DEPARTMENT CIRCULAR

DEQ-14

Nonanthropogenic Standards Development

April 2018 EDITION

GENERAL INTRODUCTION

The 2015 Montana Legislature passed Senate Bill 325, which is intended to provide a means to protect users of Montana's waters from having to clean up contaminants that those users did not create or introduce. The language from the bill was codified at §75-5-222, MCA, which contains two separate water quality standards provisions. The first provision states that the Department of Environmental Quality (Department) cannot apply a water quality standard that is more stringent than the nonanthropogenic condition of a water body. The second provision of the statute states that if contaminants upstream of a discharger are due to anthropogenic sources, a variance from standards may be appropriate under certain conditions. This document addresses the first provision of the statute (§75-5-222(1), MCA). Variances from water quality standards are addressed elsewhere in rule.

In addition to stating that the Department cannot apply water quality standards that are more stringent than the nonanthropogenic condition of a water body, MCA 75-5-222(1) also states that where a water quality standard is more stringent than the nonanthropogenic condition of the water body, the nonanthropogenic condition is the water quality standard. Determination of the nonanthropogenic condition and calculation of a nonanthropogenic water quality standard are complex subjects and are the focus of this document. The Department recommends that non-Department users consult with the Department prior to proceeding.

The first step in developing a nonanthropogenic water quality standard is to determine the nonanthropogenic condition of the water body or water bodies in question. There are several ways that this may be done, and different methods are appropriate in different situations and for different pollutants. Examples of defensible and valid methods of determining the nonanthropogenic condition of a waterbody include modeling, a reference stream approach, mass balance loading models, or other methods approved by the Department and the Board of Environmental Review. The appropriate nonanthropogenic demonstration method for a pollutant is dependent on several factors; these include the parameter's behavior in the environment, the nonanthropogenic source of the parameter and how widespread it is in the environment, and what kind of data are available for the pollutant in the affected water body or water bodies.

The second step in developing a nonanthropogenic water quality standard is selection of the standard itself. Because the means by which the nonanthropogenic condition is determined affects the methods used to derive the associated water quality standard, these are treated together in this document, by section.

The third step in the process is determining the highest attainable use of the water body under the nonanthropogenic condition. Application of a nonanthropogenic standard to a water body will almost always require a use change, and either a use attainability analysis or a use and value demonstration will accompany the use change. State and federal rules and federal guidance on use classes are available, therefore these subjects are not covered in this document.

DEFINITIONS

"Nonanthropogenic condition" means the background concentration of a parameter in surface water or groundwater due only to nonanthropogenic sources, i.e., non-human induced sources.

"Isolated primary source" means one main nonanthropogenic source contributing to an exceedance of a water quality standard.

ACRONYMS

AL	Anthropogenic Load
DEQ	Department of Environmental Quality
DNRC	Department of Natural Resources and Conservation
DON	Demonstration of Nonanthropogenic
EPA	Environmental Protection Agency
HUC	Hydrologic Unit Code
ML	Mass Load
NL	Nonanthropogenic Load
PSL	Point Source Load
ROA	Runoff Anthropogenic
TL	Total Load
USGS	United States Geological Survey

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1.0 Demonstration of Nonanthropogenic Arsenic Condition and Standard Selection for an Isolated Primary Source

This demonstration of nonanthropogenic condition and standard selection is based on an isolated primary source of arsenic. An isolated primary source means that there is one main nonanthropogenic source contributing to an exceedance of a water quality standard. An example of this is the geothermal water of the Yellowstone Park Caldera in Yellowstone National Park (YNP), which provides an isolated nonanthropogenic arsenic load to the Yellowstone and Madison Rivers and has been well documented by many researchers.

This method will incorporate a mass-balance approach to quantify the transport of arsenic in surface water. In mass-balance considerations, data on both hydrological conditions and the chemical quality of water are taken into account simultaneously. A mass load is the mass of arsenic transported at a point in a waterbody during a period of time. A nonanthropogenic arsenic standard (concentration) will be derived from the results of the mass balance approach.

