Addendum to Derivation of the Nonanthropogenic Arsenic Standards for Segments of the Upper and Middle Yellowstone River

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EXECUTIVE SUMMARY

In late 2019, the Montana Department of Environmental Quality (DEQ) released two technical reports addressing arsenic concentrations in the Yellowstone River. The first, *Demonstration of Nonanthropogenic Arsenic Levels: Yellowstone River, Montana*, detailed DEQ's assessment of the proportion of anthropogenic and nonanthropogenic arsenic in the river. The second—*Derivation of the Nonanthropogenic Arsenic Standards for Segments of the Upper and Middle Yellowstone River*—provided DEQ's recommended arsenic standards based on the river's nonanthropogenic condition. The present report is an addendum to the second document and describes work DEQ subsequently undertook which has changed the arsenic standards DEQ is recommending for the Yellowstone River. Five river segments are addressed; these are:

- Segment 1 - Montana/Wyoming border to the mouth of Mill Creek near Pray, MT
- Segment 2 - Mill Creek to the mouth of the Boulder River near Big Timber, MT
- Segment 3 - Boulder River to the mouth of the Stillwater River
- Segment 4 - Stillwater River to the mouth of the Clarks Fork of the Yellowstone River
- Segment 5 - Clarks Fork of the Yellowstone River to the mouth of the Bighorn River

This addendum contains the methods and analyses undertaken subsequent to the release of the two 2019 technical reports and provides documentation for DEQ's updated nonanthropogenic standards recommendations.

The Yellowstone River is used for drinking water, and drinking water is the beneficial use addressed in this report. Arsenic is known to cause cancer in people, and the U.S. Environmental Protection Agency (EPA) assumes there is no truly safe lower concentration in drinking water for a carcinogen like arsenic. Given these facts, DEQ applied the following reasoning:

> *If adopting the nonanthropogenic arsenic standards in a particular way—while conforming with state statutes—can demonstrably decrease cancer risk for people using the Yellowstone River as a water supply, then that is the best expression of the nonanthropogenic arsenic standards.*

DEQ then applied objective methods to evaluate how two different expressions of the nonanthropogenic standards (two seasonal medians—i.e. the originally proposed standards, or a single annual median) affect the drinking water beneficial use.

Before undertaking this work, it was first necessary for DEQ to evaluate two issues: (1) whether Yellowstone River arsenic concentrations have any relation to arsenic levels in finished drinking water originating from the river, and (2) whether annual medians comport with state law at 75-5-222, MCA.

Per 75-5-222, MCA, DEQ needed to determine if annual medians were within the Yellowstone River's nonanthropogenic condition all year round.

Regarding the first issue, analysis showed that Yellowstone River arsenic concentrations do affect arsenic levels in finished drinking water originating from the river. Variation in Yellowstone River arsenic concentrations accounted for 71% of the variation in one facility's finished drinking water. (It should be noted that, at the same time, the facility was fully compliant with the arsenic drinking water standard of 10 µg/L.) For the second issue, analysis showed that the annual median concentrations were all within the nonanthropogenic condition during each critical season. Having addressed these two issues, it was then reasonable for DEQ to proceed with the next set of analyses. River arsenic concentrations were computed for each river segment for two scenarios:

1. One in which the river's seasonal long-term average flows (High Flow, Low Flow) and associated median arsenic concentrations were combined with permitted dischargers' flows, assuming the discharges were meeting two seasonal nonanthropogenic standards (one standard for High Flow, one for Low Flow); and

2. One in which the river's seasonal long-term average flows (High Flow, Low Flow) and associated median arsenic concentrations were combined with permitted dischargers' flows, assuming the discharges were meeting a single annual nonanthropogenic standard.

For each scenario, the resulting river arsenic concentrations were then related to cancer risk via standard equations and assumptions from EPA and Department Circular DEQ-7.

In Segments 1 through 4, it was found that annual median nonanthropogenic standards result in lower potential cancer risk compared to two seasonal median nonanthropogenic standards. Relative reductions in cancer risk provided by the annual standards are small, on the order of one less case in 10,000,000 to 100,000,000. In Segment 5, either expression of the standards provides equal cancer risk. Also, Segment 5's median annual nonanthropogenic concentration is at or just below the currently-adopted arsenic standard in Circular DEQ-7 (10 µg/L), so nonanthropogenic standards are not recommended for this segment. DEQ's updated nonanthropogenic standards recommendations are shown in **Table E-1**.

Table E-1. Updated Recommendations for Nonanthropogenic Arsenic Standards for Segments of the Yellowstone River.

River Segment	Segment Description	Annual Median Nonanthropogenic Arsenic Standard (µg/L)
1	MT/WY Border to Mill Creek	28
2	Mill Creek to Boulder River	22
3	Boulder River to Stillwater River	16
4	Stillwater River to Clarks Fork Yellowstone	13
5	Clarks Fork Yellowstone to Bighorn River	n/a*

*In this segment the nonanthropogenic condition is not less than the arsenic standard in Circular DEQ-7, so the Circular DEQ-7 standard should continue to apply.

