snake R	7/18/2008	16	10	90	0.066	< 0.002	> 97%	0.614	23.1	2.65
099	Payette R-2	8/25/2008	16	7	41	0.163	< 0.002	> 99%	0.141	25.4	0.55
091	Big Wood R, L	9/22/2008	19	1	52	~ 0.043	< 0.002	> 95%	0.790	20.1	3.94
097	SF Snake R	9/24/2008	19	10	253	~ 0.035	< 0.002	> 94%	0.408	22.5	1.81
027	NF Big Lost R	7/15/2008	21	5	~ 64	0.103	< 0.002	> 98%	1.4	20.8	6.74
086	Saint Joe R	9/30/2008	21	2	174	0.084	< 0.002	> 98%	0.112	19.4	0.58
088	Selway R	9/29/2008	21	1	153	0.140	< 0.002	> 99%	~ 0.076	21.1	0.36
017	Bear R	8/13/2008	30	10	252	0.057	< 0.002	> 96%	0.486	20.0	2.44

Appendix E. Analytical Results

Site #	Site Name	Date	Species	# of Fish	Hg μg/kg ^a	As mg/kg ^b	As(i) ^c mg/kg	%Org As ^d	Se ^e mg/kg	% Solids	Se mg/kg dry wt ^f
047	Snake R-2	8/19/2008	30	10	138	0.308	< 0.002	> 99%	0.498	22.7	2.20
040	Salmon R-1	9/9/2008	36	5	674	~ 0.037	< 0.002	> 95%	0.428	20.6	2.08
005	Blackfoot R	7/19/2008	42	2	32	~ 0.030	< 0.002	> 93%	0.789	21.0	3.75
085	Portneuf R	7/20/2008	42	6	192	~ 0.038	< 0.002	> 95%	0.243	19.6	1.24
037	Blackfoot R-2	8/12/2008	44	5	92	0.054	< 0.002	> 96%	2.28	18.5	12.32
037	Blackfoot R-2, Dup	8/12/2008	44	5	79	0.090	< 0.002	> 98%	2.15	20.5	10.49
063	Payette R	8/21/2008	44	9	234	0.168	< 0.002	> 99%	0.112	26.5	0.42
050	Priest R	7/30/2008	46	4	278	0.050	< 0.002	> 96%	0.136	18.6	0.73
063	Payette R	9/25/2008	46	8	186	0.126	< 0.002	> 98%	0.114	26.7	0.43
083	Snake R-1	8/18/2008	46	10	198	0.309	< 0.002	> 99%	0.239	27.9	0.86
095	Snake R-3	8/20/2008	46	10	190	0.106	< 0.002	> 98%	0.314	20.5	1.53
099	Payette R-2	8/25/2008	46	10	276	0.158	< 0.002	> 99%	~ 0.065	26.0	0.25
012	Salmon R-3	9/11/2008	61	2	380	~ 0.041	< 0.002	> 95%	0.560	22.1	2.54
028	Salmon R-2	9/10/2008	61	9	548	0.155	< 0.002	> 99%	0.594	21.7	2.73
040	Salmon R-1	9/9/2008	61	1	253	0.066	< 0.002	> 97%	0.453	23.4	1.94
047	Snake R-2	8/19/2008	61	1	88	0.136	< 0.002	> 99%	0.570	17.5	3.25
050	Priest R	7/30/2008	61	8	156	~ 0.045	< 0.002	> 96%	0.155	19.4	0.80
063	Payette R	8/21/2008	61	6	123	0.114	< 0.002	> 98%	0.234	21.9	1.07
083	Snake R-1	8/18/2008	61	5	200	0.157	< 0.002	> 99%	0.461	20.1	2.29
095	Snake R-3	8/20/2008	61	1	318	0.078	< 0.002	> 97%	0.376	16.2	2.33
030	Cd'A R-1	8/2/2008	62	1	572	< 0.015	< 0.002	> nc	< 0.056	15.8	0.35
030	Cd'A R-1	8/2/2008	64	1	280	~ 0.029	< 0.002	> 93%	0.151	18.1	0.84
055	NF Payette R	8/28/2008	65	2	108	0.050	< 0.002	> 96%	~ 0.072	19.1	0.38
097	SF Snake R	9/24/2008	501	1	240	< 0.014	< 0.002	> 86%	0.397	15.8	2.52
999	Bigwood, USGS	8/13/2008	19	10	136	~ 0.034	< 0.002	> 94%	0.753	23.4	3.22

> 300 mg/kg Hg tissue criterion
Minimum result
Maximum result

Mean	160	0.073	>	96.2%	0.437	21.2	2.12
Max	674	0.309		99.4%	3.080	27.9	14.69
Min	29	< 0.013		85.7%	~ 0.040	14.7	0.22
n=55	5 > 300		all but 1 < 0.002				
Median	123	0.058			0.269	21.1	1.28

^a Hg = mercury; μg/kg = micrograms per kilogram. ^b As = arsenic; mg/kg = milligrams per kilogram. ^c As(i) = inorganic arsenic. ^d Org As = organic arsenic.

^e Se = selenium. ^f dry wt = dry weight. ^g < = less than detection limit. ^h ~ = between detection limit & practical quantitation limit.

Appendix E. Analytical Results

Hatchery Chinook Salmon, returning 3-ocean spawners

x99	Clearwater FH-female	9/2/2008	9	3	141	0.24	<	0.002	>	99.2%	0.16	19.1	0.84
x99	McCall FH-female	8/29/2008	9	3	151	0.17	<	0.002	>	98.8%	0.16	21.3	0.77
x99	McCall FH-male	8/29/2008	9	3	131	0.23	<	0.002	>	99.1%	0.17	20.6	0.81
x99	Pahsimeroi FH-female	8/29/2008	9	3	135	0.30	<	0.002	>	99.3%	0.18	22.0	0.80
x99	Pahsimeroi FH-male	8/29/2008	9	3	138	0.27	<	0.002	>	99.3%	0.15	17.8	0.84
x99	Rapid River FH-female	9/4/2008	9	3	134	0.18	<	0.002	>	98.9%	0.23	22.6	1.01
x99	Rapid River FH-male	9/4/2008	9	3	158	0.41	<	0.002	>	99.5%	0.21	21.3	0.99
x99	Sawtooth FH-female	9/5/2008	9	3	166	0.16	<	0.002	>	98.8%	0.17	20.8	0.82
x99	Sawtooth FH-male	9/5/2008	9	3	191	0.25	<	0.002	>	99.2%	0.15	18.5	0.79
Mean					149	0.24			>	99.1%	0.17	20.4	0.85
Max					191	0.41			>	99.5%	0.23	22.6	1.01
Min					131	0.16			>	98.8%	0.15	17.8	0.77
n=9													

Appendix E. Analytical Results

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Appendix F. Quality Control Sample Results

Field Quality Control (QC) Results

Table F-1. Field QC Results of Water Samples

Site #	QA/QC Sample Type	Date Sent to Lab	Lab Report Date	MeHg ng/L ^a	Hg ng/L ^b	As(i) μg/L ^c	As(T) ^d μg/L	Se ^e μg/L
Batch 1		6/20/2008	6/30/2008					
test	Blank				< ^f 0.15			
	Blank, breath				< 0.15			
	Blank, finger rinse				< 0.15			
Batch 2		7/14/2008	8/6/2008					
	Blank			~ ^g 0.021	< 0.15	< 0.008	< 0.06	< 0.09
Batch 3		7/22/2008	8/25/2008					
	Blank			< 0.020	< 0.15	< 0.008	< 0.06	< 0.09
Batch 4		8/7/2008	9/16/2008					
	Blank			< 0.020	< 0.15	~ 0.019	< 0.06	< 0.09
Batch 5		8/18/2008	09/23/2008					
	Blank			< 0.020	< 0.15	0.027	< 0.06	< 0.09
	Site 037			0.105	0.59	0.394	0.80	1.57
	Duplicate			0.107	0.58	0.347	0.88	1.49
	%RPD			2%	2%	13%	10%	5%
Batch 6		08/25/2008	09/25/2008					
	Blank			< 0.020	< 0.15	< 0.008	< 0.06	< 0.09
	Site 095			0.102	1.82	2.89	4.83	1.27
	Duplicate			0.103	3.91	4.28	4.85	1.08
	%RPD			1%	73%	39%	0%	16%
Batch 7		08/29/2008	10/02/2008					
	Blank			~ 0.021	< 0.15	< 0.008	< 0.06	< 0.09
	Site 055			0.098	0.7	0.138	0.26	< 0.09
	Duplicate			0.098	~ 0.39	0.143	0.29	~ 0.11
	%RPD			0%	57%	4%	11%	n/c
	Site 099			0.067	0.95	0.558	0.74	< 0.09
	Duplicate			0.068	1.67	0.549	0.7	< 0.09

