# Nonanthropogenic Standard Selection: Yellowstone River

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**WQPBWQSMTR-???**

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# ACRONYMS

| | |
|---|---|
| ARM | Administrative Rules of Montana |
| cfs | cubic feet per day |
| DEQ | Department of Environmental Quality |
| DON | Demonstration of Nonanthropogenic |
| EPA | Environmental Protection Agency |
| HUC | Hydrologic Unit Code |
| ICIS | Integrated Compliance Information System |
| kg/day | kilograms per day |
| MCA | Montana Code Annotated |
| mg/L | milligrams per liter |
| ML | Mass Load |
| MPDES | Montana Pollutant Discharge Elimination System |
| NAS | Nonanthropogenic Arsenic Standard |
| QAPP | Quality Assurance Project Plan |
| SAP | Sampling and Analysis Plan |
| TMDL | Total Maximum Daily Load |
| µg/L | micrograms per liter |
| USGS | United States Geological Survey |
| WQPB | Water Quality Planning Bureau |
| WQSM | Water Quality Standards and Modeling Section |
| WWTP | Waste Water Treatment Plant |
| YNP | Yellowstone National Park |

# 1.0 Introduction

## 1.1 Summary

This document presents the methods and results for arsenic nonanthropogenic standard (NAS) selection for the Yellowstone River. NAS selection is a process used to identify appropriate water quality standards in situations where a waterbody's levels of a pollutant are elevated due to natural (non-human) sources. This document includes the portion of the Yellowstone River watershed from the Montana/Wyoming border north of Gardiner, Montana to the mouth of the Bighorn River near Bighorn, Montana as shown in **Figure 1-1**. The Water Quality Standards and Modeling Section (WQSM) of the Montana Department of Environmental Quality (DEQ) Water Quality Division has completed this document.

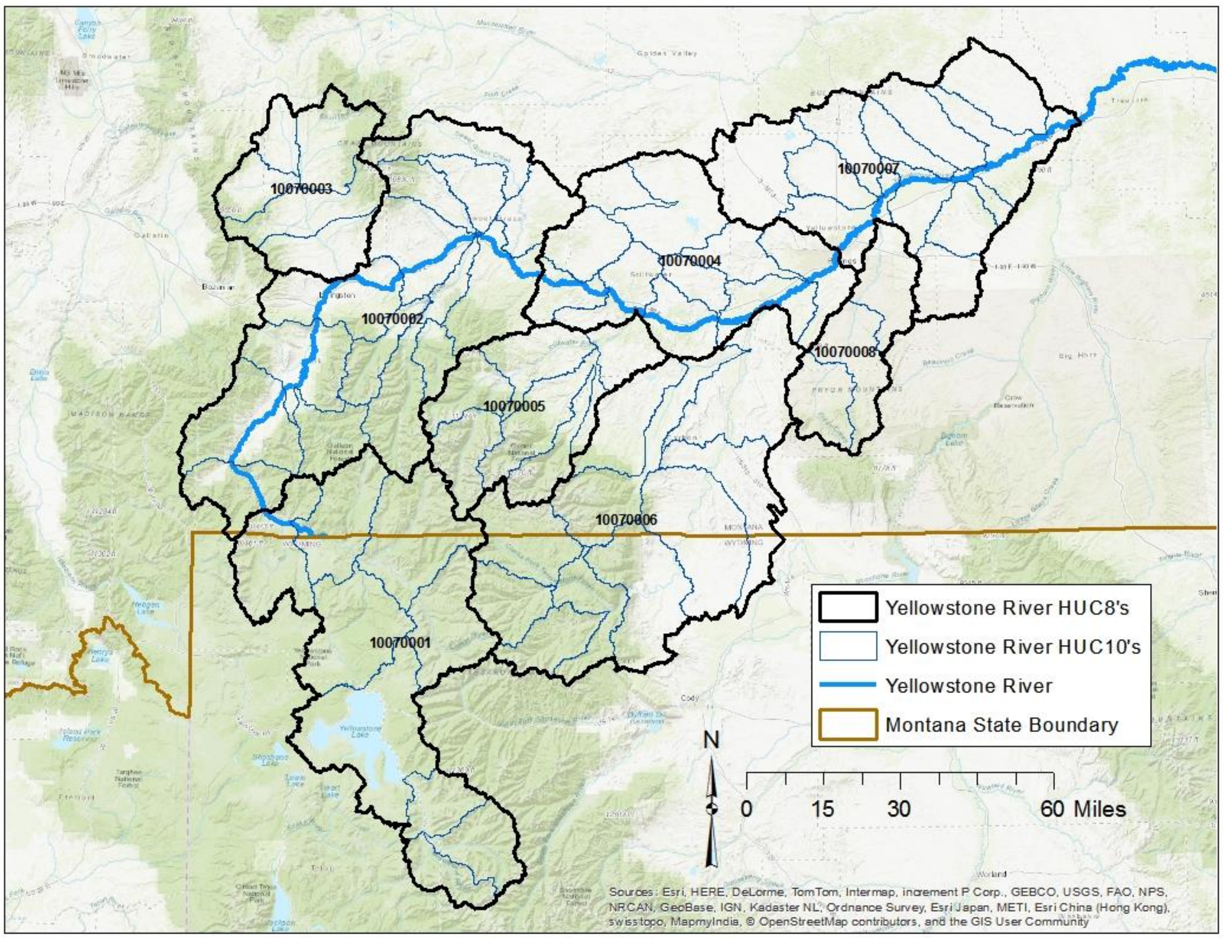


**Figure 1-1. Location of Project Sub-basins**

The NAS selected for the Yellowstone River segments are based on the median monthly nonanthropogenic concentrations calculated from modeled arsenic loads and median monthly flow rates. The Yellowstone River hydrologic segments are presented in **Figure 1-2** and **Table 1-1** and will be described in more detail in **Section 1.5**.

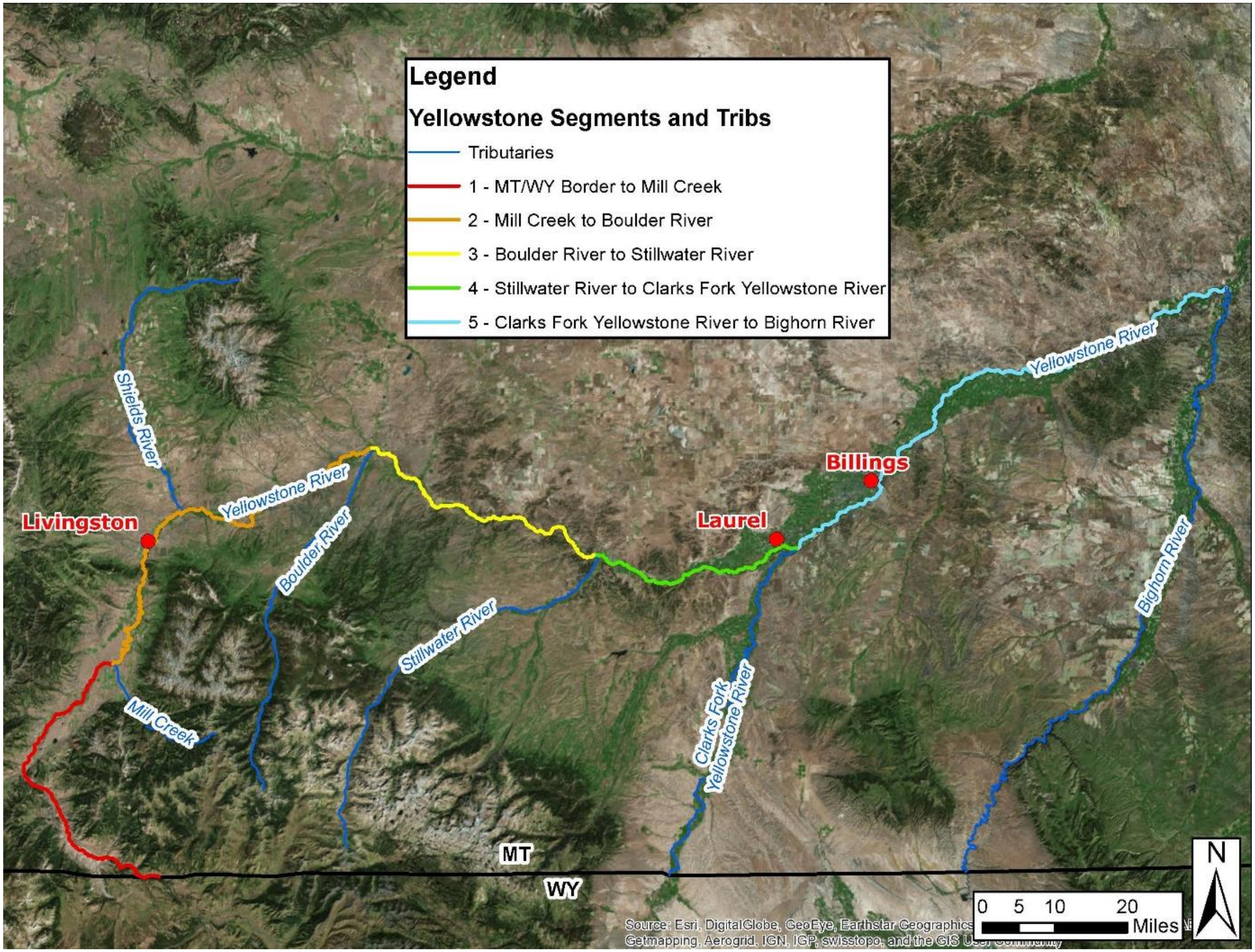


**Figure 1-2 Hydrologic Sections of the Yellowstone River**

**Table 1-1. Project Sub-basins and Associated HUCs**

| HUC | Name of Sub-basin | Description of Sub-basin |
|---|---|---|
| 10070001 | Yellowstone Headwaters | YNP to Yellowstone River at McConnell Access |
| 10070002 | Upper Yellowstone | Yellowstone River at McConnell Access to approximately 16 river miles past Big Timber |
| 10070003 | Shields | Major Tributary Basin – Shields River |
| 10070004 | Upper Yellowstone-Lake Basin | Yellowstone River, 16 river miles past Big Timber to Billings |
| 10070005 | Stillwater | Major Tributary Basin – Stillwater River |
| 1007006 | Clarks Fork Yellowstone | Major Tributary Basin – Clarks Fork Yellowstone River |
| 10070007 | Upper Yellowstone – Pompeys Pillar | Yellowstone River, Billings to confluence of Bighorn River |

The selected arsenic NAS for the Yellowstone River segments range from 32 µg/L near Yellowstone National Park to 14 µg/L at the mouth of the Clarks Fork of the Yellowstone River with a frequency and duration of "*average annual concentration not to exceed the NAS"* protecting a "*drinking water with natural arsenic*" use.

