Idaho Department of Environmental Quality

Rulemaking Docket 58-0102-1801

Statewide Arsenic Monitoring to Support Human Health Criteria Updates

Discussion Paper #2

Background

In April, 2018, The Department of Environmental Quality (DEQ) initiated rulemaking to revise Idaho's Human Health Criteria for Arsenic.

In 2010, Idaho adopted 10 µg/L as the numeric criteria for inorganic arsenic for both fish only consumption and fish + water consumption. This value was based on the Safe Drinking Water Act (SDWA) Maximum Contaminant Level (MCL), and was chosen, in part, because of concerns about background levels in Idaho waters that exceed the US Environmental Protection Agency's (EPA's) national recommendation for inorganic arsenic. EPA approved the 10 µg/L criteria in 2010.

In May 2016, EPA entered into a consent decree with Northwest Environmental Advocates to reconsider EPA's 2010 approval of Idaho's human health criteria (HHC) for arsenic. In September 2016, EPA disapproved Idaho's 10 µg/L arsenic HHC for both consumption of fish only and consumption of fish + water. The consent decree, as modified, requires that EPA propose new HHC for arsenic by November 15, 2022, and that EPA either approve an Idaho submittal of revised HHC for arsenic, or promulgate federal criteria, by July 15, 2023.

There are many issues that complicate deriving an appropriate, defensible HHC for inorganic arsenic in Idaho, including identifying appropriate bioaccumulation rates, accounting for the ratio of inorganic arsenic to total arsenic in fish tissue and water, and accounting for the elevated background of arsenic in surface waters within Idaho.

Uncertainty in Bioaccumulation and Inorganic Arsenic

Bioaccumulation can be estimated as a bioconcentration factor (BCF) through laboratory studies, where organisms take up contaminants directly from the laboratory-prepared water, or as bioaccumulation factors (BAF) that are based on field studies and include dietary exposure in addition to direct uptake from water. Because they account for dietary exposure, BAFs are generally preferred over BCFs.

Bioaccumulation of inorganic arsenic is a source of significant uncertainty when deriving HHC. EPA's recommended criteria are based on a BCF that was calculated as the geometric mean of BCF of total arsenic from two species: Eastern Oyster and Bluegill. Because this BCF is for total arsenic, includes a marine species (Eastern Oyster), and arsenic bioaccumulation is much different in marine systems than freshwater systems, this BCF value has little relevance to setting criteria in Idaho.

While it is generally accepted that inorganic arsenic is much more toxic than organic forms of arsenic, there is very little information on BCFs or BAFs for inorganic arsenic. One approach to correct for this deficiency is to apply an inorganic proportion factor based on the ratio of inorganic arsenic to total arsenic in surface waters and fish tissue.

Additional monitoring is necessary to further our understanding of bioaccumulation of arsenic and, specifically, inorganic arsenic.

Natural Background

Arsenic is a common element in the Earth's crust and can be released to the environment through natural processes such as weathering of soils and rock. Arsenic is associated with volcanism and geothermal activity. In many instances in Idaho, natural background concentrations of arsenic in waters may exceed water quality criteria that are derived using EPA's recommended procedures.

Idaho WQS has a natural background provision that states:

> Natural Background Conditions as Criteria. When natural background conditions exceed any applicable water quality criteria set forth in Sections 210, 250, 251, 252, or 253, the applicable water quality criteria shall not apply; instead, there shall be no lowering of water quality from natural background conditions. Provided, however, that temperature may be increased above natural background conditions when allowed under Section 401 (IDAPA 58.01.02.200.09).

Setting ambient water quality criteria that are well below natural background concentrations can have several negative consequences. For example, water bodies may be listed as impaired for arsenic despite not having any human caused contributions of arsenic to the water body. This could result in allocation of state resources to develop a total maximum daily load (TMDL) that would not be able to prescribe any meaningful arsenic reduction strategies.

Furthermore, water bodies identified as impaired would not be considered Tier II waters under Idaho's antidegradation policy, meaning that they would not be considered high quality waters for recreation and would only receive Tier I protections under Idaho's antidegradation policy, allowing increased degradation without review of alternatives to degradation or a socioeconomic review.

Finally, dischargers regulated under the Clean Water Act may be required to remove arsenic from wastewater to levels well below the natural background and ambient concentrations in the receiving water body.

This plan will answer the following three questions:

1. What is an appropriate BAF for inorganic arsenic in Idaho waters?
2. What is an appropriate inorganic proportion factor for arsenic in fish and water in Idaho?
3. What are the current background conditions for arsenic in surface waters around the state?

