

**U. S. DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY**

**Geochemical Processes and Baselines for Stream Waters for
Soda-Butte-Lamar Basin and Firehole-Gibbon Basin,
Yellowstone National Park**

by

William R. Miller, Allen L. Meier, and Paul H. Briggs



Open-File Report 97-550

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*U.S. Geological Survey, DFC, Box 25046, MS 973, Denver, CO 80225

Introduction

When precipitation, as rain and snow, falls within a drainage basin, water comes into contact with rock-forming minerals and chemical weathering is initiated. Chemical weathering within a basin involves the congruent dissolution of minerals such as calcite or the transformation of minerals such as plagioclase to clay minerals. These processes release elements to the natural waters of a basin. Therefore the chemical composition of natural waters that evolved within a basin that has not been effected by anthropogenic processes, is determined by the chemical composition of rocks within the basin. The major element composition of most rock types are generally known from geologic maps, and therefore the major element composition of natural waters of a basin can be predicted. This is not true with respect to trace elements which can vary two or more orders of magnitude within similar rock types.

This background geochemistry of the natural waters of a basin can be modified by input from anthropogenic processes such as nuclear fallout or the oxidation of mining wastes. There is probably no place in the world in which the natural background composition of waters of an area has not been modified to some extent by anthropogenic processes. This anthropogenic input is always superimposed on the natural background geochemistry. But areas can be selected, such as National Parks, which are only minimally effected by anthropogenic input and an approximation of the natural background geochemistry can be determined. This information is useful for an understanding of the processes controlling the chemical composition of waters of a basin. In addition, because stream water geochemistry is sensitive to changes in the environment, by monitoring stream water geochemistry over time, future changes in the environment within the basin can be determined.

The purpose of this study is to determine the natural geochemical baseline of selected stream waters in Yellowstone National Park (fig. 1), for one period of time, for a wide range of major and minor elements.

Study areas

Geochemical baselines of stream waters were determined for two study areas. The first study area (fig. 2) is the Soda Butte River to the Lamar River and the Lamar River to the Yellowstone River (referred to as Soda Butte-Lamar basin). This area was selected because of present concerns of possible environmental problems associated with mine tailings along Soda Butte Creek above Cooke City, Montana, historic mine workings in upper Miller Creek, and future concern of the proposed development of the New World gold mine near the Park boundary. Baselines were established so that future changes in the stream water geochemistry can be monitored in the future. The second study area (fig. 3) is the Firehole River and Gibbon River basins (referred to as the Firehole- Gibbon basin). This area was selected to evaluate the effects of geology and geothermal inputs on the composition of the stream waters in this area.

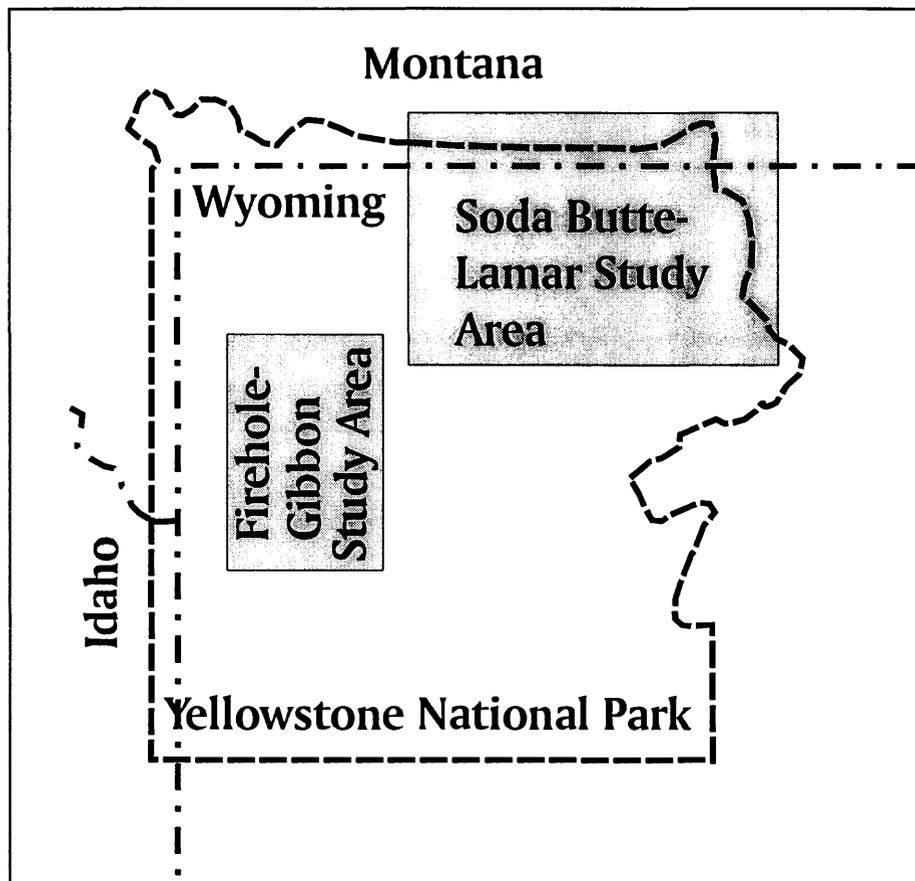


Figure 1. Map showing location of Soda Butte-Lamar Basin and Firehole-Gibbon Basin