## 1.2 Supporting Documents

The "Demonstration of Nonanthropogenic" (DON) document summarizes the methods and results for the Yellowstone River and will be referenced throughout this document (DEQ, 2018). A scientifically defensible DON is a first step in the process of developing standards based on a nonanthropogenic condition. This NAS is based on the methods and results detailed in the DON (DEQ, 2018).

The quality assurance descriptions for field data collection, data compilation and modeling described in this document were provided in the Department of Environmental Quality (DEQ) Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plans (SAP) (DEQ, 2015a, 2015b, 2016, 2017b). Full citations are in the reference section of this document.

## 1.3 Purpose

Although water quality standards are almost always expressed as a unique concentration value, water quality is not simply a static number. Water quality is almost always a distribution of concentration values which, over a long period of time, typically appears static, but in the short term, can be quite variable. The variability is a result of seasonal changes and inter-annual fluctuations. The Yellowstone River at Corwin Springs (**Figure 1-3**) serves as an excellent example of the variability of arsenic concentrations over time and the inherent difficulty in picking a unique concentration value to represent the "natural" condition of the water body. The purpose of a nonanthropogenic water quality standard is to protect the existing uses of the water body and to protect the long-term nonanthropogenic distribution of values. While it would be nearly impossible to preserve the exact distribution of values, choosing an appropriate criterion within the distribution ensures that the distribution necessary to maintain existing uses and conditions is protected.

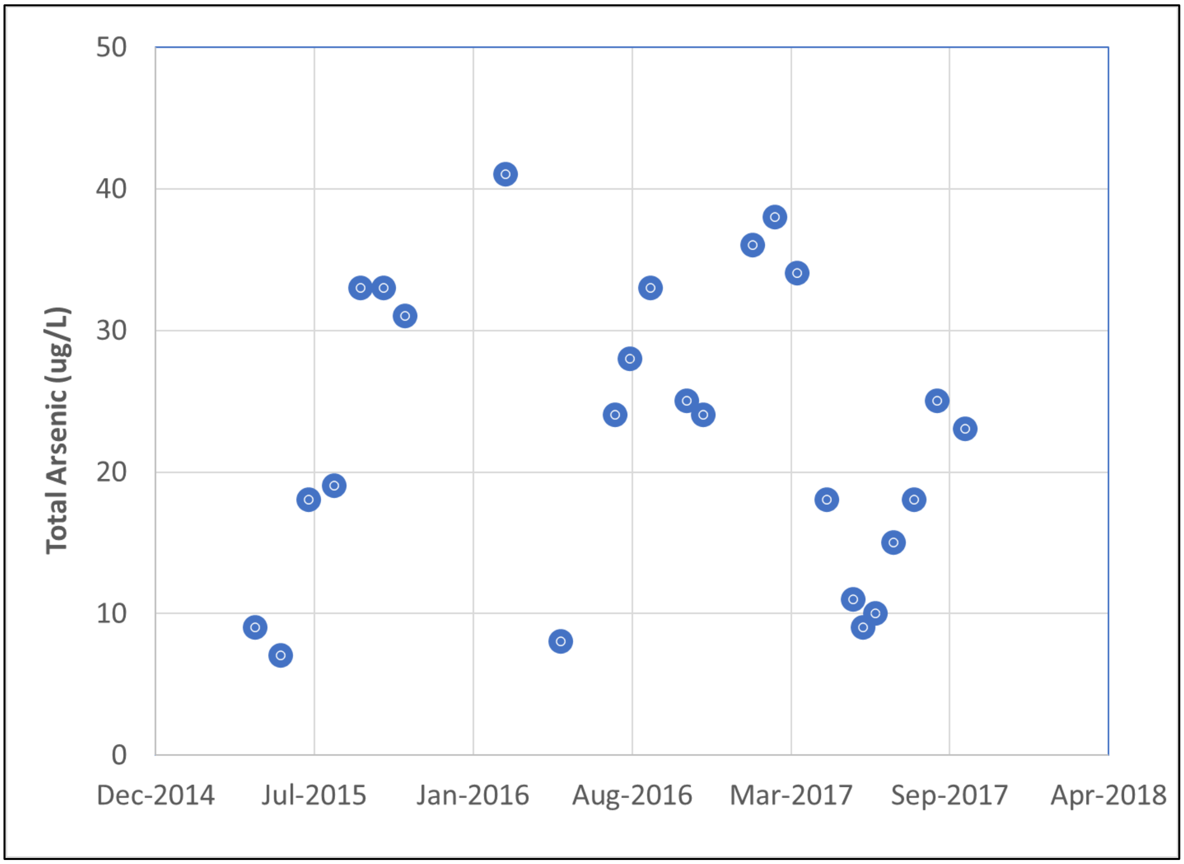


**Figure 1-3. Concentration Patterns for the Yellowstone River at Corwin Springs**

## 1.4 Background

In Yellowstone National Park (YNP), there are over 10,000 thermal features including more than 300 geysers (YNP, 2015). Many of these features drain into the Yellowstone River Basin. It is estimated that 30 percent of geothermal waters drain in the Yellowstone River Basin from the West Thumb Geyser Basin, thermal feathers in and around the shores of Yellowstone Lake, Hot Springs Basin Group, Sulfur Cauldron Hot Springs, Grand Canyon of the Yellowstone Hot Springs, Calcite Springs, and the Mammoth Geyser Basin (Norton and Friedman, 1991). The Gardner River drains much of the Mammoth Geyser Basin before joining the Yellowstone River above Gardiner, Montana. The geothermal water of the Yellowstone Park Caldera provides the largest source of arsenic loading to the Yellowstone River and has been documented by many researchers (Miller et al., 2004; Rowe et al., 1973). Arsenic concentrations of samples collected from the Yellowstone River, from the Wyoming Border to Livingston, Montana are consistently above the Montana human health criterion of 10 µg/L (DEQ, 2017c, 2012). The arsenic concentrations of the Yellowstone River, below Livingston to Laurel, Montana are consistently above the human health criterion during low flow conditions (DEQ, 2017c, 2012).

The Yellowstone River's origin is just southeast of the park and flows through YNP feeding and draining Yellowstone Lake (Uhler, 2014). The Yellowstone then flows North through the park gaining in geothermal contributions from the Gardner and Lamar Rivers. The Yellowstone River leaves the Park near Gardiner, Montana and flows into the Missouri River in North Dakota.

Per Montana law, DEQ may not apply a water quality standard to a water body that has nonanthropogenic concentration greater than the standard (75-5-222, MCA). Furthermore, Montana law has always stated that discharges are not required to discharge purer than natural (75-5-306, MCA). In this case, since the human health-based standard of 10 µg/L is below the nonanthropogenic condition, then the standard would be set at the natural arsenic condition of the water body.

The Yellowstone River has a use class of B-1 from the Montana/Wyoming border to the Laurel water supply intake. From the Laurel water supply intake to the Billings water supply intake, the use class is B-2. From the Billings water supply intake to the North Dakota state line, the Yellowstone River has a use class of B-3. Waters classified B-1 are to be maintained suitable for drinking, culinary, and food processing purposes after conventional treatment; bathing, swimming and recreation; growth and propagation of salmonid fishes and associated aquatic life, waterfowl and furbearers; and agricultural and industrial water supply. The B-2 classification has the same uses as B-1, with minor differences in the pH, turbidity and temperature narrative standards. The B-3 classification is similar to the B-2 classification, except B-3 waters are suitable for the growth and propagation of *non-salmonid* fishes and associated aquatic life.

DEQ WQSM section investigated the level of nonanthropogenic arsenic concentrations in the Yellowstone River. The specific objectives of the WQSM investigation are described in the project QAPP (DEQ, 2015a) and SAPs (DEQ, 2015b, 2016, 2017b). The results applicable to the NAS are described in this document.

## 1.5 HYDROLOGIC REGION

The Yellowstone River watershed from the Wyoming Border to the confluence with the Bighorn River is the area of interest for this study and is shown in **Figure 1-1.**

The United States Geological Survey (USGS) Hydrologic Unit Codes (HUCs) are a convenient way to classify watersheds. Using this system, the largest division for the Yellowstone River hydrologic region was a HUC8 (8 digit code), followed by a HUC10 and then a HUC12. These categories progressively divide the basin into smaller sub-basins. The Yellowstone River hydrologic region and tributaries are defined by seven HUC8 codes as listed in **Table 1-1**. These HUC8s were selected because they drain into the Yellowstone River. The region is defined from the Wyoming Border to the mouth of the Big Horn River. Smaller geographic regions within the HUC8s were recognized for modeling purposes. For example, there were 65 HUC10s within the hydrologic region (**Figure 1-1**).