This methodology of standard selection is a three-step process. The first step is the development of a demonstration of nonanthropogenic (DON) condition **(Section 1.1)**. If the resulting DON is determined to be scientifically valid by the Department, a nonanthropogenic standard is derived (**Section 1.2**). The third step is the determination and adoption of the highest attainable use **(Section 1.3)**.

1.1 Demonstration of Nonanthropogenic Arsenic Condition

This section details methods for completing a DON using a mass balance approach for arsenic that has an isolated primary source. The primary source must be quantifiable using a mass balance approach. Department guidance is available to provide specific examples of how certain parts of a DON may be carried out.

The methodology for DON development includes the following:

- Define the Hydrologic Region (i.e., the study frame)
- Data Requirements
- Mass Load Analysis
- Mass Balance Approach

This methodology is illustrated in **Figure 1-1**

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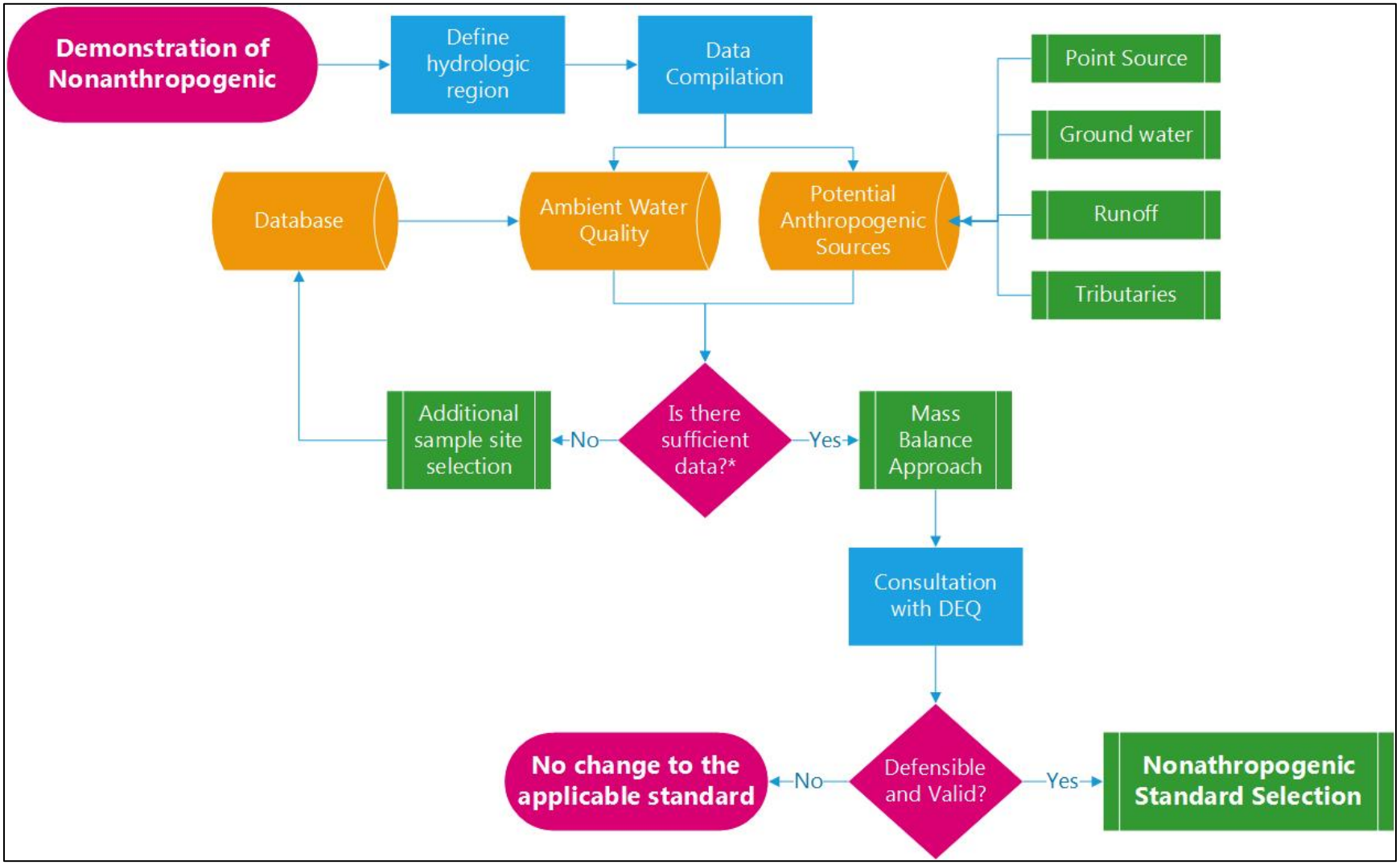