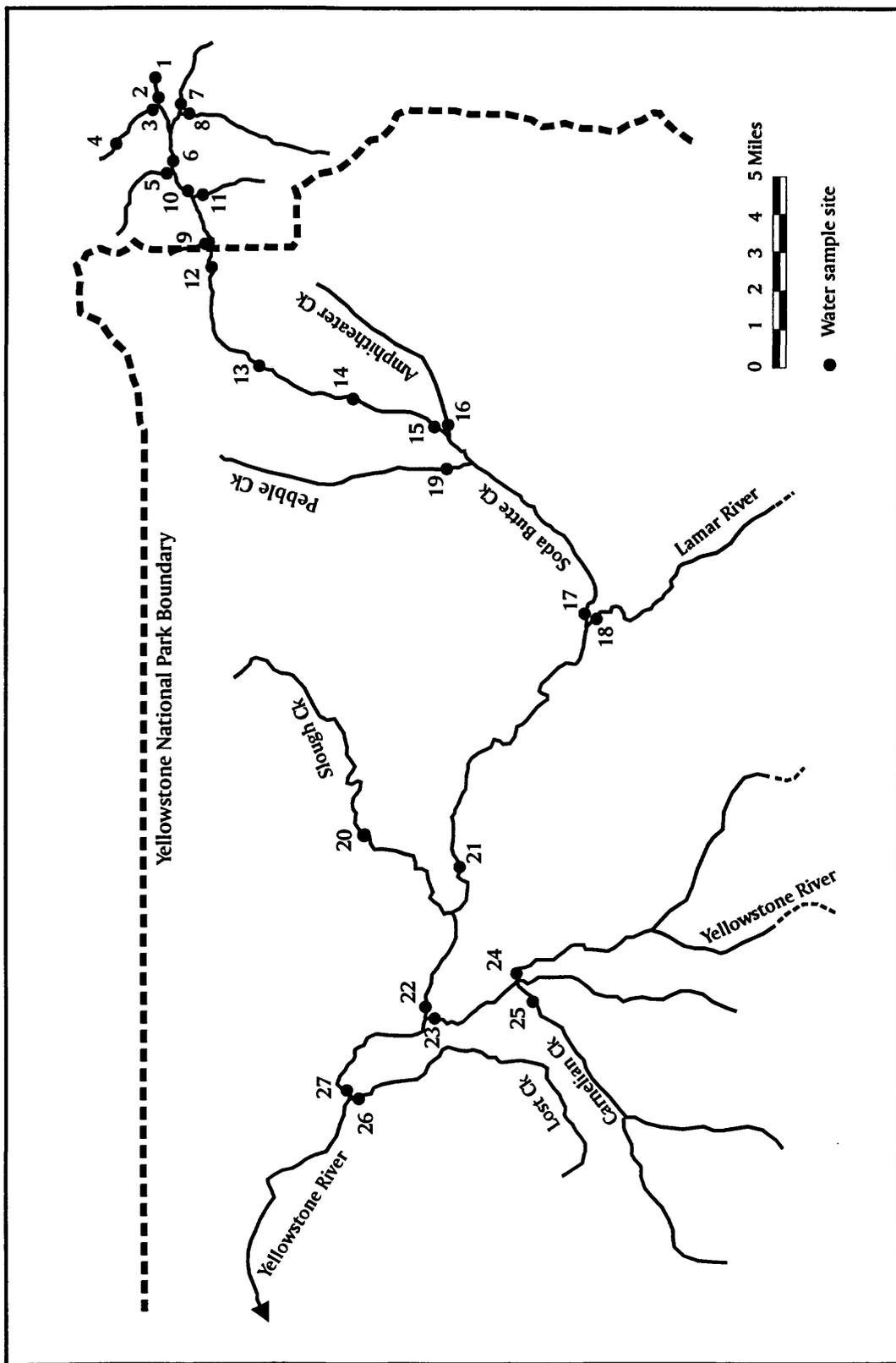


Figure 2 . Map showing location of water sample sites in the Soda Butte Creek - Lamar River basin.

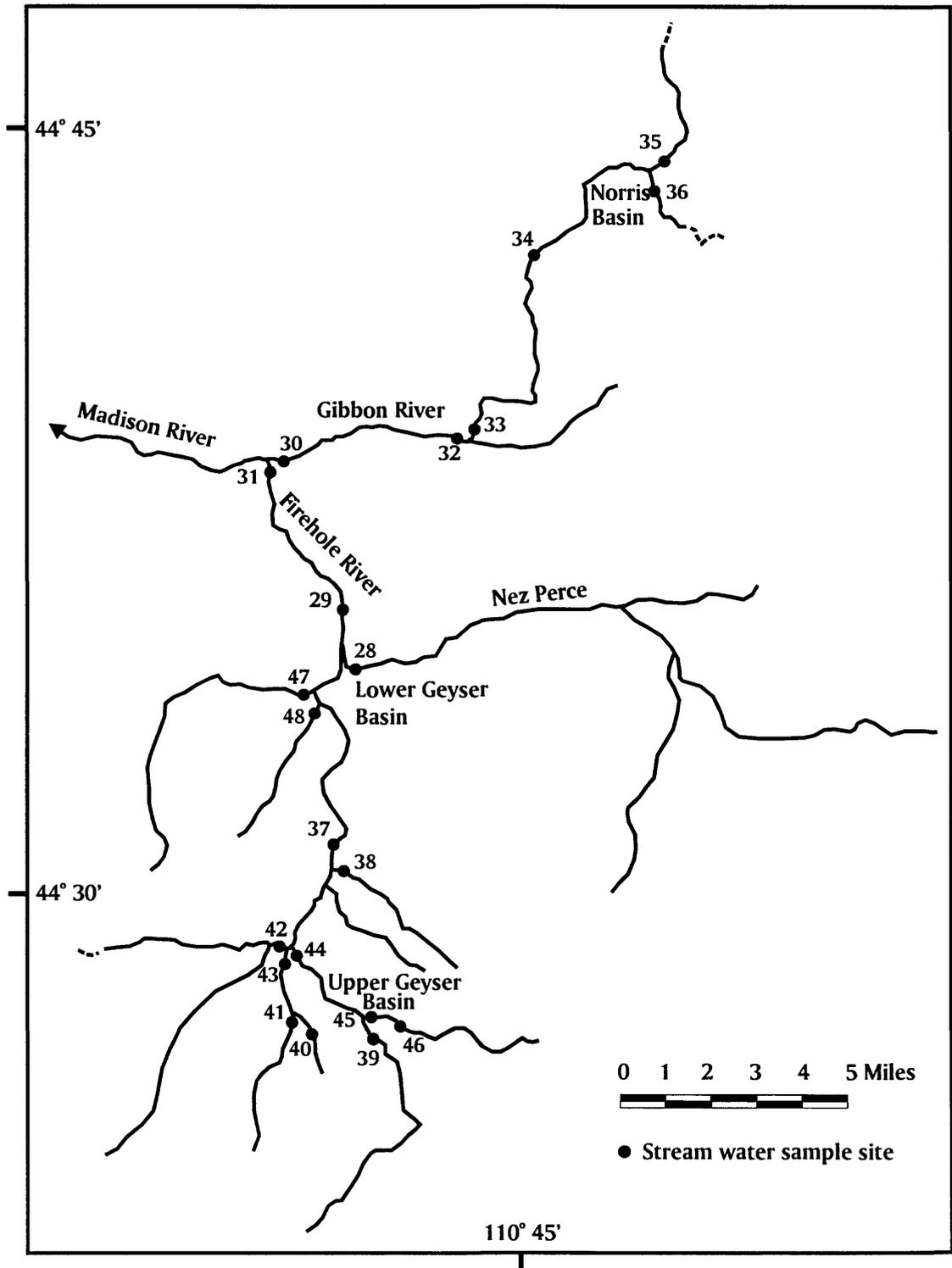


Figure 3. Map showing location of water sample sites in the Firehole-Gibbon basin, Yellowstone National Park

Currently, a stream sediment baseline survey is currently being carried out at most of the sites in this report by Maurice Chaffee of the U.S. Geological Survey.

Yellowstone National Park lies above a hot spot in the earth's crust that has been volcanically active for the last 2.2 million years (Smith and Christiansen, 1980). The dominant feature in the Park is the volcanic Yellowstone Plateau which is composed predominately of rhyolite. Numerous investigators have described the geology of Yellowstone Park. More recent summaries include Christiansen (1984), Smith and Braile (1984), and Fournier and Pitt, (1985).