Appendix F. Quality Control Sample Results

Site #	QA/QC Sample Type	Date Sent to Lab	Lab Report Date		MeHg ng/L ^a		Hg ng/L ^b		As(i) μg/L ^c		As(T) ^d μg/L		Se ^e μg/L
	%RPD				1%		55%		2%		6%		n/c
Batch 8		9/09/2008	10/07/2008										
	Blank			~	0.024	<	0.15	<	0.008	<	0.01	<	0.09
Batch 9		9/15/2008	10/07/2008										
	None												
Batch 10		09/23/2008	10/16/2008										
	Blank			<	0.020	<	0.15	~	0.012	<	0.04	<	0.09
	Site 026			<	0.020	~	0.23		0.145	~	0.19	<	0.09
	Duplicate			~	0.027	~	0.27		0.135	~	0.19	<	0.09
	%RPD				n/c		16%		7%		0%		n/c
	Henry's Fk @ Rex			~	0.044		0.62		3.34		1.27		0.74
	Duplicate			~	0.036		0.56		3.10		3.55	~	0.16
	%RPD				20%		10%		7%		95%		129%
Batch 11		10/02/2008	10/31/2008										
	No water samples												
Batch 12		10/03/2008	11/06/2008										
	None												
Batch 13													
	Blank			<	0.020	<	0.15	<	0.008	<	0.04	<	0.11
	Site 030			<	0.020		6.21		1.04		1.1	<	0.11
	Duplicate			<	0.019		4.78		1.04		1.12	<	0.11
	%RPD				n/c		26%		0%		2%		n/c

^a Me-Hg = methylmercury; ng/L = nanograms per liter

^b Hg = mercury

^c As(i) = inorganic arsenic; μg/L = micrograms per liter

^d As(T) = total arsenic

^e Se = selenium

^f < = less than detection limit

^g ~ = between detection limit & practical quantitation limit

Appendix F. Quality Control Sample Results

Site #	QA/QC Sample Type	Date Sent to Lab	Lab Report Date	MeHg ng/L ^a	Hg ng/L ^b	As(i) μg/L ^c	As(T) ^d μg/L	Se ^e μg/L
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Field QC Summary for Water

Accuracy	Blanks	Min	< 0.020	< 0.150	< 0.008	< 0.010	< 0.090
		Max n	~ 0.024 9	< 0.150 10	0.027 9	< 0.060 9	< 0.110 9
Precision	Dups	Min	0%	2%	0%	0%	5%
		Max	20%	73%	39%	95%	129%
		Mean	5%	34%	10%	18%	50%
		n	5	7	7	7	3

Table F-2. Field QC Results of Fish Tissue Samples

Site #	Site Name	Species	# of fish	Date Sampled		Hg ng/g ^a	%RPD ^b		As(i) mg/kg ^c	%RPD		As(T) ^d mg/kg	%RPD		Se ^e mg/kg	%RPD
037	Blackfoot River	44	5	8/12/2008		92		< ^f	0.002			0.054			2.28	
037	Blackfoot River	44	5	8/12/2008		79	15%	<	0.002	nc ^g		0.090	50%		2.15	6%
086	Saint Joe River	11	3	08/03/2008		37		<	0.002			0.063			0.257	
086	Saint Joe River	11	5	09/30/2008		50	30%	<	0.002	nc		0.091	36%		0.169	41%
088	Selway River	11	3	09/18/2008		49		<	0.002		<	0.013		~ ^h	0.073	
088	Selway River	11	5	09/29/2008		57	15%	<	0.002	nc	~	0.020	nc	~	0.079	8%
097	SF Snake River	11	2	09/18/2008		84		<	0.002		~	0.025			0.454	
097	SF Snake River	11	2	09/24/2008		77	9%	<	0.002	nc	<	0.013	nc		0.399	17%

^a Hg = mercury; ng/L = nanograms per liter^b RPD = relative percent difference^c As(i) = inorganic arsenic; mg/kg = milligrams per kilogram^d As(T) = total arsenic^e Se = selenium^f < = less than detection limit^g nc = not calculable^h ~ = between detection limit & practical quantitation limit**Fish Field Duplicate QC Summary**

Precision	Min	9%	nc	36%	6%
	Max	30%	nc	50%	41%
	Mean	17%	nc	43%	17%
	n	4	0	2	4

Laboratory QC Results

Table F-3. Laboratory QC Results of Water Samples

Batc h #	Report ID / Date	QA/QC sample type		Hg ng/L ^a	% Rec	% RPD ^b		Me-Hg ng/L ^c	% Rec	% RPD		As(I) µg/L ^d	% Rec	% RPD		As(T) ^e µg/L	% Rec	% RPD		Se ^f µg/L	% Rec	% RPD
1	0825050																					
	6/30/2008	Method Blank	< g	0.04																		
		Matrix Spike			107%																	
		Duplicate			102%	3%																
		Matrix Spike			120%																	
		Duplicate			110%	7%																
2	0829023																					
	8/6/2008	Method Blank	<	0.07			<	0.007			<	0.005			<	-0.01			<	0.01		
		CRM ^h			111%				106%				na				92%				90%	
		Matrix Spike			95%				109%				101%				107%				100%	
		Duplicate			106%	11%			113%	2%			92%	7%			109%	2%			100%	0.4%
3	0830026																					
	8/25/2008	Method Blank	<	0.07			<	0.009				0.009			<	-0.01			<	0.01		
		CRM			106%				93%				na				97%				97%	
		CRM							103%													
		Matrix Spike			100%				84%				90%				105%				95%	
		Duplicate			106%	5%			87%	4%			82%	6%			101%	3%			90%	3%
		Matrix Spike							105%													
		Duplicate							102%	2%												
4	0832054																					
	9/16/2008	Method Blank	<	0.08			<	0.011			<	0.101			<	-0.020			<	0.00		
		CRM			90%				99%				na				95%				92%	
		CRM															91%					

Appendix F. Quality Control Sample Results

Batc h #	Report ID / Date	QA/QC sample type		Hg ng/L ^a	% Rec	% RPD ^b		Me-Hg ng/L ^c	% Rec	% RPD			As(I) µg/L ^d	% Rec	% RPD		As(T) ^e µg/L	% Rec	% RPD		Se ^f µg/L	% Rec	% RPD
		Matrix Spike			93%				106%					113%				104%				78%	
		Duplicate			102%	8%			106%	1%				107%	4%			107%	4%			92%	17%
		Matrix Spike																111%					
		Duplicate																110%	0%				
5	0834019																						
	09/23/2008	Method Blank	<	0.13			<	0.009			<	0.006				<	0.04			<	0.03		
		CRM			89%				105%					na				97%				101%	
		Matrix Spike			117%				107%					89%				nr				114%	
		Duplicate			101%	10%			108%	1%				74%	8%			nr	1%			115%	0%
6	0835024																						
	09/25/2008	Method Blank	<	0.11			<	0.009			<	0.005				<	0.00			<	-0.04		
		CRM			102%				104%					na									
		CRM			97%				107%									92%				95%	
		Matrix Spike			92%				114%					93%				102%				100%	
		Duplicate			114%	18%			111%	1%				96%	2%			104%	1%			97%	3%
7	0835056																						
	10/02/2008	Method Blank	<	0.06			<	0.008				0.009				<	0.00			<	-0.04		
		CRM			113%				105%					na				92%				95%	
		CRM							108%														
		Matrix Spike			102%				102%					95%				97%				100%	
		Duplicate			109%	5%			103%	1%				90%	3%			101%	3%			97%	3%
8	0837030																						
	10/07/2008	Method Blank	<	0.108			<	0.007				0.009				<	-0.017			<	-0.05		
		CRM			99%				99%					na				91%				95%	
		CRM							84%														
		Matrix Spike			102%				102%					95%				105%				100%	
		Duplicate			102%	1%			107%	5%				90%	3%			105%	0%			97%	3%