In addition, DEQ had earlier recommended the Wilson Interval Method for long-term monitoring and assessment of arsenic levels in the Yellowstone River. Based on updated analyses provided in this report, it was shown that the Wilson Interval may also be used for long-term monitoring and assessment of the annual nonanthropogenic standards in **Table E-1**.

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ACRONYMS

DEQ	Department of Environmental Quality
EPA	Environmental Protection Agency
HHS	Human Health Standard
kg/day	kilograms per Day
LOADEST	Load Estimator (a USGS model)
MCA	Montana Code Annotated
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
NOAEL	No Observed Adverse Effect Level
µg/L	Micrograms per Liter
USGS	United States Geological Survey
WQSM	Water Quality Standards & Modeling Section (of DEQ)

1.0 INTRODUCTION

This document presents additional methods and analyses the Department of Environmental Quality (DEQ) used to derive arsenic standards for portions of the Yellowstone River based on the river's nonanthropogenic arsenic concentrations. The work was completed by the Water Quality Standards & Modeling Section (WQSM) with assistance provided by DEQ's Water Protection Bureau. The geographic area encompassed in this document includes the Yellowstone River from the Montana/Wyoming Border to the confluence with the Bighorn River near Bighorn, Montana.

1.1 BACKGROUND

In late 2019, DEQ released two technical reports pertaining to arsenic concentrations in the Yellowstone River. The first detailed DEQ's assessment of the proportion of anthropogenic and nonanthropogenic arsenic in the river (DEQ, 2019a). The second (DEQ, 2019b) provided DEQ's recommended arsenic standards; these standards were based on the river's nonanthropogenic condition. The recommended standards were based on the median nonanthropogenic values in **Table 1-1** below. DEQ recommended seasonal standards (one standard for the High Flow season, and one for the Low Flow) for the first four river segments. In Segment 5 during High Flow, the river's median nonanthropogenic concentration is lower than the adopted human health standard (HHS) of 10 µg/L (**Table 1-1**), and DEQ did not recommend making a change; instead, DEQ indicated the HHS would continue to apply.

Table 1-1. Yellowstone River Segments and their Median Nonanthropogenic Concentrations.

River Segment	Segment Description	High Flow Season Arsenic Conc.[1] (µg/L)	Low Flow Season Arsenic Conc.[1] (µg/L)
1	MT/WY Border to Mill Creek	11	32
2	Mill Creek to Boulder River	11	24
3	Boulder River to Stillwater River	10	18
4	Stillwater River to Clarks Fork Yellowstone	10	14
5	Clarks Fork Yellowstone to Bighorn River	8	10

[1] High Flow season for the Yellowstone River is May – July, and the Low Flow Season is August - April.

Subsequent to the time that the two technical reports (DEQ, 2019a; 2019b) were released, DEQ undertook additional analyses which have changed the arsenic standards DEQ is recommending for Yellowstone River Segments 1 through 5.

1.2 PURPOSE, SUMMARY OF APPROACH, APPLICABLE LAWS

The purpose of this addendum is to describe the methods and analyses undertaken subsequent to the release of the two arsenic technical reports (DEQ, 2019a; 2019b), and provide documentation for the updated nonanthropogenic standards recommendations.

For these subsequent analyses, DEQ applied an objective method to evaluate how two different expressions of the nonanthropogenic standards (the two seasonal medians *vs.* a single annual median) affect the beneficial use. As noted in DEQ (2019b), water drawn from the Yellowstone River for use as drinking water is the beneficial use being affected. Much of the river's nonanthropogenic arsenic concentrations are naturally above the Circular DEQ-7 HHS of 10 µg/L (**Table 1-1**). In contrast, the river's arsenic concentrations are not above the Circular DEQ-7 aquatic life standards (chronic = 150 µg/L, acute = 340 µg/L), and that beneficial use is not under consideration here.

Arsenic is a category A carcinogen, meaning it is known to cause cancer in humans (EPA, 2018). It is assumed that there is no safe lower concentration in drinking water for a carcinogen like arsenic, which is why the drinking water maximum contamination level goal (MCLG) for arsenic is zero (City of Billings, 2018; EPA, 2018). To objectively assess the best expression of the nonanthropogenic arsenic standards, DEQ applied the following line of reasoning:

> *If adopting the nonanthropogenic arsenic standards in a particular way—while conforming with state statutes—can demonstrably decrease cancer risk for people using the Yellowstone River as a water supply, then that is the best expression of the nonanthropogenic arsenic standards.*

Provided here are the three principal statutes that have relevance to the Yellowstone River's nonanthropogenic arsenic standards.