The plateau is surrounded by mountains on the north, east, and south. The magmatic-hydrothermal system at Yellowstone National Park is responsible not only for the numerous geysers and hot springs, but also for the alteration and mineralization of the volcanic rocks reflected in locations such as the Grand Canyon of the Yellowstone. This magmatic-hydrothermal system is probably responsible for the high concentrations of elements such as As and F that are reported in studies such as Thompson (1979) and this study.

Many investigators have studied hot springs and geysers beginning with Gooch and Whitfield (1888) but fewer studies have looked at the chemistry of stream waters. Previous studies of water chemistry in Yellowstone National Park are summarized in Thompson (1979). This study determines the geochemical baselines for stream waters at 48 sites for 64 elements, many of which have never been documented before.

Field and Laboratory Methods

Samples of water were collected from 48 stream sites during September 5 - 11, 1996 . During this time the weather was stable and no precipitation occurred. Samples were collected by width and depth integration (Edwards and Glysson, 1988) except site Y27, the Yellowstone River. It was not possible to wade the river at this site, but a single sample was collected below rapids where the river channel narrowed. Temperature, pH, and conductivity were measured at the site. An Orion model 250 pH meter was used with an Orion glass electrode with a Ag/AgCl junction. The conductivity was measured using an Orion model 120 conductivity meter. Samples were collected into high-density polyethylene acid-washed bottles. For the dissolved cation analyses, a 60-ml sample was filtered through a 0.45 μm -membrane filter and acidified with ultrapure reagent-grade Ultrex nitric acid to $\text{pH} < 2$. A 125-ml sample was filtered but not acidified for anion analyses and a 250-ml raw sample was collected for alkalinity measurement. The samples were stored in an ice chest and later in a refrigerator and kept cool until analyzed.

Upon return to the laboratory, alkalinity as HCO_3^- , was determined by titration with H_2SO_4 using Gran's plot technique (Orion Research, Inc., 1978). The anions were analyzed by Water Resource Division (WRD) by W. D'Angelo, analyst. Sulfate and chloride concentrations were determined by ion chromatography (IC) (Fishman and Pyen, 1979), nitrite + nitrate concentrations by colorometric technique, and fluoride by ion-specific electrode (Table 1).

Cations, shown in Table 1, were analyzed by inductively coupled plasma - atomic emission spectrometry (ICP-AES) or inductively coupled plasma - mass spectrometry (ICP-MS). Duplicate water samples, blank samples, and WRD standard reference waters were analyzed with each data set. Both precision and accuracy were acceptable by the two methods. Comparisons of chemical analyses of duplicate samples at the same site for selected elements and species are shown in Table 2. Elements which were below analytical detection for all the samples and the level of detection are shown in Table 3.

Soda Butte - Lamar Basin Study Area

This study area (fig. 2) is underlain mostly by Tertiary andesitic-composition rocks. Minor occurrences include basaltic-composition rocks, Proterozoic gneisses and schists, and Paleozoic limestones, dolomites, shales, and sandstones (Taylor and others, 1989). The occurrence of carbonate rocks and to a lesser extent, basaltic and andesitic-composition rocks plays a large role in buffering the stream waters, particularly the pH. Based on the composition of the underlying rocks, the stream waters in this study area should have good buffering capacities.

The Soda Butte Creek and Lamar River valleys were the site of Pinedale glaciation which flowed down valley from the north. Pinedale glaciation occurred 70,000 to 12,000 years ago (Pierce, 1979). Vegetation is predominately lodgepole pine with grasslands and sage brush in the valleys. Precipitation ranges up to over 50 inches at the higher elevations to less than 16 inches along Yellowstone River in the northwestern part of the study area (U.S. Dept. Agriculture, 1984). Prevailing winds are from the west and large storms that bring most of the rain and snow are from the Pacific Ocean to the west (Eversman and Carr, 1992).

Stream water samples were collected from 27 sites during September 5-8, 1996 (fig. 2). The weather was stable and no precipitation occurred during this time. Stream flow was low but slightly above base flow for September, 1996 (Smalley and others, 1997). The stream sampling began in the upper Soda Butte Creek above Cooke City, Montana, and followed Soda Butte Creek into the Park to the Lamar River and the Lamar River to the Yellowstone River. The chemical analyses of the 27 stream waters are shown in Table 4. The quality of the waters is excellent. The pH values range from 7.35 to 8.74 with a mean of 8.24. Conductivity ranged from 73 to 275 $\mu\text{S}/\text{cm}$ with a geometric mean of 171 $\mu\text{S}/\text{cm}$. The waters can be classified by dominant cation and anion. Twenty-two of the stream waters are Ca^{2+} - HCO_3^- dominant and the remaining 5 are Na^+ - HCO_3^- dominant waters. The concentrations of elements that may be a concern for health are all very low particularly for Cu, Zn, As, Mo, and U. Alkalinity, as HCO_3^- , ranges from 31 to 159 mg/l with a geometric mean of 83 mg/l. These values indicate that the stream waters are well buffered probably because of the carbonate rocks that occur in the upper part of the basin. The alkalinity decreases in the lower reaches of the basin (sites Y23, 24, 25, and 27) probably because of the input of lower pH waters from geothermal springs. Cl^- and F^-

Table 1. Method of analytical detection for elements in stream waters from Yellowstone National Park and vicinity

| ICP-AES | ICP-MS | | IC |
|---------|--------|----|---------|
| Ca | Li* | Cs | SO4 |
| Mg | Be | La | Cl |
| Na | Al* | Ce | F |
| K | Sc | Pb | NO2+NO3 |
| Si | Ti | Nd | |
| Al* | Co | Sm | |
| B | Ni | Eu | |
| Ba | Cu | Tb | |
| Fe | Zn | Gd | |
| Li* | Ga | Dy | |
| Mn | Ge | Ho | |
| P | As | Er | |
| Sr | Se | Tm | |
| V | Rb | Yb | |
| | Y | Lu | |
| | Zr | Hf | |
| | Nb | Ta | |
| | Mo | W | |
| | Ag | Au | |
| | Cd | Tl | |
| | In | Pb | |
| | Sn | Bi | |
| | Sb | Th | |
| | Te | U | |

* These elements were determined by ICP-MS except for high concentrations which were determined by ICP-AES

Table 2. Comparison of selected elements or species of duplicate samples collected at the same site.
All elements or species are in ppb except Ca and Si which are in ppm.