Appendix F. Quality Control Sample Results

Batc h #	Report ID / Date	QA/QC sample type		Hg ng/L ^a	% Rec	% RPD ^b		Me-Hg ng/L ^c	% Rec	% RPD		As(I) µg/L ^d	% Rec	% RPD		As(T) ^e µg/L	% Rec	% RPD		Se ^f µg/L	% Rec	% RPD
9	0838011																					
	10/07/2008	Method Blank	<	0.098			<	0.012			<	0.008			<	0.012				- 0.105		
		CRM			105%				102%				na				93%				98%	
		CRM							75%													
		Matrix Spike			110%				112%				96%				100%				104%	
		Duplicate			109%	1%			116%	3%			93%	2%			98%	1%			104%	0%
10	0839019																					
	10/16/2008	Method Blank	<	0.113			<	0.001			<	0.008			<	0.038				-0.13		
		CRM			100%				94%				na				92%				99%	
		CRM							102%													
		Matrix Spike			111%				110%				79%				104%				107%	
		Duplicate			109%	0%			100%	11%			85%	4%			104%	0%			106%	
		Matrix Spike															107%				110%	
		Duplicate															106%	1%			110%	0%
11	0840046	no water																				
	10/31/2008	samples																				
12	0840052																					
	11/06/2008	Method Blank		0.180			<	0.002			<	0.008			<	0.020				0.130		
		CRM			98%				87%				na				93%				93%	
		CRM																				
		Matrix Spike			103%				100%				93%				82%				76%	
		Duplicate			107%	2%			95%	5%			95%	1%			91%	4%			86%	11%
		Matrix Spike							97%				104%									
		Duplicate							88%	9%			97%	5%								
13	0843041																					
	11/17/2008	Method Blank		0.210			<	0.006			<	0.005			<	0.010				<	0.030	
		CRM			100%				111%				na				92%				95%	

Appendix F. Quality Control Sample Results

Batc h #	Report ID / Date	QA/QC sample type	Hg ng/L ^a	% Rec	% RPD ^b	Me-Hg ng/L ^c	% Rec	% RPD	As(I) µg/L ^d	% Rec	% RPD	As(T) ^e µg/L	% Rec	% RPD	Se ^f µg/L	% Rec	% RPD
		CRM		102%			88%										
		Matrix Spike		99%			95%			105%			103%			117%	
		Duplicate		102%	1%		98%	3%		103%	1%		104%	1%		115%	2%
		Matrix Spike		102%													
		Duplicate		106%	2%												

^a Hg = mercury; ng/L = nanograms per liter

^b RPD = relative percent difference

^c Me-Hg = methylmercury

^d As(i) = inorganic arsenic; µg/L = micrograms per liter

^e As(T) = total arsenic

^f Se = selenium

^g < = less than detection limit

^h = certified reference material

Lab QC Sample Summary for Water

Accuracy	MDL	0.15	0.02	0.008	0.06	0.09
Method	Min	0.040	0.001	0.005	-0.020	-0.125
Blanks	Max	0.210	0.012	0.101	0.040	0.130
	n	12	11	11	11	11
	Mean	0.106	0.007	0.016	0.006	-0.014
	# < DL	10	11	8	11	8
CRMs	Min	89%	75%	na	91%	90%
	Max	113%	111%	na	97%	101%
	n	13	18	0	11	10
	Mean	101%	98%	na	93%	96%
Spikes	Min	92%	84%	74%	82%	76%
	Max	120%	116%	113%	111%	117%
	n	28	26	24	24	24
	Mean	105%	103%	94%	103%	100%
Precision	Min	0%	1%	1%	0%	0%
Spike/Dups	Max	18%	11%	8%	4%	17%
	n	14	13	12	13	11
	Mean	5%	4%	4%	2%	4%

Appendix F. Quality Control Sample Results

Table F-4. Laboratory QC Results of Fish Tissue Samples

Batch #	Report ID / Date	QA/QC sample type		Hg ng/L (ng/g) ^a	% Rec	% RPD ^b		As(i) mg/kg ^c	% Rec	% RPD		As(T) ^d mg/kg	% Rec	% RPD		Se ^e mg/kg	% Rec	% RPD
1	0825050																	
	6/30/2008	no fish																
2	0829023																	
	08/06/2008	no fish																
3	0830026																	
	8/25/2008	Digest Blank	< ^f	0.004			<	0.0002			<	0.0008			<	0.002		
		Method Blank	<	0.02			<	-0.001			<	-0.005			<	-0.011		
		CRM ^g			88%				102%				86%				97%	
		CRM			117%								88%				99%	
		Matrix Spike			99%				72%				92%				86%	
		Duplicate			110%	14%			75%	0%			93%	9%			83%	10%
		Method Dup				0.3%				n/c				0%				4%
4	0832054																	
	9/16/2008	Digest Blank	<	0.02			<	0.0001			<	0.0008			<	0.002		
		Method Blank	<	0.11			<	0.001			<	-0.007			<	0.005		
		CRM			120%				95%				91%				92%	
		CRM							92%				87%				92%	
		Matrix Spike			120%				100%				95%				86%	
		Duplicate							91%	11%			96%	2%			87%	3%
		Method Dup				12%				n/c				n/c				9%
5	0834019																	
	09/23/2008	Digest Blank	<	0.004			<	0.0002				0.003			<	0.002		
		Method Blank	<	0.03			<	0.000			<	-0.017			<	0.001		

Appendix F. Quality Control Sample Results

Batch #	Report ID / Date	QA/QC sample type		Hg ng/L (ng/g) ^a	% Rec	% RPD ^b		As(i) mg/kg ^c	% Rec	% RPD		As(T) ^d mg/kg	% Rec	% RPD		Se ^e mg/kg	% Rec	% RPD
		CRM			111%				96%				101%				114%	
		CRM			116%				102%				94%				99%	
		Matrix Spike			109%				73%				96%				94%	
		Duplicate			98%	14%			91%	27%			98%	1%			96%	1%
		Method Dup				5%				n/c				13%				4%
6	0835024																	
	09/25/2008	Digest Blank	<	0.004			<	0.0002				0.003			<	0.002		
		Method Blank	<	0.02			<	0.000				<	-0.017		<	0.001		
		CRM			110%				96%				101%				114%	
		CRM							102%				94%				99%	
		Matrix Spike			106%				98%				95%				92%	
		Duplicate			104%	1%			93%	16%			103%	5%			98%	5%
		Method Dup				10%				n/c				0%				5%
7	0835056																	
	10/02/2008	Digest Blank	<	0.004			<	0.0002				0.0007			<	0.002		
		Method Blank	<	0.02			<	0.000				<	-0.017		<	0.001		
		CRM			110%				96%				104%				104%	
		CRM							102%				99%				98%	
		Matrix Spike			105%				73%				96%				94%	
		Duplicate			103%	5%			91%	27%			98%	1%			96%	1%
		Matrix Spike							100%				111%				75%	
		Duplicate							86%	15%			109%	1%			89%	7%
		Method Dup				3%				n/c				13%				4%
		Method Dup								n/c				2%				4%