The Yellowstone River and associated tributaries are divided into five hydrologic sections for nonanthropogenic standards development. The sections were chosen based on hydrologic divides and a measurable difference in ambient concentrations. In most cases, the hydrologic divides are large tributaries that provide significant dilution that results in a reduction in arsenic concentrations. As the river leaves YNP, arsenic concentrations are high from natural geothermal sources. Tributaries dilute these high arsenic concentrations resulting in successively lower concentrations downstream from YNP in the Yellowstone River.

The hydrologic sections are presented in **Table 1-2** and **Figure 1-2**.

**Table 1-2 Hydrologic Segments for Yellowstone River NAS**

| Segment | Beginning | End | Length (miles) |
|---|---|---|---|
| 1 | Montana/Wyoming Border | Mill Creek near Pray | 45 |
| 2 | Mill Creek near Pray | Boulder River at Big Timber | 54 |
| 3 | Boulder River at Big Timber | Stillwater River near Columbus | 37 |
| 4 | Stillwater River near Columbus | Clarks Fork of the Yellowstone River at Laurel | 27 |
| 5 | Clarks Fork of the Yellowstone River at Laurel | Bighorn River at Bighorn | 73 |

# 2.0 METHODS

The steps associated with NAS Selection are listed below and summarized in **Figure 2-1**. These steps will be discussed in the succeeding sub-sections.

- Demonstration of Nonanthropogenic (DON)
- Existing or Potential Dischargers
- Dilution Test
- Seasonality Determination
- Standard Selection

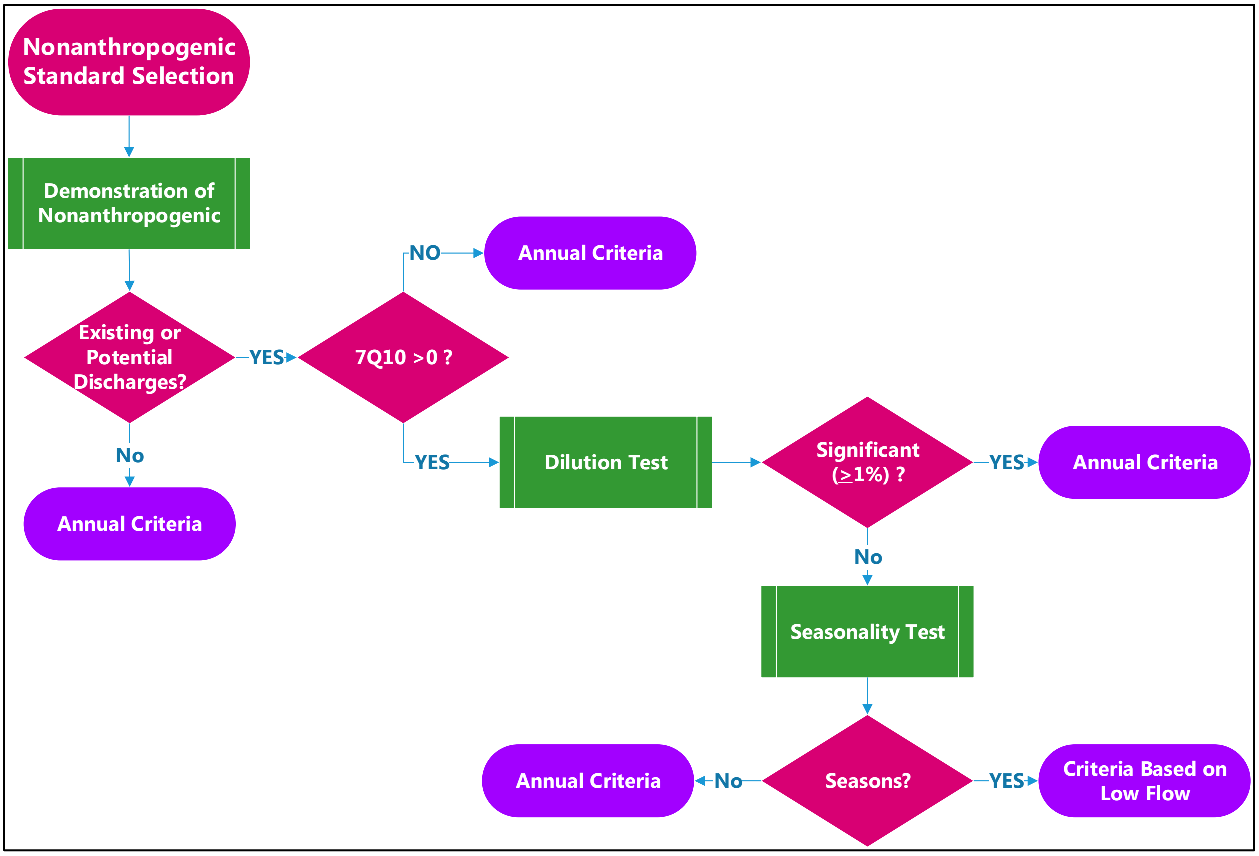


**Figure 2-1. Nonanthropogenic Standard Selection (NAS) Flow Chart**

## 2.1 DEMONSTRATION OF NONANTHROPOGENIC (DON)

A scientifically defensible DON is the first step in the process of developing criteria based on a nonanthropogenic condition. The process for calculating nonanthropogenic arsenic loads for the Yellowstone River Basin is shown in **Figure 2-2**. The DON concludes with the median nonanthropogenic arsenic load condition and is tabulated in **Table 3-1** (DEQ, 2018).

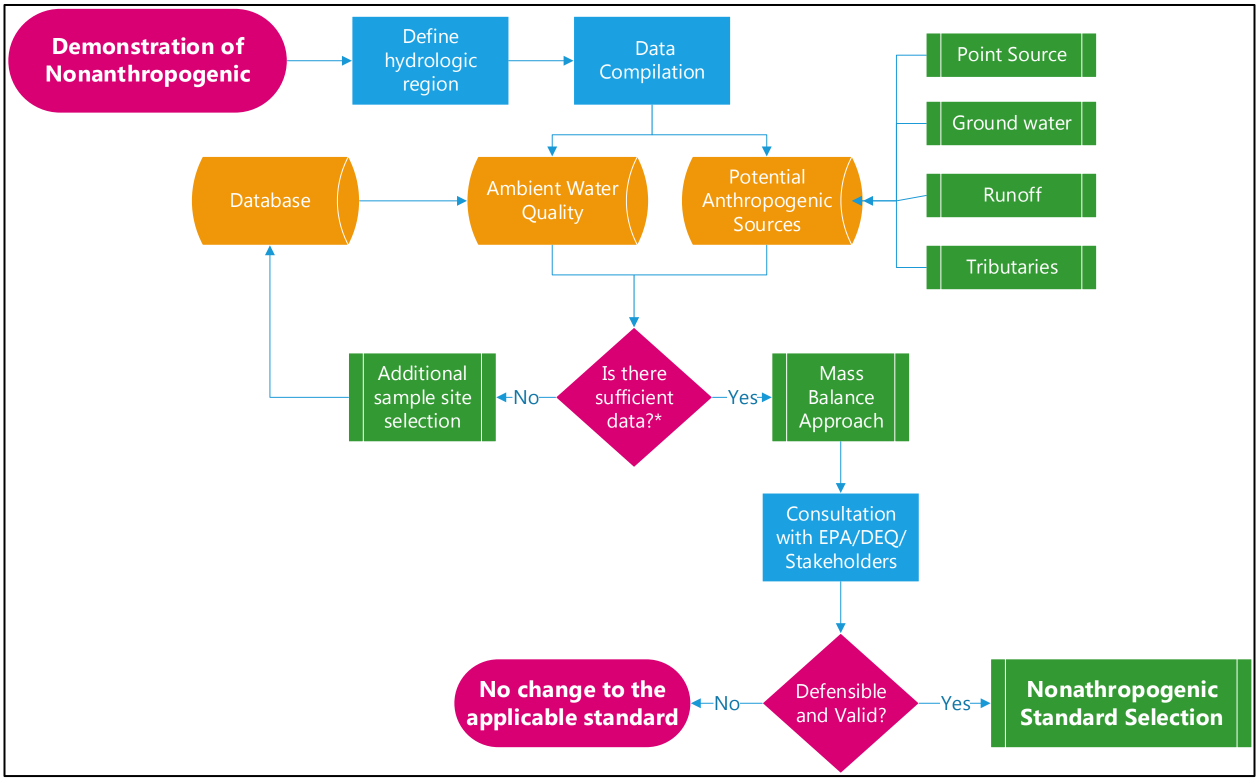


**Figure 2-2. Demonstration of Nonanthropogenic Process**

## 2.2 Potential or Existing Discharges

As shown in **Figure 2-1**, after the DON is completed and determined valid, the presence of permitted discharges (or planned discharges) that are discharging anthropogenic arsenic are determined. Permitted discharges include major facilities legally and actively discharging into the project waterbodies. The arsenic concentration data is extracted from the EPA Integrated Compliance Information System (ICIS) database.

Current or future discharges have the potential to shift the nonanthropogenic arsenic distribution of the water body in a manner inconsistent with the protection of beneficial uses. Arsenic concentrations in Montana are greater during low flow conditions compared to high flow conditions. Therefore, setting a criterion based on year-round arsenic concentrations is more conservative than setting a criterion based on low-flow arsenic concentrations. The more conservative approach will be selected if there are no dischargers in a reach. In the future, if there are new dischargers in the reach, the new discharger will be held to the more conservative criterion, and any discharges may be further limited because they will have to provide for attainment and maintenance of downstream water quality. This concept is further explained in the next section.

## 2.3 Dilution Test

The dilution test estimates if current or future discharges have the potential to shift the nonanthropogenic arsenic distribution of the water body in a manner inconsistent with the protection of beneficial uses.