| Duplicate Pair | Ca | Si | Al | Cu | Zn | Mo | As | W | U |
|----------------|-----|-----|------|------|------|-----|------|-------|------|
| Y02 | 38 | 4 | 2 | 0.5 | 0.60 | 0.1 | <0.5 | <0.05 | 0.13 |
| 201 | 36 | 3.9 | 2 | 0.6 | <0.5 | 0.1 | <0.5 | 0.54 | 0.1 |
| Y14 | 33 | 6.4 | 4 | 0.7 | <0.5 | 0.6 | 0.8 | <0.05 | 0.22 |
| 203 | 33 | 6.6 | 2 | 0.6 | <0.5 | 0.7 | 0.9 | 0.07 | 0.22 |
| Y30 | 8.4 | 34 | 0.23 | 1.4 | 1.4 | 7.9 | 74 | 4.5 | 1.2 |
| 205 | 8.3 | 34 | 0.24 | 1.3 | 1.3 | 8.2 | 76 | 4.4 | 1.2 |
| Y40 | 5 | 29 | 11 | <0.5 | <0.5 | 2.6 | 23 | 1.1 | 0.15 |
| 207 | 4.9 | 29 | 11 | <0.5 | <0.5 | 2.7 | 24 | 1.2 | 0.16 |

| Duplicate Pair | F | Cl | SO4 | NO2+NO3 |
|----------------|------|-----|-----|---------|
| Y05 | <0.1 | 0.1 | 5.9 | <0.02 |
| 202 | <0.1 | 0.1 | 5.9 | <0.02 |
| Y30 | 4 | 25 | 15 | 0.07 |
| 206 | 3.8 | 25 | 15 | 0.07 |
| Y40 | 3.7 | 7 | 2.6 | <0.02 |
| 208 | 3.7 | 7 | 2.7 | <0.02 |

Table 3. Elements in stream waters in which all samples were below level of detection, Yellowstone National Park and vicinity

| Element | Lower level of analytical detection in ppb |
|---------|--|
| Ag | < 0.05 |
| Cd | < 0.1 |
| Co | < 0.5 |
| Cr | < 1 |
| Ni | < 1 |
| Ti | < 2 |
| Sc | < 10 |
| Zr | < 0.1 |
| Se | < 5 |
| Nb | < 0.1 |
| In | < 0.05 |
| Sn | < 1 |
| Te | < 0.5 |
| Eu | < 0.05 |
| Tb | < 0.05 |
| Ho | < 0.05 |
| Er | < 0.05 |
| Tm | < 0.05 |
| Yb | < 0.05 |
| Lu | < 0.05 |
| Ta | < 0.05 |
| Au | < 0.01 |
| Tl | < 0.1 |

Table 4. Chemical analyses of stream waters from Soda Butte - Lamar Basin

| Field No. | Temperature degree C | pH | Conductivity uS/cm | Ca ppm | Mg ppm | Na ppm | K ppm | Si ppm | Alkalinity ppm HCO3 | SO4 ppm | Cl ppm | F ppm |
|-----------|-------------------------|------|-----------------------|-----------|-----------|-----------|----------|-----------|------------------------|------------|-----------|----------|
| Y001 | 5.8 | 8.41 | 235 | 38 | 7.2 | 1.3 | 0.60 | 3.9 | 147 | 3 | 0.3 | <0.1 |
| Y002 | 8.0 | 8.40 | 239 | 38 | 6.9 | 1.3 | 0.53 | 4.0 | 137 | 6.2 | 0.2 | <0.1 |
| Y003 | 9.2 | 8.27 | 193 | 30 | 4.1 | <1 | 0.53 | 3.3 | 73 | 26 | 0.2 | <0.1 |
| Y004 | 8.0 | 8.10 | 171 | 26 | 3.8 | <1 | 0.39 | 2.5 | 159 | 22 | 0.1 | <0.1 |
| Y005 | 7.0 | 8.39 | 155 | 20 | 6.0 | 1.8 | 0.33 | 2.9 | 81 | 5.9 | 0.1 | <0.1 |
| Y006 | 9.6 | 8.31 | 177 | 23 | 5.2 | 4.5 | 0.44 | 5.6 | 87 | 9.2 | 0.3 | <0.1 |
| Y007 | 1.4 | 7.92 | 90 | 9.0 | 2.6 | 6.6 | 0.21 | 6.0 | 43 | 2 | 0.1 | <0.1 |
| Y008 | 1.7 | 7.98 | 114 | 13 | 3.7 | 5.1 | 0.26 | 6.6 | 59 | 2.3 | 0.1 | <0.1 |
| Y009 | 3.7 | 8.55 | 217 | 26 | 6.6 | 7.9 | 0.42 | 4.5 | 119 | 6.3 | 0.2 | <0.1 |
| Y010 | 4.8 | 8.35 | 214 | 28 | 6.7 | 3.3 | 0.41 | 4.7 | 102 | 11 | 0.2 | <0.1 |
| Y011 | 2.4 | 7.88 | 73 | 5.6 | 1.9 | 7.5 | 0.24 | 6.5 | 34 | 2.8 | 0.2 | <0.1 |
| Y012 | 6.0 | 8.42 | 195 | 26 | 6.1 | 4.0 | 0.42 | 4.9 | 103 | 9.3 | 0.2 | <0.1 |
| Y013 | 9.1 | 8.52 | 246 | 33 | 8.6 | 4.0 | 0.63 | 5.6 | 130 | 10 | 0.3 | <0.1 |
| Y014 | 10.3 | 8.58 | 241 | 33 | 9.0 | 3.7 | 0.79 | 6.4 | 135 | 9.4 | 0.3 | <0.1 |
| Y015 | 12.8 | 8.63 | 245 | 34 | 9.4 | 3.8 | 0.83 | 6.8 | 139 | 9.2 | 0.4 | <0.1 |
| Y016 | 7.6 | 7.96 | 82 | 6.2 | 3.5 | 3.9 | 1.8 | 14 | 41 | 2.4 | 0.2 | <0.1 |
| Y017 | 14.5 | 8.14 | 275 | 34 | 11 | 4.6 | 1.9 | 9.2 | 157 | 7.7 | 0.6 | 0.1 |
| Y018 | 15.0 | 8.00 | 161 | 11 | 4.5 | 17 | 1.1 | 12 | 58 | 12 | 0.8 | 0.3 |
| Y019 | 9.4 | 8.55 | 200 | 25 | 8.8 | 1.9 | 1.5 | 9.2 | 119 | 2.2 | 0.2 | 0.1 |
| Y020 | 8.1 | 8.23 | 205 | 27 | 7.8 | 3.0 | 1.4 | 7.9 | 120 | 3.4 | 0.5 | 0.1 |
| Y021 | 9.3 | 8.34 | 218 | 22 | 7.9 | 12 | 1.5 | 11 | 110 | 10 | 0.7 | 0.2 |
| Y022 | 10.3 | 8.74 | 207 | 22 | 7.6 | 9.6 | 1.6 | 10 | 115 | 8.6 | 0.7 | 0.2 |
| Y023 | 13.9 | 7.60 | 144 | 6.4 | 2.6 | 16 | 2.7 | 9.7 | 37 | 15 | 8 | 0.8 |
| Y024 | 15.0 | 7.35 | 136 | 6.4 | 2.7 | 17 | 2.5 | 10 | 35 | 15 | 7.9 | 0.8 |
| Y025 | 11.8 | 8.12 | 81 | 7.2 | 2.4 | 6.3 | 1.3 | 14 | 31 | 1.9 | 0.6 | 0.7 |
| Y026 | 12.3 | 8.62 | 238 | 25 | 8.2 | 14 | 2.0 | 14 | 128 | 11 | 1.8 | 0.5 |
| Y027 | 14.5 | 8.04 | 148 | 8.0 | 3.1 | 15 | 2.9 | 9.8 | 42 | 14 | 7.3 | 0.8 |