Appendix F. Quality Control Sample Results

Batch #	Report ID / Date	QA/QC sample type		Hg ng/L (ng/g) ^a	% Rec	% RPD ^b		As(i) mg/kg ^c	% Rec	% RPD		As(T) ^d mg/kg	% Rec	% RPD		Se ^e mg/kg	% Rec	% RPD
8	0837030																	
	10/07/2008	Digest Blank	<	0.004			<	0.0002			<	0.0007			<	0.002		
		Method Blank	<	0.012			<	0.000			<	0.004			<	-0.001		
		CRM			121%				123%				104%				104%	
		CRM											99%				98%	
		Matrix Spike			102%				100%				111%				75%	
		Duplicate			113%	10%			86%	15%			109%	1%			89%	7%
		Method Dup				15%				n/c				2%				4%
9	0838011																	
	10/07/2008	Digest Blank	<	0.004			<	0.0002			<	0.0007			<	0.002		
		Method Blank	<	0.012			<	0.000			<	0.004			<	-0.001		
		CRM			121%				123%				104%				104%	
		CRM											99%				98%	
		Matrix Spike			102%				100%				111%				75%	
		Duplicate			113%	10%			86%	15%			109%	1%			89%	7%
		Method Dup				15%				n/c				2%				4%
10	0839019																	
	10/16/2008	Digest Blank	<	0.004			<	0.0002			<	0.0007			<	0.002		
		Method Blank	<	0.004			<	0.000				-0.023			<	-0.035		
		CRM			110%				92%				98%				98%	
		CRM							100%				97%				101%	
		Matrix Spike			93%				79%				107%				103%	
		Duplicate			92%	2%			81%	3%			104%	2%			91%	6%
		Method Dup				6%				n/c				n/c				10%

Appendix F. Quality Control Sample Results

Batch #	Report ID / Date	QA/QC sample type		Hg ng/L (ng/g) ^a	% Rec	% RPD ^b		As(i) mg/kg ^c	% Rec	% RPD		As(T) ^d mg/kg	% Rec	% RPD		Se ^e mg/kg	% Rec	% RPD
11	0840046																	
	10/31/2008	Digest Blank	<	0.030			<	0.0002			<	0.0007			<	0.002		
		Method Blank	<	0.15			<	-0.001			<	-0.007			<	0.004		
		CRM			113%				100%				94%				102%	
		CRM			118%				96%				92%				99%	
		Matrix Spike			114%				109%				95%				94%	
		Duplicate			109%	0%			109%	4%			101%	1%			96%	4%
		Matrix Spike			108%													
		Duplicate			109%	2%												
		Method Dup				1%				n/c				7%				5%
		Method Dup				2%												
		Method Dup				10%												
12	0840052																	
	11/06/2008	Digest Blank	<	0.030			<	0.0002			<	0.0007			<	0.002		
		Method Blank	<	0.15			<	-0.001			<	0.002			<	-0.010		
		CRM			113%				100%				88%				101%	
		CRM			118%				96%				85%				94%	
		Matrix Spike			103%				93%				102%				98%	
		Duplicate			112%	7%			102%	20%			96%	4%			82%	8%
		Matrix Spike							104%				96%				92%	
		Duplicate							104%	8%			96%	12%			95%	12%
		Method Dup				10%				n/c				n/c				1%
		Method Dup								n/c				3%				8%

Appendix F. Quality Control Sample Results

Batch #	Report ID / Date	QA/QC sample type	Hg ng/L (ng/g) ^a	% Rec	% RPD ^b	As(i) mg/kg ^c	% Rec	% RPD	As(T) ^d mg/kg	% Rec	% RPD	Se ^e mg/kg	% Rec	% RPD
13	0843041													
	11/17/2008	no fish												

^a Hg = mercury; ng/L = nanograms per liter; ng/g = nanograms per gram

^b RPD = relative percent difference

^c As(i) = inorganic arsenic; mg/kg = milligrams per kilogram

^d As(T) = total arsenic

^e Se = selenium

^f < = less than detection limit

^g = certified reference material

Laboratory QC Sample Summary for Fish Tissue

Accuracy		Min	< 0.004	< 0.0001	< 0.0007	< 0.002
	Digest	Max	< 0.030	< 0.0002	0.003	< 0.002
	Blanks	n	10	10	10	10
		Mean	< 0.011	< 0.0002	< 0.001	< 0.002
	Method	MDL	0.04	0.002	0.015	0.04
	Blanks	Min	0.004	-0.001	-0.023	-0.035
		Max	0.15	0.001	0.004	0.005
		n	10	10	10	10
		Mean	0.053	0.000	-0.008	-0.005
	CRMs	Min	88%	92%	85%	92%
		Max	121%	123%	104%	114%
		n	10	10	14	14
		Mean	112%	100%	93%	99%
Matrix	Min	92%	72%	92%	75%	
Spikes	Max	120%	109%	111%	103%	
	n	19	20	20	20	
	Mean	106%	91%	99%	91%	
Precision	Min	0%	0%	1%	1%	
	Spike/Dups	Max	14%	27%	12%	12%
	n	9	10	10	10	

Appendix F. Quality Control Sample Results

Laboratory QC Sample Summary for Fish Tissue

	Mean	6%	13%	4%	6%
Method	Min	0%	nc	0%	1%
Duplicates	Max	15%	nc	13%	10%
	n	10	0	7	10
	Mean	6%	nc	5%	5%

Appendix G. QA / QC Evaluation

Data Quality Assessment for Fish Mercury Study in Statewide Rivers, Idaho Department of Environmental Quality

Prepared by Xin Dai, DEQ Technical Services
Feb. 11, 2009

This report applies to the data obtained for IDEQ's study entitled "Mercury in Fish Tissue – A Statewide Assessment of Rivers". Data quality assessment is primarily based on criteria listed in the QAPP (version 1.1) of the study. Following criteria are used: method detection limits (MDL) requirements, data precision as measured by relative percent difference (RPD) between duplicate samples, data accuracy as measured by recovery rates of spiked matrix with certified reference materials and blank concentrations, data representativeness as determined by sampling scheme, data comparability and data completeness.

The rivers in the study are random selected as described in the QAPP. For the selected rivers, the water and fish tissue samples were obtained. Representativeness of the data in this study is assumed met by the randomization sampling process. Obtained samples were analyzed using EPA standard methods. For the fish tissue samples, species and size of the fishes were recorded. Sample collection and analysis were carried out with precautions to avoid contamination. Data comparability is assumed met for this data set. These two criteria will not be further discussed in following text.

Water Samples

QA/QC was carried out to the 64 water sample data reported by Brooks Rand Laboratories. The data set consists 49 water samples, 8 field duplicates and 7 blanks. The highest analytical water duplicate RPD is 18% for total Hg of batch 6, meeting the QAPP requirement of less than 25%. Field blank RPDs are reported as information and not used as QA/QC criterion.

One water sample *Henry's Fk @ Rex* is suspected for its arsenic result. The sample and its duplicate were analyzed twice to confirm the results. Total arsenic in the sample is 1.27 µg/l, for inorganic arsenic, it is 3.34 µg/l. The duplicate results are 3.55 µg/l and 3.10 µg/l respectively. QA/QC of the batch don't disqualify the data due to laboratory errors. Field blank does not show contamination. Selenium concentration of the sample is 0.74 µg/l, with duplicate concentration is 0.16 µg/l. High RPD rate is not explainable. Although QA/QC procedure does not disqualify the analytical results for this sample, it is recommended be excluded for future analysis on total arsenic and selenium. **The water sample analytic results meet the precision objective.**

CRM spike recovery rates of the water samples are within 75-125%, meeting the QAPP requirement. Also none of the matrix spike recovery exceed the 65-135% QAPP requirement for inorganic arsenic. Water blanks are less than designated acceptable levels in Table 3. of the QAPP. **The water sample analytic results meet the accuracy objective.**

Methylmercury is not included in the QA/QC section of the QAPP. Its spike recovery rate ranges from 75-116%. Highest field blank MMHg concentration is 0.024 ng/L.

The QAPP defines completeness as 100% of the target number of site samples for water. 35 rivers are targeted by random sampling. The 64 water samples are from 34 random sites and 6 additional sites from Statewide Trend Monitoring Network and sampled by USGS. **The water sample analytic results meet the completeness objective.**

Fish Tissue Samples

QA/QC was carried out to the 66 fish tissue sample data reported by Brooks Rand Laboratories. This data set includes 4 field duplicates. The QAPP requires fish tissue composite duplicates be created at the ten percent of the number of field sample delivered to the laboratory. This requires at least 6 fish tissue composite duplicate.