The nonanthropogenic distribution of arsenic concentrations in a large river is much better protected against potential changes caused by permitted arsenic discharges than is the arsenic distribution of a smaller stream with lower flows. To assess this volume-based sensitivity, a dilution test is carried out by comparing a water body's 7Q10 flow (the lowest average 7-day low flow that occurs once every 10 years on average) to existing and potential discharge volumes. The 7Q10 or methodologies for calculating the 7Q10 for many Montana waterbodies can be found in Appendix E of the USGS publication, Montana Stream Stats (USGS, 2015). Use of the 7Q10 for the dilution test is meant to evaluate the potential for a shift in the distribution of arsenic concentration values during some of the lowest expected flows (i.e. in the worst-case scenario for dilution purposes).

If the 7Q10 value of a stream is zero cfs, then current or future discharges to that stream are significant and an annual standard based on the median monthly nonanthropogenic concentrations would be applied (**Figure 2-1**). If the 7Q10 is greater than 0, then a ratio of the cumulative point sources' discharge volumes (existing and any planned discharges) to 7Q10 flow is calculated. If the ratio is greater than or equal to 1%, the collective discharge is considered significant and an annual standard based on the median monthly nonanthropogenic concentrations would be applied. If the ratio is less than 1%, then a seasonality determination is required (1% was chosen because there is precedence for using 1% dilution to indicate that sufficient dilution will occur). The seasonality determination is described in detail in **Section 2.4**. The dilution test qualifications are summarized in **Table 2-1**.

**Table 2-1. Dilution Test for NAS Selection**

| Case | 7Q10 (cfs) | Point Source Discharge Volume % of 7Q10 | Standard Selection or Action |
|---|---|---|---|
| 1 | 0 | N/A | Select Annual Standard |
| 2 | > 0 | 0 | Select Annual Standard |
| 3 | > 0 | ≥ 1% | Select Annual Standard |
| 4 | > 0 | < 1% | Perform Seasonality Determination |

## 2.4 Seasonality Determination

If the dilution test demonstrates that a seasonality determination is appropriate (**Table 2-1**), the modeled nonanthropogenic arsenic concentration for the water body is analyzed for variability under high flow versus low flow conditions. This determines if the annual standard will be based on the median concentrations of all months or just the low flow months. This will be done per the method identified in Suplee (2007) and summarized in this section.

The USGS daily flow data and the median monthly arsenic concentrations calculated from the median of the daily flow data are used in the seasonality determination. First, high flow and low flow months are determined. To do this, at least five years of continuous flow data are necessary (this will normally be drawn from a USGS gaging station or stations within the reach). The recorded flows for each day of the year for the entire period of record are averaged and plotted on a flow duration hydrograph. The runoff period is then bracketed by determining the two points of inflection (where runoff and begins and ends) and rounding to the nearest end-of-month or mid-month date. The runoff period represents the high flow months, and the rest of the year represents the low flow months. An example of the daily mean flow hydrograph for the Yellowstone River at Corwin Springs is shown in **Figure 2-3**. The high flow period is identified as starting and ending at the two inflection points on each side of the flow peak (111 and 222 days).

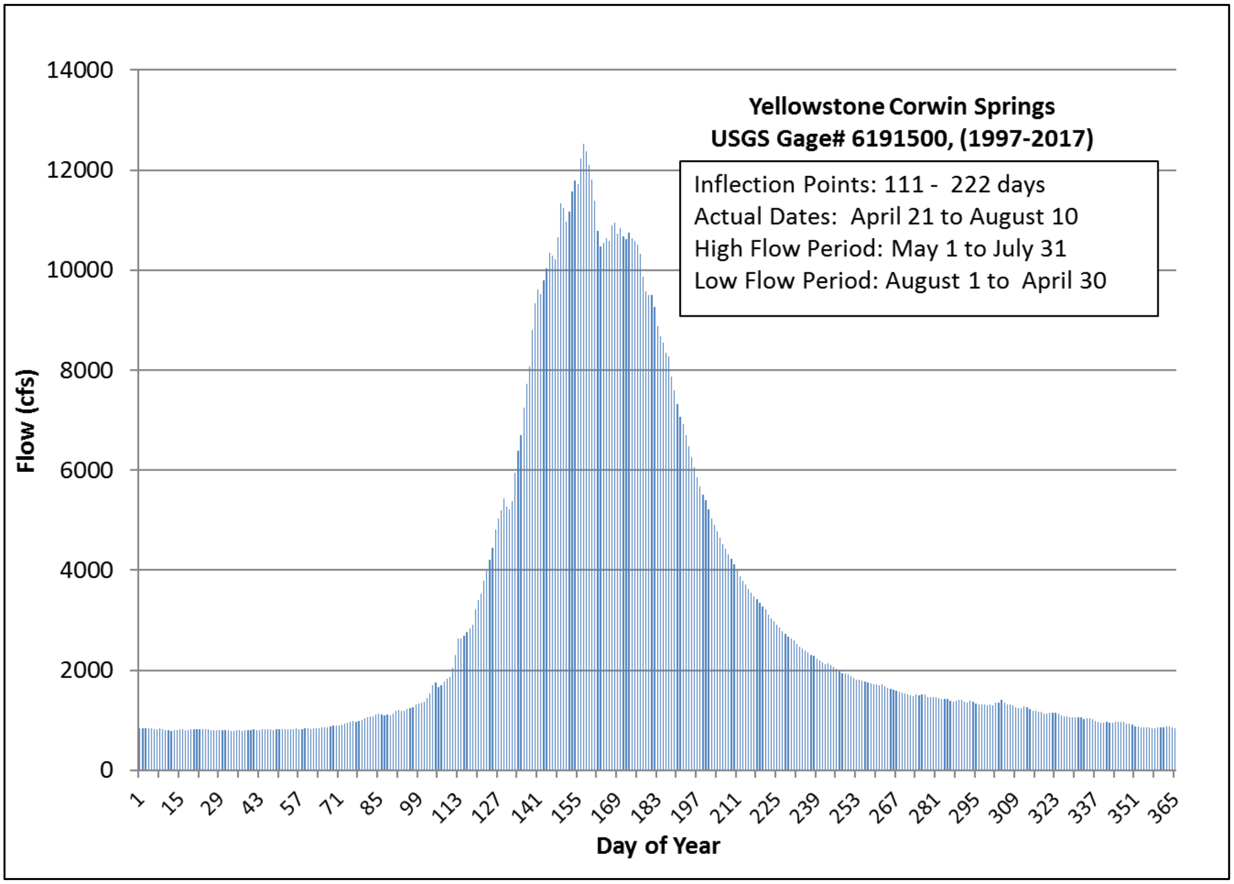


**Figure 2-3. Example Daily Mean Flow Duration Hydrograph for Yellowstone River at Corwin Springs**

After determining the high flow and low flow months, the model-derived monthly arsenic concentrations from the two time periods are tested for a significant difference (95% confidence, $\alpha$= .05) using the Mann-Whitney test. The Mann-Whitney test is a nonparametric hypothesis test to determine whether two populations have the same population median.

The hypotheses are:

$H_0$: $x_1 = x_2$ versus $H_1$: $x_1 \neq x_2$, where x is the population median

The test does not require the data to come from normally distributed populations but the sample sets should have similar shape and be independent of each other. The test uses the ranks of the sample data, instead of their specific values, to detect statistical significance. The selected $\alpha$ (significance level) is the maximum acceptable level of risk for rejecting a true null hypothesis ($H_0$). The test calculates a p-value (between 0 and 1) and determines the appropriateness of rejecting $H_0$ in the hypothesis test. The p-value must be less than the selected $\alpha$ (0.05) to reject $H_0$ in favor of the alternate hypothesis ($H_1$), thus concluding that the two populations are different. Alternately, a test that results in a p-value greater than $\alpha$ does not support the hypothesis that there is a difference between the population medians.

If the median arsenic concentrations for the high and low flow seasons are significantly different per the Mann-Whitney test, then seasonal criteria will be calculated and one annual standard will be applied based on the median monthly concentrations of the low flow season. Alternately, if the median arsenic concentrations for the high and low flow seasons are not significantly different per the Mann-Whitney test, then one annual standard based on the median monthly arsenic concentrations is applied.

In summary, this approach protects water bodies when they are most vulnerable to change during low flow conditions or if point source discharges make up a significant portion of the flow. It also allows a slightly higher standard if the water body's arsenic concentrations are protected from changes due to higher flows and therefore higher dilution.

## 2.4 Standard Selection

As mentioned in the previous section, the water quality standard, whether seasonal or annual, is based on the 50th percentile (median) of the nonanthropogenic distribution. The nonanthropogenic condition is determined via a loading analysis and the standard is calculated based on the long-term median flow for the designated period. This approach establishes the water quality standard at a value that is protective locally (i.e., representative of the nonanthropogenic condition), with the 50th percentile as the best representation of the central tendency of the nonanthropogenic distribution of the data points.

A standard calculated based on ambient concentrations is less complicated than a standard calculated from a nonanthropogenic condition. For instance, to establish a standard based on ambient condition, a statistically valid number of concentration data points are collected, representing seasonal and annual fluctuations and a median concentration is calculated from this data to represent an annual or seasonal standard. There are many more steps when the standard is developed from the nonanthropogenic condition.

The first step in selecting the NAS is to calculate the nonanthropogenic condition as outlined in **Figure 2-2** and defined in the DON (DEQ, 2018). The DON not only demonstrates that the source of arsenic is mainly nonanthropogenic, but also establishes the monthly nonanthropogenic arsenic mass load. Standards are set as concentrations; therefore, the nonanthropogenic arsenic mass load must be converted to a concentration. A mass load is converted to a concentration using a flow volume, as defined in the following equation:

***EQUATION 1:*** $C = ML/(Q \times T \times cf)$

Where,

C – Concentration (µg/L or mg/L)
ML – Mass Load (pounds or kilograms per unit of time)
Q – Flow of water at a point (cubic feet per second, cfs)
T – unit of time (season, month, or year)
cf – conversion factor for mass load calculation (variable depending on units of individual terms)

While the 7Q10 flow is used to determine the worst-case scenario in the dilution test, the median flow volume is used for calculating the arsenic standard. The median flow volume corresponds to a mid-level arsenic concentration rather than a very high arsenic concentration, and the intent is to select the central tendency for the standard rather than an outlier. The median monthly flow volume is calculated from USGS gage data as described in **Section 2.2**.