| NO2+NO3 ppm | B ppb | Ba ppb | Fe ppm | Mn ppb | P ppb | Sr ppb | V ppb | Li ppb | Be ppb | Al ppb | Cu ppb | Zn ppb | Ga ppb |
|----------------|----------|-----------|-----------|-----------|----------|-----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|
| <0.02 | <10 | 52 | <0.02 | <1 | <50 | 97 | <1 | 0.8 | <0.2 | 3 | 0.6 | <0.5 | <0.5 |
| <0.02 | <10 | 46 | <0.02 | 1.4 | <50 | 110 | <1 | 0.7 | <0.2 | 2 | 0.5 | 0.6 | <0.5 |
| <0.02 | <10 | 29 | <0.02 | <1 | <50 | 88 | <1 | <0.3 | <0.2 | 6 | 2.6 | 1.6 | <0.5 |
| <0.02 | <10 | 22 | <0.02 | 1.5 | <50 | 75 | <1 | <0.3 | <0.2 | 6 | 4.0 | 1.3 | <0.5 |
| <0.02 | <10 | 14 | <0.02 | <1 | <50 | 88 | 1.6 | 0.5 | <0.2 | 3 | <0.5 | 1.1 | <0.5 |
| 0.06 | <10 | 17 | <0.02 | 14 | <50 | 82 | 2.8 | <0.3 | <0.2 | 4 | 0.7 | 1.2 | <0.5 |
| <0.02 | 10 | 10 | <0.02 | <1 | 63 | 60 | 4.3 | 0.4 | <0.2 | 11 | 0.7 | <0.5 | <0.5 |
| <0.02 | <10 | 4.7 | <0.02 | <1 | 60 | 49 | 2.9 | <0.3 | <0.2 | 7 | <0.5 | 2.1 | <0.5 |
| <0.02 | <10 | 10 | <0.02 | <1 | <50 | 100 | 3.8 | 1.6 | <0.2 | 2 | <0.5 | <0.5 | <0.5 |
| 0.06 | <10 | 18 | <0.02 | 6.0 | <50 | 100 | 1.8 | 0.7 | <0.2 | 3 | 0.6 | <0.5 | <0.5 |
| <0.02 | <10 | 3.9 | 0.038 | <1 | <50 | 47 | 5.4 | <0.3 | <0.2 | 22 | <0.5 | <0.5 | <0.5 |
| 0.04 | <10 | 16 | <0.02 | 3.6 | <50 | 100 | 2.3 | 0.6 | <0.2 | 3 | 0.5 | <0.5 | <0.5 |
| 0.06 | <10 | 17 | <0.02 | 2.6 | <50 | 110 | 2.3 | 0.9 | <0.2 | 2 | <0.5 | <0.5 | <0.5 |
| 0.03 | <10 | 16 | <0.02 | 2.0 | <50 | 100 | 2.7 | 1.0 | <0.2 | 4 | 0.7 | <0.5 | <0.5 |
| 0.02 | <10 | 16 | <0.02 | 2.1 | <50 | 100 | 2.8 | 0.9 | <0.2 | 2 | 0.8 | <0.5 | <0.5 |
| <0.02 | <10 | 6.5 | <0.02 | <1 | 68 | 35 | 5.7 | 0.3 | <0.2 | 8 | 0.8 | <0.5 | <0.5 |
| <0.02 | 59 | 22 | <0.02 | 13 | <50 | 110 | 3.8 | 2.8 | <0.2 | 2 | 0.7 | <0.5 | <0.5 |
| <0.02 | 110 | 9.1 | 0.061 | 12 | <50 | 67 | 5.4 | 3.6 | <0.2 | 57 | 1.5 | 1.2 | <0.5 |
| <0.02 | <10 | 21 | <0.02 | <1 | <50 | 54 | 3.5 | 0.4 | <0.2 | 2 | <0.5 | <0.5 | <0.5 |
| <0.02 | <10 | 44 | 0.033 | 3.4 | <50 | 93 | 1.6 | 1.1 | <0.2 | 2 | <0.5 | <0.5 | <0.5 |
| <0.02 | 78 | 16 | 0.023 | 5.3 | <50 | 90 | 4.2 | 3.3 | <0.2 | 21 | 0.7 | <0.5 | <0.5 |
| <0.02 | 59 | 23 | 0.025 | 2.8 | <50 | 92 | 3.8 | 2.7 | <0.2 | 20 | 0.5 | 0.5 | <0.5 |
| 0.07 | 300 | 14 | 0.035 | 7.0 | <50 | 52 | 1.1 | 7.1 | <0.2 | 63 | <0.5 | 1.9 | <0.5 |
| 0.06 | 280 | 12 | 0.040 | 6.9 | <50 | 52 | <1 | 65 | <0.2 | 64 | <0.5 | 0.9 | <0.5 |
| <0.02 | 12 | 9.6 | 0.032 | 6.5 | <50 | 37 | 2.4 | 2.1 | <0.2 | 7 | <0.5 | <0.5 | <0.5 |
| <0.02 | 38 | 37 | 0.022 | 2.8 | <50 | 260 | 3.8 | 4.2 | <0.2 | 2 | 0.7 | 0.6 | <0.5 |
| 0.07 | 280 | 16 | 0.039 | 7.2 | <50 | 56 | 1.5 | 7.2 | <0.2 | 60 | <0.5 | 0.8 | <0.5 |