Figure 1-1. Demonstration of Nonanthropogenic Condition, Mass Balance Approach for an Isolated Primary Source

1.1.1 Defining the Hydrologic Region

The first step in completing a DON is defining the hydrologic region. The hydrologic region will include both the delineated segment of the water body where a nonanthropogenic arsenic standard (NAS) may apply, as well as all the tributaries of the water body. The hydrologic region should be defined using the United States Geological Survey (USGS) Hydrologic Unit Codes (HUCs) in which the largest division for a hydrologic region is a HUC8 (8 digit code), followed by a HUC10 and then a HUC12. These categories progressively divide the basin into smaller sub-basins.

In order to determine what size HUC to use, the area of interest needs to be identified. All waters above (including tributaries draining to) the area of interest must be included in the hydrologic region. Additionally, the hydrologic region must extend an appropriate distance downstream so that potential future impacts may be identified. Depending on where the NAS is proposed, it may be necessary to define an entire HUC8 as the hydrologic region, or alternatively, smaller geographic regions within the HUC8 may be more appropriate for defining the hydrologic boundaries of the DON.

Individual tributaries within the hydrologic region must be defined as major or minor. This will determine how much data must be collected. A major tributary is defined as a percent of the total volume of the main river. Major tributaries are determined based on their low flow volumes (defined as flows from August through April). The major tributaries have average low flow volumes greater than 5 percent of the median low flow volume of the study water body. Minors are all the remaining tributaries.

1.1.2 Data Needs

A DON requires certain data be collected for purposes of statistical validity. The necessary data for the DON includes both nonanthropogenic and anthropogenic arsenic loads which are calculated from concentrations and flow volumes. Due diligence must be used to assess and collect all available anthropogenic and nonanthropogenic data. Potential arsenic sources to the subject water body may include point sources, overland runoff, groundwater, and tributaries.

A thorough search of all available databases will likely produce enough information to determine whether there are anthropogenic influences in the watershed. After completing all database searches and compiling the anthropogenic and nonanthropogenic data into one dataset, a statistically rigorous analysis must be performed to determine whether sufficient data exist to complete a defensible and valid DON. If there is a question regarding anthropogenic influence, missing data in tributaries, or other concerns about data limitations, additional sampling is necessary.

Determining the appropriate data needs for the DON is a two-stage process. In this process, a minimum of 12 preliminary paired water quality and flow samples with seasonal and annual representation for a minimum of two years is compiled for the major tributaries and study water body. This initial data approximates the population's relative standard deviation and the necessary sample size using a 90% confidence level and 15% relative error. Then, if the required sample size is less than what has already

been collected, data collection is complete. If the required sample size is larger than what has already been collected, more data will be needed.

The formula for calculating sample size is:

EQUATION 1: $n = (Z_{1-\alpha/2} * \eta / d_r)^2$

Where n is the required number of samples, Z is the standard normal deviate for the confidence level desired (90%), α is the desired significance level (10%), η is the coefficient of variation or relative standard deviation of the initial dataset, and d_r is the pre-specified relative error from the mean (15%).

Equation 1 may yield in some cases very large sample sizes (n). However, the Department will not require more than 36 pair water quality and flow samples with a minimum of two years of annual and seasonal fluctuations regardless of the calculated (Equation 1) number of samples.

1.1.3 Mass Load Analysis

A mass load analysis quantifies all anthropogenic and nonanthropogenic sources of a contaminant in a water body using concentration of the contaminant and flow of the surface water. Mass load is a calculation of the total mass of a substance (e.g. pounds) that is carried past a particular point on a water body for a given time period, and assists in determining the magnitude of impact on the downstream water body. The result from the mass load analysis is the total arsenic load for the subject water body and is the total load (TL) variable in the mass balance equation (**Section 1.1.4**).