With the obtained 66 samples, the highest RPD is 27%, meeting the less than 40% requirement in the QAPP. Highest RPD is 50% for the field duplicates. Precision for field duplicates is reported as information and not a criterion of the data quality. **The fish tissue sample analytic results meet the precision objective.**

CRM spike recovery rates of the fish tissue samples are within 75-125% for total Hg, total As and selenium, meeting the QAPP requirement. Matrix spike recovery rate is 72% for inorganic arsenic of batch 3. % recovery limits in the Brooks Rand Laboratories is 65-135%. The QAPP requires 75-125%. The CRM recovery rate is 102%. Inorganic As measurements in Batch 3 are valid. None of the fish sample blanks exceed designated acceptable levels in Table 3. of the QAPP. **The fish tissue sample analytic results meet the accuracy objective.**

The QAPP defines completeness as 75% of the target number of fish samples. 53 fish samples are targeted in the QAPP. And 62 fish samples were taken. **The fish tissue sample analytic results meet the completeness objective.**

REFERENCE

Don Essig and Jason Pappani, Idaho Department of Environmental Quality, 2007. Mercury In Fish Tissue – A Statewide Assessment Of Rivers, Quality Assurance Project Plan (QAPP), Version 1.1, Summer, 2008.

Appendix H. Cumulative Distribution Plots

Fish Tissue

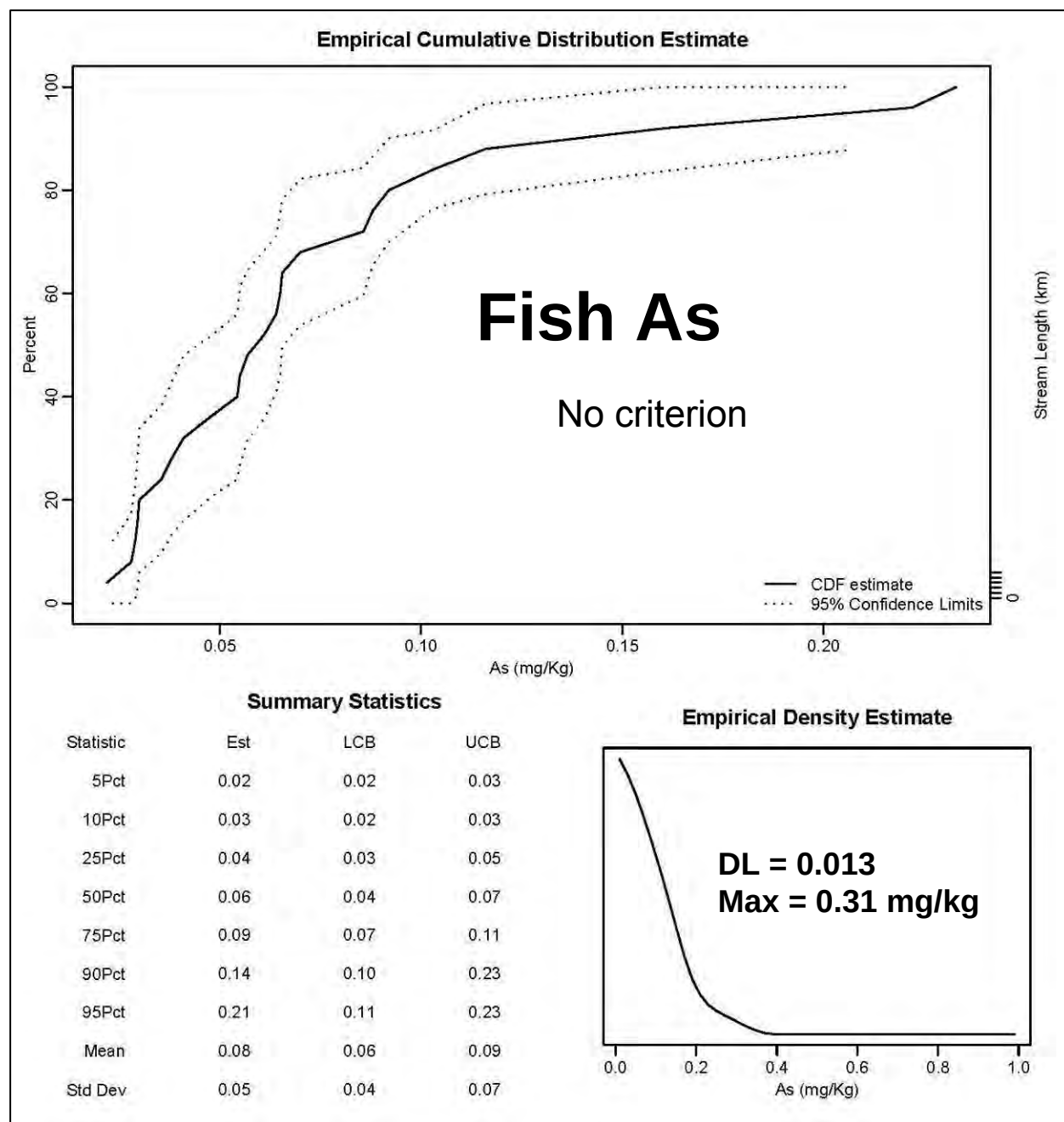


Figure H-1. Cumulative Distribution Plot of Arsenic in Fish Tissue

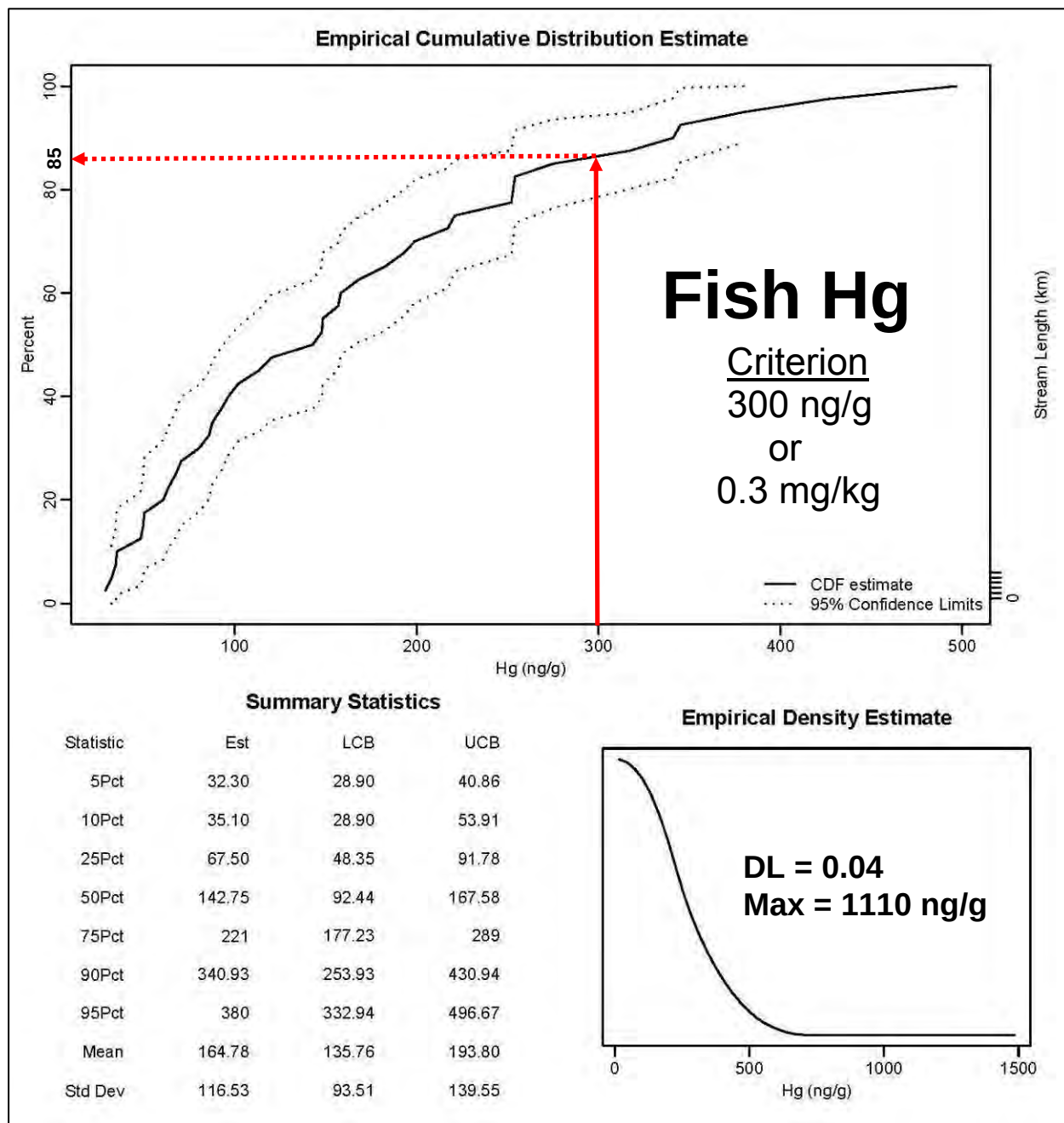


Figure H-2. Cumulative Distribution Plot of Mercury in Fish Tissue

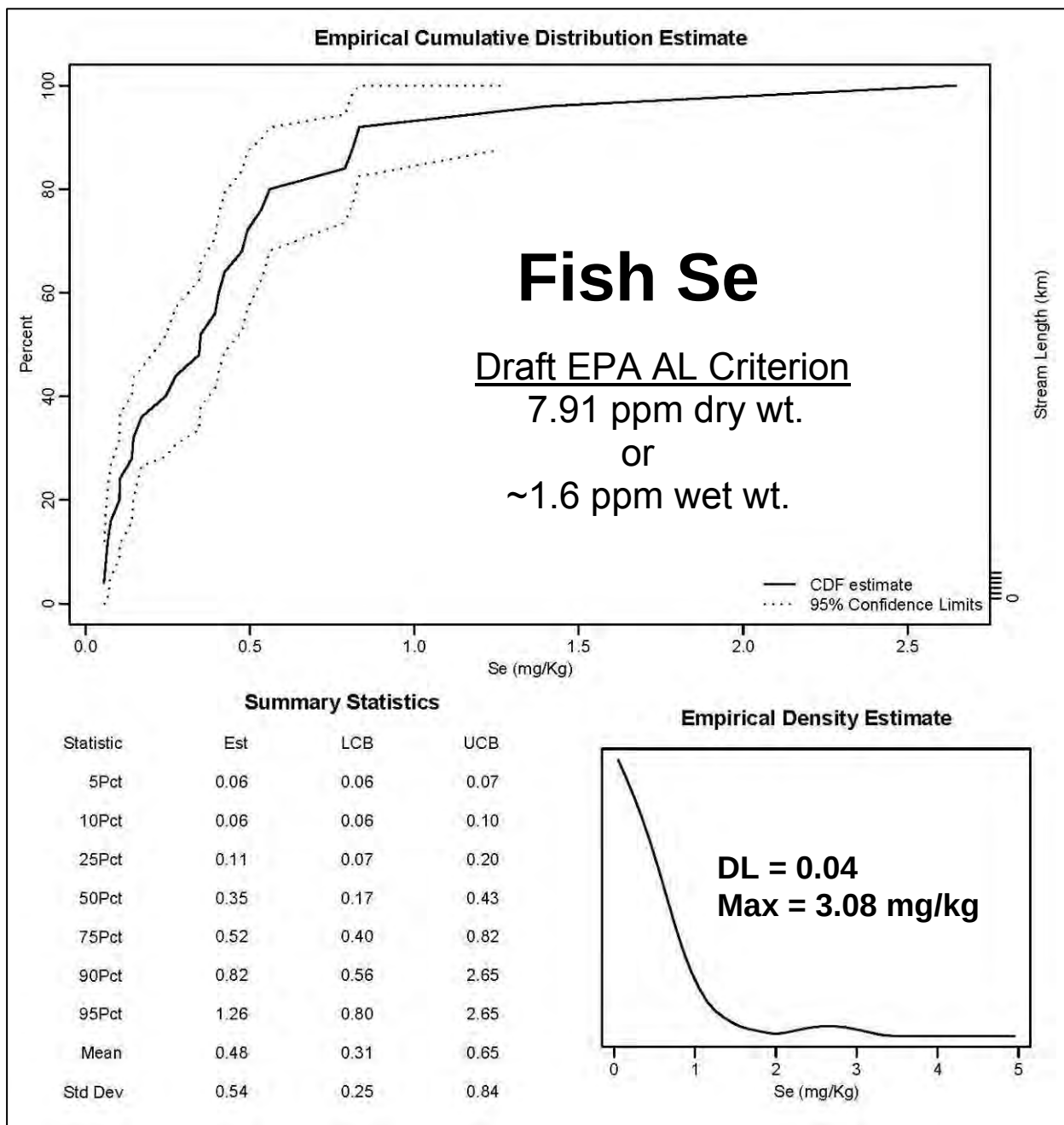
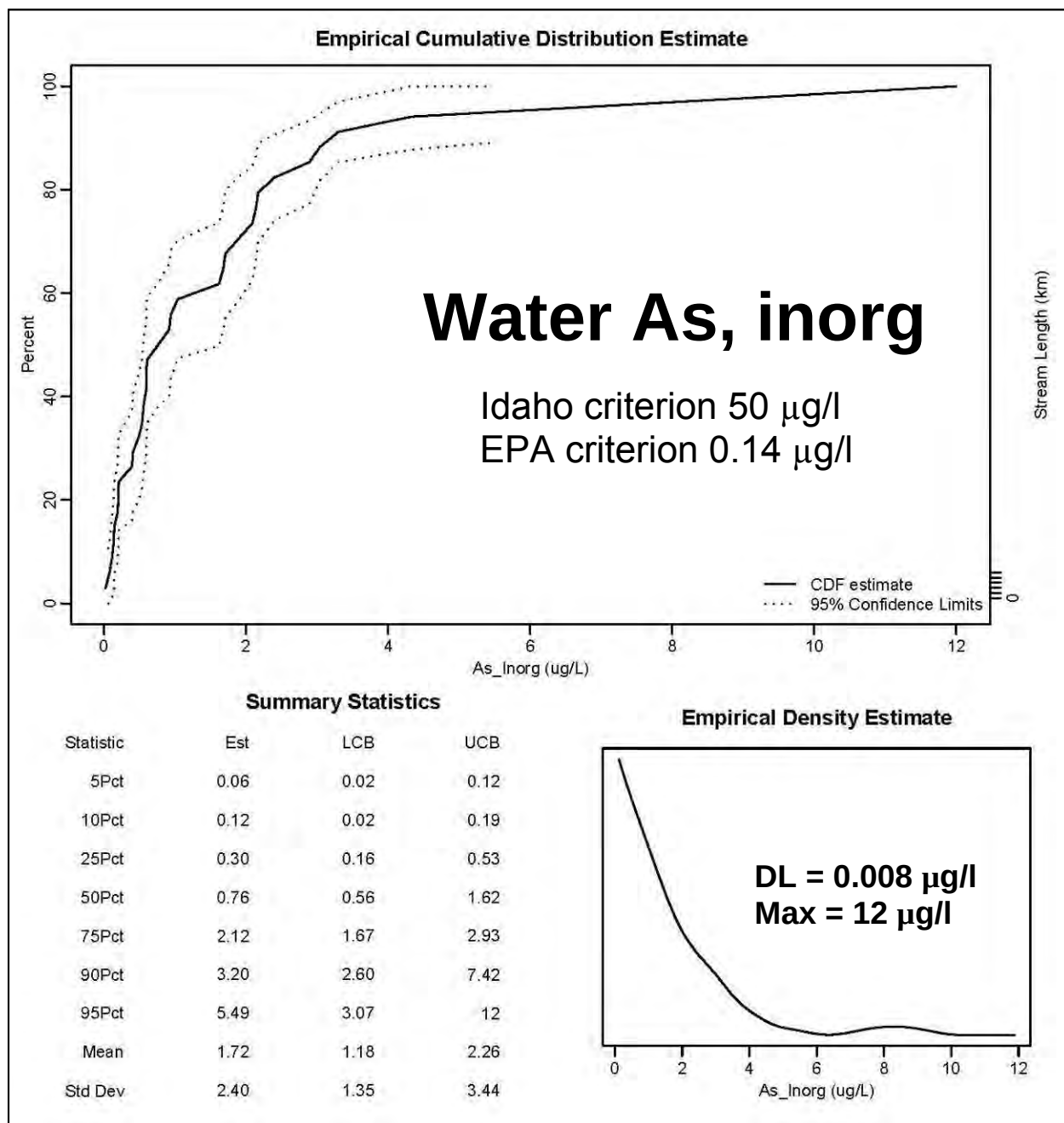