# 3.0 RESULTS

## 3.1 DEMONSTRATION OF NONANTHROPOGENIC

For the Yellowstone River segments, the modeled median monthly and annual median anthropogenic arsenic loads are tabulated in **Table 3-1**. Additional detail can be found in the DON (DEQ, 2018).

**Table 3-1. Median Nonanthropogenic Loads for Yellowstone River (From DEQ, 2018)**

| Month | 1 - MT/WY Border to Mill Creek | 2 - Mill Creek to Boulder River | 3 - Boulder River to Stillwater River | 4 - Stillwater River to Clarks Fork Yellowstone River | 5 - Clarks Fork Yellowstone River to Bighorn River |
|---|---|---|---|---|---|
| **Monthly (kg/month)** | | | | | |
| October | 3,096 | 3,087 | 2,718 | 2,905 | 3,024 |
| November | 2,244 | 2,548 | 2,476 | 2,893 | 2,496 |
| December | 2,399 | 2,436 | 2,142 | 2,343 | 2,225 |
| January | 2,177 | 2,390 | 2,164 | 2,279 | 2,298 |
| February | 2,182 | 2,262 | 2,123 | 2,180 | 2,279 |
| March | 2,580 | 2,716 | 2,737 | 2,589 | 2,876 |
| April | 3,466 | 3,599 | 3,557 | 3,696 | 3,797 |
| May | 5,633 | 6,350 | 6,936 | 8,806 | 8,910 |
| June | 6,044 | 6,942 | 8,411 | 11,856 | 12,752 |
| July | 4,635 | 4,843 | 4,422 | 4,776 | 4,763 |
| August | 3,695 | 3,786 | 3,425 | 3,261 | 2,593 |
| September | 3,077 | 3,209 | 2,733 | 2,478 | 2,248 |
| **Annual (kg/year)** | | | | | |
| **Annual** | 41,229 | 44,167 | 43,842 | 50,062 | 50,260 |

## 3.2 DILUTION TEST

As described in **Section 2.2**, a dilution test is carried out by comparing a water body's 7Q10 flow to existing and potential discharge volumes. The list of permitted dischargers, facility, receiving body, maximum facility discharge and maximum facility concentration are shown in **Table 3-2**. As discussed in the DON, these are not the only permitted dischargers in the Yellowstone basin but are the only permitted dischargers with arsenic limits and arsenic effluent monitoring (DON, 2018). The other permitted dischargers are assumed to not be discharging significant arsenic concentrations to the Yellowstone River. Please refer to the DON for additional discussions on point sources (DEQ, 2018).

The maximum discharge was used in this analysis (**Table 3-2**) to illustrate a high-case scenario or the maximum discharge quantity for the facilities history. There were two dischargers from the Montana/Wyoming Border to the mouth of Mill Creek (hydrologic segment 1), one discharger from the Mouth of Mill Creek to the mouth of the Boulder River (segment 2), no potential dischargers identified from the Boulder River to the Stillwater River (segment 3), one discharger from the Stillwater River to the Clarks Fork of the Yellowstone River (segment 4), and four dischargers from the Clarks Fork of the Yellowstone River to the mouth of the Bighorn River (segment 5). The sum of these discharges, the river's 7Q10, and the results of the dilution test are shown in **Table 3-3**.

**Table 3-2. Permitted Discharges with Arsenic Discharges**

| MPDES No. | Facility | Hydrologic Segment Discharge | Maximum Flow (cfs) | Max Conc. (µg/L) |
|---|---|---|---|---|
| MT0030252 | TVX MINERAL HILL INC | 1 | 0.42 | 0.014 |
| MT0022705 | GARDINER WWTF | 1 | 0.65 | 0.1 |
| MT0020435 | CITY OF LIVINGSTON WWTP | 2 | 1.7 | 0.004 |
| MT0000264 | CENEX HARVEST STATES COOP. | 4 | 2.2 | 0.08 |
| MT0000281 | WESTERN SUGAR COOPERATIVE | 5 | 3.2 | 0.004 |
| MT0000256 | PHILLIPS 66 - BILLINGS REFINERY | 5 | 1 | 0.006 |
| MT0000477 | EXXONMOBIL REFINING & SUPPLY | 5 | 3.9 | 0.012 |
| MT0022586 | CITY OF BILLINGS WWTP | 5 | 23 | 0.004 |

**Table 3-3. Results of Yellowstone River Dilution Test**

| Hydrologic Section | USGS Station Number | 7Q10 (cfs) | Discharger Max Flow (cfs) | Dilution Test (MAX/7Q10) | Conclusions |
|---|---|---|---|---|---|
| 1 - MT/WY Border to Mill Creek | 6191500 | 504 | 1.07 | 0.20% | Use Seasonal Determination |
| 2- Mill Creek to Boulder River | 6192500 | 766 | 1.7 | 0.20% | Use Seasonal Determination |
| 3 - Boulder River to Stillwater River | N/A | 907 | 0 | 0 | Annual Criteria |
| 4 - Stillwater River to Clarks Fork Yellowstone | N/A | 1047 | 2.2 | 0.20% | Use Seasonal Determination |
| 5 - Clarks Fork of the Yellowstone River to Bighorn River | 6214500 | 1197 | 31.1 | 2.60% | Annual Criteria |

For all five hydrologic segments of the Yellowstone River, the 7Q10 is greater than 0. The ratio of the cumulative point sources' discharge volumes (existing and any planned discharges) to 7Q10 flow is calculated (**Table 3-3**). The 7Q10 of the USGS station located within the segment is used in the calculation. For segments 3 and 4, there are no USGS stations located within the segment. For this reason, an addition-by-parts method was used to estimate daily flows in segment 3 and 4. Using USGS gage data at other locations, the flow at a downstream point was set equal to the flow at a gaged upstream point, plus all the gaged tributary flows that come in between them. To test this rough approximation, the sum at Billings was calculated and compared to the gaged daily data at Billings.

The formula is:
*Yellowstone River at Billings*$_i$ *= Yellowstone River at Livingston*$_{i-2}$ *+ 1.008*Shields River*$_{i-2}$ *+ 1.004*Boulder River*$_{i-1}$ *+ 1.082*Stillwater River*$_{i-1}$ *+ 1.326*Clarks Fork Yellowstone River*$_i$

Where i is the iteration value. In this case, the iteration is reported flow by day to account for travel time. Using segment 4 as an example (Stillwater River to Clarks Fork of Yellowstone), each tributary has a drainage area adjustment based on where the gage is located within the watershed, and estimated travel times were used to approximate which days to compare (i.e. to Billings there is a 2 day travel time from Livingston and Shields River, a 1 day travel time from Boulder and Stillwater River, and <1 day travel time from the Clarks Fork of Yellowstone River).

This calculation for the period 1989-2017 (29 years) resulted in an excellent match between observed and calculated data. Modeling metrics were good, with overall relative error at 0.4%, the slope of model fit at 1.005, and a Nash-Sutcliffe coefficient of Efficiency (NSE) of 0.97. The main discrepancies are in the winter flows (the addition-by-parts method overpredicts and under predicts winter flows equally), possibly due to ice issues. Overall, this appears to be a reliable method for obtaining an approximation of daily flows without considering minor tributaries, irrigation, point source withdrawals, etc.

After determining that this method works well on segment 4, it was used to estimate the daily flow for segment 3 (downstream of the Stillwater River confluence) using the formula below.

*Yellowstone River at Columbus*$_i$ *= Yellowstone River at Livingston*$_{i-1}$ *+ 1.008*Shields River*$_{i-1}$ *+ 1.004*Boulder River*$_i$ *+ 1.082*Stillwater River*$_i$

There are no permitted or known potential discharges for the Yellowstone River from the Boulder River to the Stillwater River (segment 3). Thus, per **Table 2-1**, the standard would be one annual criteria based on median monthly nonanthropogenic concentrations. The Yellowstone River from the mouth of the Clarks Fork of the Yellowstone River to the mouth of the Bighorn River has a dilution ratio greater than 1%; therefore, potential anthropogenic discharge is considered significant and one annual standard is applied and is based on the median monthly nonanthropogenic concentrations. The Yellowstone River from Montana/Wyoming Border to the mouth of Mill Creek (segment 1), the mouth of Mill Creek to the mouth of the Boulder River (segment 2), and the mouth of the Stillwater River to the mouth of the Carks Fork of the Yellowstone River (segment 4) have a dilution ratio less than 1% and requires a seasonality determination for NAS selection. The seasonality determination is described in **Section 3.3**.

## 3.3 Seasonality Determination

Segments 1, 2, and 4 as shown in **Table 3-3** require a seasonality determination to select a NAS. Twenty years of daily flow data for the most applicable USGS gaging station is averaged and plotted on a hydrograph. The hydrograph for segment 1 is shown in **Figure 2-3**. The hydrographs for segments 3 and 4 are located in Appendix A.

The runoff period is bracketed by two points of greatest inflection and rounded to the nearest end-of-month. For all three segments, the high flow runoff period is May 1 to July 31 and the low flow period is August 1 to April 30.

The model-derived monthly nonanthropogenic arsenic concentrations from the high and low flow periods are tested for significant differences (95% confidence, or $\alpha$= .05) using the Mann-Whitney test. The median monthly concentrations were calculated from the modeled nonanthropogenic arsenic load (**Table 3-1**) using **Equation 1** and the methodology described in **Section 2.4**. An example of the model derived median nonanthropogenic loads, flow rates, and resulting concentrations for segment 1 are shown in **Table 3-4**. The low flow months are shown in red (August through April) and high flow months shown in blue (May through July). The corresponding model derived values for segments 3 and 4 are in **Appendix A**.