Monitoring Strategy

In order to answer these questions, DEQ is planning two separate monitoring approaches:

1. **Probabilistic Arsenic Accumulation**: Probabilistic monitoring of sites throughout the state for fish tissue and water to calculate BAF and to identify the ratio of inorganic to total arsenic in Idaho waters.

2. **Targeted Ambient Arsenic in Water:** Targeted monthly samples of ambient to determine background concentrations of arsenic in waters throughout Idaho.

Probabilistic Arsenic Accumulation

DEQ will employ a probabilistic sampling design to identify sites for collection of data for estimating BAF. Probabilistic survey designs allow statistically valid estimates of results for the entire population being studied while sampling only a fraction of the population. In this instance, we will be able to extrapolate results from relatively few locations to the entire state. In addition, by employing a probabilistic survey we will be able to make comparisons to previous efforts in Idaho.

The probabilistic design will allow DEQ to determine a statistically valid assessment of arsenic bioaccumulation rates based on the sites sampled. In addition, the probabilistic design will provide representative samples from which to derive an appropriate inorganic proportion factor that can be used to estimate inorganic arsenic based on total arsenic results. The probabilistic design will also ensure that the full range of ambient arsenic conditions found in Idaho surface waters are represented.

Site Selection

Sites were generated using the spsurvey 2.6 package for R statistical software based on a general random tessellation stratified (GRTS) survey design.

The target population included all perennial streams that were outside of Indian Reservations and designated wilderness areas. A total of 24 sites, represented by a single set of coordinates that fall upon a stream (known as the x-site) will be sampled.

Sites are categorized as either Large River (Strahler Order ≥ 6) or Small Stream (Strahler Order <6), and stratified based on Idaho administrative basin (Bear, Clearwater, Panhandle, Salmon, Southwest, and Upper Snake). Four sites will be sampled from each of the six administrative basins, following the site evaluation process identified in the survey design file.

Figure 1 displays the locations of Probabilistic Fish Tissue sites and Targeted Ambient Water Quality sites.

