Demonstration of Nonanthropogenic Arsenic: Yellowstone River, Montana

August 2018

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WQSMTECH-01

EXECUTIVE SUMMARY

This document presents the methods and results for the demonstration of nonanthropogenic (DON) arsenic for the Yellowstone River Basin. The Yellowstone River includes the Yellowstone River watershed from the Wyoming Border south of Gardiner to the mouth of the Bighorn River near Bighorn, Montana and all associated tributaries and drainages. The river is divided into five hydrologic segments for the purposes of this DON. Hydrologic modeling and mass balance techniques are used to calculate the nonanthropogenic condition of the Yellowstone River. The Water Quality Standards and Modeling Section (WQSM) of the Montana Department of Environmental Quality's (DEQ) Water Quality Planning Bureau (WQPB) completed this demonstration.

The geothermal water of the Yellowstone Park Caldera provides the largest source of arsenic loading to the Yellowstone River and arsenic concentrations are consistently above the human health standard (10 µg/L) for much of the river. Per recent legislation, DEQ may not apply a water quality standard to a water body that has a nonanthropogenic concentration greater than the standard. Thus, the nonanthropogenic condition is calculated for arsenic standard development.

The anthropogenic arsenic load at the Montana/Wyoming border is assumed to be zero due to the Yellowstone River watershed being almost entirely contained within Yellowstone National Park upstream of the border. The arsenic mass balance shows that the nonanthropogenic load of the Yellowstone River at the confluence of the Bighorn River is 94.3% nonanthropogenic. The remaining 5.7% is either anthropogenic arsenic (2.5%) or unaccounted-for mass load/error. The 2.5% anthropogenic load at Billings is the cumulative anthropogenic arsenic load from the Montana/Wyoming border to the confluence with the Bighorn River and has resulted from industrial, agricultural, and mining discharge directly to the river, gaining segments of groundwater recharge, or runoff.

Table of Contents

LIST OF TABLES

LIST OF FIGURES

ACRONYMS

AAL	Anthropogenic Arsenic Load
BLM	Bureau of Land Management
CV	Coefficient of Variation
CCA	Chromated copper arsenate
CECRA	Comprehensive Environmental Cleanup and Responsibility Act
DEQ	Department of Environmental Quality
DON	Demonstration of Nonanthropogenic
EPA	Environmental Protection Agency
GIS	Geographical Information System
GW	Groundwater
GWIC	Groundwater Information Center
HAWQS	Hydrologic and Water Quality System
HUC	Hydrologic Unit Code
ICIS	Integrated Compliance Information System
kg/day	kilograms per day
LOADEST	Load Estimator Model
LUST	Leaking Underground Storage Tank
MBMG	Montana Bureau of Mines and Geology
MCA	Montana Code Annotated
mg/kg	milligrams per kilogram
ML	Mass Load
MLE	Maximum Likelihood Estimation
MPDES	Montana Pollutant Discharge Elimination System
MUSLE	Modified Universal Soil Loss Equation
NAL	Nonanthropogenic Arsenic Load
NAS	Nonanthropogenic Standard
NGS	National Geochemical Survey
NLCD	National Land Cover Database
NSE	Nash-Sutcliffe Coefficient of Efficiency
PSL	Point Source Load
QAPP	Quality Assurance Project Plan
R^2	Coefficient of Determination
RO	Total Runoff
ROA	Runoff - Anthropogenic
RRS	Remediation Response Sites
SAP	Sampling and Analysis Plan
SWAT	Soil and Water Assessment Tool
TAL	Total Arsenic Load
TMDL	Total Maximum Daily Load
Trib	Tributary
µg/L	micrograms per liter
USFS	United States Forest Service

USGS	United States Geological Survey
USLE	Universal Soil Loss Equation
WQPB	Water Quality Planning Bureau
WQSM	Water Quality Standards and Modeling Section
WDEQ	Wyoming Department of Environmental Quality
YNP	Yellowstone National Park

1.0 INTRODUCTION

This document presents the methods and results for the demonstration of nonanthropogenic (DON) arsenic for the Yellowstone River Basin. The Yellowstone River includes the Yellowstone River watershed from the Wyoming Border south of Gardiner to the mouth of the Bighorn River near Bighorn, Montana and all associated tributaries and drainages. For this demonstration, the terms natural and nonanthropogenic are synonymous and mean the background concentration of arsenic due only to non-human induced sources. The Water Quality Standards and Modeling Section (WQSM) of the Montana Department of Environmental Quality's (DEQ) Water Quality Planning Bureau (WQPB) has completed this demonstration.

Many figures within this document are not appropriate for grayscale and best viewed when printed in color.

1.1 PURPOSE

The purpose of this DON is for nonanthropogenic arsenic standard development for the Yellowstone River. A scientifically defensible DON is a first step in the process of developing standards based on a nonanthropogenic condition. The second step in the nonanthropogenic process is the nonanthropogenic standard (NAS) selection and is detailed in a separate document (DEQ, 2018a)

1.2 SUPPORTING DOCUMENTS

Investigations completed by the United States Geological Survey (USGS) and other researchers conclude that the likely sources of the elevated arsenic concentrations in the Yellowstone River are from nonanthropogenic sources. The geothermal water of the Yellowstone Caldera in Yellowstone National Park (YNP) provides the largest source of arsenic loads to the Yellowstone River and has been well documented by the following list of researchers. The complete citations are located in the reference section of this document.

- John D. Hem, 1985.
- K.A. Miller, M.L. Clark, and P.R. Wright, 2004
- Jack J. Rowe, Robert O. Fournier, and G. W. Morey, 1973.

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

1.3 BACKGROUND

In YNP, there are over 10,000 thermal features including more than 300 geysers (YNP, 2015). 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). Geothermal waters in the park drain into the Yellowstone River Basin from the West Thumb Geyser Basin, thermal features 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 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. The Yellowstone River 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 a nonanthropogenic concentration greater than the standard (75-5-222, MCA). Furthermore, Montana law has stated since 1967 that discharges are not required to discharge purer than natural (75-5-306, MCA). In this case, the standard would be set at the nonanthropogenic condition of the water body. 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, 2017b, 2012). The arsenic concentrations in the Yellowstone River, below Livingston to the mouth of the Clarks Fork of Yellowstone River, are consistently above the human health criterion during low flow conditions (DEQ, 2017b, 2012).

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

2.0 METHODS

The steps associated with the Yellowstone River DON for arsenic are listed below:

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

The specific methods for the DON steps are summarized in the following sections. The results of these steps are presented in **Section 4.0**.

2.1 HYDROLOGIC REGION

The first step is to define the hydrologic region of interest. 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 2-1.**

The United States Geological Survey (USGS) Hydrologic Unit Codes (HUCs) is a convenient way to classify watersheds. Using this system, the largest division for the Yellowstone River 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. The Yellowstone River hydrologic region is defined by eight HUC8 codes as listed in **Table 2-1**. These HUC8s were selected because they drain into the Yellowstone River. The region is defined from the Wyoming Border to the mouth of the Bighorn River. Smaller geographic regions within this HUC8 were recognized for modeling purposes. For example, there were 65 HUC10s within the hydrologic region (**Figure 2-1**).

Table 2-1. Project Sub-basins and Associated HUC's

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
10070008	Pryor	Headwaters of Pryor Creek to confluence with Yellowstone River

Individual tributaries within the hydrologic region were defined as major or minor. A major tributary was defined as contributing greater than 5 percent of the 7Q10 flow of the Yellowstone River. The 7Q10 is the lowest 7-day average flow that occurs (on average) once every 10 years.

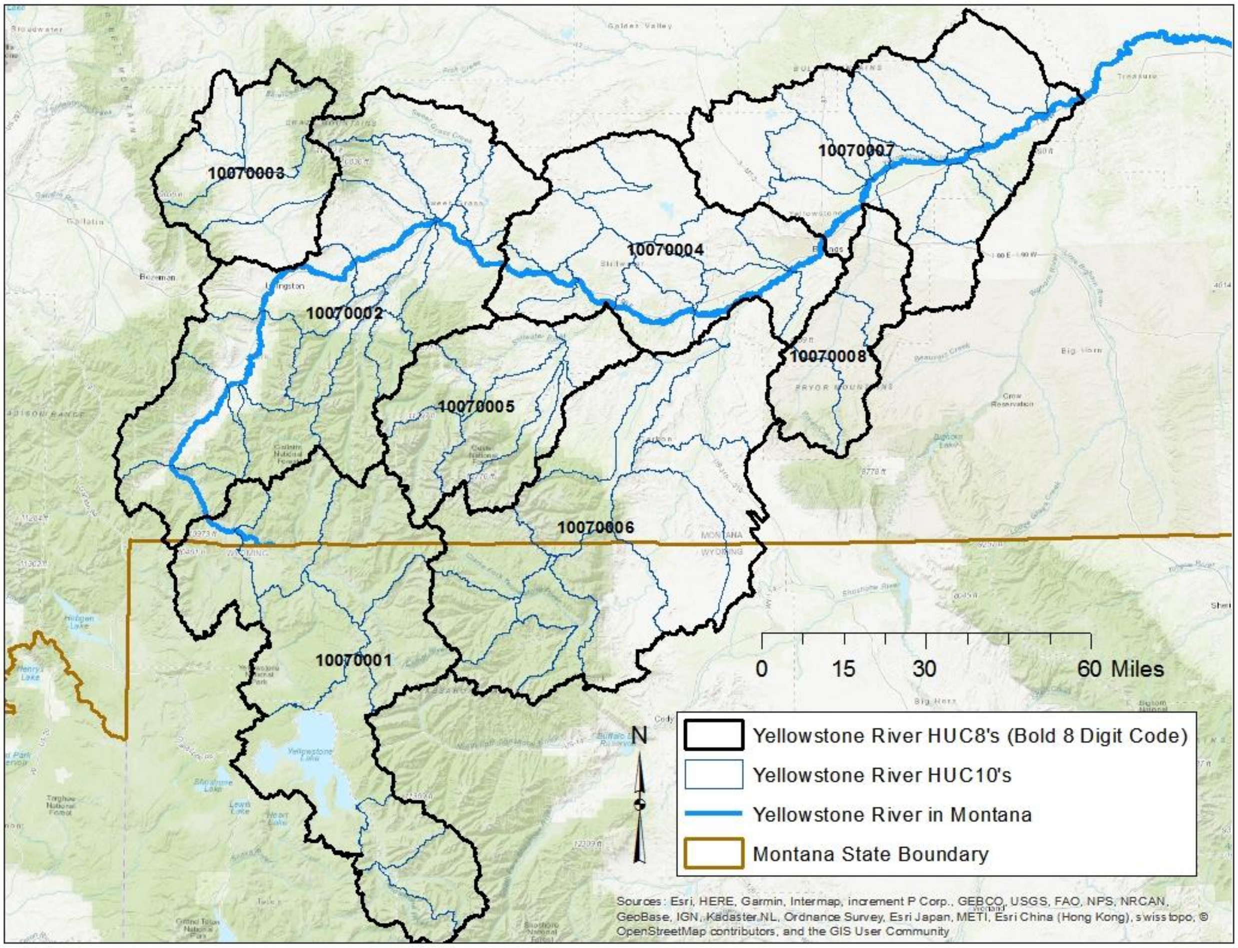


Figure 2-1. Location of Project Sub-basins

2.2 DATA COMPILATION

The necessary data for the DON included both nonanthropogenic and anthropogenic arsenic loads calculated from concentrations and flow volumes.

Existing data for the Yellowstone Basin were compiled using the methodology described in the project QAPP (DEQ, 2015a). The results of this task were used to develop additional sampling efforts as described in the project SAPs (DEQ, 2015b, 2016a, 2017a). The sampling objectives, sampling design, and data quality objectives are described in the project QAPP (DEQ, 2015a). Total recoverable arsenic concentrations, dissolved arsenic concentrations, total suspended solids, and flow volume for the mainstem of the Yellowstone River along with tributary data were compiled. Historical data locations and additional sampling locations are shown on **Figure 2-2**. The arsenic concentrations and flow data for the Yellowstone River and associated tributaries are maintained at DEQ and are available upon request (DEQ, 2017b).

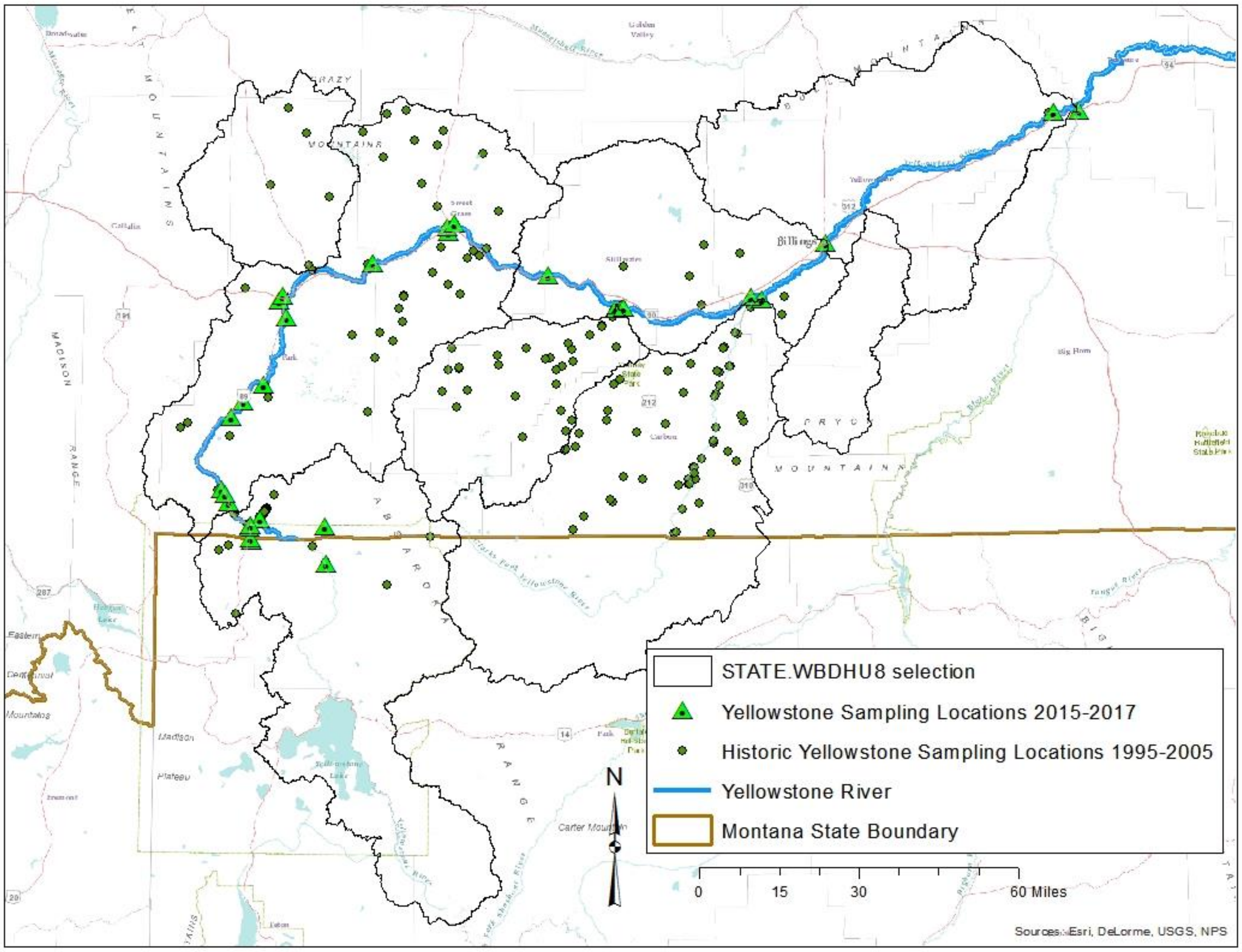


Figure 2-2. Map Showing Historic and Additional Sampling Locations

Due diligence was used to assess and collect data to determine the sources of arsenic to the Yellowstone River. The following is a list of potential sources of both anthropogenic and nonanthropogenic arsenic and will be discussed in more detail in the following sections:

- Point Sources
- Overland Runoff
- Groundwater
- Tributaries

A publication that summarizes the different anthropogenic sources of arsenic in Montana is found at: http://toxsci.oxfordjournals.org/content/123/2/305.long.

2.2.1 Point Sources

2.2.1.1 Permitted Point Sources

Permitted dischargers included major facilities legally and actively discharging into the project waterbodies. The arsenic concentration data was extracted from the EPA's Integrated Compliance

Information System (ICIS) database. Only Montana facilities with effective or administratively extended permits in the project sub-basins were analyzed and discussed in **Section 4.0**.

Permitted discharges in Wyoming were accessed through the Environmental Protection Agency (EPA) Enviro Mapper program (https://www.epa.gov/emefdata/em4ef.home) and the Wyoming Department of Environmental Quality (WDEQ) permitting website (http://deq.wyoming.gov/wqd/permitting-2/). Within the watershed there are 23 WDEQ permits, 21 of these are oil and gas production and construction storm water general permits that are not potential sources of arsenic. There are two individual permits, one is a fish hatchery located 22 miles northwest of Powell, Wyoming and the other is a wastewater treatment facility at Canyon Village in Yellowstone National Park. Neither permit has permit limits for arsenic nor are they required to monitor for arsenic. These discharges are not considered potential sources of arsenic to the Yellowstone River Basin.