**Table 3-4. Segment 1: Model Derived Median Monthly Nonanthropogenic Arsenic Loads, Flow Rates, and Concentrations.**

| Month* | Median Nonanthropogenic Arsenic Load (kg/month) | Median Flow Rate (cfs) | Median Nonanthropogenic Arsenic Concentration (µg/L) |
|---|---|---|---|
| October | 3096 | 1360 | 31 |
| November | 2244 | 1460 | 21 |
| December | 2399 | 903 | 36 |
| January | 2177 | 878 | 33 |
| February | 2182 | 903 | 32 |
| March | 2580 | 1070 | 32 |
| April | 3466 | 2535 | 18 |
| May | 5633 | 7340 | 10 |
| June | 6044 | 9120 | 9 |
| July | 4635 | 3860 | 16 |
| August | 3695 | 2060 | 24 |
| September | 3077 | 1305 | 32 |

******High Flow Period in Blue and the Low Flow Period in Red.*

The results of the Mann-Whitney test showed a p-value (0.0002) less than the chosen alpha (.05) concluding that the median arsenic concentrations for the high and low flow seasons are significantly different. Therefore, for the Yellowstone River at Corwin Springs, the standard will be one annual criterion based on the low flow median monthly nonanthropogenic concentrations. Segments 3 and 4 also showed a statistically significant difference in low flow and high flow concentrations. The Mann Whitney test results are in **Appendix B**.

## 3.4 Criteria Selection

The modeled loads, flow rates, and resulting median monthly nonanthropogenic concentrations for segment 1 are presented in **Table 3-4**. The median monthly nonanthropogenic concentration results for the remaining Yellowstone River segments are shown in Appendix B. The monthly median anthropogenic arsenic concentration is calculated from the median anthropogenic arsenic load and the median flow rate using **Equation 1** (**Section 2.4**).

For segments 1, 2, and 4, the selected NAS is one annual standard based on the median value of the modeled low flow months. For segment 3, the annual standard is based on the median value of all monthly modeled data. The NAS are presented in **Table 3-5**.

**Table 3-5. Yellowstone River Segments and Selected NAS**

| Yellowstone River Hydrologic Segments | Basis For NAS | NAS (µg/L) |
|---|---|---|
| N1 - MT/WY Border to Mill Creek | Annual Standard Based on Low Flow Months | 32 |
| 2 - Mill Creek to Boulder River | Annual Standard Based on Low Flow Months | 24 |
| 3 - Boulder River to Stillwater River | Annual Standard Based on All Months | 16 |
| 4 - Stillwater River to Clarks Fork Yellowstone | Annual Standard Based on Low Flow Months | 14 |
| 5* - Clarks Fork Yellowstone to Bighorn River | Not Selected | Not Selected |

*Anthropogenic condition (9 µg/L) is lower than current MCL (10 µg/L)

The proposed arsenic criteria for the Yellowstone River segments 1, 2, 3, and 4 are shown in **Table 3-5.** The median nonanthropogenic condition for segment 5 (9 µg/L) is less than the current MCL of 10 µg/L (DEQ, 2012). For segment 5 (mouth of the Clarks Fork of the Yellowstone to the mouth of the Bighorn River), a NAS will not be adopted and the current MCL (10 µg/L) will remain the standard.

## 3.5 Frequency and Duration

A specified frequency and duration must accompany the proposed Arsenic NAS for the Yellowstone River Segments. Since the NAS is not derived from toxicity and the NAS represents the median condition of the water body, a "shall not" exceed is not necessary. Thus, the proposed frequency and duration for the Yellowstone River Arsenic NAS is "*average annual concentration not to exceed the NAS*." The average annual concentration is based on the arithmetic mean.

## 3.6 Highest Attainable Use

A critical step in developing a NAS is determining the highest attainable use of the water body under the nonanthropogenic condition. State and federal regulations (MCA 75-5-301 and 302, ARM 17.30.606 and 621 through 629, 40 CFR 131.10) and federal guidance on use designation are available from the Department and the Environmental Protection Agency. For the Yellowstone River, application of the arsenic nonanthropogenic standard requires a use change for transparency to the public. The Yellowstone River DON is a robust "use and value" demonstration (DEQ, 2018). The proposed use change for hydrologic segments 1, 2, 3, and 4 (**Table 3-5**) is from "*drinking water with conventional treatment*" to "*drinking water with natural arsenic.*"

# 4.0 Implementation

The NAS also includes procedures for implementation including provisions that ensure protection of downstream water quality standards.

Implementation includes the following:

- Assessment Method
- Nondegradation
- Effluent limit calculations
- Mixing zones
- Total maximum daily load calculations
- Remediation requirements
- Other activities as appropriate

These applications are described in more detail in the following sections.

## 4.1 Assessment Method

Water quality and beneficial use assessments determine if water quality continues to meet the level of nonanthropogenic water quality originally characterized by the NAS. Because the NAS is based on the 50th percentile, it would be expected that over the long term, half of the years assessed will exceed the NAS and half will be below it. To account for this natural variability in future assessments, the following assessment method has been developed.

### 4.1.1 Data Needs

The data should generally be collected at a single station in the reach where the NAS standard is adopted, preferably near the downstream end. All data within the reach collected in the same month will be reduced to a single monthly average (month=duration). If the dataset happens to comprise multiple sites within the reach, the different sites' data collected during the same month will be collated and reduced to a single value for that month. If only a single sample has been collected during a month, that sample will be considered representative of that month.

If the NAS standard was based only on the low-flow period, 9 data points collected during the low-flow period are required as a minimum. If the NAS standard was based on year-round data, then a minimum of 9 data points must be collected with high and low flow periods represented with no more than 70% representation from low flow months.

### 4.1.2. Wilson's Interval Tests

A statistical approach is used based on the confidence interval to determine whether an assessed dataset can be considered significantly different from the nonanthropogenic condition that was used to derive the standard. The approach is based on the Colorado Department of Public Health and Environment confidence intervals, calculated using the Wilson Interval, in water quality assessments (CDPHE, 2013). The confidence interval is most easily understood as the region around an estimate (the 50th percentile of the assessed data) within which the true value is likely to be located (CDPHE, 2013). The width of the confidence interval, and therefore the range of values it spans, is determined in part by the desired level of confidence. Each calendar year's data is separately evaluated using the lower confidence level (LCL) set at 90% confidence of the Wilson's Interval for the 50$^{th}$ percentile test (p-hat = 0.5, **Table 2, Appendix C**).

## 4.1.3 Exceedance Frequency

Each calendar year's data is separately evaluated using the lower confidence level (LCL) set at 90% confidence of the Wilson's Interval for the 50$^{th}$ percentile test (p-hat = 0.5, **Table 2, Appendix C**). Any LCL arsenic concentration determined from the test dataset found to be higher (greater than) the NAS is considered an exceedance of the standard. For example, if the NAS is 50 µg/L and the LCL value determined from the 2018 monitoring dataset is 55 µg/L, this is an exceedance.

The NAS will have a zero annual (no years) exceedance rate of the criterion using the Wilson's Interval tests. Monitoring should carry out (or compile, if existing data are found) two calendar years of sampling which meet the minimums described above.

Based on the outcomes from the two - yearly Wilson's Interval tests:

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

If the water body is determined non-compliant for arsenic, the water body will either be referred for a TMDL or for redevelopment of the NAS depending on the suspected cause of the exceedance, as outlined in **Figure 4-1**.

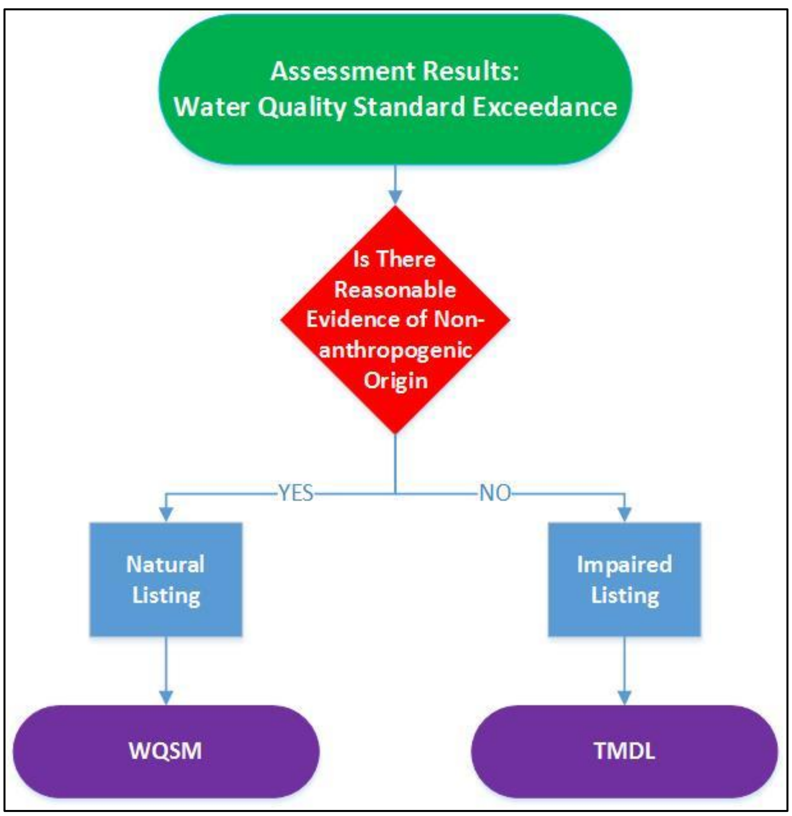


**Figure 4-1. Decision Chart for Arsenic NAS Assessment Exceedance Using Wilson's Interval Method.**

If there is no evidence that the NAS has been exceeded due to anthropogenic causes, it may be necessary to establish a new natural standard; for this reason, that scenario leads back to the WQSM in **Figure 4-1**.