75-5-222(1), MCA: *The department may not apply a standard to a water body for water quality that is more stringent than the nonanthropogenic condition of the water body. For the parameters for which the applicable standards are more stringent than the nonanthropogenic condition, the standard is the nonanthropogenic condition of the parameter in the water body. The department shall implement the standard in a manner that provides for the water quality standards for downstream waters to be attained and maintained.*

75-5-101, MCA: ***Policy.*** *It is the public policy of this state to: (1) conserve water by protecting, maintaining, and improving the quality and potability of water for public water supplies, wildlife, fish and aquatic life, agriculture, industry, recreation, and other beneficial uses; (2) provide a comprehensive program for the prevention, abatement, and control of water pollution; and (3) balance the inalienable rights to pursue life's basic necessities and possess and use property in lawful ways with the policy of preventing, abating, and controlling water pollution in implementing the program referred to in subsection (2).*

75-5-301(2), MCA: *…the board shall: (2) formulate and adopt standards of water quality, giving consideration to the economics of waste treatment and prevention.*

2.0 METHODS

DEQ carried out analyses to address the following question:

> *Downstream from permitted arsenic discharges, which expression of the nonanthropogenic arsenic standards (two seasonal medians, one annual median, or some other temporal expression) results in lower cancer risk to people who use drinking water originating from the Yellowstone River?*

Before addressing this question, it was first necessary for DEQ to evaluate two issues: (1) whether Yellowstone River arsenic concentrations are related to arsenic levels in finished drinking water originating from the river, and (2) whether nonanthropogenic annual median concentrations comport with state law at 75-5-222, MCA. These subjects are covered in the next two sections.

2.1 INFLUENCE OF YELLOWSTONE RIVER ARSENIC CONCENTRATIONS ON ARSENIC IN FINISHED DRINKING WATER

Prior to being provided to municipal users, drinking water undergoes treatment to remove impurities. If the drinking water treatment process were to reduce arsenic in finished drinking water in such a way that no relationship could be observed between arsenic concentrations in the source (Yellowstone River) and arsenic concentrations in the finished drinking water, then arsenic cancer risk would be unrelated to arsenic variation in the river. And, as a result, there would be no point in addressing the question posed above. Therefore, DEQ first examined the drinking water-river concentration relationship.

DEQ explored the relationship between Yellowstone River arsenic concentrations and arsenic concentrations in finished drinking water from the Billings water supply (PWS No. MT0000153). DEQ acquired arsenic concentration data for Billing's finished drinking water from quarterly compliance reports (2009 to 2017). The finished drinking water data were collected by the city during the Yellowstone River's High Flow period and its Low Flow period. The compliance reports provided the day and concentration for each sample. These data were joined (by corresponding day) to DEQ's daily LOADEST-modeled Yellowstone River arsenic concentrations[1] (anthropogenic + nonanthropogenic) from the Billing's USGS gage, which is just downstream from the Billings drinking water intake. DEQ confirmed that water removed from the river is treated and then enters the drinking water delivery system within a few hours, therefore matching the data by corresponding day was appropriate. The results are shown in **Figure 2-1**.

The results show that there is a good relationship between arsenic concentrations in the Yellowstone River and arsenic concentrations in Billing's finished drinking water. Arsenic variation in the river explains 71% of the arsenic variation in the finished drinking water. This indicates that anything that would cause arsenic concentrations in the river to go up or down will result in corresponding changes in arsenic concentrations in the finished drinking water. Since the MCLG for arsenic in drinking water is

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[1] DEQ's LOADEST model provides a modeled river arsenic concentration for each day of the year for each year during the period from 2009 to 2018 (DEQ, 2019b).

zero (see **Section 1.2**), DEQ can evaluate difference expressions of the nonanthropogenic arsenic standards by calculating how each expression might increase or decrease the arsenic concentrations in the Yellowstone River. The version that reduces arsenic concentrations most would be the better expression of the standards.