| Ge ppb | As ppb | Rb ppb | Y ppb | Zr ppb | Mo ppb | Sb ppb | Cs ppb | La ppb | Ce ppb | Pr ppb | Nd ppb | Sm ppb | Gd ppb |
|-----------|-----------|-----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| <0.2 | <0.5 | 0.9 | <0.1 | <0.1 | 0.1 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | <0.5 | 0.9 | <0.1 | <0.1 | 0.1 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | <0.5 | 1.2 | <0.1 | <0.1 | 0.7 | 0.12 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | <0.5 | 0.7 | <0.1 | <0.1 | 0.4 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | <0.5 | 0.2 | <0.1 | <0.1 | 0.4 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | 0.6 | 0.4 | <0.1 | <0.1 | 0.6 | 0.07 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | 0.6 | 0.2 | <0.1 | <0.1 | 0.3 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | 0.7 | 0.2 | <0.1 | <0.1 | 0.7 | 0.08 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | 0.5 | 0.3 | <0.1 | <0.1 | 0.3 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | 0.5 | 0.4 | <0.1 | <0.1 | 0.8 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | 0.6 | 0.2 | <0.1 | <0.1 | 0.9 | <0.05 | <0.05 | 0.07 | 0.08 | <0.05 | 0.07 | <0.05 | <0.05 |
| <0.2 | <0.5 | 0.3 | <0.1 | <0.1 | 0.7 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | 0.6 | 0.6 | <0.1 | <0.1 | 0.7 | 0.08 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | 0.8 | 0.7 | <0.1 | <0.1 | 0.6 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | 0.8 | 0.8 | <0.1 | <0.1 | 0.6 | 0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | 0.5 | 2.1 | <0.1 | <0.1 | 0.2 | <0.05 | <0.05 | 0.06 | <0.05 | <0.05 | 0.06 | <0.05 | <0.05 |
| <0.2 | 0.8 | 2.1 | <0.1 | <0.1 | 0.5 | 0.06 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | 1.4 | 1.7 | <0.1 | <0.1 | 1.0 | 0.05 | <0.05 | 0.07 | 0.12 | <0.05 | 0.08 | <0.05 | <0.05 |
| <0.2 | <0.5 | 1.6 | <0.1 | <0.1 | 0.2 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | <0.5 | 1.1 | <0.1 | <0.1 | 0.2 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | 1.1 | 1.8 | <0.1 | <0.1 | 0.7 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| <0.2 | 0.9 | 1.8 | <0.1 | <0.1 | 0.6 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| 0.5 | 18 | 10 | <0.1 | <0.1 | 1.4 | 0.84 | 2.0 | 0.09 | 0.18 | <0.05 | 0.10 | <0.05 | <0.05 |
| 0.5 | 17 | 9.9 | <0.1 | <0.1 | 1.3 | 0.80 | 1.9 | 0.11 | 0.17 | <0.05 | 0.10 | <0.05 | <0.05 |
| <0.2 | 0.7 | 2.9 | 0.1 | <0.1 | 0.5 | <0.05 | <0.05 | 0.06 | 0.06 | <0.05 | 0.06 | <0.05 | <0.05 |
| <0.2 | 2.5 | 2.0 | 0.1 | <0.1 | 0.8 | 0.07 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| 0.5 | 16 | 9.3 | <0.1 | <0.1 | 1.2 | 0.76 | 1.8 | 0.10 | 0.14 | <0.05 | 0.08 | <0.05 | <0.05 |

| Dy ppb | Hf ppb | W ppb | Pb ppb | Bi ppb | Th ppb | U ppb |
|-----------|-----------|----------|-----------|-----------|-----------|----------|
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.09 | < 0.05 | 0.16 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.08 | < 0.05 | 0.13 |
| < 0.05 | < 0.05 | < 0.05 | 0.06 | 0.08 | < 0.05 | 0.11 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.09 | < 0.05 | 0.12 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.08 | < 0.05 | 0.07 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.08 | < 0.05 | 0.13 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.08 | < 0.05 | 0.02 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.08 | < 0.05 | 0.02 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.08 | < 0.05 | 0.09 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.08 | < 0.05 | 0.21 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.08 | < 0.05 | 0.03 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.07 | < 0.05 | 0.19 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.09 | < 0.05 | 0.22 |
| < 0.05 | 0.15 | < 0.05 | < 0.05 | 0.08 | < 0.05 | 0.22 |
| < 0.05 | 0.07 | < 0.05 | < 0.05 | 0.08 | < 0.05 | 0.22 |
| < 0.05 | 0.05 | < 0.05 | < 0.05 | 0.09 | < 0.05 | 0.22 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.08 | < 0.05 | < 0.02 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.07 | < 0.05 | 0.24 |
| < 0.05 | 0.05 | 0.13 | < 0.05 | 0.08 | < 0.05 | 0.05 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.08 | < 0.05 | 0.14 |
| < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.09 | < 0.05 | 0.32 |
| < 0.05 | < 0.05 | 0.07 | < 0.05 | 0.08 | < 0.05 | 0.15 |
| < 0.05 | < 0.05 | 0.06 | < 0.05 | 0.08 | < 0.05 | 0.20 |
| < 0.05 | 0.07 | 2.2 | < 0.05 | 0.09 | < 0.05 | < 0.02 |
| < 0.05 | 0.05 | 2.2 | < 0.05 | 0.08 | < 0.05 | < 0.02 |
| < 0.05 | < 0.05 | 0.10 | < 0.05 | 0.07 | < 0.05 | 0.04 |
| < 0.05 | < 0.05 | 0.05 | < 0.05 | 0.07 | < 0.05 | 0.46 |
| < 0.05 | < 0.05 | 2.0 | < 0.05 | 0.08 | < 0.05 | 0.05 |

concentrations are also very low in the stream waters until input from hot springs in the lower reaches of the basin.

Possible environmental problems associated with mining and mine and mill tailings would have the most effect in upper Soda Butte Creek, above Cooke City, and Miller Creek (fig. 4). Values of pH range from 7.88 to 8.63 and alkalinity (as HCO_3^-), from 34 to 159 mg/l. Site Y11, an unnamed tributary one mile east of the Park boundary, had the lowest pH and alkalinity values in the upper basin. The most likely cause of this lower quality may be sanitary leach pads from houses upstream from the site. The water had a greenish cast and was difficult to filter. It would be prudent to determine bacteria counts in the vicinity of site Y11.