1.1.4 Mass Balance

The mass balance quantifies the transport of arsenic in surface water by determining loads contributed by various sources. In mass balance considerations, data on both hydrological conditions and the chemical quality of water are taken into account simultaneously. A mass load is the mass of arsenic transported at a point in a waterbody during a period of time and is defined by the following equation. All components of the equations below must be included in the DON.

EQUATION 2: **TL = IPL + PSL + GW + Trib + RO**

Where,

TL – Total Load

IPL – Isolated primary load, resulting from nonanthropogenic activity

PSL – Point source load, permitted discharge operations

GW – Groundwater load contribution

Trib – arsenic load associated with surface water discharge into the mainstems from the major tributaries

RO – Non-point source runoff arsenic load

The individual terms in ***Equation 2*** describe a mass load. Each mass load is defined by the mass load equation (***Equation 3***).

EQUATION 3: **ML = C x Q x t x cf**

Where,

ML – Mass Load (pounds or kilograms, per unit of time)

C – Concentration (µg/L or mg/L)

Q – Flowrate at a point (cubic feet per second, cfs)

t – A period of time (season, month, or year)

cf – conversion factor for mass load calculation (variable depending on units of individual terms)

The isolated primary load (IPL) must be a quantifiable load within the subject water body. For example, the arsenic load in both the Madison and Yellowstone Rivers at the Yellowstone National Park boundary with Montana is an IPL resulting from the geothermal activity of the Yellowstone Caldera.

TL is the total load of arsenic in the stream which includes both "nonanthropogenic" and "anthropogenic" sources. Therefore, TL is rewritten to express this relationship.

EQUATION 4: **TL = NL + AL**

Where,

NL = Nonanthropogenic Load

AL = Anthropogenic Load

It is important to understand the relative contribution of a nonanthropogenic load versus that known to occur from anthropogenic sources. To distinguish between nonanthropogenic and anthropogenic sources, the mass balance equation (***Equation 2***) is written as:

EQUATION 5: **TL = IPL + PSL + GWA + GWN + TribA + TribN + ROA + RON**

Where,

GWA – Groundwater mass load contributions considered anthropogenic

GWN – Groundwater mass load contributions considered nonanthropogenic

TribA – Tributary mass load contributions considered anthropogenic

TribN – Tributary mass load contributions considered nonanthropogenic

ROA – Surface water runoff with anthropogenic derived arsenic loading

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RON – Surface water runoff with nonanthropogenic derived arsenic loading

Equations 2, 4, and 5 are rearranged to solve for the nonanthropogenic load (**NL**) and expressed as:

EQUATION 6: **NL = TL - PSL - GWA - TribA – ROA**

1.1.5 Documentation of Findings

Once the nonanthropogenic load is determined, it must be expressed as monthly and annual median contaminant loads in a report containing the data and process followed for the DON. These nonanthropogeinc loads will then be used in the NAS selection process detailed in **Section 1.2**.

1.2 Nonanthropogenic Arsenic Standard Selection

This subsection details the methodology for arsenic specific nonanthropogenic standard (NAS) selection. NAS selection is a process used to identify appropriate water quality standards in situations where a waterbody's levels of a contaminant are elevated due to nonanthropogenic sources.

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 concentrations. Choosing an appropriate standard within the distribution can help ensure that the important part of the distribution necessary to maintain existing uses and conditions is protected.

The first step in NAS Selection is the DON and was detailed in **Section 1.1.**

After the demonstration of nonanthropogenic condition is made, the standard selection process begins. Arsenic concentrations in Montana rivers are higher during low flow conditions than during high flow conditions. Additionally, there are many different size streams in Montana that may have nonanthropogenically high arsenic concentrations. Many large rivers and streams have high enough flows that it would be unlikely for dischargers to change the arsenic concentrations in those rivers and streams. This method accounts for those factors through determination of existing or potential dischargers, a dilution test, and a seasonality determination prior to selecting the appropriate standard. These steps are summarized in **Figure 1-3** and are discussed in the following sub-sections.