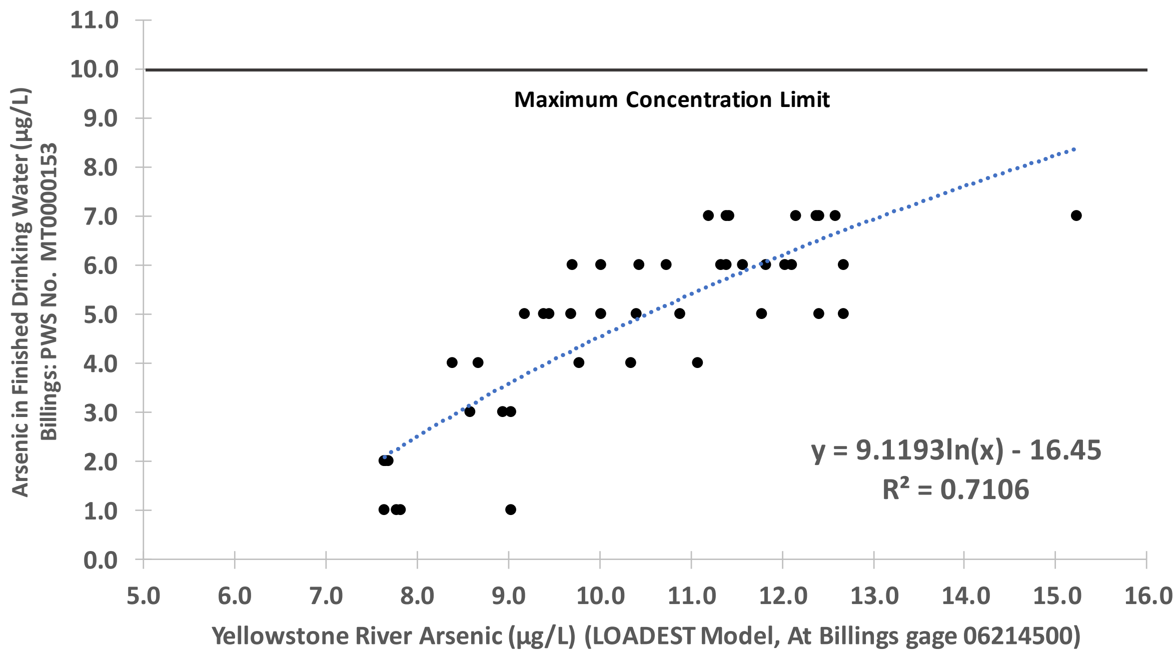

Figure 2-1. Relationship between LOADEST-modeled Total Arsenic Concentrations in the Yellowstone River at Billings, MT and Arsenic Concentrations in Billing's Finished Drinking Water (2009-2017). Note that all concentrations in the finished drinking water are below the MCL of 10 µg/L and comply with the current drinking water standard.

The next step was to evaluate whether annual median concentrations met the intent of state law at 75-5-22, MCA.

2.2 Evaluating if Annual Medians Meet 75-5-222(1), MCA

Montana law states that "for the parameters for which the applicable standards are more stringent than the nonanthropogenic condition, the standard is the nonanthropogenic condition of the parameter in the water body" (75-5-222(1), MCA). Although this statute directs DEQ to identify the nonanthropogenic standard, it also limits the nonanthropogenic standard to the nonanthropogenic condition. If a nonanthropogenic standard was expressed in such a way that it was at a *higher* concentration than the nonanthropogenic condition during some critical period, then that expression of the nonanthropogenic standard would not comply with statute.

As noted in DEQ (2019a), there are two distinct periods during the year for arsenic (Low Flow, High Flow), and during High Flow arsenic concentrations are lowest in the Yellowstone River (**Table 1-1**). The annual nonanthropogenic median arsenic concentrations for Segments 1 through 5 are shown below in **Table 2-1.** To comport with 75-5-22, MCA, the annual nonanthropogenic median concentrations must occur (even if uncommonly) during the High Flow period when the river's concentrations are lowest. All five river segments were examined, and it results that for each segment the annual nonanthropogenic median is within the High Flow nonanthropogenic condition (**Table 2-1**, last column). Thus, all the annual nonanthropogenic concentrations comport with 75-5-222(1), MCA.

Table 2-1. Yellowstone River Segments and their Annual Median Nonanthropogenic Arsenic Concentrations, and Maximum Nonanthropogenic Concentrations During the High Flow Period.

River Segment	Segment Description	Annual Median Nonanthropogenic Arsenic Concentration (µg/L)	High Flow Season* Maximum Nonanthropogenic Concentration (µg/L)
1	MT/WY Border to Mill Creek	28	31
2	Mill Creek to Boulder River	22	23
3	Boulder River to Stillwater River	16	17
4	Stillwater River to Clarks Fork Yellowstone	13	14
5	Clarks Fork Yellowstone to Bighorn River	10	11
*High Flow occurs annually from May through July.			

In this section and in the previous, it has been shown that arsenic levels in finished drinking water originating from the Yellowstone River vary with the river's arsenic levels, and that nonanthropogenic annual median concentrations are within the nonanthropogenic condition during the High Low period. Since these two important conditions have been met, in the next section DEQ examines the influence of different expressions of the nonanthropogenic standards on human cancer risk.

2.3 Evaluating the Best Expression of the Nonanthropogenic Arsenic Standards

A cancer risk *vs.* arsenic concentration relationship was computed based on the factors shown in **Table 2-2** using the current EPA equation applicable to arsenic, and assuming consumption of water and organisms (EPA, 2002).

Table 2-2. Values Used to Compute Arsenic Cancer Risk.

Input Variable	Value (units)	Source
Cancer Potency Factor (q1*)	1.75 (per mg/kg·day)	EPA (2002)
Bioconcentration Factor (BCF)	44 (L/kg)	Circular DEQ-7
Body Weight	80 (kg)	Circular DEQ-7
Water Consumed	2.4 (L/day)	Circular DEQ-7
Fish Consumed	0.0220 (kg/day)	Circular DEQ-7

The relationship between arsenic concentrations in water and human cancer risk based on the factors in **Table 2-2** is shown in **Figure 2-2**.

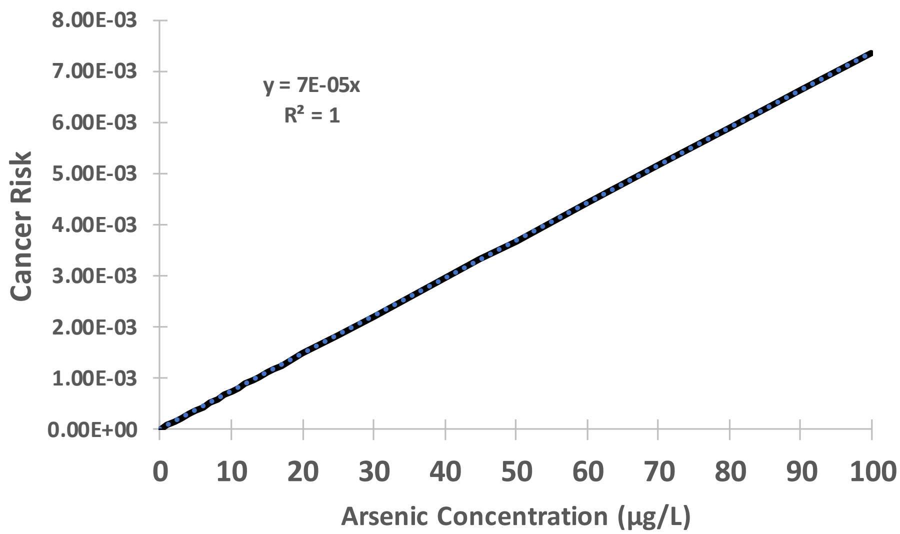

Figure 2-2. Relationship Between Cancer Risk and Arsenic Concentrations in Water.