Additional research was performed to determine if there were any other point source discharges. Other potential sources included active or inactive mining operations, remediation sites, leaking underground storage tank sites, or hazardous waste sites. These sites are described in the following sections.

2.2.1.2 Active Mines

There is one active permitted mine in the project boundaries, the TVX Mineral Hill Mine Inc (MPDES permit MT0030252). Based on the Montana Pollutant Discharge Elimination System (MPDES) permit data this facility does contribute arsenic to Bear Creek, a tributary to the Yellowstone River. The arsenic loading from this facility is summarized in **Section 4.2.1**.

Permitted mines in the Wyoming portion of the watershed were accessed through the EPA Enviro Mapper program (https://www.epa.gov/emefdata/em4ef.home). The program identified three sand and gravel mines, and one granite mine. All mines are under 10 acres in size and based on the type of mining operations they are not potential sources of arsenic.

2.2.1.3 Abandoned Mines

The Montana DEQ Abandoned Mines program maintains information on abandoned mines in a Geographical Information System (GIS) database. The database identifies the location of known inactive mining projects, soil and water quality data is limited to only a small percentage of the sites. Typically, only the high priority abandoned mines have associated soil or water quality data. The sampling results for high priority abandoned mines were accessed on the DEQ website at http://deq.mt.gov/Land/AbandonedMines/priority. Internal DEQ and public GIS information was also searched at: http://svc.mt.gov/deq/wmadst and https://deqgis.mt.gov/arcgis/rest/services.

Additional information regarding water quality from abandoned mines was available from the Montana Bureau of Mines and Geology (MBMG) Groundwater Information Center (GWIC) database at http://mbmggwic.mtech.edu. The GWIC database contained primarily water well information but also included springs, mines and other miscellaneous sources. The database was searched under the site type category with the phrases “mine”, “mine drainage”, “adit”, or “tailings pond” to find any data potentially related to mining activities.

Abandoned mine inventory or site information for the Wyoming portion of the watershed was not available through WDEQ.

The results of the DEQ GIS inventory, internal records, and GWIC searches are summarized in Section 4.2.2.

2.2.1.4 Remediation Response Sites

A DEQ GIS inventory of contaminant releases for remediation response sites throughout Montana includes the location, site name, DEQ contact name if available, and the period of operation. Specific information including water quality for some of these sites is available via the listed DEQ contact or the DEQ website at one of the following links:

- http://deq.mt.gov/Land/FedSuperfund
- http://deq.mt.gov/Land/statesuperfund
- http://deq.mt.gov/Land/brownfields

Internal DEQ and public GIS information is available at: https://svc.mt.gov/deq/wmadst and https://deqgis.mt.gov/arcgis/rest/services, respectively. Two sites were identified that could potentially contribute arsenic to the Yellowstone river via groundwater: Mouat Industries in Columbus and Yale Oil of South Dakota – Billings Facility (Yale Oil). In addition, a historic tailings site (Jardine Arsenic Tailings) is likely contributing arsenic to the Yellowstone river via Bear Creek, just north of YNP. The arsenic load migrating from these three sites are described in **Section 4.2.3**. Three other active and inactive remediation sites (Burlington Northern Livingston Complex, Lockwood Solvent Site, and the 2015 Silvertip Pipeline Oil Spill) did not have arsenic as a contaminant of concern and therefore were not included in the assessment of remediation-related arsenic sources.

Information on remediation sites in the Wyoming portion of the watershed is limited to sites in the Wyoming Voluntary Remediation Program: http://deq.wyoming.gov/shwd/voluntary-remediation-program/resources/site-lists-maps/ . The inventory showed four sites within the Yellowstone watershed. Three of the sites were petroleum hydrocarbon leaks, remediated prior to 2012, and not potential sources of arsenic. The fourth site was a natural gas well blowout and not a potential source of arsenic to the Yellowstone watershed.

2.2.1.5 Underground Storage Tanks (USTs)

An inventory of known leaking underground storage tank (LUST) sites in Montana is located at http://deq.mt.gov/Land/lust/luststites. Internal DEQ and public GIS information was also searched at: http://svc.mt.gov/deq/wmadst/ and https://deqgis.mt.gov/arcgis/rest/services, respectively. The DEQ Petroleum Tank Cleanup Section does not have a database for water quality data collected from LUST sites, however the data is available in hard copy. Petroleum discharge sites are not typically a source of arsenic, therefore without specific information indicating an arsenic discharge petroleum LUST sites were not included as anthropogenic arsenic sources for this assessment.

2.2.1.6 Hazardous Waste

DEQ maintains a GIS inventory of hazardous waste handlers including the site name and the locations. These sites are not associated with contaminant releases unless they are indicated as a remediation response site (see **Section 2.2.1.3**). Additional research was necessary if information indicated that these sites were a source of contamination. Internal DEQ and public GIS information was searched and is available at: http://svc.mt.gov/deq/wmadst/ and https://deqgis.mt.gov/arcgis/rest/services, respectively. There were no hazardous waste sites that were also identified as remediation response sites.

2.2.2 Overland Runoff

The arsenic load attributed to overland runoff includes both anthropogenic and nonanthropogenic sources. The nonanthropogenic sources are from the naturally occurring arsenic in the native soils and stream bank sediment. The anthropogenic inputs are from agricultural practices and any exposed surface conditions that result from mining or other industries. The databases for these specific industries are covered in previous sections. This section is focused on the naturally occurring arsenic composition in the native soils and anthropogenic land uses (primarily agriculture related) in the Yellowstone Basin.

2.2.2.1 Soil/Stream Sediment

The arsenic composition of the native soil is used for estimating the load to surface water from runoff events. The databases previously described for abandoned mines and hazardous waste sites has soil quality data for several sites, but this soil data is applicable to limited areas in the watershed and not applicable for extrapolation on a watershed scale. Additional soil information not associated with a potential release of contaminants is available via a USGS report (Smith et al., 2014). This report summarizes the results of randomly distributed soil sampling across the United States, including 25 sites in the Yellowstone Basin. The soil samples were collected at several depths and analyzed for numerous parameters including arsenic. The report and data are available at: https://pubs.usgs.gov/of/2014/1082. DEQ maintains a GIS layer of all the sampling locations in Montana.

Stream sediment data in both Montana and Wyoming is available through the USGS. The USGS, in collaboration with other federal and state government agencies, industry, and academia conducted the National Geochemical Survey (NGS) to produce a body of geochemical data for the United States based primarily on stream sediments (USGS, 2008), and is available at: https://mrdata.usgs.gov/geochem. The goal of the NGS was to analyze at least one stream sediment sample in every 289 km^2 area by a single set of analytical methods across the entire nation (in some areas the data concentration is much higher due additional sampling as part of the National Uranium Resource Evaluation Hydrogeochemical and Stream Sediment Reconnaissance Program: https://pubs.usgs.gov/of/1997/ofr-97-0492/nurehist.htm). Sediment data is also available through the USGS National Water Information Service (NWIS) database: https://waterdata.usgs.gov/nwis.

Additional stream sediment quality for Montana streams is available via the abandoned mines databases described in **section 2.2.1.3**.

2.2.2.2 Agriculture

Agricultural practices in the Yellowstone Basin may result in an increased anthropogenic load of arsenic to the Yellowstone River. As irrigation water percolates through soil it has the potential to cause migration of contaminants that may be present in the soils and/or fertilizers/herbicides into local surface waters. Also, irrigation water may be diverted from one surface water source to another, thereby potentially migrating contaminants across watershed boundaries.

The Montana State Extension Service was contacted for purposes of determining whether arsenic is a common component in locally applied herbicides and pesticides. Dr. Cecil Tharp, a Pesticide Education Specialist at Montana State University, confirmed that lead arsenate pesticides have been effectively eliminated from use within the past 50 years. However, due to its persistence, it is possible that some soils still carry residuals. The use of arsenate pesticides was most common in late 19th and early 20th

century orchards. Orchards are not common in the Yellowstone Basin. Therefore, the anthropogenic risk of arsenic loading from arsenate pesticides is unlikely for the Yellowstone Basin.

The DNRC water rights database for Montana was searched for agricultural points of diversion, points of use, and types of use. The types of uses include domestic, industrial, stock watering, agricultural irrigation, and lawn and garden. For purposes of determining anthropogenic effects, typically the use of concern is irrigation as that water is diverted, distributed on the land and a certain portion is eventually returned to surface water. Groundwater rights are also included in the database. The potential for agricultural inputs of arsenic to the Yellowstone River is summarized in **Section 4.3.1**.

2.2.2.3 Modeling Sediment and Arsenic Runoff

Sediment runoff from land uses into surface water is estimated using the web-based version of the Soil and Water Assessment Tool (SWAT) also known as the Hydrologic and Water Quality System (HAWQS). HAWQS calculates sediment loading based on land cover, land management practices, soil composition, soil erodibility, land slope, and climate using the Modified Universal Soil Loss Equation (MUSLE). The HAWQS predicted sediment runoff load is combined with the estimated soil arsenic concentration to estimate an anthropogenic arsenic load to the Yellowstone Basin from runoff.

The sediment load from each of the 65 Yellowstone watershed HUC10s is first modeled under anthropogenic (existing) land uses and conditions. To determine the corresponding sediment loads under pre-anthropogenic (natural) conditions the existing land uses are modified to reflect the most probable land use under natural conditions. The modifications include setting all urban and cropland (including hay/alfalfa) land uses to near zero (HAWQS doesn't allow a land use to be reduced completely to zero) and changing those land uses to one of the natural condition land uses such as rangeland, forest, or wetland. As most anthropogenic land uses occur in rangeland instead of forested or wetland areas, anthropogenic land uses are converted to rangeland where possible. Due to the structure of HAWQS, conversion of land uses is limited to land uses that exist in each sub-basin and to the same soil type. Thus, in some cases anthropogenic land uses are converted to forest or wetland when rangeland is not available. Conversions of land uses are only done in similar soils so that an existing anthropogenic land use is not converted to a natural land use in a different soil type which could have different runoff characteristics. Despite being limited by the HAWQS structure in completely removing anthropogenic land uses, 96% of the anthropogenic land uses are converted to natural land uses. The 4% of anthropogenic land uses not converted are comprised predominantly of hay/alfalfa. This does not create significant error in the final results since the average sediment loading calculated by HAWQS for hay/alfalfa (0.0142 tons/acre) is nearly identical to the average sediment loading for rangeland (0.0139 tons/acre). The remaining 0.2% of the anthropogenic land uses that could not be converted to natural land uses is urban or winter wheat land uses. In those cases, the HAWQS results are modified externally to match sediment load from a natural land use (rangeland or forest) in the same soil type from another sub-basin. The difference in sediment loads between the two model scenarios (existing conditions and natural conditions) is attributed to anthropogenic land uses.

The arsenic concentration of the anthropogenically derived sediment load estimated using HAWQS is extrapolated from the soil data (Smith et al., 2014) discussed in **Section 2.2.2.1**. The top 5 cm of soil data is used in the analysis since it is the soil most likely to be transported with runoff. A summary of this data by land use and associated land uses for the entire Yellowstone Basin are presented in **Figures 2-3 and 2-4**. The average soil arsenic concentration (7.7 mg/kg) of the one anthropogenic land use identified in the USGS report (Smith et. al., 2014) (planted/cultivated) is similar to the rangeland land use (herbaceous upland) in the report, 7.5 mg/kg. These similar concentrations support using the same soil arsenic concentration for anthropogenic land uses that were converted to rangeland in the HAWQS model natural conditions scenario.

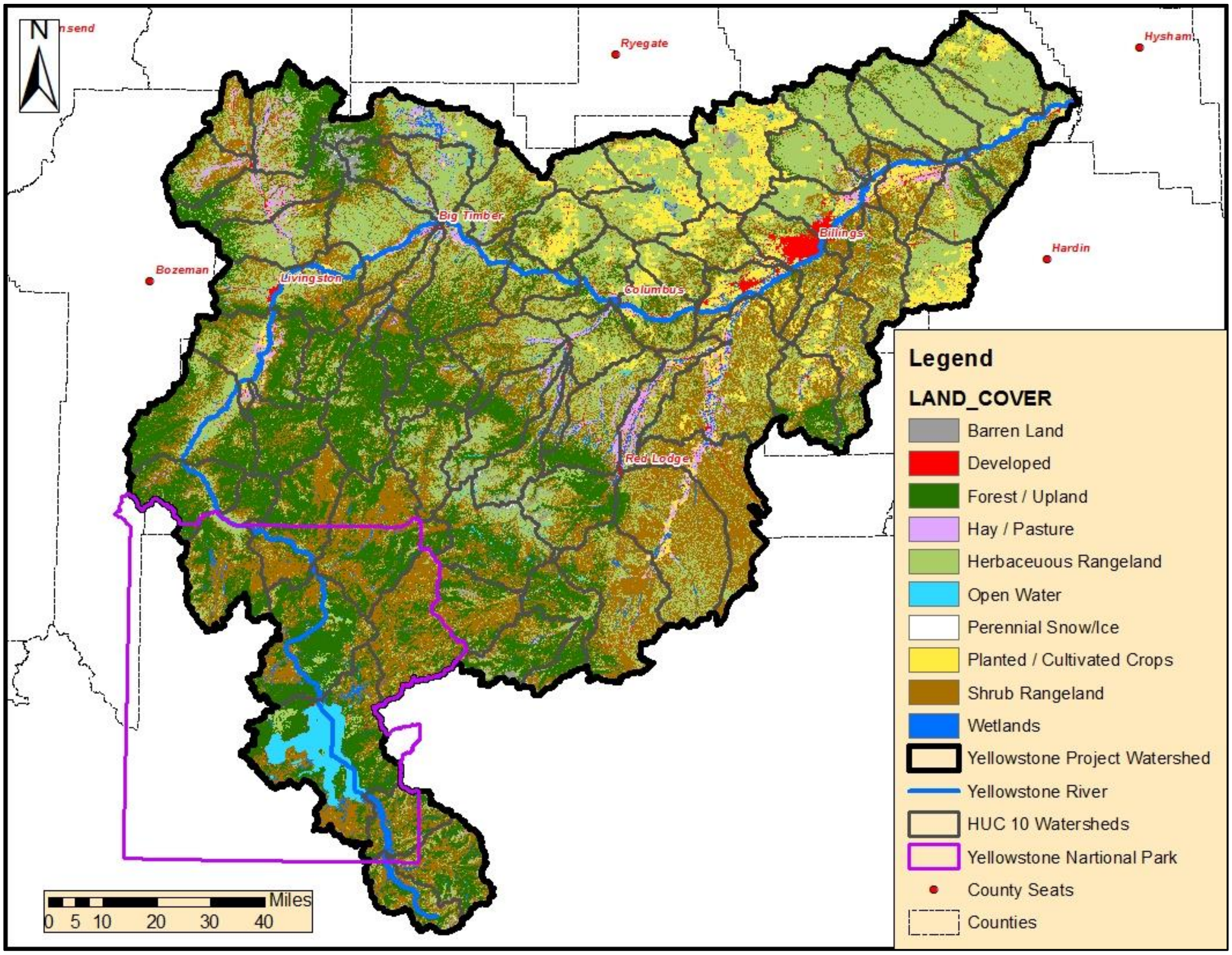


Figure 2-3. Land use Map

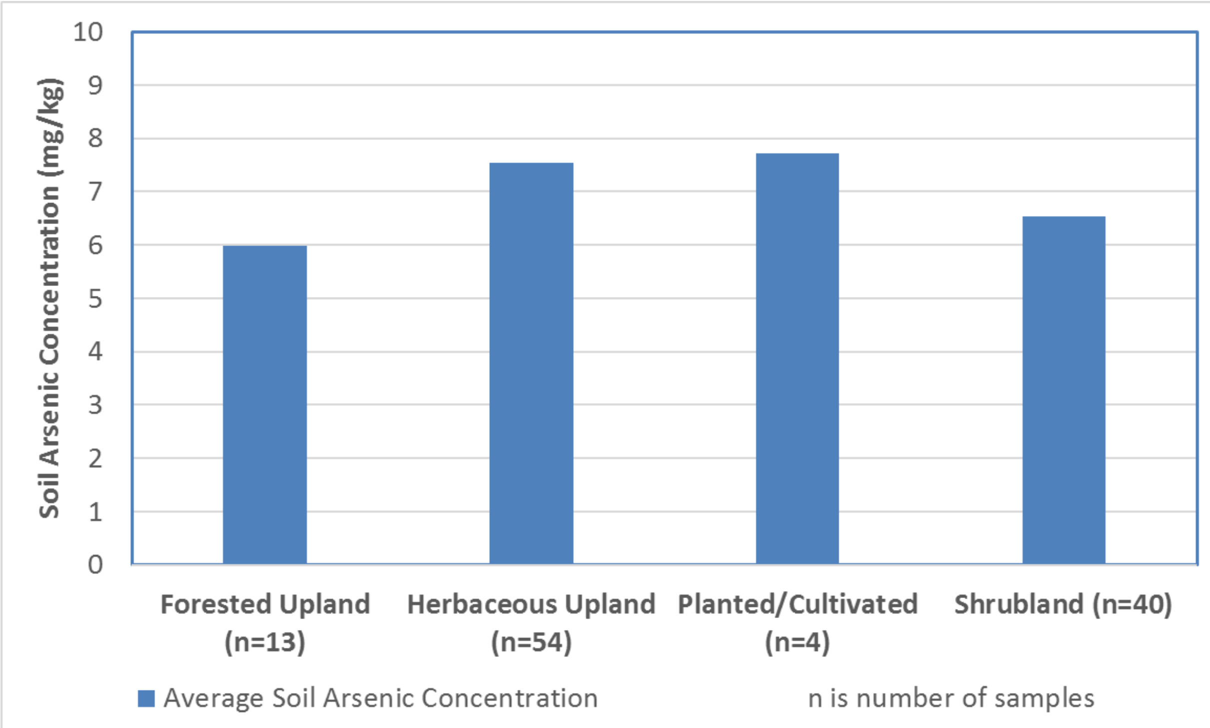


Figure 2-4. Soil Arsenic Concentrations in Upper and Lower Yellowstone Watershed (adapted from Smith et al., 2014)

2.2.3 Groundwater

Concentrations of naturally occurring arsenic in groundwater varied locally primarily due to geologic conditions. Arsenic concentrations in groundwater are assumed to be naturally occurring and originating from the local geologic conditions when no anthropogenic sources can be identified through database searches. When anthropogenic sources of arsenic are identified the arsenic load to surface water from the groundwater is estimated from the available aquifer data.