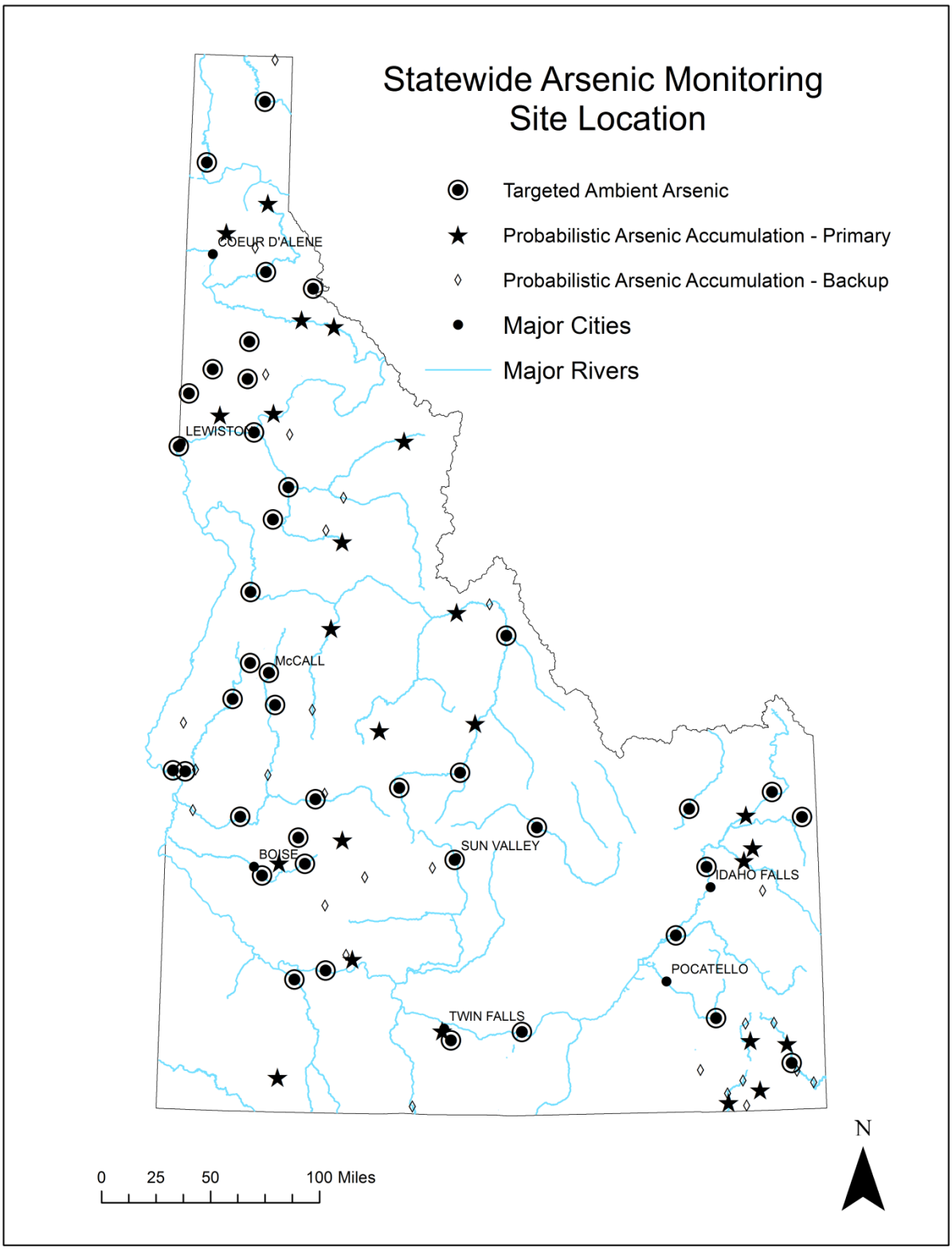

Figure 1. Location of Probabilistic Arsenic Accumulation and Targeted Ambient Arsenic sites.

Sample Collection

Sites will be monitored for both fish tissue and water chemistry during late summer/fall base flow conditions.

Stream reaches will be located so that the coordinates of the x-site are within the delineated reach. Stream reaches will be 40x the wetted width, with a minimum reach length of 100 m and a maximum reach length of 4000 m.

Grab samples for analysis of total and inorganic arsenic in water will be collected from the thalweg or other well-mixed portion of the stream at the x-site, or as near as is practicable. Fish for tissue analysis may be collected using boat or backpack electrofishing or by hook-and-line when conditions preclude electrofishing.

DEQ will identify and measure all fish captured within the reach. When necessary, fish may be collected from beyond the reach, provided that they are captured from the same assessment unit (AU) as the site.

DEQ will collect a composite of up to five individual fish from each of two species for fish tissue analysis of total and inorganic arsenic.

DEQ will target individuals from the two most-abundant gamefish species at each site. To control for size, the smallest fish in a composite sample must be at least 75% of the total length of the largest fish. Fish for tissue analysis may be collected using boat or backpack electrofishing or by hook-and-line when conditions preclude electrofishing. If the target number of individual fish from the target species are not collected, a composite sample of the fish collected will be analyzed. If no fish from the target species are collected, tissue from the species that is either most likely to be consumed, or is of a size that could be consumed will be collected.

DEQ will collect a second water sample in the spring during runoff conditions.

Targeted Ambient Arsenic

DEQ will use a targeted sampling design to determine ambient arsenic conditions at select locations throughout Idaho. Sites will be sampled monthly for total and inorganic arsenic in the water column.

Site Selection

Sites were selected based on the following factors:

1. Accessibility: sites must be easily accessible during all times of the year
2. Near areas of interest: DEQ selected sites near population centers or other areas where there would be a particular interest in understanding upstream or background arsenic conditions.
3. Above major anthropogenic inputs: to the extent possible, DEQ selected sites that were not immediately within or downstream of points of discharge or other sources of anthropogenic arsenic input

4. State representation: sites were selected to provide for a distribution around Idaho and within major Idaho watersheds; DEQ avoided clustering sites or having all sites located in headwater streams.

Sample Collection

Grab water samples for analysis of total and inorganic arsenic will be collected from the thalweg or other well-mixed portion of the stream at the x-site, or as near as is practicable. Samples will be collected approximately monthly.

Sample Analysis

The following table describes the analytical method, method detection limits (MDL), and number of samples expected from this project:

Probabilistic Arsenic Accumulation

Media	Analyte	Method	MDL	N
Fish Tissue	Total As	ICP-MS	0.009 mg/kg	48
	Inorganic As	EPA-1632	0.004 mg/kg	48
Water	Total As	ICP-MS	0.011 µg/L	48
	Inorganic As	SOP BAL-4100	0.004 µg/L	48

Ambient Arsenic in Water

Media	Analyte	Method	MDL	N
Water	Total As	ICP-MS	0.011 µg/L	480
	Inorganic As	SOP BAL-4100	0.004 µg/L	480

Summary

DEQ is initiating monitoring to determine an appropriate BAF for inorganic arsenic, an appropriate inorganic proportion factor for fish and water, and to begin to identify background conditions for arsenic in surface waters around the Idaho. Monitoring will include probabilistic arsenic accumulation monitoring of fish tissue and water in order to calculate BAFs and inorganic proportion factors, and targeted monthly samples of ambient arsenic in surface waters to determine background concentrations of both total and inorganic arsenic in Idaho waters.

These data will help to ensure that DEQ uses appropriate, Idaho-specific, scientifically defensible inputs to the HHC equation.