Next, for each segment, DEQ calculated the river's harmonic mean[2] for the High Flow and Low Flow periods (2009-2018). Median river arsenic concentrations (based on the LOADEST model; DEQ, 2019a) for the corresponding flow periods (and span of years) were also calculated. New river arsenic concentrations were then computed for each river segment for two scenarios:

3. Combining the river's seasonal harmonic mean flows (High and Low Flow) and associated median arsenic concentrations with the sum of the permitted discharger' flows discharging at the two seasonal median nonanthropogenic standards (one standard for High Flow, one for Low Flow); and

4. Combining the river's seasonal harmonic mean flows (High, Low) and associated median arsenic concentrations with the sum of the permitted discharger' flows discharging at the annual median nonanthropogenic standard.

For each segment, the new river arsenic concentration (C_{new}, µg/L) resulting from each scenario was calculated as:

$$C_{new} = [(C1 \times Q1) + (C2 \times Q2)] \div (Q1 + Q2) \qquad \textbf{Equation 1}$$

where C1 is the river segment's median seasonal arsenic concentration, Q1 is the river segment's seasonal harmonic mean flow, C2 is the discharge concentration assumed to be at the segment's applicable nonanthropogenic standard (either High Flow, Low Flow, or Annual), and Q2 is the sum of the permitted discharge flows in the segment (**Table 2-3**). C_{new} was computed for both High and Low Flow periods.

[2] Human cancer risk is based on the assumption that water is consumed over a 70-year period. For computing effects of carcinogens in mixing calculations, EPA recommends the harmonic mean as the best representation of a river's long-term average flow (EPA, 1991).

Once the river's new arsenic concentration was computed for each segment and scenario, cancer risk from the river water was calculated using the relationship in **Figure 2-1**. Since the High Flow period is 3 months/year and the Low Flow is 9 months/year, each seasonally-calculated risk factor was weighted (0.25 and 0.75 for High and Low Flow, respectively) and the results summed.

Table 2-3. Input Flow and Concentration Variables by Segment.

River Segment	C1 (µg/L)		Q1 (ft^3/sec)		C2 (µg/L)			Q2 (ft^3/sec)
	High Flow	Low Flow	High Flow	Low Flow	High Flow	Low Flow	Annual	*Assumed same all year*
1	11.53	33.11	6285	1147	11	32	28	1.1713
2	11.25	24.43	7423	1633	11	24	22	3.0945
3	9.78	18.17	9023	1963	10	18	16	1.5473*
4	9.99	14.26	10234	2283	10	14	13	3.0404
5	7.77	9.99	12225	3290	10	10	10	53.52

*There is no permitted arsenic discharge in this segment; flow is hypothetical for purposes of assessing the segment.

To double check these results and to further understand the effect of expressing the nonanthropogenic standards at different timescales, DEQ carried out additional computations using **Equation 1** and the daily flow and daily LOADEST-modeled arsenic concentrations[3]. With this approach it was possible to compute the effects of monthly nonanthropogenic standards[4] and even "daily" nonanthropogenic standards (i.e., a scenario in which there would be a different nonanthropogenic arsenic standard for each day of the year). Daily standards are impractical to implement and DEQ never considered setting the nonanthropogenic standards at a daily scale, but they were computed here for comparative purposes. This work was undertaken on Segments 1 and 4 to ascertain the effect of different timescale expressions at different ends of the river (upper, lower) where seasonal arsenic concentration patterns are quite different (see arsenic patterns in Appendix C of DEQ, 2019b).

2.4 Method for Assessing Ambient River Arsenic Conditions

For the two seasonal standards, DEQ earlier recommended the Wilson Interval for assessing long-term changes in arsenic concentrations in the Yellowstone River (see Section 4.1 in DEQ, 2019b). To ascertain if the Wilson Interval could also be used to assess nonanthropogenic standards expressed as an annual median, DEQ repeated the bootstrap analysis using the same dataset. To assess river compliance with a single annual standard, DEQ will need to carry out proportional sampling corresponding to the length of time associated with the Low Flow (75% of the year) and High Flow (25% of the year) periods. To conform with this, the bootstrap analysis was modified so that each re-sampling event randomly selected data from the High and Low Flow periods in the proper proportions to create each bootstrap dataset. In the future DEQ will collect whole-number sample datasets, therefore the bootstrap analysis was limited to samples sizes of 8, 12, 16, 20, 24, and 28. As before, 1000 randomly-generated datasets for each sample size were generated.