Background groundwater concentration data not related to a particular remediation site is available through two databases: the MBMG GWIC database (http://mbmggwic.mtech.edu); and the USGS NWIS database (https://www.waterqualitydata.us/portal_userguide). Both databases compile information from outside entities (DEQ, EPA, BLM, USFS, county agencies, and private watershed groups). The two database queries are combined and edited to remove duplicate data. A state-wide groundwater arsenic map and corresponding GIS database was created by DEQ for identifying locations with high arsenic groundwater concentrations (DEQ, 2016b). The database was not published but is available from DEQ upon request. For this DON, the existing DEQ groundwater database was updated with data from the GWIC and NWIS databases collected since 2016 as well as pre-2000 data from the DEQ abandoned mines program. The resulting updated arsenic groundwater database is used to identify any anthropogenic and/or nonanthropogenic groundwater sources to the total arsenic load in the Yellowstone River.

Additional groundwater concentration data is available through databases described in previous sections focusing on remediation response sites.

2.2.4 Tributaries

The major tributaries are assessed for anthropogenic and nonanthropogenic arsenic loads. This assessment includes existing data or data collected during the monitoring portion of the project. The arsenic mass load contribution is likely nonanthropogenic unless anthropogenic sources are identified, or values are unusually high or different than nearby reference streams. If an anthropogenic influence is identified, a percentage of the loading due to anthropogenic input is determined. The process of determining the anthropogenic sources in each of the tributaries is the same as discussed in the previous sections for the mainstems.

2.3 MASS LOAD ANALYSIS

2.3.1 LOADEST Modeling

Mass load is also referred to as mass flux when there is a continuous record of concentration and discharge (Aulenbach et al., 2007). Mass flux (Φ) is the product of constituent concentration (C) and discharge (Q) integrated over time (t).

Equation 1:

$$\Phi = \int C(t)Q(t)dt$$

The approach used to estimate concentrations continuously through time is a regression-model method for estimating fluxes (Aulenbach et al., 2007). The regression-model method, also known as the rating-curve method, is a standard statistical technique that is used to estimate concentration continuously, thus enabling a direct calculation of mass flux (Aulenbach et al., 2007). This method uses a regression model relating concentration to continuous variables such as discharge or time.

A computer program used for estimating arsenic load is the USGS program LOADEST (LOAD ESTimator). Given a time series of streamflow, additional data variables, and arsenic concentrations, LOADEST produces regression models for the estimation of arsenic (Runkel et al., 2004). Explanatory variables within the regression model include various functions of streamflow, decimal time, and additional user-specified data variables. The formulated regression model is then used to estimate loads over a user-specified time interval. Mean load estimates, standard errors, and 95 percent confidence intervals are developed on a monthly and/or seasonal basis. The calibration and estimation procedures within LOADEST are based on statistical estimation methods. LOADEST output includes diagnostic tests and warnings to assist in determining the appropriate estimation method and in interpreting the estimated loads (Runkel et al., 2004). Essentially the program finds a best fit data model of flux as a function of discharge, then extrapolates these relationships to estimate flux from daily flow data. The two input files are flow data and water quality data. For this project, daily flow data are obtained from existing USGS gaging stations, and water quality data (total recoverable arsenic concentrations) are obtained from periodic grab samples taken by either USGS or DEQ. These samples are typically collected monthly and include an associated flow value. The model requires a minimum of twelve concentration data points. The model outputs include annual and monthly load averages (kg/day) and concentration averages (µg/L), daily load (kg/day) and concentration (µg/L) estimates, and calibration and modeling statistics. The outputs presented in this document incorporate a Maximum Likelihood Estimation (MLE) technique for the daily and monthly loads.

2.3.2 Synoptic Mass Load Analysis

When there is less concentration data and/or the river or stream location is not a USGS gaging station, the alternative synoptic mass load analysis is used to calculate a mass load. This approach is also used for point source discharges. The mass load analysis is defined by a direct calculation of mass load using the following equation:

EQUATION 2: **ML = C x Q x t x cf**

Where,

ML – Mass Load (pounds or kilograms)

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)

For each sample pair collected (flow and concentration), a mass load is calculated. A median or average of the calculated mass load is used in the mass balance equation (**Section 2.4**).

This process is simpler than the process described in **Section 2.3.1**. The advantage of using synoptic mass load analysis is that a load is estimated with less data and without a USGS gaging station. The disadvantage is that the results are only as reliable as the data collected. For instance, if the data is highly variable with limited seasonal representation, the mass load results have the same limitations. For all mass load calculations, incorporating more data with seasonality and annual fluctuations is best for statistically valid results. Data needs and statistical validity for mass load analysis are discussed further in **Section 3**.

2.4 Mass Balance Approach

The mass balance approach offers a useful technique for quantifying the transport of trace elements such as arsenic in surface water. In mass balance considerations, data on both hydrological conditions and the chemical quality of water are considered simultaneously. A mass load is the mass of arsenic transported at a point in a waterbody during a period of time.

A simple mass balance model was used for the Yellowstone River arsenic load. The equation is as follows:

EQUATION 3: **TAL = YNP + PSL + GW + Trib + RO**

Where,

TAL – Total arsenic load

YNP - Geothermal arsenic load from the Yellowstone Caldera

PSL – Point source arsenic load, permitted discharge operations

GW – Groundwater arsenic 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 3*** describe a mass load. Each mass load is defined by the mass load equation (***Equation 2***). **TAL** is the total arsenic load in the stream which includes both "nonanthropogenic" and "anthropogenic" sources. Therefore, TAL was rewritten to express this relationship.

EQUATION 4: **TAL = NAL + AAL**

Where,

NAL = Nonanthropogenic Arsenic Load

AAL = Anthropogenic Arsenic Load

It is important to understand the relative contribution of nonanthropogenic arsenic load versus that known to occur from anthropogenic sources. To distinguish between nonanthropogenic and anthropogenic sources of arsenic, the mass balance equation (***Equation 3***) is written as:

EQUATION 5: **TAL = YNP + 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

RON – Surface water runoff with nonanthropogenic derived arsenic loading

Equations 3, 4, and 5 are rearranged to solve for NAL and expressed as:

EQUATION 6: **NAL = TAL - PSL - GWA - TribA - ROA**

The final product of the mass balance and this DON is the NAL. The Yellowstone River NAL is necessary for the Nonanthropogenic Standard Selection (NAS) (DEQ,2018a).

3.0 DATA NEEDS

A thorough search of all available databases, as described in **Section 2.0**, produced enough information to determine whether there are anthropogenic influences in the watershed. However, there are questions regarding anthropogenic influence, missing data in tributaries, or other concerns about data limitations, additional sampling was required. In the Yellowstone River, there is adequate sampling on the main-stem and the major tributaries, but after reviewing the minor tributaries, several tributaries with either some mining history or high arsenic soil concentrations have no data available, and several others have old data where detection limits are very high. Therefore, additional sampling was performed on several tributaries to fill in these data gaps.

3.1 DETERMINATION OF SUFFICIENT DATA

Figure 3-1 is a decision flowchart showing the process of determining whether additional sampling is needed.

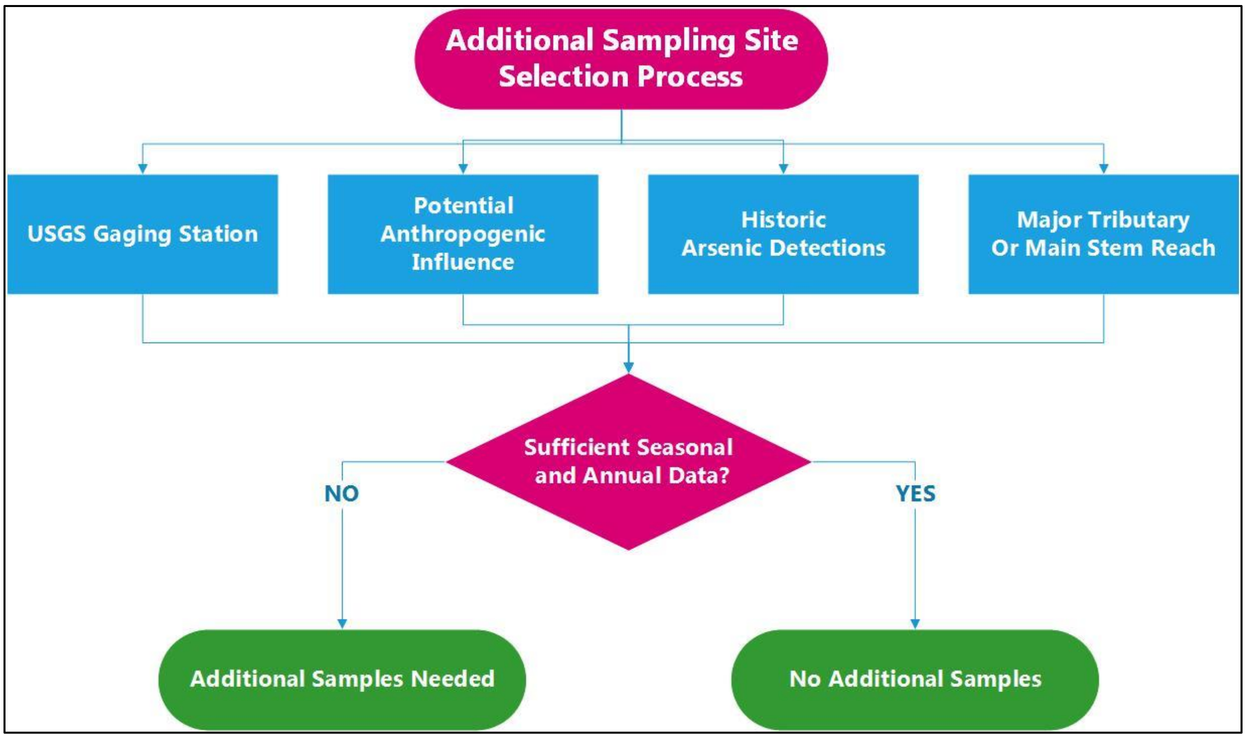


Figure 3-1. Decision Flow Chart for Additional Sampling for Tributaries

After completing all database searches and compiling the anthropogenic and nonanthropogenic data into one dataset, an analysis is performed as to whether sufficient data exists to complete a defensible and valid DON. The process of determining whether there is sufficient data is presented in **Figure 3-2**.

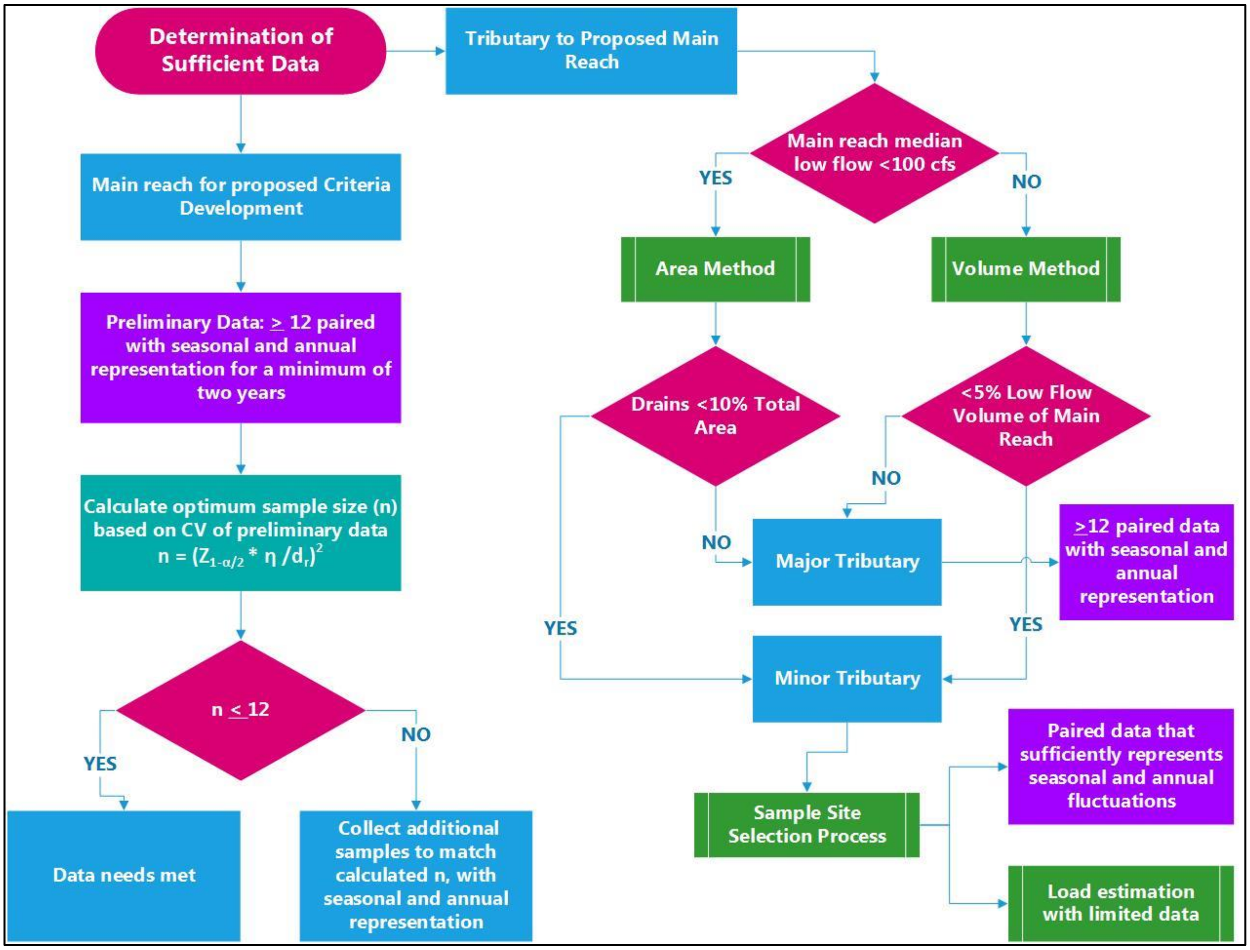


Figure 3-2. Flow Chart for Determination of Sufficient Data

For the major tributaries and main reaches in the Yellowstone River watershed, 12 paired water quality and flow samples with seasonal and annual representation for a minimum of two years was collected. The following sections explain how these numbers are determined.

3.2 Sample Size Determination

Most methods for sample size determination require some knowledge about the desired outcome and population in advance, including:

- Desired accuracy of results
- Confidence level; and
- Variability of data

While the desired accuracy and confidence can be determined *a priori*, understanding the variability of the data requires some knowledge of the population. Metrics such as standard deviation (σ), mean (μ), and the coefficient of variation (CV) or relative standard deviation (σ/μ) have a huge influence on the spread of the data and thus confidence intervals, prediction intervals, etc. The central tendency of datasets with high variability can be very difficult to characterize by sampling. Consider which population in **Figure 3-3** would be easier to characterize with just a few samples. Stream B would be easier to characterize with fewer samples since there is less variability in the concentration data.