## 4.2 PERMITTING

Permits exist to control pollution from point sources that may affect soil, water, or air (e.g., pollution from industrial applications, waste water treatment plants, etc.). Nonpoint sources are also sources of pollution but are not regulated in permits. Implementation of a NAS in MPDES permits is explained in the following sections.

A MPDES permit or a Montana Ground Water Pollution Control System permit is required from DEQ to construct, modify or operate a disposal system or to construct or use any outfall for discharge of sewage, industrial, or other wastes into state surface or ground water. Components of a permit include effluent characterization, reasonable potential analysis, nondegradation review (this is part of the effluent limit calculation for new or increased sources), and calculation of effluent limits. Another consideration in the permitting process is also necessary for developing effluent limits from NASs: protection of downstream water quality standards. These components are all discussed in the sections below.

### 4.2.1 Reasonable Potential Analysis

A crucial step in the surface water discharge permit process is effluent characterization. The objective of effluent characterization is to project receiving water values based upon existing effluent quality to determine if an excursion above ambient criterion occurs, or has the reasonable potential to occur. In determining reasonable potential, DEQ will consider controls on point and nonpoint sources, the variability of the pollutant parameter in the effluent, and any dilution of downstream waters. All estimates must assume discharge at critical conditions (currently the annual 7Q10 for arsenic). Therefore, a conservative assumption is used to determine if an impact is projected to occur (EPA, 1991).

With criteria based on nonanthropogenic conditions, if a proposed discharge containing the pollutant has the potential to elevate the concentration of the pollutant in the receiving water body, reasonable potential would generally exist and necessitate effluent limits.

### 4.2.2 Application of Nondegradation

DEQ uses a parameter by parameter approach for nondegradation analysis for determining high quality waters. Therefore, a specific receiving water body can be high quality for some parameters but not others. Because the arsenic NAS is set at the nonanthropogenic condition of the Yellowstone River, assimilative capacity does not exist. Therefore, although it is considered high quality from the perspective that it is not "impaired" by exceeding a standard, the Yellowstone river will ***not*** be considered a high quality water for the purposes of applying nondegradation rules for permitting activities (i.e., Tier 1 equivalent for CWA). A nonsignificance review for these waters is not applicable to new or increased sources of the pollutant, because existing water quality is already right at the criterion. Any concentration of the pollutant above the NAS will cause an exceedance of the NAS and could shift the long-term distribution above the NAS. For this reason, neither nonsignificance reviews nor authorizations to degrade are applicable. Essentially, a new or increased source must discharge at a concentration no higher than the NAS, at a load that is small enough that it would not impact downstream water quality standards.

### 4.2.3 Protection of Downstream Water Quality

Prior to DEQ issuing or renewing a MPDES permit implementing the NAS, the permit applicant must provide sufficient information demonstrating that the discharge will not negatively affect downstream water quality. Models used for this purpose could be simple mass balance calculations or more complicated models depending on the complexity of the situation. Information needed for the analyses includes the proposed concentration of the pollutant in the effluent and the volume of the proposed discharge, as well as whether the discharge will be continuous or intermittent and if the effluent characteristics would vary over time (e.g. seasonally).

If modeling demonstrates that an effluent limit based on the NAS has the potential to negatively impact downstream water quality, then the permitted effluent limit, and if necessary, load, will be determined based on the highest modeled effluent that will not negatively impact downstream water quality and existing uses.

### 4.2.4 Effluent Limit Calculations

In general, because the NAS will be calculated to reflect the nonanthropogenic condition of the water body *and to* protect highest attainable uses, the criteria can be implemented in permits directly as average (arithmetic mean) monthly effluent limits. These criteria are to be applied at the end of pipe only—mixing zones are not applicable with NASs. A maximum daily limit may then be calculated using methods suggested in the Technical Support Document for Water Quality-based Toxics Control or another method approved by DEQ and accepted by EPA.

# 5.0 References

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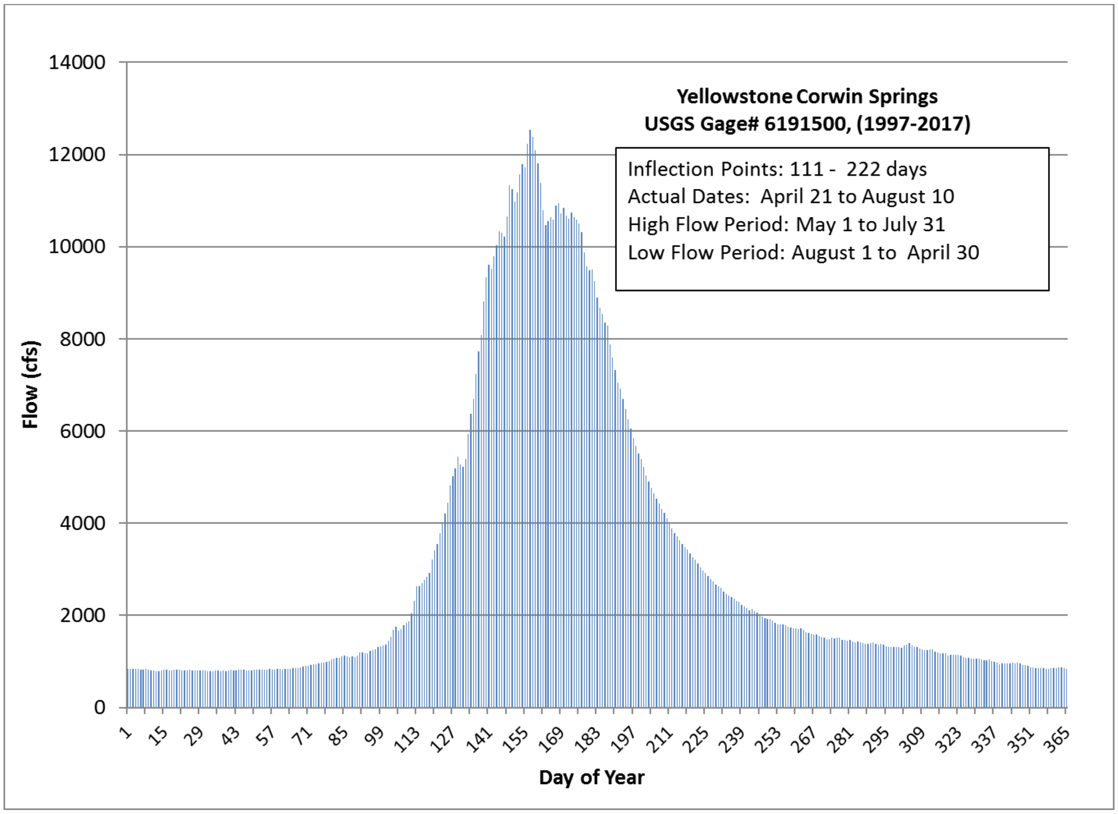
# APPENDICES

# APPENDIX A – SEASONALITY TEST RESULTS

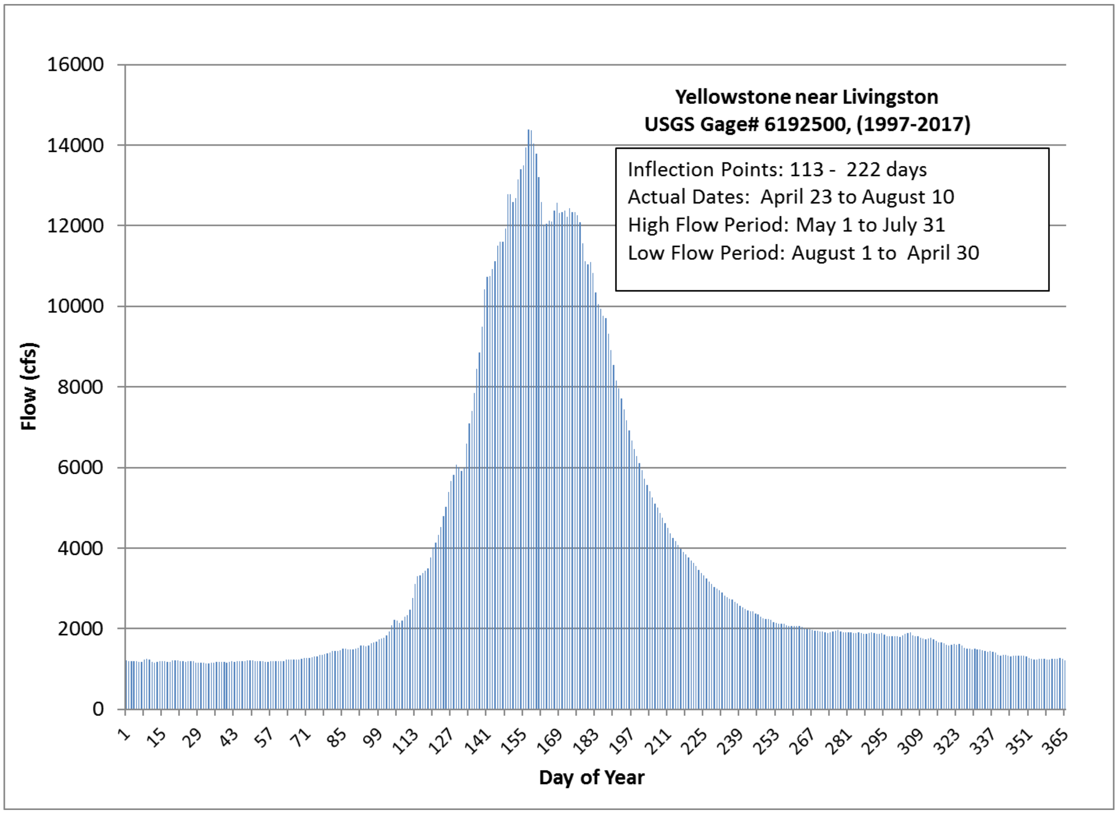



**Results for: Segment 1: MT/WY Border to Mill Creek**

**Mann-Whitney Test and CI: C1, C2**

| | N | Median |
|---|---|---|
| C1 | 9 | 10.000 |
| C2 | 16 | 29.500 |

Point estimate for η1 - η2 is -16.000
95.6 Percent CI for η1 - η2 is (-24.003,-10.003)
W = 50.5
Test of η1 = η2 vs η1 ≠ η2 is significant at 0.0002
The test is significant at 0.0002 (adjusted for ties)
alpha = .05
p-value = .0002
p<alpha; therefore, the data does support the hyposthesis that there is a difference between the population medians.
Signifcant
Seasonality