[3] All of the computations described in **Section 2.3** are available from DEQ upon request; contact the supervisor or staff of the Water Quality Standards & Modeling Section.

[4] Although DEQ ultimately did not present monthly nonanthropogenic arsenic standards in its previous technical documents (DEQ, 2019a, 2019b), we did discuss them internally as a potentially viable approach for expressing the arsenic standards.

3.0 RESULTS

3.1 BEST EXPRESSION OF THE NONANTHROPOGENIC ARSENIC STANDARDS

In Segments 1 through 4, a single annual median nonanthropogenic standard results in lower cancer risk compared to the two seasonal median nonanthropogenic standards (**Table 3-1**). In Segment 5, either expression of the standards provides equal risk. Relative reductions in cancer risk provided by the annual median nonanthropogenic standards on the order of one less case in 10,000,000 to 100,000,000.

Table 3-1. Relative Cancer Risk, by Segment, for Two Different Expressions of the Nonanthropogenic Arsenic Standards.

		Comparison of Total Cancer Risk Resulting from Different Expressions of the Standard*			
River Segment	**Segment Description**	**Two Seasonal Standards[†]**	**One Annual Standard[†]**	**Reduction in Risk Provided by the Lower-risk Expression of the Standard**	**More Protective Standard**
1	MT/WY Border to Mill Creek	2.04184E-03	2.04167E-03	**1.67E-07**	One Annual Standard
2	Mill Creek to Boulder River	1.55715E-03	1.55702E-03	**1.25E-07**	One Annual Standard
3	Boulder River to Stillwater River[‡]	1.18377E-03	1.18370E-03	**6.81E-08**	One Annual Standard
4	Stillwater River to Clarks Fork of the Yellowstone	9.71936E-04	9.71872E-04	**6.39E-08**	One Annual Standard
5	Clarks Fork of the Yellowstone to Bighorn River[a]	6.95312E-04	6.95312E-04	**0.00E+00**	Equal

*Raw river water, no drinking water treatment considered. Drinking water treatment reduces arsenic conc. by ~50% at Billings.

[†]Standards were computed as the median of the nonanthropogenic concentration.

[‡] There are no point sources in this segment. 1 MGD was input to the model to assess the standards.

[a] In DEQ (2019b), DEQ recommended leaving the DEQ-7 standard for High Flow, adopting the nonanthropogenic standard for Low Flow.

As noted in **Section 2.3**, additional timescales were analyzed in Segment 1 and Segment 4. In Segment 1, expressing the nonanthropogenic standards as “daily” standards had the highest relative cancer risk, followed by monthly standards, followed by two seasonal standards, and the lowest cancer risk occurred when the standard was expressed as a single annual value. In Segment 4, the order (from highest cancer risk to lowest) was (1) two seasonal standards, (2) “daily” standards, (3) monthly standards, and (4) the single annual standard. These results corroborate the finding in **Table 3-1** and, in spite of the fact that there are different temporal patterns of risk manifested in Segments 1 and 4, the single annual standard is always the lowest cancer risk option.

Finally, DEQ explored the effect of increasing the discharge volumes of the permitted discharges to determine if the results presented here would continue to occur under increased effluent discharge volumes. The results showed that effluent discharge volumes would have to be far in excess of the Yellowstone river’s highest flow volumes in order to alter the results. Thus, for all practical purposes, the results here will occur under any foreseeable arsenic permitting situation.

3.2 ASSESSING AMBIENT RIVER ARSENIC CONDITIONS

The bootstrap analysis showed that, with respect to arsenic concentrations, there were differences among the segments, and that the upper part of the river was different from the lower. The simplest long-term monitoring strategy consists of assessing Segments 1 and 2 using one method and Segments 3 and 4 with a slightly different one. These are detailed below.

- **For Segments 1 and 2:** A total of 16 samples should be collected in each segment over one to two calendar years, proportionally sampling the High Flow (May to July) and Low Flow (August to April) periods. This equates to 4 samples during High Flow and 12 during Low Flow. Each dataset (and segment) should be assessed using the Wilson Interval specific to the 50^{th} percentile (p-hat = 0.5) with a confidence level set at 90%. This will provide false positive rates in the 0-2% range, and DEQ will be able to detect a 25% (or smaller) change in the river's median arsenic concentration.

- **For Segments 3 and 4:** A total of 16 samples should be collected in each segment over one to two calendar years, proportionally sampling the High Flow (May to July) and Low Flow (August to April) periods. This equates to 4 samples during High Flow and 12 during Low Flow. Each dataset (and segment) should be assessed using the Wilson Interval specific to the 50^{th} percentile (p-hat = 0.5) with a confidence level set at 95%. This will provide a false positive rate <10%, and DEQ will be able to detect a 17% (or smaller) change in the river's median arsenic concentration.

Each segment (1 through 4) should be assessed separately (i.e., 16 samples are required for each).

Arsenic data may be collected by DEQ or come from sources other than DEQ. If a dataset comprises multiple sampling sites within a segment, the different sites' data collected on the same day (or almost the same day) will be collated and reduced to a single average value to represent that day (i.e., the sites are NOT considered spatially independent). Based on the outcomes from the Wilson Interval calculations:

1. Zero (0) exceedances = full compliance
2. One (1) exceedance = non-compliance

An exceedance is not a single river sample above the standard; it is a statistically significant change in the river's median arsenic concentration. The regularity at which DEQ's Monitoring & Assessment Section carries out assessments on the river is at the discretion of the section manager and/or included in the section's long-term monitoring strategy.