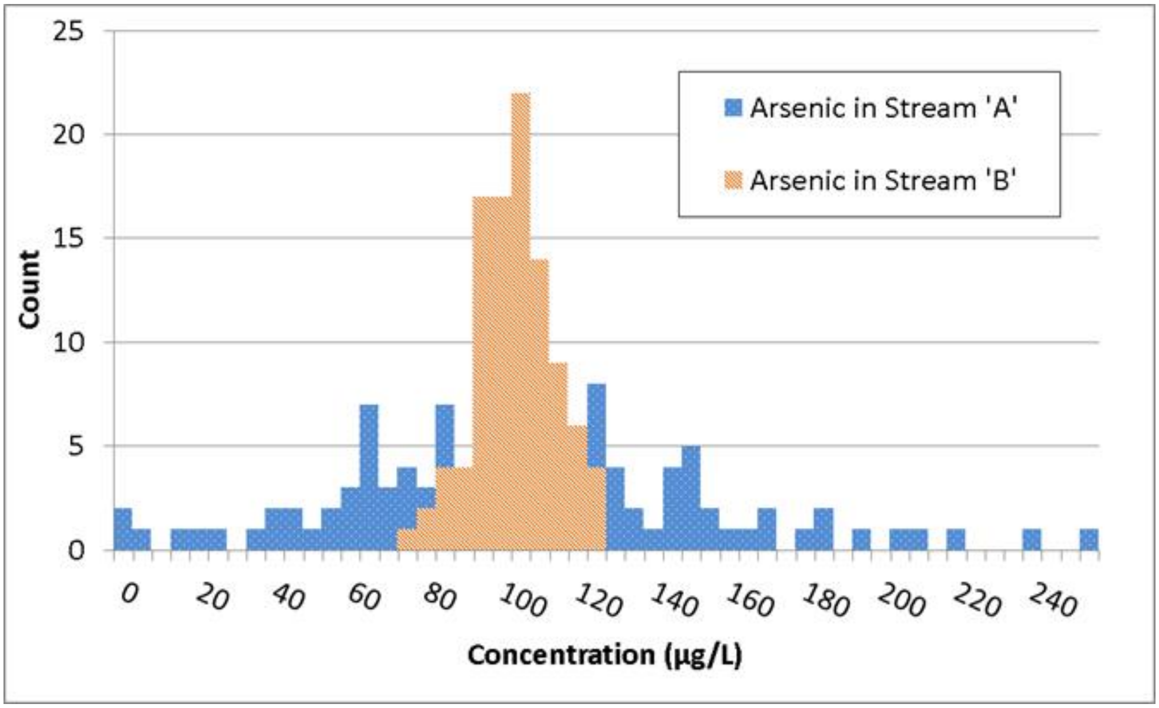


Figure 3-3. Examples of Variability Between Environmental Datasets

The CV is very useful as it allows comparison of any given sample dataset's standard deviation to all other sample dataset's standard deviations (DEQ, 2011), regardless of whether the arsenic concentrations in the datasets are high, low, or in between. The required sample size depends on the coefficient of variation (CV). Data sets with a low CV require a handful of samples to achieve a strong estimate of means, whereas datasets with a high CV require hundreds of samples.

One of the most common methods to determine sample size in environmental data is to implement a two-stage sampling procedure. In this process, preliminary data is collected from the population to approximate the relative standard deviation, and then the necessary sample size is calculated from this data (with a predetermined confidence level and acceptable 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 is needed. This method is common (Gilbert, 1987) and provides a good estimate of needed sample size. The formula for calculating sample size with a pre-determined relative error is:

EQUATION 7: $$n = (Z_{1-\alpha/2} * \eta / d_r)^2$$

Where n is the required number of samples, Z is the standard normal deviate (often looked up in statistical tables) for the confidence level desired, α is the desired significance level, η is the coefficient of variation or relative standard deviation, and d_r is the pre-specified relative error from the mean. The advantage of this method is simplicity, but one disadvantage is that it may not account for asymmetry and non-normal distributions.

The size of the preliminary data set is somewhat arbitrary, but 12 samples are suggested. This sample size is more than 10, which several sources suggest is a minimum for capturing adequate seasonal and annual variability, and less than the 30 that is typically considered a large data set in statistics. Thus, to determine the required sample size, 12 preliminary samples were collected (making sure they were spatially and/or temporally independent as needed) to determine the approximate variance and mean. Then, using a pre-specified relative error and a confidence interval, the required sample size was determined. At this point, more samples may have been required.

The Yellowstone River concentration data sets described in the next section had optimal sample sizes ranging from 6 to 25 based on a 90% confidence level and 15% error. In other words, a minimum collection of 6 samples allows 90% confidence that the average concentration calculated for the Yellowstone River at Billings station is within ± 15% of the *true* average concentration. This low sample minimum is due to the lesser variability in seasonal concentrations. The actual number of samples collected for the Yellowstone River at Billings was 28. A much greater minimum sample collection for the Yellowstone River at Corwin Springs of 25 was calculated due to the greater seasonal variability in concentration.

Another methodology that was available is the bootstrap method. The bootstrap method (or bootstrapping) refers to any test or metric that relies on random sampling with replacement and assigns measures of accuracy such as a confidence interval or standard deviation based on this random sampling (Qumsiyeh, 2013). The bootstrap method provides an alternative estimate of medians and sample size. The bootstrap method requires a large amount of data up front, and assumes that this data accurately represents the true population. These requirements were not met with the Yellowstone River datasets. An example of a much more robust dataset is the Madison River dataset and the DON incorporates the bootstrap method (DON 2017c)

4.0 RESULTS

4.1 HYDROLOGIC SEGMENTS

The Yellowstone River and associated tributaries were divided into five hydrologic sections for the mass balance analysis. The sections were based on the regional hydrologic divisions, and are shown in **Figure 4-1**. The five hydrologic sections are:

- Segment 1 - Montana/Wyoming Border to the Mouth of Mill Creek near Emigrant
- Segment 2 - Mill Creek to the Mouth of the Boulder River near Big Timber
- 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

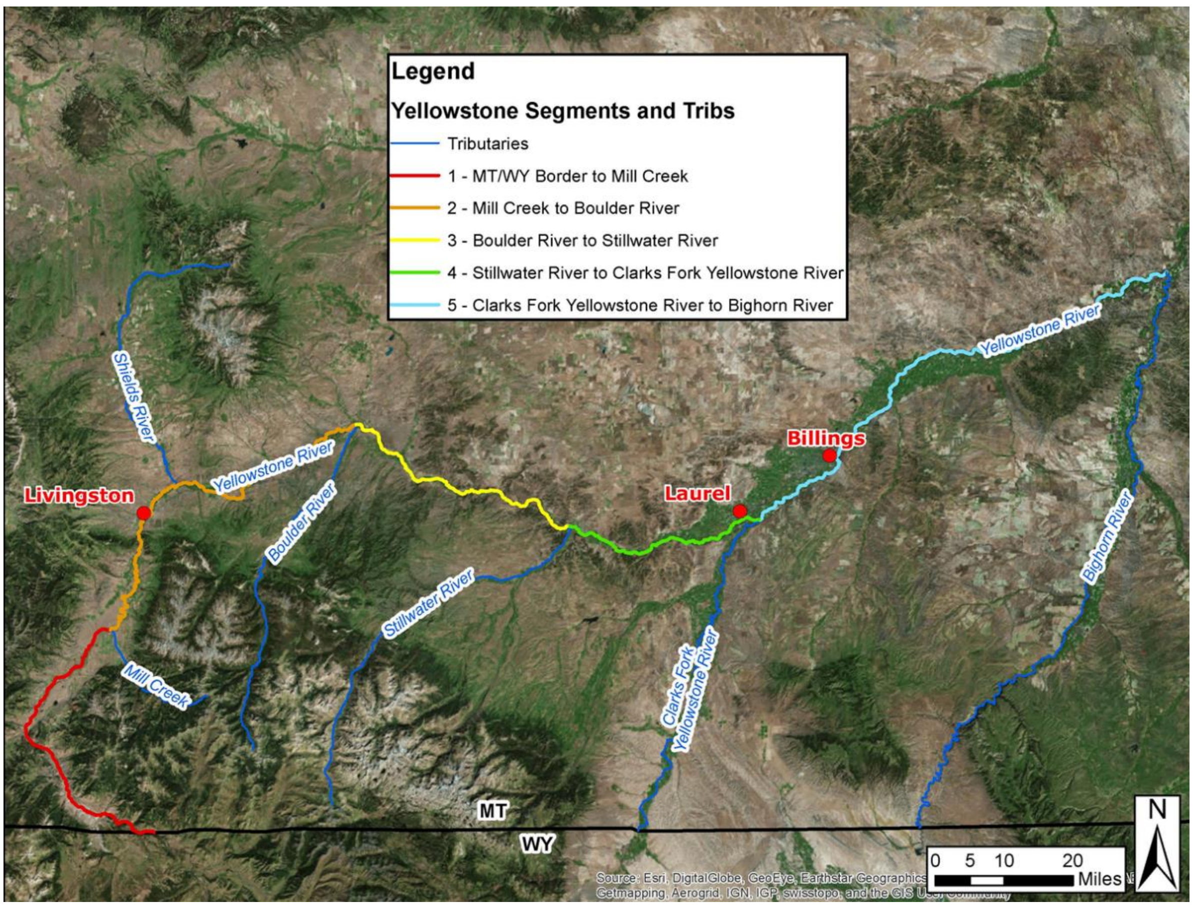


Figure 4-1. Hydrologic Sections of the Yellowstone River for Mass Balance Analysis

Each segment has a different median concentration. 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 arsenic concentration falls below 10 µg/L in the Yellowstone River after the confluence with the Bighorn River. Thus, this DON ends at the Bighorn River.

4.2 POINT SOURCES

4.2.1 Permitted Discharges

There are 98 identified MPDES and/or Groundwater Pollution Control System permitted dischargers in the project area. These permitted discharges, as shown on **Figure 4-2**, are broken down into 22 storm water permits, 7 groundwater permits, 47 general permits, and 22 individual permits. In addition to the Montana discharges an additional 19 discharges were identified in Wyoming along the border. Of the 98 Montana permits, only 8 permitted dischargers had effluent monitoring for arsenic. None of the Wyoming permitted dischargers monitor for arsenic. Due diligence was completed to assess whether any permitted discharges, monitoring for arsenic or not, have potential to contribute anthropogenic arsenic to the Yellowstone Basin.

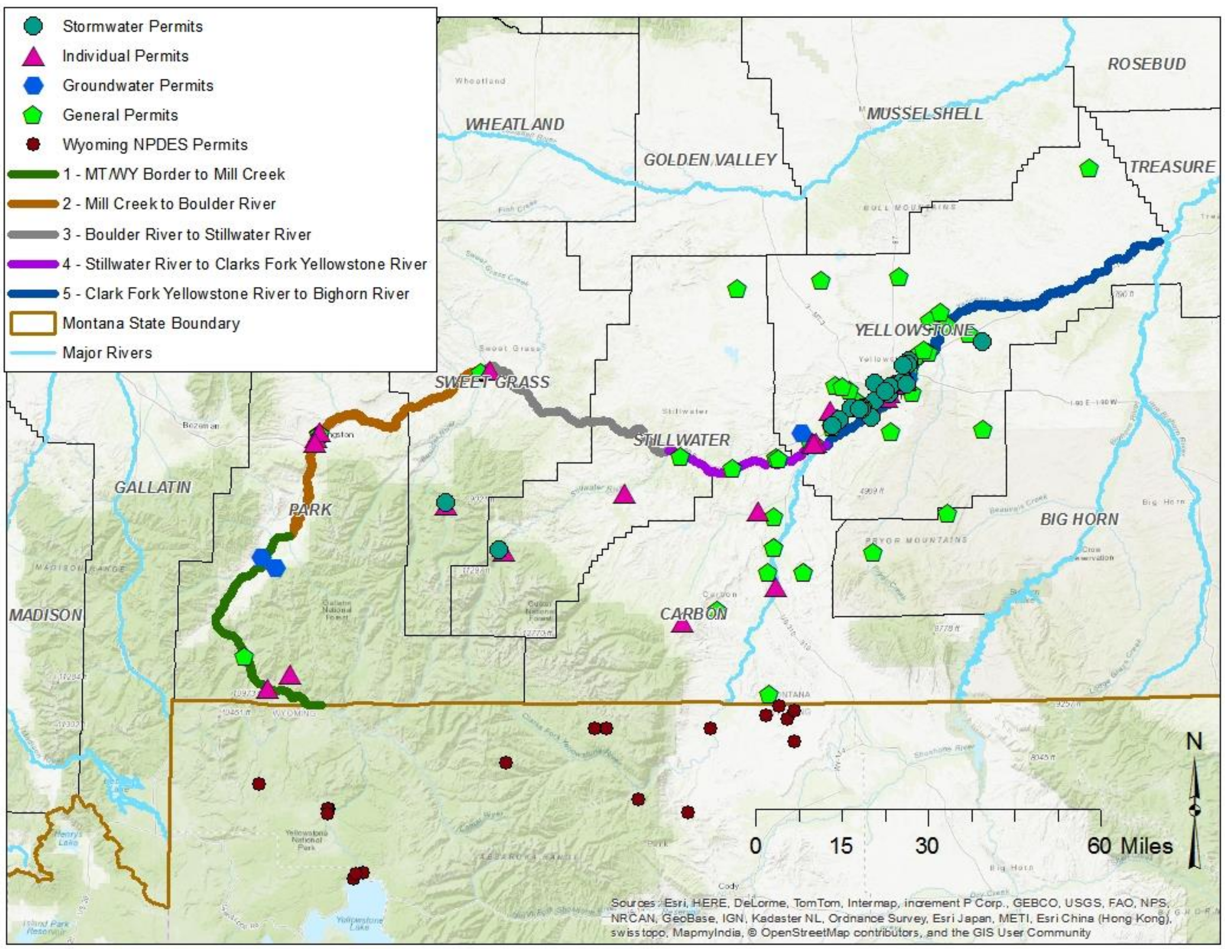


Figure 4-2. Permitted Point Sources

Only 8 permitted discharges with effluent monitoring for arsenic have quantifiable arsenic loads to the Yellowstone Basin (**Table 4-1**). A high flow (June) and low flow (December) arsenic load and the associated percentage of the total arsenic load in the river is presented in **Table 4-1**. In the case of limited data, the discharge load was estimated for the entire year. This resulted in equal low and high flow permitted loads.

Table 4-1. Permitted Discharges with Quantifiable Anthropogenic Arsenic Loads

MPDES No.	Facility	Receiving Body	Facility Load (Kg/ Month)	River Load at Facility (Kg/ Month)	% of River Load	Facility Load (Kg/ Month)	River Load at Facility (Kg/ Month)	% of River Load
			June			*December*		
MT0030252	TVX MINERAL HILL INC - TVX MINERAL HILL MINE	BEAR CREEK	0.19	6,044	0.003%	0.39	2,399	0.016%
MT0022705	GARDINER WWTF	YELLOWSTONE RIVER	4.44	6,044	0.073%	2.25	2,399	0.094%
MT0020435	CITY OF LIVINGSTON WWTP	YELLOWSTONE RIVER	0.50	6,942	0.007%	0.50	2,436	0.021%
MT0000264	CENEX HARVEST STATES COOP.	YELLOWSTONE RIVER	3.64	11,355	0.032%	5.37	2,277	0.236%
MT0000281	WESTERN SUGAR COOPERATI VE	YEGEN DRAIN	0.95	12,752	0.007%	0.74	2,225	0.033%
MT0000256	PHILLIPS 66 - BILLINGS REFINERY	YEGEN DRAIN	0.31	12,752	0.002%	0.45	2,225	0.020%
MT0000477	EXXON MOBIL REFINING & SUPPLY	YELLOWSTONE RIVER	1.67	12,752	0.013%	2.54	2,225	0.114%
MT0022586	CITY OF BILLINGS WWTP	YELLOWSTONE RIVER	6.81	12,752	0.053%	6.81	2,225	0.306%
Total From All Permittees at Billings			**18.52**	**12,752**	**0.682%**	**12,752**	**0.145%**	**0.816%**

Bear Creek is a tributary to the Yellowstone River near the Yellowstone Park Boundary. There is a current and historic mining operation within this tributary drainage that is contributing anthropogenic arsenic to the Yellowstone Basin. For more detailed discussions on Bear Creek, see **Sections 4.2.2, 4.2.3. and 4.3.1**.

The Yegen Drain is a Billings drainage canal that flows into the Yellowstone River. Thus for this mass balance, discharges into the Yegen Drain are essentially discharging into the Yellowstone River.
For facilities with untreated source water originating from the Yellowstone River, the initial arsenic load of the Yellowstone River is subtracted from the discharge load to avoid duplicate accounting in the Mass Balance.

The anthropogenic arsenic loads from the permitted discharges account for less than 1% percent of the total arsenic load in the Yellowstone River for both the high flow and low flow seasons.

4.2.2 Mining

The Montana DEQ has inventoried 421 abandoned mines in the Yellowstone watershed. 17 of these mines are considered high priority sites and have limited data regarding pollutant concentrations for sediment and surface water. There is no comparable data on abandoned mines available in the Wyoming portion of the watershed. Using the DEQ abandoned mine data, USGS sediment data, and MBMG GWIC data, the potential for arsenic loading to the watershed is discussed in this section.

Sediment arsenic concentrations for the Yellowstone watershed are shown on **Figure 4-3**. The sources for this data included a USGS geochemical database (USGS, 2008), the online USGS NWIS database, and the DEQ abandoned mines program. The highest concentrations occur in the upper section of the watershed near YNP. There are two significantly elevated sediment arsenic concentrations (207 and 300 mg/kg) collected from Bear Creek below the Jardine Arsenic Tailings site and the TVX Mineral Hill Mine (**Figure 4-3**). The instream arsenic concentrations near the mouth of Bear Creek are also elevated most likely due to those two sources. Thus, the entire arsenic load from Bear Creek is assumed to be from anthropogenic sources.