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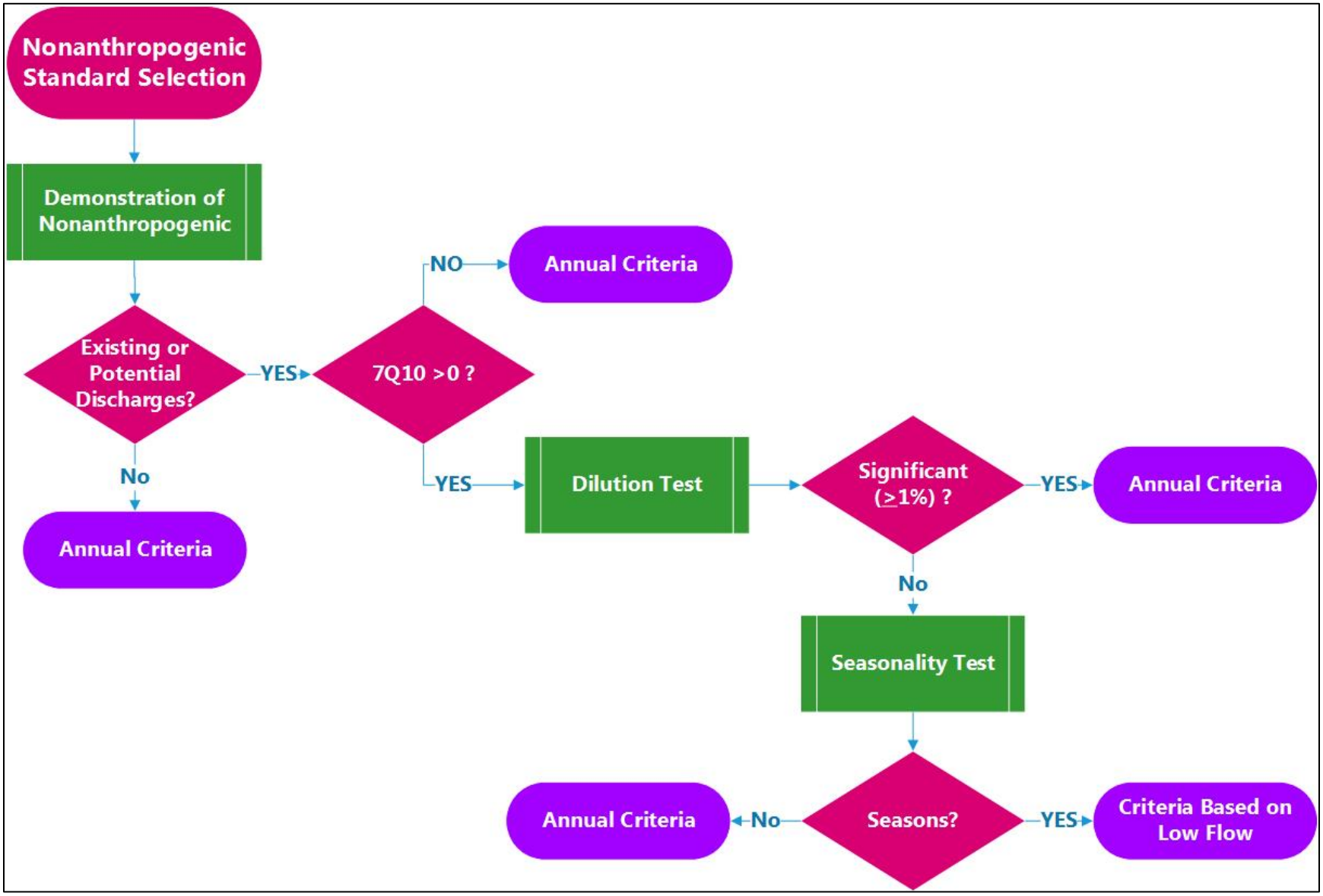

Figure 1-3. Nonanthropogenic Standard Selection (NAS) Flow Chart

1.2.1 Potential or Existing Discharges

As shown in **Figure 1-3**, after the DON is completed the presence of existing or future planned discharges must be determined. Permitted discharges include facilities actively discharging into the project waterbodies. The arsenic concentration data is extracted from the Environmental Protection Agency's (EPA) Integrated Compliance Information System database. Additional research must be performed to determine if there are any other discharges from other point sources. Other potential sources may include active or inactive mining operations, remediation sites, leaky underground storage sites, or hazardous waste sites.