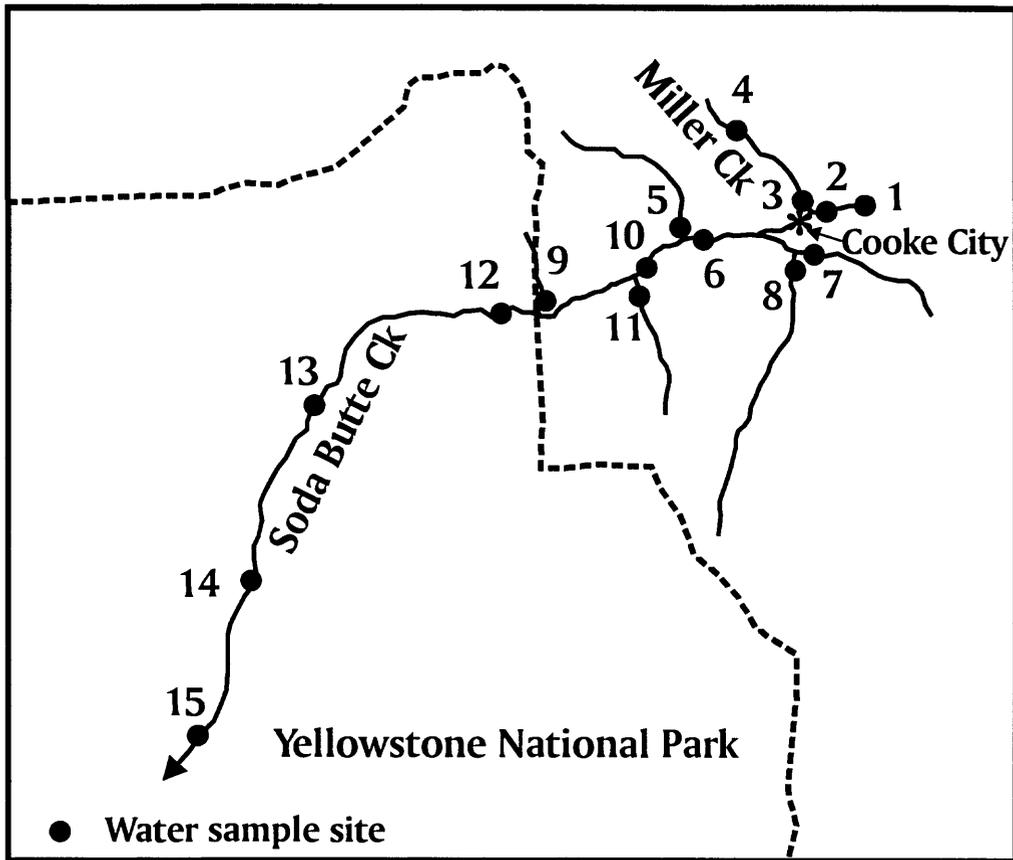
There is minimal to no effect on the chemistry of Soda Butte Creek from the presence of mine workings or tailings above Cooke City for this time of year. Cu and Zn concentrations at site Y02, along Soda Butte Creek and just downstream from the mine tailings, is 0.5 $\mu\text{g/l}$ and 0.6 $\mu\text{g/l}$, respectively. Cu concentration in Upper Miller Creek (site Y04) below historic mine workings, is 4 $\mu\text{g/l}$, but this decreased to 2.6 $\mu\text{g/l}$ and at the junction with Soda Butte Creek (site Y03). Zn concentrations at sites Y04 and Y03 is low at 1.3 $\mu\text{g/l}$ and 1.6 $\mu\text{g/l}$. The concentrations of Cu and Zn are lower than water quality standards of the Environmental Protection Agency. Other than site Y11, near Silver Gate, the water quality in the upper basin is excellent.

Gibbon - Firehole Basin Study Area

The geology of this area is different from the Soda Butte - Lamar basin. The drainage basin of the Firehole and Gibbon Rivers is underlain mostly by Quaternary rhyolitic-composition lavas and ash flow tuffs (Taylor and others, 1989). The rocks in the Soda Butte - Lamar River basin are mainly andesitic in composition with minor sedimentary and metamorphic rocks. Therefore a comparison can be made as to the effect of different rock composition on the evolution of natural waters of an area.

Vegetation is predominately lodgepole pine with grasslands and sage brush in the valleys. Precipitation ranges from greater than 60 inches at higher elevations to 30 inches along the Firehole and Gibbon River valleys (U.S. Dept. Agriculture, 1984).

Stream water samples were collected from 21 sites during September 9 - 11, 1996 (fig.3). The weather was stable and no precipitation occurred during this time. Rain began falling on the afternoon of September 11, after the sampling was completed. Stream flow was low but slightly above base flow for September, 1996 (Smalley and others, 1997). Chemical analyses of the 22 stream waters are shown in Table 5. The pH values ranged from 6.88 to 8.41 with a mean of 7.71. Conductivity ranged from 51 to 490 $\mu\text{S/cm}$ with a geometric mean of 161. Twenty of the stream waters are Ca^{2+} - HCO_3^- dominant and one is Na^+ - HCO_3^- dominant water. The concentrations of Cu, Zn, and U are low and pose no environmental problem. The concentrations of Cl⁻, F⁻, As, and W are high compared to average surface water (Table 6),



0 5 miles

Figure 4. Map showing locations of stream water samples collected in upper Soda Butte Creek

Table 5. Chemical analyses of stream waters from the Firehole - Gibbon Basin

| Field No. | Temperature | pH | Conductivity | Ca ppm | Mg ppm | Na ppm | K ppm | Si ppm | Alkalinity ppm HCO ₃ | SO ₄ ppm | Cl ppm | F ppm |
|-----------|-------------|------|--------------|--------|--------|--------|-------|--------|---------------------------------|---------------------|--------|-------|
| Y028 | 13.8 | 7.74 | 318 | 7.8 | 0.88 | 53 | 6.7 | 41 | 76 | 26 | 26 | 6.4 |
| Y029 | 14.0 | 7.99 | 411 | 5.5 | 0.50 | 74 | 6.6 | 43 | 106 | 11 | 50 | 7.2 |
| Y030 | 12.8 | 7.26 | 308 | 8.4 | 1.3 | 52 | 7.0 | 34 | 108 | 15 | 25 | 4 |
| Y031 | 16.4 | 8.25 | 410 | 5.4 | 0.50 | 74 | 6.2 | 43 | 104 | 10 | 50 | 7.2 |
| Y032 | 16.5 | 7.67 | 270 | 8.2 | 1.3 | 42 | 6.8 | 33 | 69 | 18 | 26 | 3.4 |
| Y033 | 16.8 | 7.88 | 127 | 6.6 | 1.2 | 17 | 3.5 | 28 | 51 | 1.6 | 2.9 | 4 |
| Y034 | 16.0 | 7.21 | 210 | 7.4 | 1.4 | 30 | 5.9 | 27 | 50 | 17 | 20 | 2.6 |
| Y035 | 14.0 | 6.88 | 83 | 4.8 | 0.82 | 9.8 | 2.3 | 15 | 30 | 3.9 | 2.6 | 2 |
| Y036 | 15.6 | 7.27 | 121 | 6.2 | 0.79 | 14 | 4.9 | 27 | 37 | 9.2 | 3.8 | 2.6 |
| Y037 | 15.0 | 7.94 | 227 | 4.5 | <0.5 | 40 | 4.4 | 34 | 60 | 5 | 25 | 4.9 |
| Y038 | 21.0 | 7.65 | 89 | 8.6 | <0.5 | 7.8 | 3.2 | 34 | 24 | 5.6 | 0.7 | 5.1 |
| Y039 | 9.8 | 7.27 | 80 | 3.6 | <0.5 | 9.8 | 2.8 | 21 | 17 | 2.5 | 6.7 | 2.1 |
| Y040 | 16.4 | 7.73 | 114 | 5.0 | 0.73 | 16 | 3.2 | 29 | 34 | 2.6 | 7 | 3.7 |
| Y041 | 10.0 | 7.81 | 56 | 3.7 | <0.5 | 5.5 | 3.0 | 24 | 15 | 2.2 | 0.8 | 2.8 |
| Y042 | 16.1 | 8.03 | 101 | 5.8 | 0.50 | 14 | 2.6 | 27 | 33 | 6 | 3.6 | 3.3 |
| Y043 | 22.2 | 8.41 | 241 | 4.2 | <0.5 | 44 | 5.1 | 38 | 70 | 4.2 | 26 | 5.5 |
| Y044 | 20.9 | 8.39 | 242 | 3.5 | <0.5 | 46 | 3.8 | 32 | 56 | 4 | 33 | 4.5 |
| Y045 | 14.9 | 7.56 | 74 | 4.7 | 0.68 | 8.6 | 2.5 | 22 | 26 | 2.1 | 0.9 | 2.9 |
| Y046 | 13.1 | 7.56 | 51 | 4.2 | 0.64 | 4.4 | 2.3 | 19 | 20 | 1.4 | 0.7 | 2.2 |
| Y047 | 8.5 | 7.67 | 156 | 6.1 | 0.90 | 29 | 2.8 | 28 | 52 | 2.9 | 16 | 3.9 |
| Y048 | 14.4 | 7.79 | 490 | 4.9 | 0.54 | 95 | 4.1 | 42 | 130 | 7.3 | 63 | 9.3 |