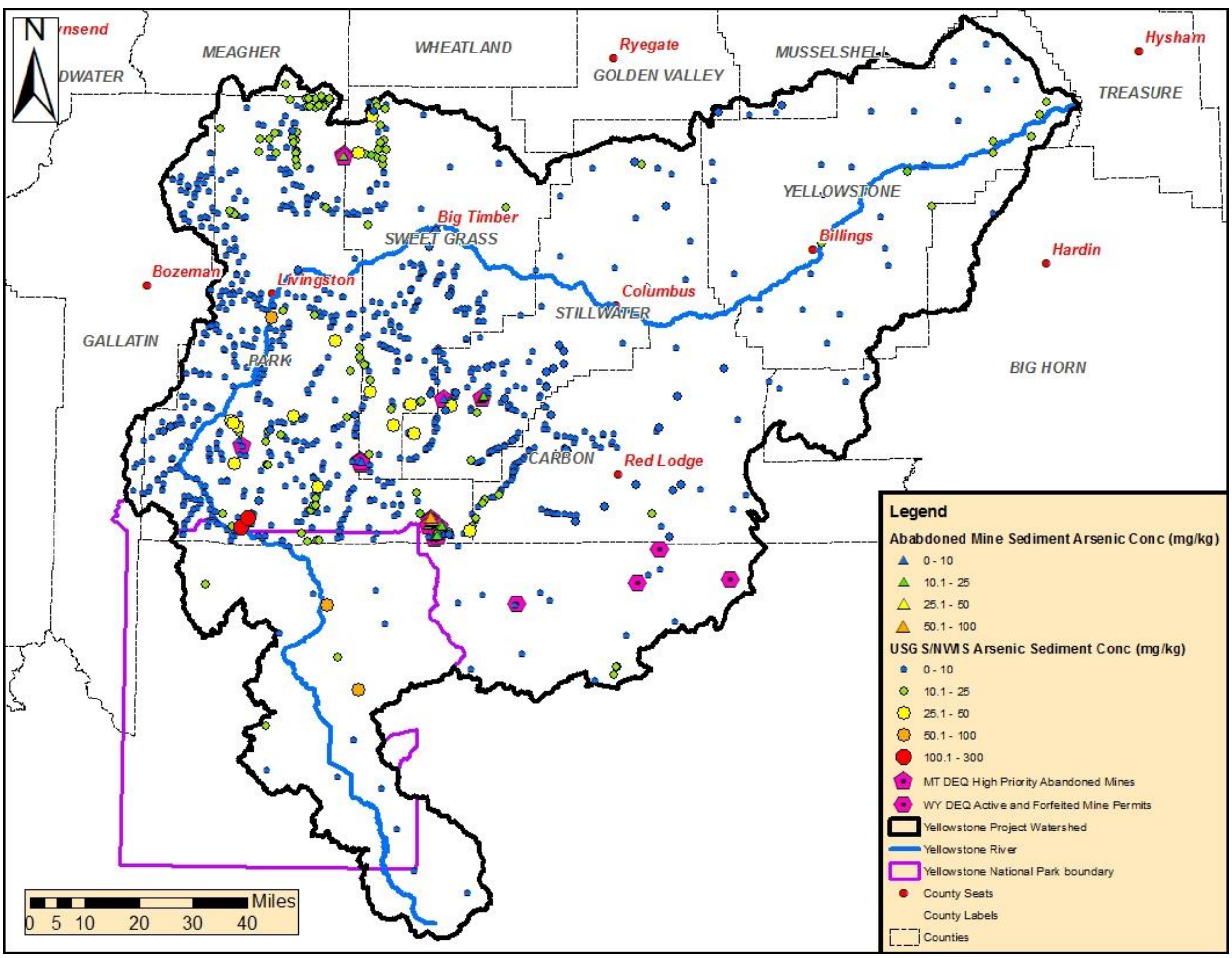


Figure 4-3. Sediment Arsenic Concentrations for Yellowstone Watershed

The Montana abandoned mine sediment data shown in **Figure 4-3** is limited to the 17 high priority mines. Nine of those mines are located within and around the New World Mining district near the northeast corner of YNP, which is an area of naturally elevated metals due to the local geology. Between 1989 and 2003 there were 650 surface water samples (including adits, seeps and springs) analyzed for arsenic from the New World Mining District. Only 10 of those samples exceeded the arsenic standard of 10 µg/L, the highest being 54 µg/L from a spring or adit in the Daisy Creek headwaters. All 10 samples exceeding the standard were collected in tributaries of the main streams in the New World Mining District (Daisy Creek, Stillwater River, Fisher Creek and Clarks Fork Yellowstone). There were 117 arsenic samples collected on those main streams, none were above the arsenic standard. This indicates that the New World Mining District is not a significant source of arsenic to the Yellowstone Basin. The four Wyoming mines shown on **Figure 4-3** consist of three sand and gravel mines and one granite mine. Based on the type of mining, the Wyoming mines have a low potential for contributing arsenic to the basin.

Surface water arsenic concentrations from the DEQ's Abandoned Mines program database and the MBMG GWIC database are shown on **Figure 4-4.** Only the western and central portions of the watershed are shown since there were no surface water samples related to mining in the far eastern portion of the watershed. Surface water samples were collected downstream of the mine workings at 12 of the 17 high priority abandoned mines in the Yellowstone Basin. Sites listed as "mine drainage" in the MBMG GWIC data base are also shown on **Figure 4-4**. These mining related arsenic concentrations were all below 6.5 µg/L, which indicates that abandoned mines are not a significant source of arsenic in the Yellowstone Basin.

4.2.3 Other Anthropogenic Sources

Chromated copper arsenate (CCA) is still in use as a wood preservative in industry, but there is no evidence of industrial wood treatment facilities in the Yellowstone Basin. Other common commercial uses of CCA have been discontinued for over 50 years and residuals are not expected to be present in the watershed.

There are 722 inventoried LUST sites in the Montana Yellowstone Bain and three sites in Wyoming (**Figure 4-5)**. Half of the Montana sites have been remediated. Arsenic is not typically a contaminant of concern at petroleum sites and have a low potential to contribute arsenic to the watershed. However, petroleum spills can in some cases alter the chemistry in the soil and allow previously immobile arsenic that occurs naturally in the soil to become mobile and migrate to groundwater. One site where this may have occurred is the Phillips 66 refinery in Billings, which has a Montana Hazardous Waste Permit for on-going corrective actions. There are elevated groundwater arsenic concentrations beneath this property, however due to corrective actions the arsenic plume has been maintained on-site and is not impacting the adjacent Yellowstone River. Thus, an anthropogenic arsenic load to the Yellowstone River was not assigned to this groundwater arsenic plume.

Other potential anthropogenic point sources of contaminants to the Yellowstone River are also shown in **Figure 4-5**. These sources are based on the Montana DEQ and Wyoming DEQ databases for remediation response sites (RRS). Most of the RRS are small and based on a review of the available site investigation summaries via the Montana DEQ mapping program these sites have a low potential to contribute arsenic to the watershed.

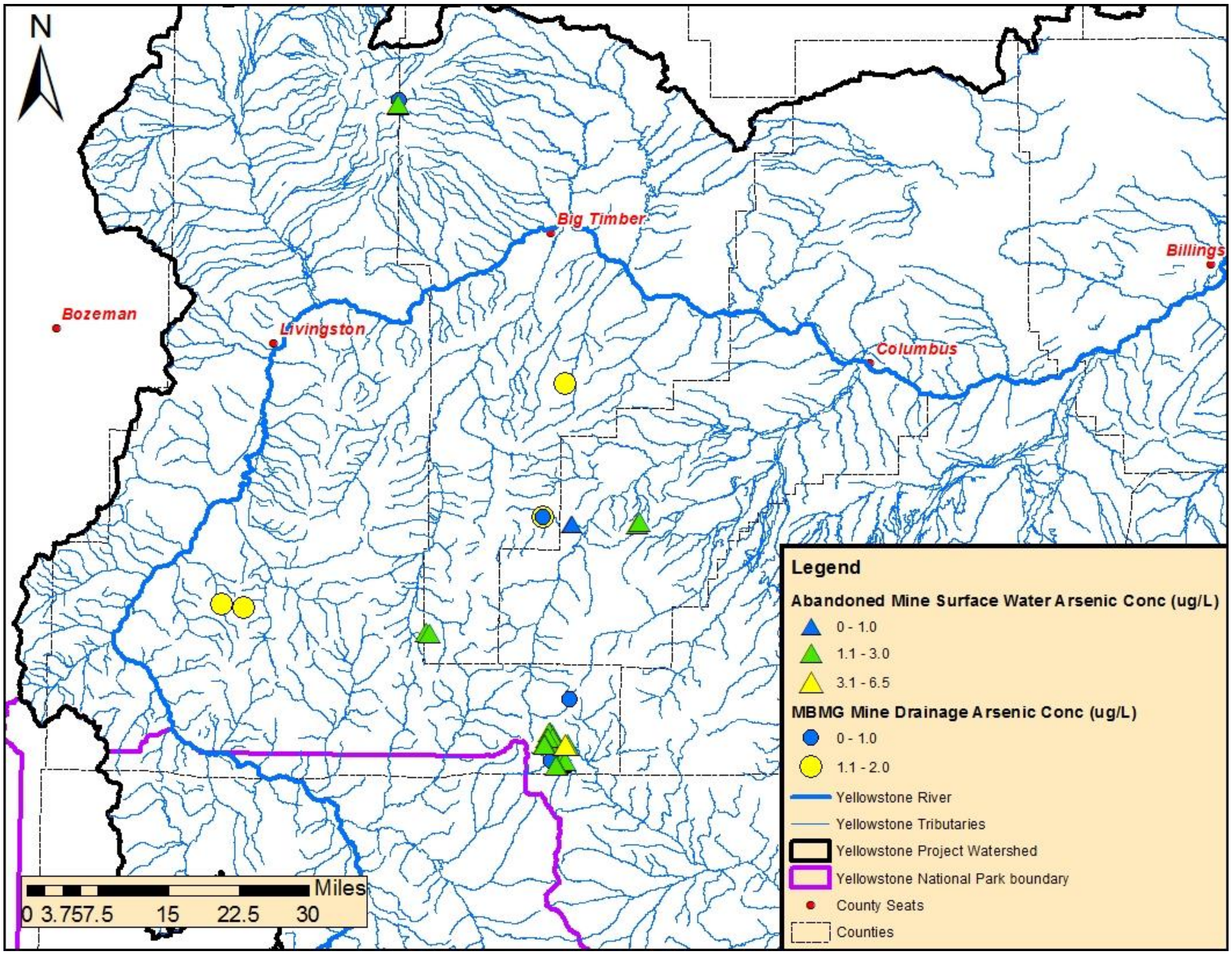


Figure 4-4. DEQ's Abandoned Mines Program and MBMG GWIC Mine Drainage Arsenic Concentrations in the Yellowstone Watershed

There are six larger RRS sites in the Yellowstone watershed, three are not suspected sources of arsenic and three are. The three sites that are not arsenic sources include: the Lockwood solvent site, a federal Superfund site located east of Billings; the Burlington Northern Livingston Complex, a state Comprehensive Environmental Cleanup and Responsibility Act (CECRA) site in Livingston; and the 2011 Silvertip Pipeline Oil spill, a CECRA site near Laurel. These three sites are not monitoring for arsenic and are not considered potential arsenic sources.

The three RRS sites identified as potential sources of arsenic are shown on **Figure 4-5.** The first site is within the city of Billings, Yale Oil of South Dakota Facility (Yale Oil), an oil refinery that operated until 1949. The site remediation is ongoing and arsenic concentrations in the groundwater beneath the site exceeds the water quality standard of 10 µg/L. Using existing hydrogeology studies of the site the direction and volume of groundwater flow beneath the site was estimated. The groundwater flow volume was combined with the available groundwater arsenic concentration data to estimate the arsenic load to the Yellowstone River (0.0035 kg/month). The Yale Oil groundwater load is included as an anthropogenic load in the mass balance calculations in **section 4.7**.

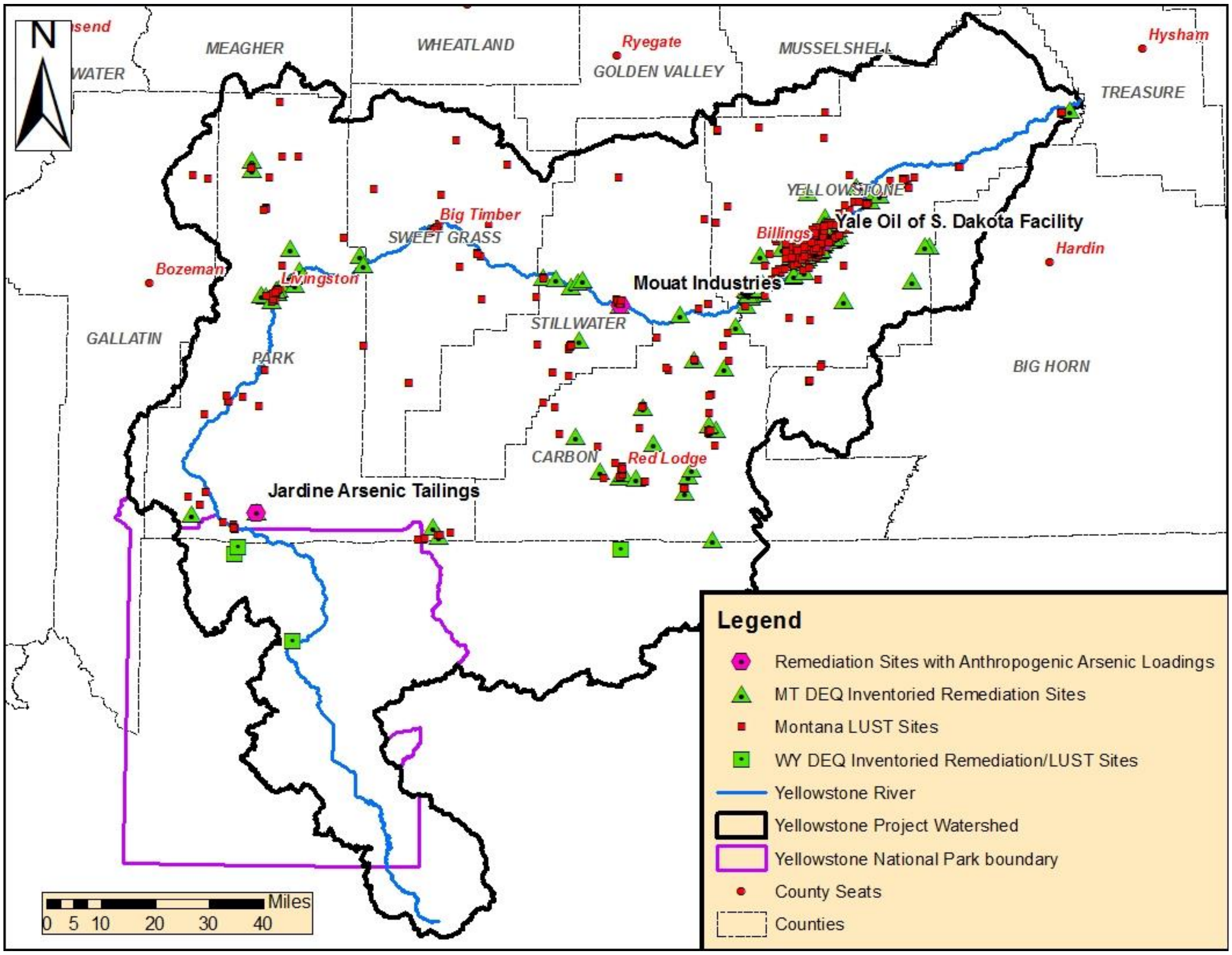


Figure 4-5. DEQ Remediation Response Sites in Yellowstone Watershed.