Current or future discharges have the potential to shift the nonanthropogenic arsenic distribution of the water body. The maximum discharge load for the facilities' history is used in this analysis in order to estimate a discharger's greatest potential to shift the natural condition of the water body. If there is more than one discharger for the receiving water body, then the maximum discharge flow rates must be added together prior to performing the dilution test.

1.2.2 Dilution Test

The dilution test estimates if current or future discharges have the potential to shift the nonanthropogenic arsenic distribution of the water body. The nonanthropogenic distribution of arsenic concentrations in a large river is much better buffered against potential changes caused by permitted arsenic discharges than is the arsenic distribution of a smaller stream with lower flows. In order to assess this volume-based sensitivity, a dilution test is carried out by comparing a water body's 7Q10 flow to existing and potential discharge volumes. 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). Four dilution test scenarios are summarized in **Table 1-1**.

Table 1-1. Dilution Test for NAS Selection

Case	7Q10 (cfs)	Dilution Test % (Equation 7)	Standard Selection or Action
1	0	N/A	Select Annual Standard based on all median monthly concentrations
2	> 0	0	Select Annual Standard based on all median monthly concentrations
3	> 0	$\geq$ 1%	Select Annual Standard based on all median monthly concentrations
4	> 0	< 1%	Perform Seasonality Determination

For case 1, when the 7Q10 value of a stream is zero cfs, current or future discharges to that stream are considered significant and a more conservative annual standard based on all median monthly nonanthropogenic concentrations will be applied (**Figure 1-3**). If there are no discharges in a reach (case 2), then the more conservative standard, similar to case 1, will be applied. Additionally, if a 7Q10 cannot be determined for a stream, the more conservative annual standard based on all median monthly

concentrations will be selected. For case 2, any future discharges in the reach will be held to this more conservative criterion, and any discharges may be further limited because they will have to provide for attainment and maintenance of downstream water quality standards.

If the 7Q10 is greater than 0 and there are existing and/or future discharges (case 3), then a ratio of the cumulative point sources' discharge volumes (existing and any planned discharges) to 7Q10 flow is calculated as shown in the following equation.

Equation 7: **Dilution Test % = Max Discharge/7Q10**

Where,

Max Discharge = Maximum Discharge Volume (cfs) of Point Source Discharger

7Q10 = Water body's 7Q10 design flow volume (cfs)

If the ratio is greater than or equal to 1%, the collective discharge is considered significant and an annual standard based on all the median monthly nonanthropogenic concentrations must be derived. If the ratio is less than 1% (case 4), 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 1.2.3**.

1.2.3 Seasonality Determination

If the dilution test demonstrates that a seasonality determination is appropriate (**Table 1-1,** case 4), the modeled nonanthropogenic arsenic concentration for the water body is analyzed for variability under high flow versus low flow conditions. Arsenic concentrations in Montana are higher during low flow conditions compared to higher flow conditions. Therefore, setting a criterion based on the median year-round arsenic concentration is more conservative than setting a criterion based on the median low-flow arsenic concentration. This determines if the annual standard will be based on the median concentrations of all months or just the low flow months. Overall, this approach protects water bodies when 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 flow volume and therefore higher dilution.

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. In order 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 low flow 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.

If the water body does not meet the minimum five years of daily flow data, then the seasonality test cannot be performed. In this case the more conservative annual standard based on the median year-round arsenic concentration will be selected for that water body.

After determining the high flow and low flow months, the model-derived monthly arsenic concentrations from these two time periods are tested for a significant difference (i.e. 95% confidence, α= .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 α (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 α (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 α does not support the hypothesis that there is a difference between the population medians. An α equal to 0.05 must be used for the seasonality determination.

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 all the median monthly arsenic concentrations will be applied.