Figure H-3. Cumulative Distribution Plot of Selenium in Fish Tissue

Water**Figure H-4. Cumulative Distribution Plot of Inorganic Arsenic in Water**

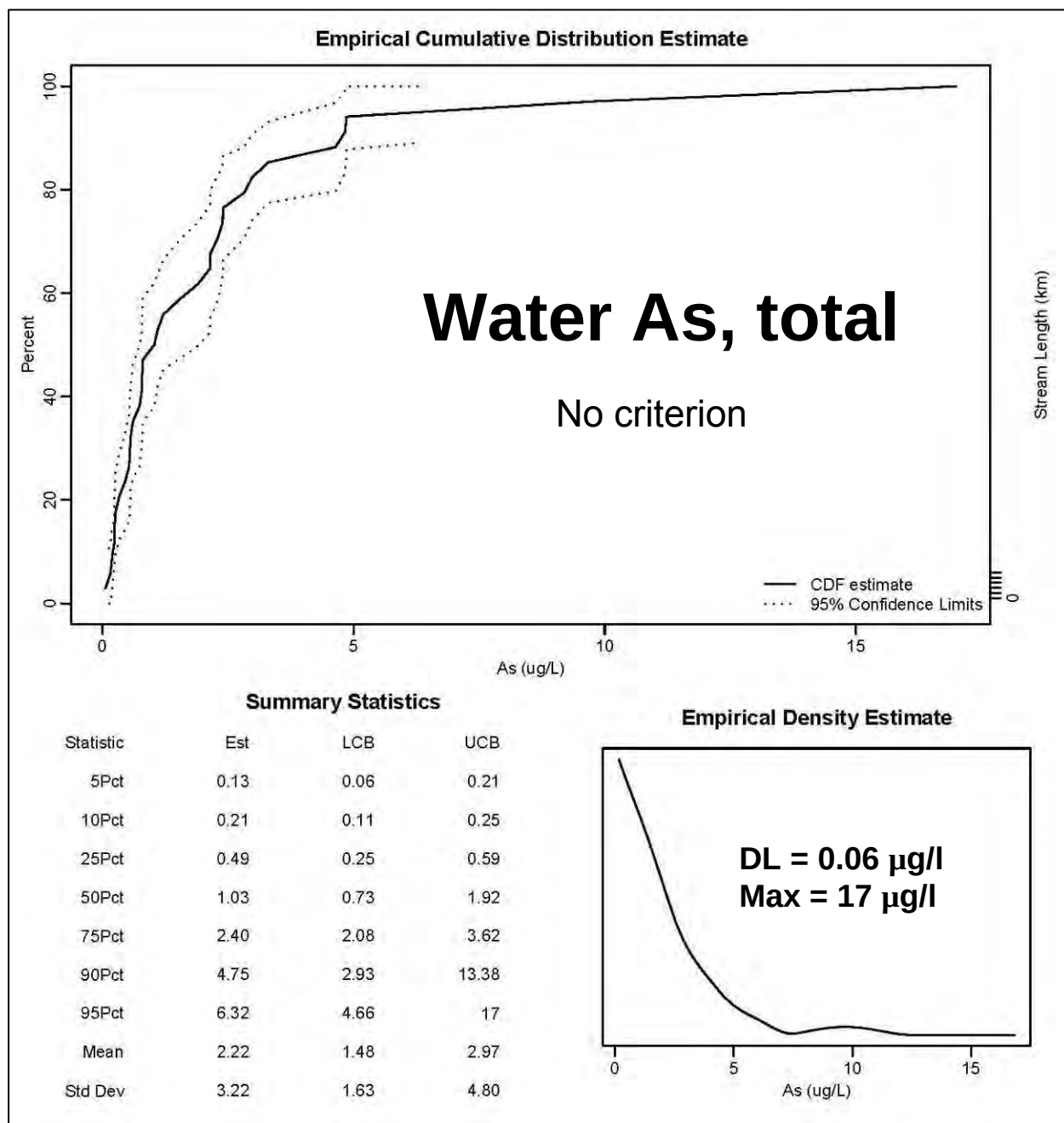


Figure H-5. Cumulative Distribution Plot of Total Arsenic in Water

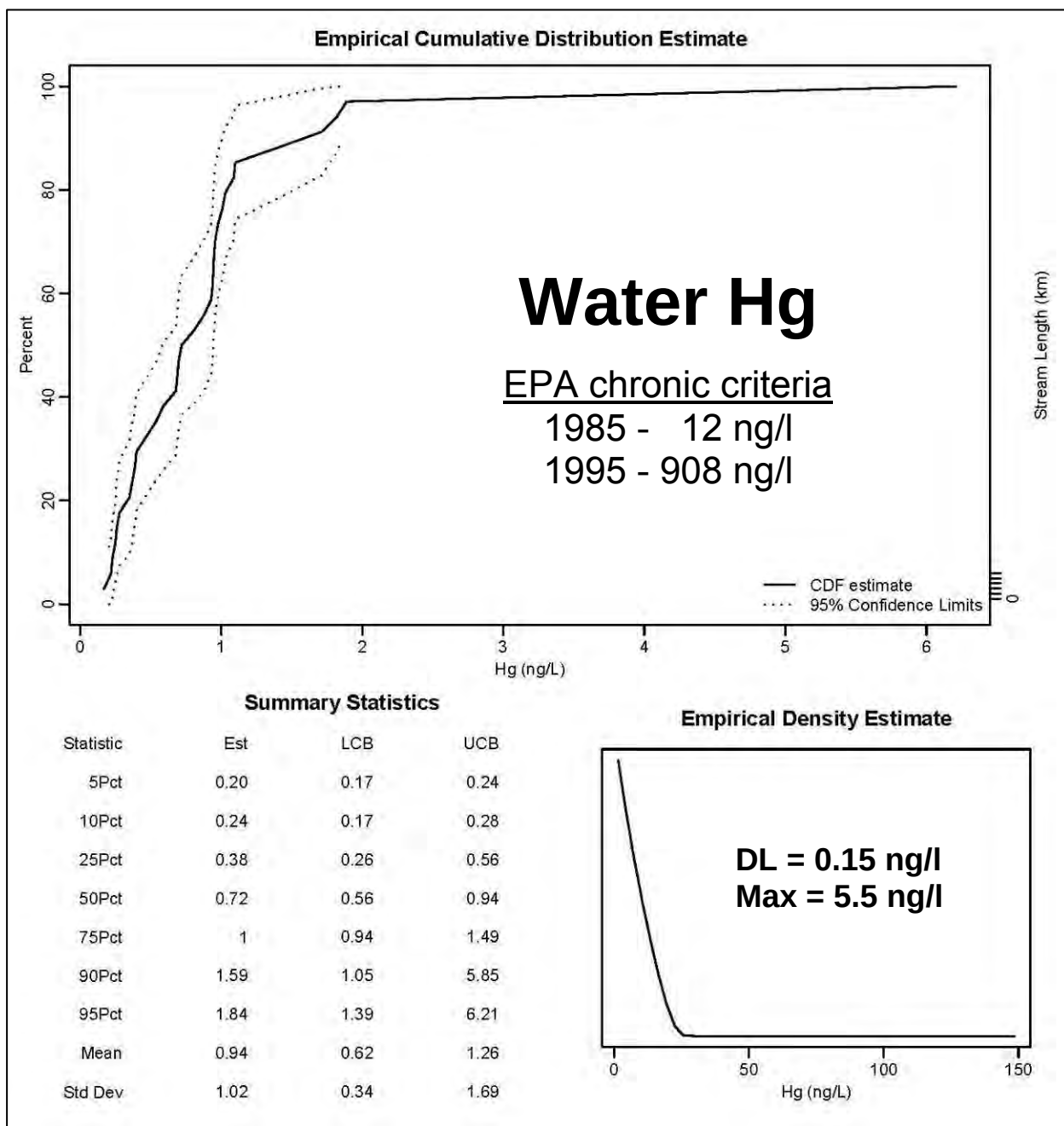