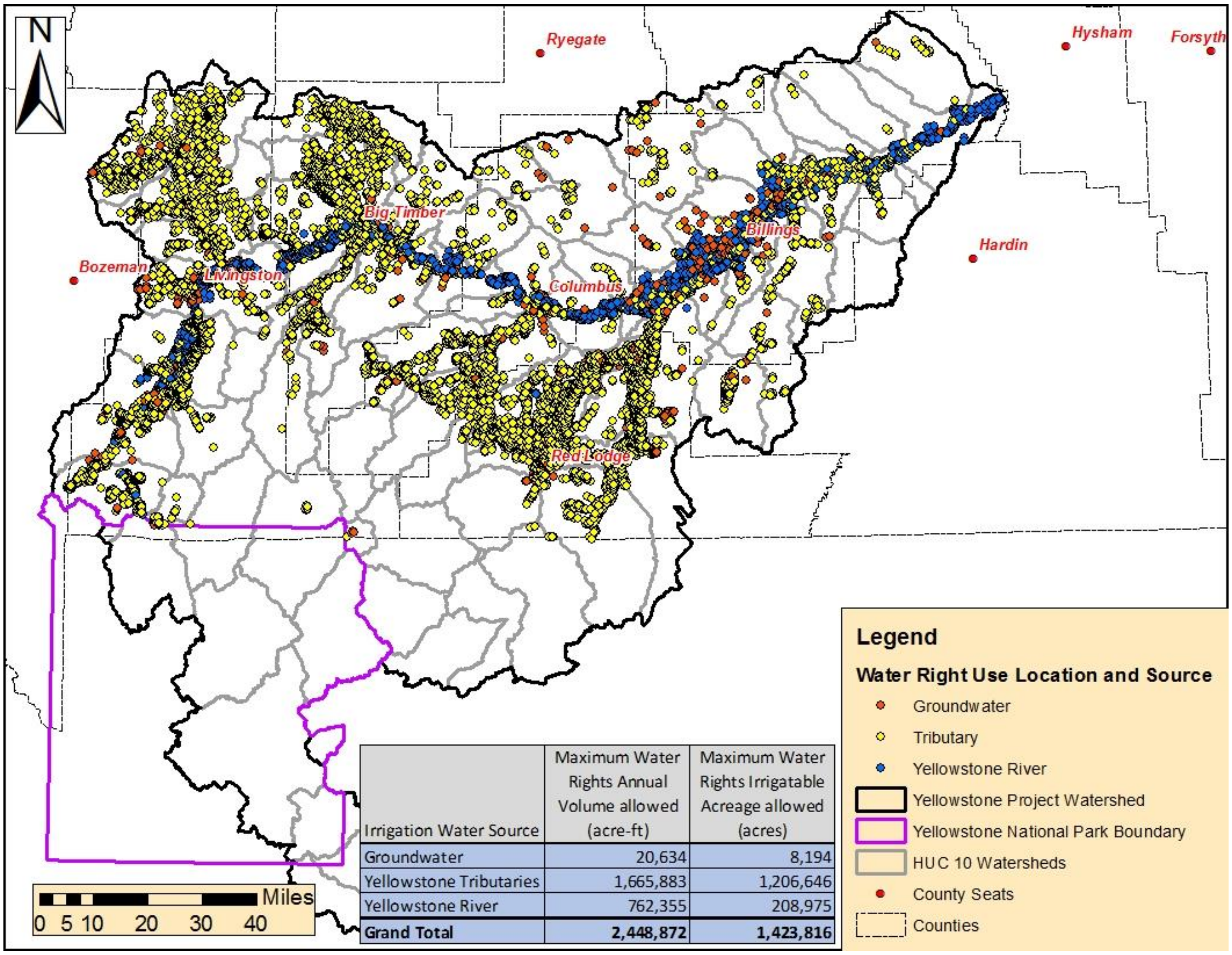
The second site, Mouat Industries of Columbus, Montana, was a chromite ore processing site that operated from 1957 to 1962. Remediation efforts were completed in 2008, but residual arsenic exists in the groundwater beneath and downgradient of the site that eventually enters the Yellowstone River. Using existing hydrogeology studies of the site the direction and volume of groundwater flow beneath the site was estimated. The groundwater flow volume was combined with the available groundwater arsenic concentration data to estimate the arsenic load to the Yellowstone River (0.11 kg/month). The Mouat Industries groundwater load is included as an anthropogenic load in the mass balance calculations in **section 4.7**.

The third site is the Jardine Tailings. The runoff and groundwater from the tailings flow into Bear Creek which enters the Yellowstone River immediately north of YNP (more detail in **Sections 4.2.2 and 4.4**). The arsenic load in Bear Creek fluctuates monthly in response to flow rates in the creek. The monthly arsenic load is an estimate from measured stream discharge rates and instream arsenic concentrations. The arsenic load in Bear Creek ranges from 14.97 kg/month during low flow months to 58.72 kg/month during high flow months. The Bear Creek load is included as an anthropogenic load in the mass balance calculations in **section 4.7**.

4.3 Runoff

4.3.1 Agriculture

As irrigation water percolates through soil it has the potential to cause migration of contaminants that may be present in the soils into local surface waters. Also, water that is diverted from one surface water source may be used in a location that drains to a different surface water source thereby potentially migrating contaminants to different basins. **Figure 4-6** shows the DNRC water rights source and use locations for all surface water irrigation rights in the Yellowstone Basin. Similar water rights data for the Wyoming portion of the watershed are not available.



Irrigation Water Source	Maximum Water Rights Annual Volume allowed (acre-ft)	Maximum Water Rights Irrigatable Acreage allowed (acres)
Groundwater	20,634	8,194
Yellowstone Tributaries	1,665,883	1,206,646
Yellowstone River	762,355	208,975
Grand Total	**2,448,872**	**1,423,816**

Figure 4-6. DNRC Water Rights Showing Use Location and Source for Irrigation-Related Water Rights

The Yellowstone River has higher arsenic concentrations than most of its tributaries and groundwater in the basin. The median arsenic concentration of the Yellowstone River ranges from 30 µg/L above the confluence with the Lamar River inside YNP to 9 µg/L at Forsyth (DEQ, 2018). The median arsenic concentration in tributaries ranged from below detection limit, 0.5 µg/L, to 6 µg/L (DEQ, 2017b); those concentrations do not include two other tributaries, Gardner River and Bear Creek, which have elevated median arsenic concentrations of 85 and 9 µg/L, respectively. The Gardner River originates in YNP and the elevated arsenic is due to the natural geologic sources in YNP. The elevated Bear Creek arsenic concentrations are due to mining-related sources. The median groundwater concentration in the

Yellowstone Basin is 2.50 µg/L. Based on the tributary and groundwater information, return flow to the Yellowstone River from irrigated lands through runoff, tributaries, or groundwater will likely dilute the arsenic concentration in the Yellowstone River.

4.3.2 HAWQS Sediment Runoff Modeling

The amount of arsenic associated with sediment runoff from anthropogenic land uses was estimated using measured and extrapolated soil concentrations and simulated sediment runoff from the HAWQS watershed model (electronic version of the HAWQS model parameters and results are available upon request). **Figure 4-7** shows the estimated soil arsenic concentrations for each HUC10 in the Yellowstone watershed that were extrapolated from the 25 USGS soil sample locations in the watershed (Smith et al., 2014). The soil arsenic concentrations were used to estimate monthly and annual arsenic load runoff in the individual HUC10's using the monthly sediment loading estimates from the HAWQS model discussed in **Section 2.2.2.3**. **Table 4-2** shows the difference in estimated annual arsenic load between the anthropogenic and nonanthropogenic conditions. The arsenic load in the last column of **Table 4-2** is the annual anthropogenic arsenic loads from runoff (ROA) component of the Mass Balance Equation (**Section 2.4**) for all five hydrologic sections. The annual ROA is broken down by each HUC10 in **Figure 4-8**. The monthly and annual ROA to the five hydrologic sections of the Yellowstone River are listed in **Table 4-3**. The annual ROA is less than 1 percent of the total arsenic in the Yellowstone River for all five hydrologic sections, and will be used in the mass balance equation to calculate the nonanthropogenic load.

The Yellowstone Basin overland sediment runoff estimated using the HAWQS model was not calibrated to measured concentrations, however the sediment load rate was compared to a calibrated SWAT model run on the Flint Creek Basin that discharges to the Clarks Fork River near Drummond, MT. Comparing just those land uses that the two basins have in common (alfalfa/hay, rangeland, evergreen forest, barley, spring wheat, and urban development) the sediment loading rates were similar. The average sediment load rates for the common land uses in the Yellowstone Basin and Flint Creek Basin indicates the Yellowstone sediment loading rates are reasonable and consistent with the calibrated model and therefore provide a good tool for estimating anthropogenic contributions of sediment to the Yellowstone River.

Table 4-2. HAWQS Annual Estimate of Arsenic Runoff from Land Uses Due to Anthropogenic Effects

Region	HAWQS Anthropogenic (Existing Condition) Sediment Load (t/yr)	HAWQS Nonanthropogenic Condition Sediment Load (t/yr)	HAWQS Sediment Load Due to Anthropogenic Land Uses (t/yr)[1]	Annual Anthropogenic Arsenic Load (kg/yr)[2]
Yellowstone R. from MT/WY border to Mill Ck.	15,193.58	14,330.92	862.66	7.65
Yellowstone R. from Mill Ck. to Boulder R.	38,708.2	24,875.7	13,832.4	133.70
Yellowstone R. from Boulder R. to Stillwater R.	22,584.7	19,444.7	3,140.0	24.82
Yellowstone R. from Stillwater R. to Clarks Fork Yellowstone	40,397.6	23,095.1	17,302.5	117.93
Yellowstone R. from Clarks Fork Yellowstone to Bighorn R.	53,240.3	11,607.9	41,632.5	364.48
TOTAL	**170,124.36**	**93,354.29**	**76,770.06**	**648.58**

[1]Calculated by subtracting nonanthropogenic condition load from existing condition load.
[2]Calculated by using average soil concentrations for each HUC 10 multiplied by the sediment load due to anthropogenic conditions.

Table 4-3. Anthropogenic Arsenic Contribution to Yellowstone River from Runoff (ROA)

Month	MT/WY Border to Mill Ck.	Mill Ck. to Boulder R.	Boulder R. to Stillwater R.	Stillwater R. to Clarks Fork Yellowstone	Clarks Fork Yellowstone to Bighorn R.
	kg/mo	**kg/mo**	**kg/mo**	**kg/mo**	**kg/mo**
October	0.16	2.07	1.21	4.13	5.09
November	0.10	5.94	0.50	3.57	7.75
December	0.02	9.28	0.87	6.18	23.84
January	0.00	8.50	0.72	3.53	12.20
February	0.02	6.03	0.79	4.15	10.15
March	0.62	18.62	1.32	18.76	49.40
April	2.50	30.68	0.80	20.19	12.06
May	2.20	17.43	5.51	25.42	90.22
June	2.40	29.26	7.68	19.77	45.18
July	0.00	0.91	1.16	0.93	4.00
August	0.00	1.68	0.28	0.51	13.62
September	0.00	3.30	3.99	10.79	90.97
ANNUAL (KG/YR)	8.02	133.70	24.82	117.93	364.48

[1] *Percent of total arsenic in the Yellowstone River.*

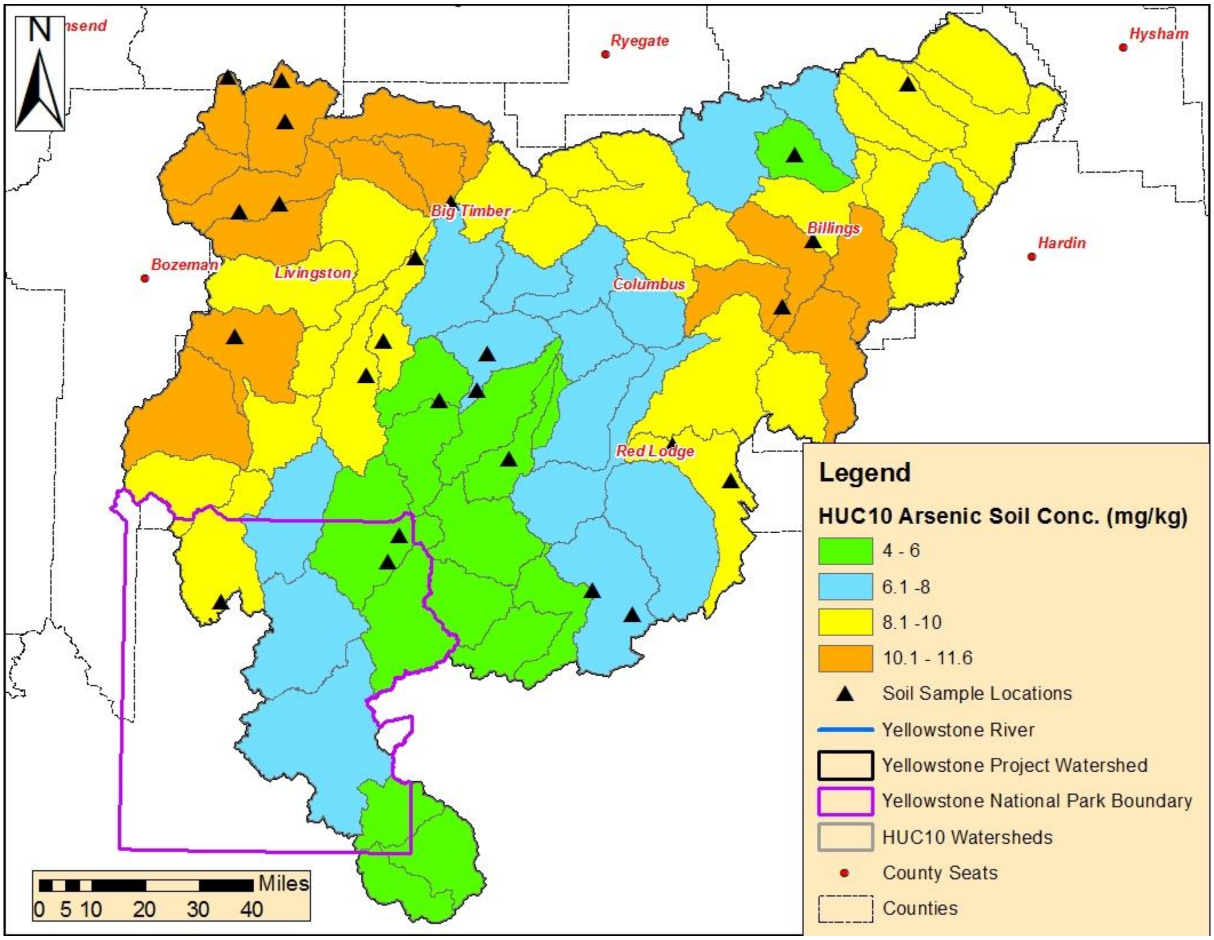


Figure 4-7. Extrapolated Soil Arsenic Concentrations for the Yellowstone Watershed (Smith et al., 2014)

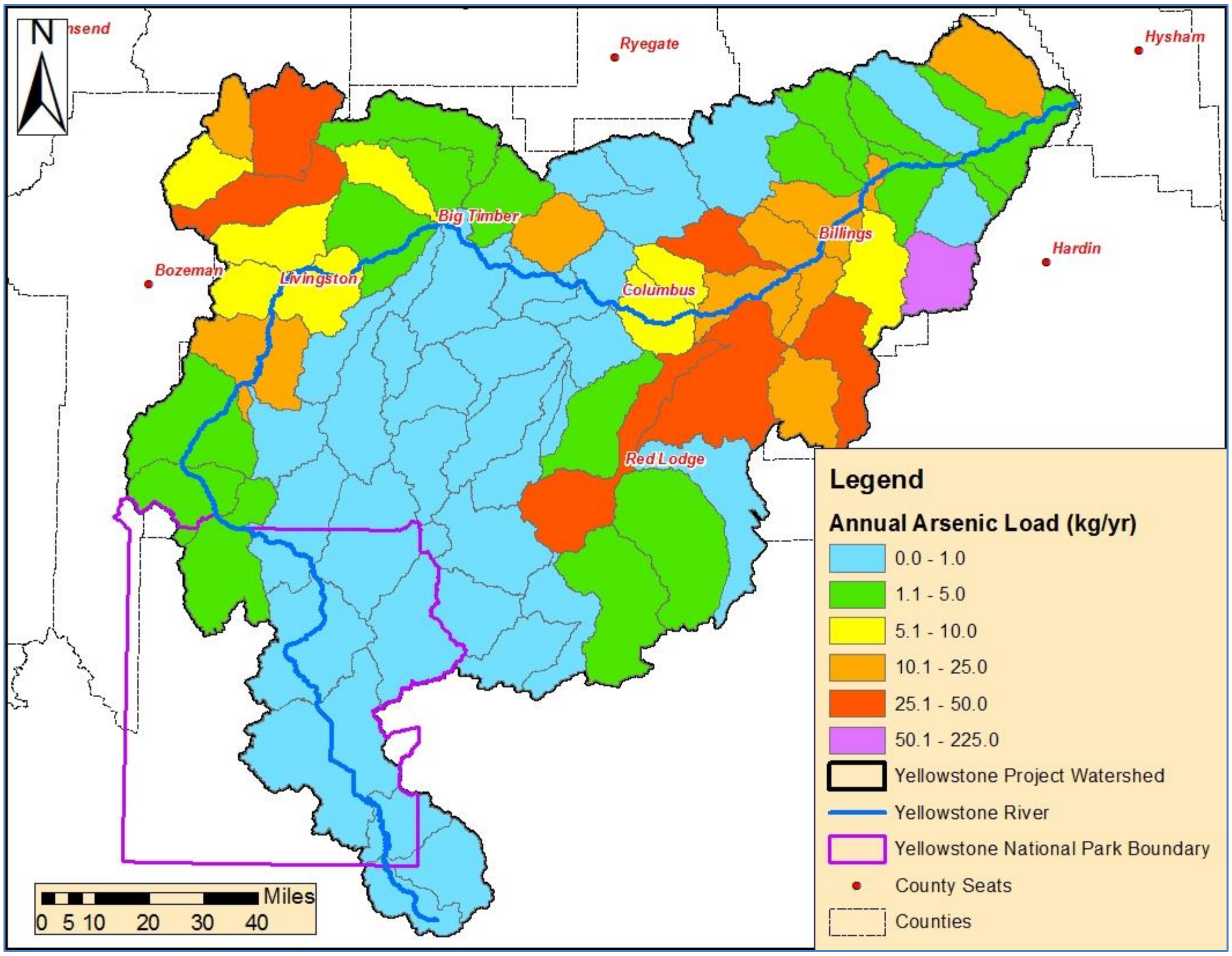


Figure 4-8. Arsenic Loads from HAWQS Model for Yellowstone Watershed

4.4 GROUNDWATER

Groundwater concentrations are shown in **Figure 4-9** (DEQ, 2016b). The groundwater data shows most samples are below the water quality standard (10 µg/L), with several areas of noticeably higher concentrations. Two areas near the northern border of YNP have elevated arsenic concentrations, these are located near Bear Creek and LaDuke Hot Springs. The Bear Creek drainage includes a mining tailings pile that has high arsenic concentrations that is contributing arsenic to Bear Creek (see **section 4.2.3**) and is likely also contributing to groundwater as the groundwater data indicates. The elevated arsenic in the groundwater near LaDuke hot springs is a naturally occurring geothermal spring with total arsenic concentrations measured as high as 23 µg/L. The groundwater in the Hailstone basin area north of Columbus also has numerous elevated arsenic concentrations. The Hailstone area has naturally high heavy metal concentrations due to evaporation in this hydrologically closed basin. Because it is a closed basin it does not contribute surface water or groundwater to the Yellowstone River and therefore was not accounted for in this project. The cluster of elevated groundwater arsenic concentrations near Columbus are related to the Mouat Industries federal superfund site which was evaluated and included as an anthropogenic source of arsenic to the Yellowstone River (see **section 4.2.3**). Two other isolated wells that are not near any known anthropogenic arsenic sources contained elevated arsenic concentrations. The first is a domestic well near Red Lodge that is completed in the Lance formation known to contain trace metals including arsenic (USGS, 1999). The second is a shallow monitoring well on the Montana State University Agricultural Research Center near Huntley. The arsenic concentration in the well increased from less than 10 µg/L in 2002 to 62 µg/L in 2011; however, many other parameter concentrations increased between 2002 and 2011 including nitrate from 0.8 to 4.5 mg/L. The increase of nitrate and other parameters indicate the elevated arsenic concentration is due to land management practices at the center. However, the extent of the elevated arsenic is likely minimal and not a significant source of arsenic to the Yellowstone River since a similar monitoring well 2,500 to the west of this well had a low arsenic concentration of 6.9 µg/L on the same date in 2011.