The median monthly concentrations are calculated from the modeled nonanthropogenic arsenic load and the median flow rate. The modeled nonanthropogenic load is calculated as part of the DON (**Section 1.1.4**). This nonanthropogenic load is converted to a concentration using the following equation:

EQUATION 8: $C = ML/(Q \times T \times cf)$

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)

There are scenarios where the ambient concentration data set can be used for the seasonality determination as long as the nonanthropogenic load is at least 95% of the ambient condition. For

example, if there are only 2 modeled high flow months and 10 modeled low flow months as determined from the daily mean flow duration hydrograph, using the monthly modeled nonanthropogenic concentrations would only provide an n=2 for the high flow months. This is not enough data to complete a valid statistical test. Under these circumstances, a larger dataset is necessary to determine seasonality and the ambient concentration data set can be used for seasonality determination. For this scenario, the ambient concentration data would be divided into two data sets, representing the high flow (2 months) and the low flow (10 months) periods. For instance, a water body may have a dataset consisting of 30 data points with an n=8 for the high flow period and an n=22 for the low flow period, which is enough data to complete a valid statistical test.

1.2.4 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. If the nonanthropogenic condition is determined via a loading analysis, the standard will be calculated based on the long-term median flow for the designated time period. This approach establishes the water quality standard at a locally protective value (i.e., largely representative of the nonanthropogenic condition) even if relatively large discharges were ultimately allowed that could move in-stream water quality concentrations nearer to the established standard. In other words, distributions of concentration data, if there are many dischargers and little dilution, will always change; in these cases, the central tendency will move towards the water quality criterion concentration (which would be equal to the 50th percentile), and the 50th percentile is about the best representation of the central tendency of the nonanthropogenic distribution of the data points.

The first step in selecting the NAS is to calculate the nonanthropogenic condition as outlined in **Figure 1-1** and defined in **Section 1.1**. The DON process 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 as defined by **Equation 8** in **Section 1.2.3**.

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. If applicable to the stream body, the median monthly flow volumes can be calculated from USGS gage data. However, if there is no USGS gage or other type of gage, the median flow rate is based on the flow rates collected as part of sampling efforts. Statistically valid paired (flow and concentration) data sets are used in the DON. Thus, the median will be calculated from this statistically valid dataset even when there is no applicable gaging station.

If the nonanthropogenic load is at least 95% of the ambient load as calculated during the DON process (**Section 1.1**), the ambient concentrations for the water body can be used in the NAS selection. The 5% discrepancy between the ambient and nonanthropogenic loads allows for inherent error that is associated with mass balance calculations and the resulting nonanthropogenic loads. Therefore, the

median monthly ambient concentrations would be substituted for the median monthly modeled nonanthropogenic concentrations during the NAS process.

1.2.4.1 Frequency and Duration

Water quality standards have three components: magnitude, duration, and frequency. Magnitude is the concentration of the pollutant and is represented by a number (for example, 10 µg/L), as described above in **Section 1.2.4**. Duration is the defined period of time over which sample concentrations are to be averaged, and frequency is the number of times the pollutant can be over the standard concentration without exceeding the water quality standard. An "exceedance" occurs when samples averaged over the defined duration result in concentrations higher than the magnitude of the standard more often than the allowed frequency. The duration associated with arsenic standards derived via methods in this Circular is one month, and the standards can be exceeded no more than once every three years, on average, assessed using the Wilson's Interval with a 90% confidence level.

1.2.4.2 Documentation of Findings

Once the NAS is calculated, a report must be compiled containing the data and process followed in generating the NAS.

1.3 Highest Attainable Use

The next step is to determine whether the drinking water designated use is appropriate, or if it should be changed. Using information that is available from the demonstration of nonanthropogenic conditions, the Department will provide a use and value demonstration and propose use changes where the current arsenic criteria are more stringent than the nonanthropogenic arsenic levels. The best attainable use under the nonanthropogenic arsenic condition will be proposed. Use changes must be adopted by the Board of Environmental Review (the Board) and approved by EPA.

1.4 Submittal and Review

The DON and the NAS must be submitted to the Department for review and approval. The Department will review the documents for completeness and statistical validity. If the Department finds that the DON and the NAS are complete and statistically valid, the NAS may then go through the public review process. If the DON and the NAS are not complete or statistically valid, the Department may require more information to be submitted.

2.0 Placeholder Section for Additional Approach

Selected References

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