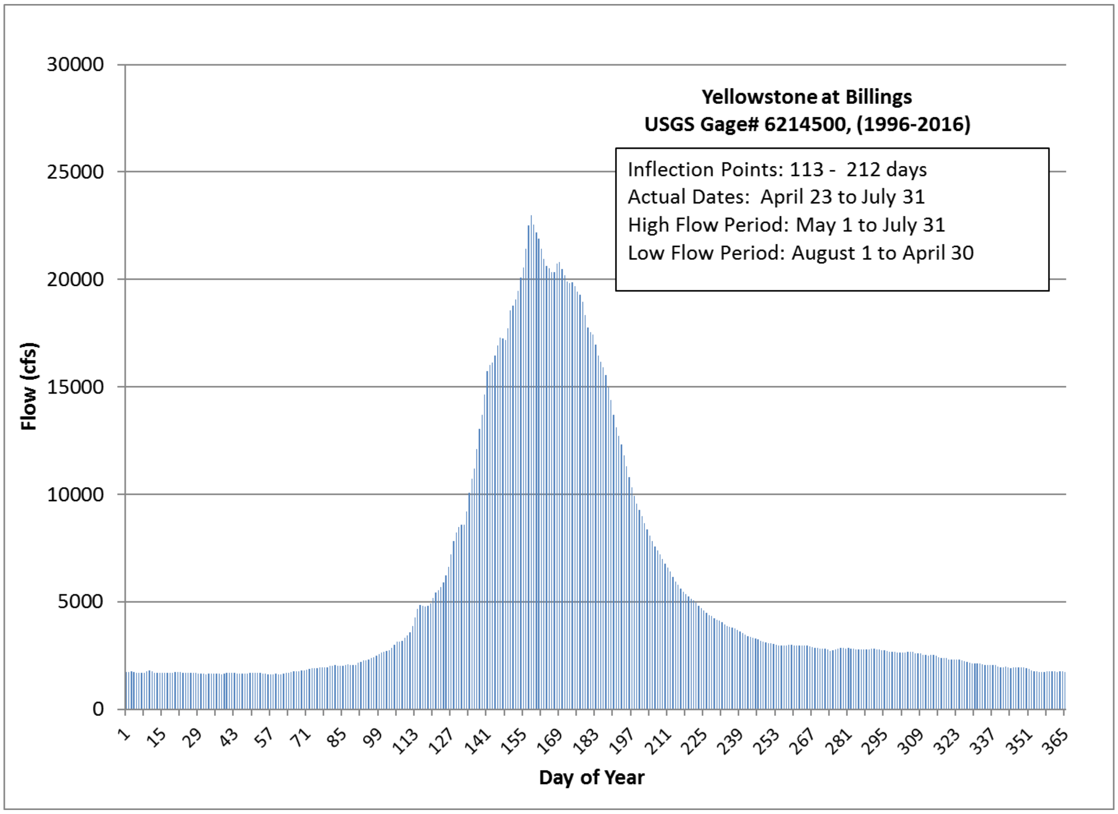



**Results for: Segment 2, Mill Creek to Boulder River**

**Mann-Whitney Test and CI: C1, C2**

| | N | Median |
|---|---|---|
| C1 | 15 | 13.000 |
| C2 | 22 | 22.500 |

Point estimate for η1 - η2 is -10.000
95.1 Percent CI for η1 - η2 is (-13.000,-7.000)
W = 136.0
Test of η1 = η2 vs η1 ≠ η2 is significant at 0.0000
The test is significant at 0.0000 (adjusted for ties)
alpha = .05
p-value = .0000
p<alpha; therefore, the data does support the hypothesis that there is a difference between the population medians.
Significant
Seasonality




**Results for: Segment 4, Stillwater River to Clarks Fork of the Yellowstone**

**Mann-Whitney Test and CI: C1, C2**

| | N | Median |
|---|---|---|
| C1 | 9 | 10.000 |
| C2 | 13 | 12.000 |

Point estimate for η1 - η2 is -3.000
95.5 Percent CI for η1 - η2 is (-4.000,-0.002)
W = 71.5
Test of η1 = η2 vs η1 ≠ η2 is significant at 0.0354
The test is significant at 0.0331 (adjusted for ties)
alpha = .05
p-value = 0.0331
p<alpha; therefore, the data does support the hypothesis that there is a difference between the population medians.
Significant
Seasonality

# Appendix B - Model Derived Median Monthly Nonanthropogenic Arsenic Loads, Flow Rates, and Concentrations

| ***Segment 1 - MT/WY Border to Mill Creek*** | | | |
|---|---|---|---|
| **Month** | **Median Nonanthropogenic Arsenic Load (kg/month)** | **Median Flow Rate (cfs)** | **Median Nonanthropogenic Concentration (µg/L)** |
| October | 3096 | 1360 | 31 |
| November | 2244 | 1460 | 21 |
| December | 2399 | 903 | 36 |
| January | 2177 | 878 | 33 |
| February | 2182 | 903 | 32 |
| March | 2580 | 1070 | 32 |
| April | 3466 | 2535 | 18 |
| May | 5633 | 7340 | 10 |
| June | 6044 | 9120 | 9 |
| July | 4635 | 3860 | 16 |
| August | 3695 | 2060 | 24 |
| September | 3077 | 1305 | 32 |
| **Annual Standard Applied Monthly Based on Low Flow Months** | | | **32** |

| ***Segment 2 - Mill Creek to Boulder River*** | | | |
|---|---|---|---|
| **Month** | **Median Nonanthropogenic Arsenic Load (kg/month)** | **Median Flow Rate (cfs)** | **Median Nonanthropogenic Concentration (µg/L)** |
| October | 3087 | 2180 | 19 |
| November | 2548 | 1890 | 18 |
| December | 2436 | 1380 | 24 |
| January | 2390 | 1200 | 27 |
| February | 2262 | 1210 | 25 |
| March | 2716 | 1390 | 26 |
| April | 3599 | 2655 | 18 |
| May | 6350 | 8620 | 10 |
| June | 6942 | 11850 | 8 |
| July | 4843 | 5060 | 13 |
| August | 3786 | 2630 | 19 |

| | | | |
|---|---|---|---|
| September | 3209 | 1800 | 24 |
| **Annual Standard Applied Monthly Based on Low Flow Months** | | | **24** |
| ***Segment 3 - Boulder River to Stillwater River*** | | | |
| **Month** | **Median Nonanthropogenic Arsenic Load (kg/month)** | **Median Flow Rate (cfs)** | **Median Nonanthropogenic Concentration (µg/L)** |
| October | 2718 | 2186 | 17 |
| November | 2476 | 2325 | 14 |
| December | 2142 | 1665 | 17 |
| January | 2164 | 1511 | 19 |
| February | 2123 | 1731 | 16 |
| March | 2737 | 1842 | 20 |
| April | 3557 | 3751 | 13 |
| May | 6936 | 10410 | 9 |
| June | 8411 | 15700 | 7 |
| July | 4422 | 5470 | 11 |
| August | 3425 | 2892 | 16 |
| September | 2733 | 2003.5 | 18 |
| **Annual Standard Applied Monthly Based on Low Flow Months** | | | **17** |
| ***Segment 4 - Stillwater River to Clark Fork Yellowstone River*** | | | |
| **Month** | **Median Nonanthropogenic Arsenic Load (kg/month)** | **Median Flow Rate (cfs)** | **Median Nonanthropogenic Concentration (µg/L)** |
| October | 2905 | 2791 | 14 |
| November | 2893 | 2824 | 14 |
| December | 2343 | 2098 | 15 |
| January | 2279 | 2033 | 15 |
| February | 2180 | 2131 | 14 |
| March | 2589 | 2196 | 16 |
| April | 3696 | 4224 | 12 |
| May | 8806 | 11750 | 10 |
| June | 11856 | 19810 | 8 |
| July | 4776 | 6833 | 9 |

| | | | |
|---|---|---|---|
| August | 3261 | 3492 | 13 |
| September | 2478 | 2496 | 13 |
| **Annual Standard Applied Monthly Based on Low Flow Months** | | | **14** |
| ***Segment 5 - Clark Forks of the Yellowstone River to Bighorn River*** | | | |
| **Month** | **Median Nonanthropogenic Arsenic Load (kg/month)** | **Median Flow Rate (cfs)** | **Median Nonanthropogenic Concentration (µg/L)** |
| October | 3024 | 4600 | 9 |
| November | 2496 | 4250 | 8 |
| December | 2225 | 3150 | 9 |
| January | 2298 | 2720 | 11 |
| February | 2279 | 2830 | 11 |
| March | 2876 | 3190 | 12 |
| April | 3797 | 5370 | 10 |
| May | 8910 | 15000 | 8 |
| June | 12752 | 24600 | 7 |
| July | 4763 | 7670 | 8 |
| August | 2593 | 3260 | 11 |
| September | 2248 | 3000 | 10 |
| **Annual Standard Applied Monthly** | | | **9** |

# APPENDIX C – WILSON'S INTERVAL METHOD

See electronic Appendix C for Table 2