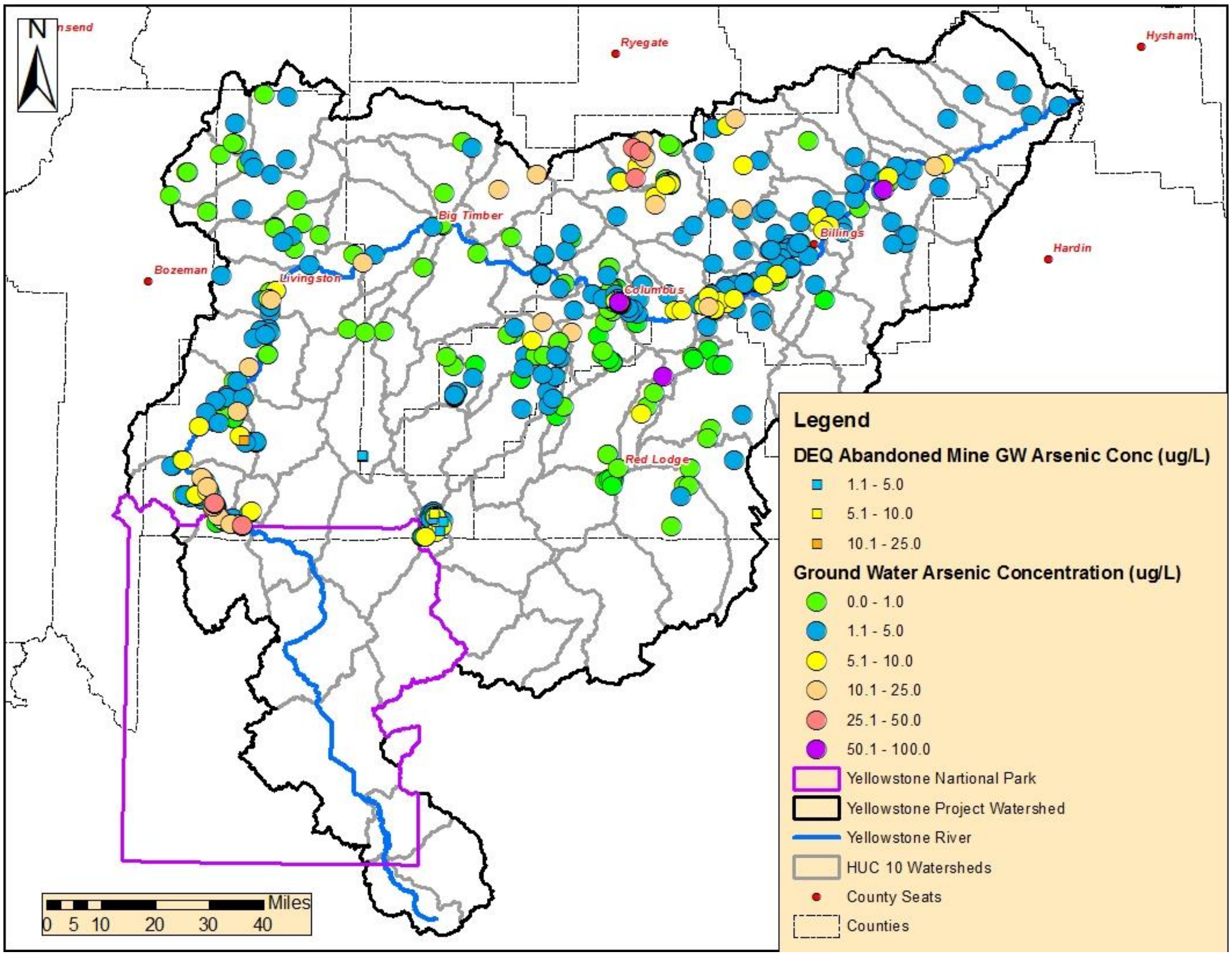


Figure 4-9. Groundwater (1971-2018) Arsenic Concentrations in Yellowstone Watershed (DEQ, 2016d)

Based on the available data, the average arsenic groundwater concentrations in the Upper Yellowstone Basin is 4.94 mg/L, which is similar to the statewide average of 4.44 mg/L. However, the median value in the Upper Yellowstone Basin is 2.50 mg/L, which is over double the statewide median of 1.07 mg/L. The higher median values are likely due to the naturally higher groundwater concentrations north of YNP and in the Hailstone basin area.

4.5 TRIBUTARIES

Major tributaries were determined based on their low flow volumes (defined as flows from August through April). Many of the tributaries had existing USGS flow gages or had been gaged for a historic period of record. The tributaries that were considered major had average low flows greater than 5 percent of the 7Q10 low flow of the Yellowstone River. The major tributaries to the Yellowstone River in the modeled area are the Gardner, Shields, Boulder, Stillwater, Clarks Fork of the Yellowstone, and the Bighorn Rivers.

At least 12 paired flow and concentration samples were collected near the mouth of the major tributaries with seasonal and annual representation. All the major tributaries had USGS gages with daily flow measurements. The data was used for total mass load analysis using the methodologies described in **Section 2.3.2**. The anthropogenic contribution to the Yellowstone River from the tributaries is captured in the runoff loads. The anthropogenic arsenic loads from runoff events flow directly into the mainstem or into tributaries that eventually flow into the Yellowstone River.

Not all minor tributaries in the Yellowstone River watershed were measured for flow or concentration. These tributaries either (1) had no historical record and there was no evidence to suggest they had a potential anthropogenic source or (2) may not have been sampled due to private land access issues or because their contributing area was so small that it was impractical to sample them. Tributaries that were directly measured are shown in **Figure 4-10**. The Yellowstone River basin and tributary area modeled is 96,690 square miles. The total accounted for area (i.e. tributary contributions that were directly measured) is 87 percent and the unaccounted-for area with limited or no data is 13 percent of the total area as shown in **Table 4-4** and **Figure 4-10**.

Unaccounted-for drainages still contribute total arsenic load to the Yellowstone River and were included in the mass balance. For each of the locations on the Yellowstone River (**Table 4-4)**, a ratio of unaccounted for and accounted for drainage area was developed. This ratio was then multiplied by the total arsenic load contribution of the accounted for drainages within the three Yellowstone segments to provide an arsenic load estimate for the unaccounted-for drainages. Since the accounted for and unaccounted-for area within the Yellowstone have similar physiographic, land use, and geologic conditions, this ratio method can provide a reliable estimate for the total arsenic load from the tributaries that have no arsenic data.

Table 4-4. Accounted and Unaccounted for Drainage Area in the Yellowstone Watershed

Location	Accounted for Area ($mile^2$)	Unaccounted for Area ($mile^2$)	Ratio of Unaccounted/ Accounted	% of Drainage Area Unaccounted
MT/WY Border	6,718	0	0	0%
Mouth of Mill Creek	1,817	956	0.5	11.2%
Mouth of Boulder River	5,978	2,201	0.4	15.2%
Mouth of Stillwater River	5,996	2,218	0.4	10.8%
Mouth of Clarks Fork Yellowstone	9,675	2,442	0.3	8.1%
Mouth of Bighorn River	66,505	4,563	0.1	4.7%

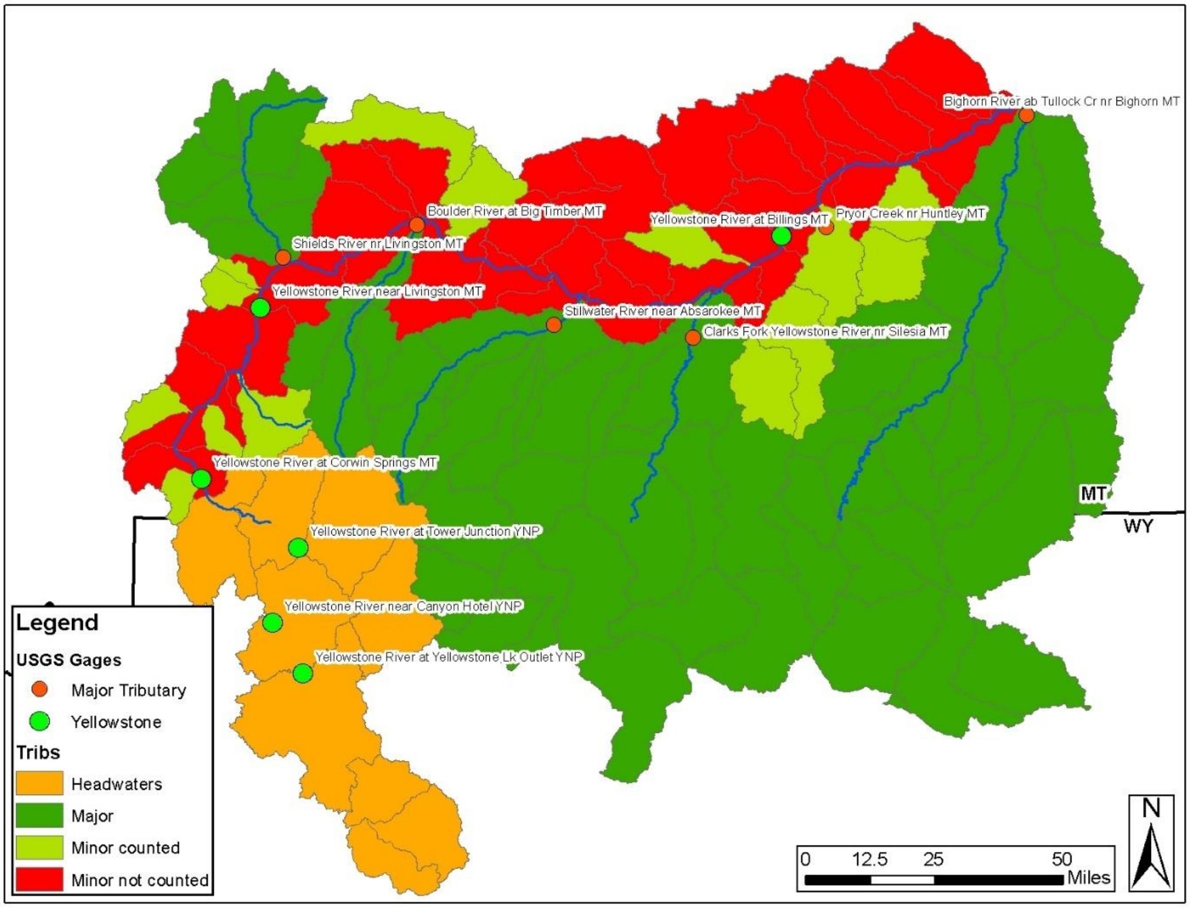


Figure 4-10. Tributaries to the Yellowstone River and Their Associated Drainage Areas

Tributary load calculations were based on presumed high and low flow conditions and the median concentrations of those flow conditions. In this area, high flow conditions were defined as those occurring from May through July, and low flow conditions as those occurring from August through April. Many of the tributaries have non-detectable arsenic concentrations and the arsenic loads for these drainages were calculated using one half of the laboratory detection limit. The calculations are in Appendix B.

The total arsenic load contribution from all the tributaries is shown monthly in **Table 4-5**. The total arsenic load includes both anthropogenic (TribA) and nonanthropogenic sources (TribN). The HAWQS model arsenic load analysis from sediment runoff estimates includes the anthropogenic land use input for all the tributaries in the Yellowstone Basin. Therefore, the tributary anthropogenic input (TribA) is included in the ROA values presented in **Table 4-3**.

The tributary arsenic load is assumed to be mainly nonanthropogenic as evidenced in the mass balance results (**Section 4.7**). The total arsenic load to the Yellowstone River from the tributaries is 8,023 kg/year. A small percentage (8%) of this load is considered anthropogenic and had already been accounted for in the runoff estimates. The total nonanthropogenic arsenic load from the tributaries is 7,376 kg/year. Annually, the total tributary arsenic load is 14% (8,023 kg) of the total arsenic load in the Yellowstone River at the mouth of the Bighorn and only 1% (647 kg) is estimated to be an anthropogenic input from the tributaries. Since the anthropogenic tributary arsenic load is such a small percentage of the total arsenic in the Yellowstone River, accounting for every arsenic contribution of all Yellowstone basin tributaries is not necessary. The method of estimating arsenic tributary loads (**Table 4-4**) of unaccounted for drainages is acceptable for the Yellowstone Basin since it is unlikely that any one tributary would contribute a significant arsenic load to the Yellowstone River.

Table 4-5. Summary of Total Arsenic Load Contribution to Yellowstone River from All Tributaries

Month	MT/WY Border to Mill Creek	Mill Creek to Boulder River	Boulder River to Stillwater River	Stillwater River to Clark Fork Yellowstone	Clark Fork Yellowstone to Bighorn River
kg/month					
October	18.6	28.7	34.8	54.9	384.0
November	18.6	28.7	34.8	54.9	384.0
December	18.6	28.7	34.8	54.9	384.0
January	18.6	28.7	34.8	54.9	384.0
February	18.6	28.7	34.8	54.9	384.0
March	18.6	28.7	34.8	54.9	384.0
April	18.6	28.7	34.8	54.9	384.0
May	60.6	180.0	148.0	288.9	433.8
June	60.6	180.0	148.0	288.9	433.8
July	60.6	180.0	148.0	288.9	433.8
August	18.6	28.7	34.8	54.9	384.0
September	18.6	28.7	34.8	54.9	384.0
kg/year					
Annual	*349.0*	*798.8*	*757.1*	*1361.2*	*4757.2*

4.6 LOADEST MODELING

The total arsenic loads were modeled for the five hydrologic segments on the Yellowstone River and are listed in **Table 4-6**.

Segments 1, 2, and 5 have existing USGS gaging stations with a minimum of twenty years of average daily flow data. There are limited active USGS gaging stations on the Yellowstone River. 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 first calculated and compared to the gaged daily data at Billings (segment 5).