Start and end points of Yellowstone River *assessment* units—which are the base units for assessment purposes—do not align with the segment start and end points in this report (assessment units can be found in DEQ's Clean Water Act Information Center, on DEQ's website). For purposes of assessment, any segment found to be out of compliance within an assessment unit would result in the entire Yellowstone River assessment unit being considered impaired for arsenic.

If the water body is determined impaired for arsenic, the water body will either be referred for a TMDL or for redevelopment of the standard depending on the suspected cause of the exceedance. If there is no evidence that the standard has been exceeded due to anthropogenic causes, it may be necessary to establish a new nonanthropogenic standard.

4.0 DISCUSSION

Our analysis shows that arsenic in Billing's finished drinking water varies in accordance with arsenic variation in the Yellowstone River (**Figure 2-1**). Others have documented similar findings. Wilson et al. (2002) show that arsenic levels in finished drinking water in Illinois vary in accordance with arsenic levels in the source water (mainly groundwater in their case).

In this report it has been shown that in the Yellowstone River, annual medians are—from a cancer risk perspective—the better choice for expressing the nonanthropogenic arsenic standards. Why might this be? The answer lies in the annual pattern of runoff, the timing of the river's relative dilution strength, and the way these interact with the different expressions of the standards. Essentially, the annual standards provide greater dilution when it matters most.

Figure 4-1 shows daily arsenic concentrations for Segment 1 and includes the annual standard (**Figure 4-1A**) and the two seasonal standards (**Figure 4-1B**). The figure also shows the river's dilution factor (right vertical axis), which is calculated as *[river flow + discharge flow] ÷ discharge flow*. During High Flow (days 122 to 213, horizontal-axis), the river's dilution factor is at times two orders of magnitude higher than during Low Flow. When the standard is expressed as a single annual median, a discharge will dilute river arsenic concentrations during Low Flow but concentrate them during High Flow (**Figure 4-1A**). For the two seasonal standards, a discharge also dilutes river arsenic concentrations during Low Flow, and either dilutes or concentrates river arsenic concentrations during High Flow depending on the time (**Figure 4-1B**). The amount of dilution provided by the discharge—that is, the vertical distance between the river's arsenic concentration and the standard—is greater and occurs longer during Low Flow for the annual standard compared to the two seasonal standards. This dilution occurs precisely when the river's volume is lowest and river arsenic concentrations are highest. During High Flow, the river's volume is far greater and the river's dilution factor is high enough that it matters very little if a discharge increases or decreases the river's arsenic concentration; the river's strong dilution essentially nullifies either result. Annually, it is the greater dilution provided by the annual standard during Low Flow that results in greater overall reduction in river arsenic concentrations (and corresponding cancer risk).

Compared to the two seasonal standards, the relative cancer risk reduction from the annual median nonanthropogenic standards is small, on the order of one less case in 10,000,000 to 100,000,000 (**Table 3-1**). For comparison, EPA maintains that one excess case in 100,000 to 1,000,000 is generally acceptable for establishing standards for carcinogens for the general population (EPA, 2000). Nevertheless, EPA is also clear that states can adopt criteria at lower cancer risks than 1 in 1,000,000 if they choose (EPA, 2000). The important point here is that, even if the cancer risk reductions are small, the methods used in this document provide an objective way to identify the best way to express the nonanthropogenic arsenic standards from among several possible options.