Figure H-6. Cumulative Distribution Plot of Mercury in Water

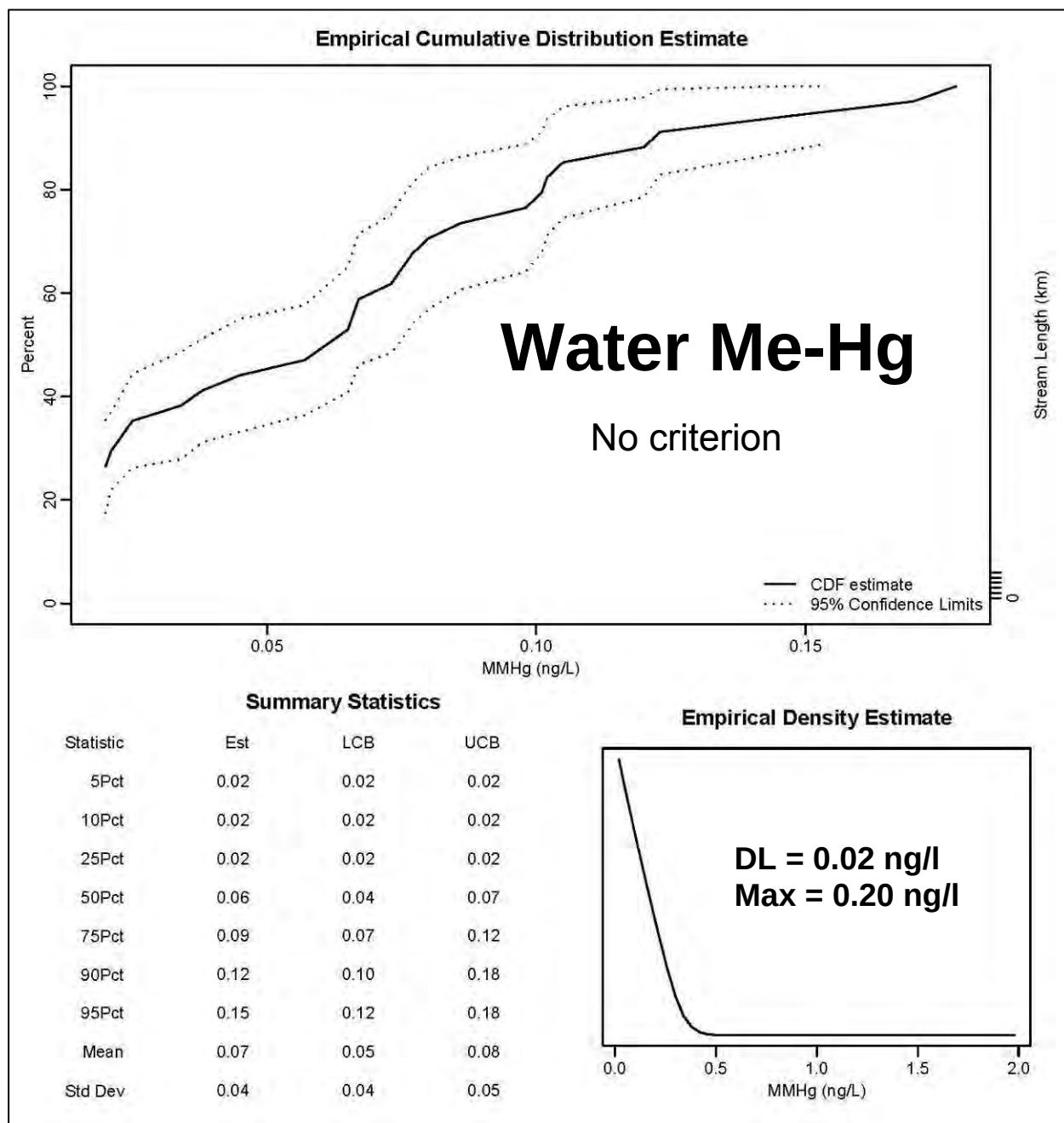


Figure H-7. Cumulative Distribution Plot of Methylmercury in Water

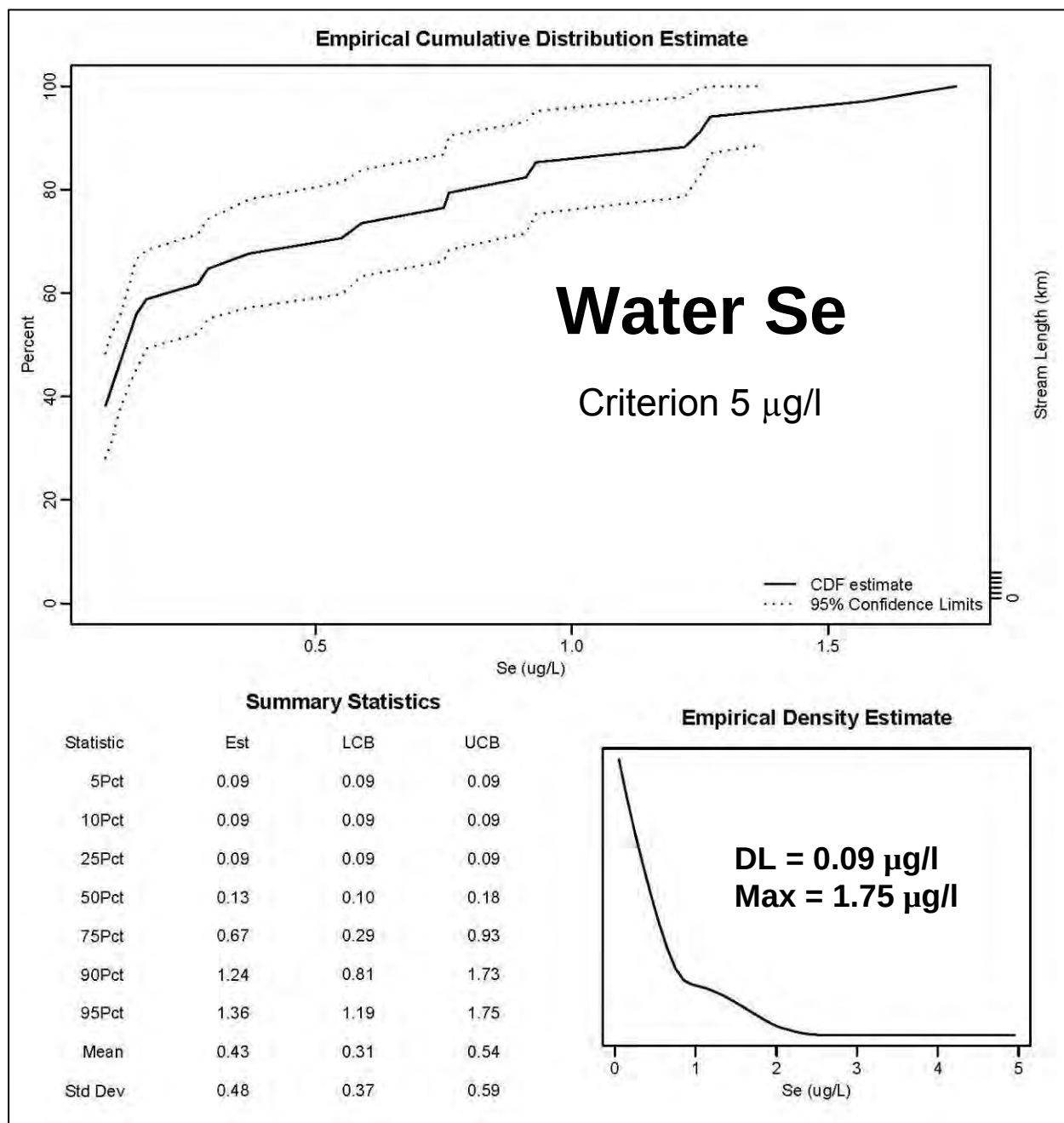


Figure H-8. Cumulative Distribution Plot of Selenium in Water