Table 4-6. Yellowstone River Stations Modeled using LOADest

USGS ID	Station Description	Hydrologic Section	Latitude	Longitude	# Data (n)
06191500	Yellowstone River at Corwin Springs	1 – WY/MT Border to Mill Creek	45.11212	-110.794	25
06192500	Yellowstone River near Livingston	2 – Mill Creek to Boulder Creek	45.59721	-110.566	37
N/A	Yellowstone River near Big Timber	3 – Boulder Creek to Stillwater River	45.63472	-109.262	18
N/A	Yellowstone River near Laurel	4 – Stillwater River to Clarks Fork Yellowstone River	45.65411	-108.760	19
06214500	Yellowstone River at Billings	5 – Clarks Fork Yellowstone River to Bighorn River	45.80012	-108.468	28

The formula was:
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 a temporal iteration value. In this case, the iteration is reported flow by day to account for travel time. For example, 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 (**Figure 4-11**). 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 seems to overpredict and under predict winter flows equally). This is 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*$_i$

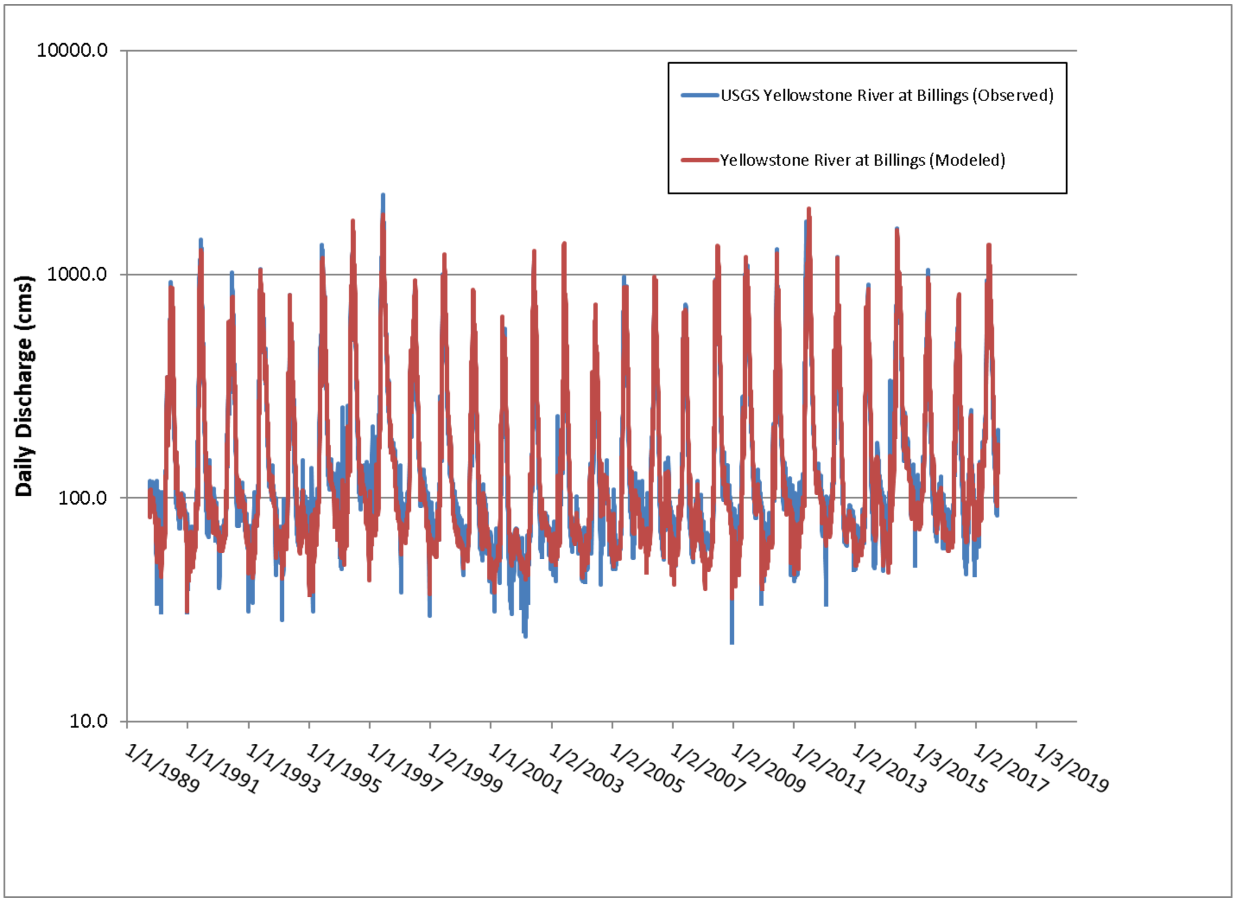


Figure 4-11. Comparison of USGS gage Yellowstone River at Billings and the Addition-By-Parts Calculation

The input files to LOADest include daily flow data and synoptic concentration data from 1997 to 2017. For each station (**Table 4-6**) there are greater than 19 concentration and flow data points. The model only requires a minimum of 12 paired concentration and flow data points to calibrate.

Modeling statistics are presented in **Table 4-7**; absolute relative error, Nash-Sutcliffe model efficiency coefficient (NSE) and the coefficient of determination (R^2). The absolute relative error is the absolute difference between the observed and simulated values, divided by the observed value. In other words, it measures the relative error between the simulated and observed time series. The Nash-Sutcliffe model efficiency coefficient (NSE) is a measure of how well the simulated data predicts the observed data. The closer the NSE is to 1, the better the fit. R^2 is a statistical measure of how close the data are to the fitted regression line and measures how well the regression line approximates the real data points. Like the NSE, the closer the R^2 to 1, the better the approximation. The R^2 value is consistent for all hydrologic segments suggesting there is similar variance in the data for all five segments. Based on acceptable ranges used by the USGS (Anderson and Rounds, 2010), the modeling statistics are acceptable for all five stations.

Model output files are located in **Appendix C**. The model outputs daily and monthly loads with estimated concentration data. A summary of the monthly modeled loads is shown in **Figure 4-12**. The monthly results are also listed in **Table 4-8**. These monthly loads are the median of the model estimated loads and include both anthropogenic and nonanthropogenic sources of arsenic.

Table 4-7. LOADEST Arsenic Load Model Run Statistics

Hydrologic Segment	Mean Absolute Relative Error %	NSE	R^2
1 – WY/MT Border to Mill Creek	8.53	0.96	0.96
2 – Mill Creek to Boulder River	5.03	0.96	0.96
3 – Boulder River to Stillwater River	15.49	0.96	0.96
4 – Stillwater River to Clarks Fork Yellowstone River	8.62	0.99	0.96
5 – Clarks Fork Yellowstone River to Bighorn River	12.06	0.96	0.97
USGS Acceptable Range	*0 - 50*	*0.6 – 1.0*	*0.6 - 1.0*

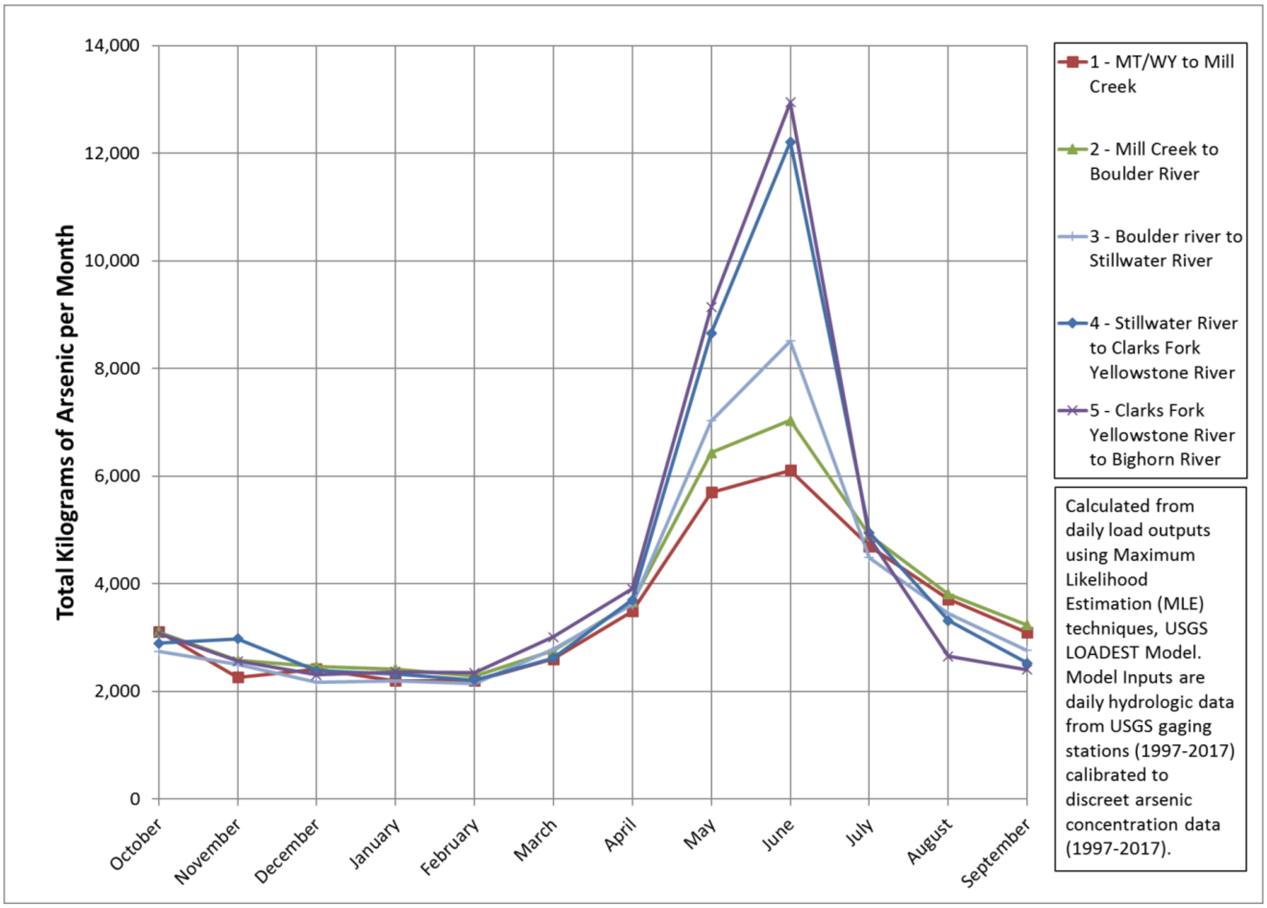


Figure 4-12. LOADEST Output of Median Monthly Arsenic Load

Table 4-8. LOADEST Estimated Median Monthly Arsenic Load

Month	1 – WY/MT 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
kg/month					
October	3,096	3,087	2,811	2,814	3,024
November	2,244	2,548	2,577	2,801	2,496
December	2,399	2,436	2,221	2,277	2,225
January	2,177	2,390	2,231	2,221	2,298
February	2,182	2,262	2,189	2,119	2,279
March	2,580	2,716	2,838	2,505	2,876
April	3,466	3,599	3,690	3,551	3,797
May	5,633	6,350	7,275	8,404	8,910
June	6,044	6,942	8,978	11,355	12,752
July	4,635	4,843	4,554	4,540	4,763
August	3,695	3,786	3,509	3,088	2,593
September	3,077	3,209	2,798	2,335	2,248
kg/year					
Annual	41,229	44,167	45,671	48,009	50,260

4.7 Mass Balance Results

The modeling results and other calculated anthropogenic and nonanthropogenic loads were used in the mass balance equations. The mass balance equation was used to calculate the final nonanthropogenic condition of the Yellowstone River. The mass balance equation that defines the Nonanthropogenic Arsenic Load (NAL) is shown in ***Equation 6*** **(Section 2.4)**.

EQUATION 6: **NAL = TAL - PSL - GWA - TribA - ROA**

The mass balance results are presented using the median monthly results of nonanthropogenic and anthropogenic loads. The monthly total arsenic loads (TAL), point source loads (PSL), and anthropogenic run off loads (ROA) were calculated in previous sections and are used in the equation to calculate NAL. As discussed in previous sections, the anthropogenic tributary load (TribA) is accounted for in the ROA. The groundwater anthropogenic contribution (GWA) was zero for all segments with the exception of the last hydrologic segment **(Section 4.4)**. Thus, the equation is rewritten and presented as ***Equation 8***.

EQUATION 8: **NAL = TAL - PSL – ROA - GWA**

The median monthly NAL is presented in **Table 4-9**. An annual summary for the five segments is presented in **Table 4-10**.

Table 4-9. Median Monthly Arsenic Load Summary for Yellowstone River

Month	Median Total Arsenic Load (TAL)	Source Loads (PSL + GWA)	Anthropogenic Runoff Load (ROA)	Running Total Anthropogenic Loads (PSL + ROA + GWA)	Median Nonanthropogenic Loads (NAL)
MT/WY Border to Mill Creek (kg/month)					
October	3,114	17.3	0.2	17.5	3,096
November	2,261	17.5	0.1	17.6	2,244
December	2,417	17.5	0.0	17.5	2,399
January	2,195	17.8	0.0	17.8	2,177
February	2,201	18.7	0.0	18.7	2,182
March	2,601	19.4	0.6	20.0	2,580
April	3,489	19.8	2.5	22.3	3,466
May	5,698	62.8	2.2	65.0	5,633
June	6,109	62.5	2.4	64.9	6,044
July	4,697	61.8	0.0	61.8	4,635
August	3,712	17.2	0.0	17.2	3,695
September	3,094	17.2	0.0	17.2	3,077
Mill Creek to Boulder River (kg/month)					
October	3,107	0.5	2.1	20.1	3,087
November	2,572	0.5	5.9	24.0	2,548
December	2,463	0.5	9.3	27.3	2,436
January	2,416	0.5	8.5	26.8	2,390
February	2,287	0.5	6.0	25.3	2,262
March	2,755	0.5	18.6	39.2	2,716
April	3,653	0.5	30.7	53.4	3,599
May	6,433	0.5	17.4	83.0	6,350
June	7,037	0.5	29.3	94.6	6,942
July	4,906	0.5	0.9	63.2	4,843
August	3,805	0.5	1.7	19.4	3,786
September	3,230	0.5	3.3	21.0	3,209
Boulder River to Stillwater River (kg/month)					
October	2,832	0.0	1.2	21.3	2,811
November	2,602	0.0	0.5	24.5	2,577
December	2,250	0.0	0.9	28.2	2,221
January	2,259	0.0	0.7	27.5	2,231
February	2,215	0.0	0.8	26.1	2,189
March	2,878	0.0	1.3	40.5	2,838
April	3,744	0.0	0.8	54.2	3,690
May	7,363	0.0	5.5	88.5	7,275
June	9,081	0.0	7.7	102.3	8,978
July	4,618	0.0	1.2	64.4	4,554
August	3,529	0.0	0.3	19.7	3,509

September	2,823	0.0	4.0	25.0	2,798
Stillwater River to Clarks Fork Yellowstone River (kg/month)					
October	2,847	7.4	4.1	32.8	2,814
November	2,838	9.4	3.6	37.5	2,801
December	2,316	5.0	6.2	39.3	2,277
January	2,257	4.6	3.5	35.6	2,221
February	2,154	5.3	4.2	35.5	2,119
March	2,568	3.7	18.8	63.0	2,505
April	3,628	3.2	20.2	77.7	3,551
May	8,521	2.5	25.4	116.4	8,404
June	11,482	5.0	19.8	127.1	11,355
July	4,610	4.4	0.9	69.7	4,540
August	3,114	6.1	0.5	26.2	3,088
September	2,376	5.5	10.8	41.3	2,335
Clarks Fork Yellowstone River to Bighorn River (kg/month)					
October	3,081	19.2	5.1	57.1	3,024
November	2,560	19.2	7.8	64.4	2,496
December	2,307	18.5	23.8	81.7	2,225
January	2,363	17.3	12.2	65.1	2,298
February	2,344	18.6	10.2	64.3	2,279
March	3,007	18.4	49.4	130.8	2,876
April	3,906	19.0	12.1	108.7	3,797
May	9,135	18.9	90.2	225.5	8,910
June	12,943	18.7	45.2	191.0	12,752
July	4,855	19.2	4.0	92.9	4,763
August	2,651	18.8	13.6	58.6	2,593
September	2,399	19.2	91.0	151.5	2,248

Table 4-10. Median Annual Arsenic Load Summary for Yellowstone River

Segments	Median Total Arsenic Load (TAL)	Source Loads (PSL + GWA)	Anthropogenic Runoff Load (ROA)	Running Total Anthropogenic Loads (PSL + ROA + GWA)	Median Non-anthropogenic Loads (NAL)
kg/year					
1 - MT/WY Border to Mill Creek	41,587	349.6	8.0	357.6	41,229
2 - Mill Creek to Boulder River	44,664	6.0	133.7	497.3	44,167
3 - Boulder River to Stillwater River	46,193	0.0	24.8	522.1	45,671
4 - Stillwater River to Clarks Fork Yellowstone River	48,711	62.1	117.9	702.1	48,009
5 - Clarks Fork Yellowstone River to Bighorn River	51,551	225.0	364.5	1,291.6	50,260

5.0 CONCLUSIONS

The arsenic mass balance for the Yellowstone River is summarized in **Table 5-1**. The anthropogenic arsenic load at the Montana/Wyoming border is assumed to be zero due to the Yellowstone River watershed being almost entirely contained within Yellowstone National Park upstream of the border. From the Montana/Wyoming border to the confluence with the Big Horn River, the Yellowstone River accumulates 1,292 kg/year of anthropogenic arsenic. Most of the net gain of nonanthropogenic arsenic is due to tributary nonanthropogenic arsenic (7,376 kg/year). The remaining arsenic load (1,655 kg/year) was not accounted for, but is only 3.2 percent of the total arsenic accumulation.

Table 5- 1. Mass Balance and Nonanthropogenic Load Summary

Mass Balance	Load at Bighorn (kg/year)	% of TAL at Bighorn
1. Start: MT/WY Border	41,229	80%
2. Anthropogenic Arsenic Load	1,292	2.5%
3. Nonanthropogenic Tributary Load	7,376	14.3%
4. Unaccounted for Mass Load/Error	1,655	3.2%
5. End: Mouth of the Big Horn River (kg/year) (1+2+3+4)	51,552	100.0%
Total Nonanthropogenic Arsenic from MT/WY Border to the Confluence of the Bighorn River (5-4-2)	48,606	94.3%

The original YNP arsenic load is 80 percent of the total arsenic load at the confluence with the Big Horn River and is the primary source of the elevated arsenic concentrations in the Yellowstone River. Nonanthropogenic tributary and runoff arsenic loads accounts for an additional 14.3 percent of the total arsenic load. Therefore, the total nonanthropogenic arsenic represents at least 94.3 percent of the total arsenic load at the confluence with the Big Horn River. The remaining 5.7 percent of the arsenic load is composed of anthropogenic arsenic (2.5 percent) and unaccounted for/error (3.2 percent). Accordingly, the majority of the arsenic load is natural and anthropogenic sources account for a very minor portion of the total anthropogenic arsenic load in the Yellowstone River.

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Appendices

A. HAWQS Model

See Electronic File

B. Tributary Load Calculations

See Electronic File

C. LOADEST Model Output

See Electronic File

D. Mass Balance Calculations

See Electronic File