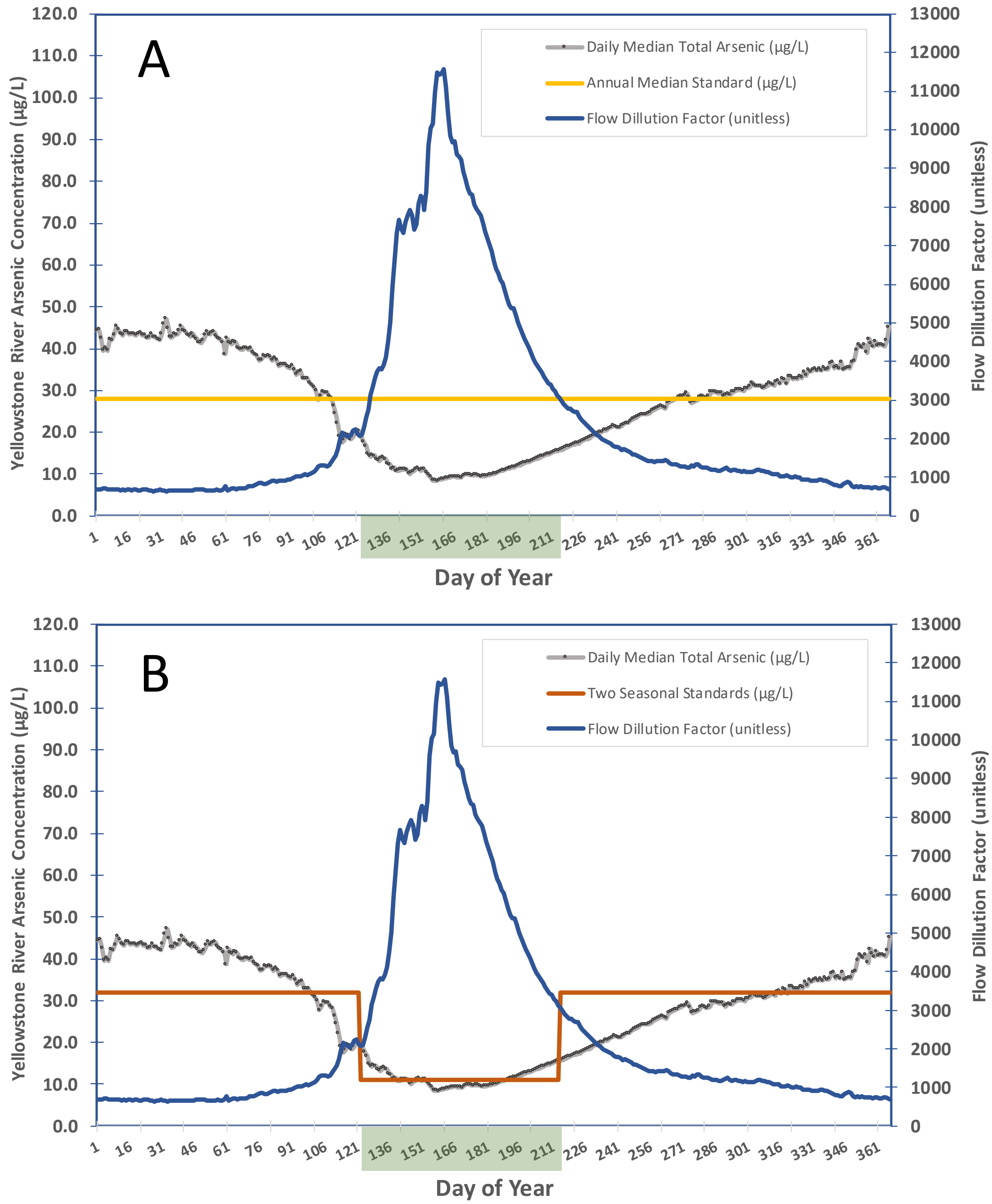

Figure 4-1. Annual Variation in Yellowstone River Arsenic Concentrations, Flow Dilution Factor, and Different Expressions of the Nonanthropogenic Standards, for Segment 1.
Panel A. Annual river arsenic patterns and river dilution shown along with the annual median nonanthropogenic standard. Panel B. Annual river arsenic patterns and river dilution shown along with the two seasonal median nonanthropogenic standards. Green shaded area is High Flow.

The work described in this addendum made it clear to DEQ that each waterbody will be different, so each nonanthropogenic case will have to be considered individually; an effluent-dominated waterbody would not have the same results for arsenic as were found for the Yellowstone River.

In the future, DEQ anticipates that other types of nonanthropogenic standards will be formulated. For those future nonanthropogenic standards, the basic method applied here—properly modified according to the beneficial use and standards being evaluated—can be used. For example, non-carcinogens (i.e., toxic compounds) are not harmful to people at all concentrations. They typically have a lower threshold below which they do not cause harm, referred to as the no observed adverse effect level (NOAEL; Laws, 2000). A nonanthropogenic standard involving a toxic compound of this type would have to be assessed differently than what was done here for arsenic. And as for all water quality standards, during the rule adoption process consideration must be given to the full suite of applicable laws governing the water quality standard.

5.0 CONCLUSION

Using reduction in human cancer risk associated with decreased river arsenic concentrations, it has been shown in this document that a single annual median is the best expression of the nonanthropogenic arsenic standards for Segments 1 through 4 of the Yellowstone River (from the Montana/Wyoming border to the confluence with the Clarks Fork of the Yellowstone). In Segment 5, either expression of the nonanthropogenic standards (two seasonal medians or one annual median) results in the same cancer risk. In Segment 5, the river's median annual nonanthropogenic concentration is at or just below the currently-adopted arsenic HHS in Circular DEQ-7 (10 µg/L), and nonanthropogenic standards are not recommended there. DEQ recommends the nonanthropogenic standards shown in **Table 5-1**.

Table 5-1. Recommended Nonanthropogenic Arsenic Standards for Segments of the Yellowstone River.

River Segment	Segment Description	Annual Median Nonanthropogenic Arsenic Standard (µg/L)
1	MT/WY Border to Mill Creek	28
2	Mill Creek to Boulder River	22
3	Boulder River to Stillwater River	16
4	Stillwater River to Clarks Fork Yellowstone	13
5	Clarks Fork Yellowstone to Bighorn River	n/a*
*In this segment the nonanthropogenic condition is not less than the arsenic standard in Circular DEQ-7, so the Circular DEQ-7 standard should continue to apply.		

The Wilson Interval Method may be used for long-term monitoring and assessment of the recommended standards in Segments 1 through 4 (**Table 5-1**). Sampling and data evaluation using the Wilson Interval should proceed according to the details provided in **Section 3.2**.

6.0 REFERENCES

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