| NO2+NO3 ppm | B ppb | Ba ppb | Fe ppm | Mn ppb | P ppb | Sr ppb | V ppb | Li ppb | Be ppb | Al ppb | Cu ppb | Zn ppb | Ga ppb |
|----------------|----------|-----------|-----------|-----------|----------|-----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|
| <0.02 | 410 | 4.8 | 0.058 | 4.1 | <50 | 12 | <1 | 190 | 1.4 | 190 | <0.5 | 0.7 | <0.5 |
| <0.02 | 630 | 3.2 | 0.038 | 4.3 | <50 | 7.1 | <1 | 520 | 0.9 | 75 | <0.5 | <0.5 | 0.6 |
| 0.07 | 440 | 7.8 | 0.13 | 28 | <50 | 21 | <1 | 260 | 1.8 | 230 | <0.5 | 1.4 | <0.5 |
| <0.02 | 630 | 3.0 | 0.035 | 3.6 | <50 | 7.0 | <1 | 500 | 0.9 | 64 | <0.5 | <0.5 | 0.5 |
| 0.07 | 460 | 8.8 | 0.16 | 42 | <50 | 21 | <1 | 260 | 1.5 | 250 | <0.5 | 1.7 | <0.5 |
| <0.02 | 45 | 2.3 | <0.02 | 1.1 | <50 | 9.2 | <1 | 90 | 0.4 | 43 | <0.5 | 1.1 | <0.5 |
| 0.09 | 380 | 9.8 | 0.18 | 60 | <50 | 22 | <1 | 170 | 0.9 | 200 | <0.5 | 1.4 | <0.5 |
| 0.04 | 67 | 5.3 | 0.059 | 48 | <50 | 18 | <1 | 37 | <0.2 | 25 | <0.5 | 1.9 | <0.5 |
| 0.13 | 71 | 5.7 | 0.12 | 19 | <50 | 12 | <1 | 59 | 0.7 | 74 | <0.5 | 1.2 | <0.5 |
| <0.02 | 320 | 2.5 | 0.026 | 2.7 | <50 | 5.9 | <1 | 270 | 0.6 | 36 | <0.5 | <0.5 | <0.5 |
| <0.02 | 11 | 2.6 | <0.02 | 7.0 | <50 | 12 | <1 | 11 | 2.8 | 27 | <0.5 | <0.5 | <0.5 |
| <0.02 | 88 | 2.9 | 0.036 | 4.6 | <50 | 6.0 | <1 | 34 | 0.4 | 31 | <0.5 | <0.5 | <0.5 |
| <0.02 | 98 | 1.7 | <0.02 | 1.2 | <50 | 6.4 | <1 | 50 | 0.4 | 11 | <0.5 | <0.5 | <0.5 |
| <0.02 | 13 | 1.1 | <0.02 | 1.3 | <50 | 4.4 | <1 | 18 | 0.4 | 24 | <0.5 | 0.8 | <0.5 |
| <0.02 | 64 | 1.7 | 0.030 | 4.5 | <50 | 5.4 | <1 | 37 | 0.4 | 25 | <0.5 | <0.5 | <0.5 |
| <0.02 | 320 | 1.4 | <0.02 | 2.1 | <50 | 5.0 | <1 | 280 | 0.5 | 31 | <0.5 | <0.5 | <0.5 |
| <0.02 | 390 | 2.6 | 0.034 | 4.3 | <50 | 6.2 | <1 | 340 | 0.4 | 55 | <0.5 | 0.5 | 0.6 |
| <0.02 | 16 | 7.4 | 0.060 | 5.1 | <50 | 12 | <1 | 17 | <0.2 | 21 | <0.5 | <0.5 | <0.5 |
| <0.02 | <10 | 6.6 | 0.057 | 5.7 | <50 | 10 | <1 | 8.6 | <0.2 | 26 | <0.5 | <0.5 | <0.5 |
| <0.02 | 240 | 1.6 | 0.056 | 8.2 | <50 | 5.8 | <1 | 120 | 0.2 | 24 | <0.5 | <0.5 | <0.5 |
| <0.02 | 840 | 1.1 | 0.059 | 8.3 | <50 | 4.9 | <1 | 460 | 0.5 | 43 | <0.5 | <0.5 | 1.2 |

| Ge ppb | As ppb | Rb ppb | Y ppb | Zr ppb | Mo ppb | Sb ppb | Cs ppb | La ppb | Ce ppb | Pr ppb | Nd ppb | Sm ppb | Gd ppb |
|-----------|-----------|-----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 2.0 | 29 | 40 | 0.4 | 0.2 | 9.0 | 0.66 | 9.4 | 0.18 | 0.29 | 0.05 | 0.20 | 0.05 | < 0.05 |
| 6.2 | 240 | 35 | 0.2 | < 0.1 | 7.3 | 8.6 | 18 | 0.08 | 0.15 | < 0.05 | 0.08 | < 0.05 | < 0.05 |
| 2.1 | 74 | 42 | 0.5 | < 0.1 | 7.9 | 2.8 | 9.2 | 0.16 | 0.29 | < 0.05 | 0.16 | < 0.05 | 0.05 |
| 6.2 | 240 | 34 | 0.2 | < 0.1 | 6.8 | 8.5 | 17 | 0.09 | 0.14 | < 0.05 | 0.08 | < 0.05 | < 0.05 |
| 1.9 | 80 | 41 | 0.5 | < 0.1 | 4.3 | 3.3 | 9.9 | 0.21 | 0.40 | 0.06 | 0.25 | 0.05 | 0.07 |
| < 0.2 | 1.4 | 24 | 0.2 | < 0.1 | 3.1 | < 0.05 | 2.4 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| 1.4 | 56 | 35 | 0.5 | < 0.1 | 3.1 | 1.9 | 7.5 | 0.19 | 0.38 | 0.06 | 0.23 | 0.06 | 0.06 |
| < 0.2 | 0.6 | 11 | 0.2 | < 0.1 | 1.8 | < 0.05 | 0.98 | 0.06 | 0.10 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| 0.4 | 6.5 | 27 | 0.4 | < 0.1 | 1.2 | 0.15 | 1.8 | 0.10 | 0.17 | < 0.05 | 0.13 | < 0.05 | < 0.05 |
| 3.5 | 100 | 23 | 0.3 | 1.1 | 3.8 | 3.8 | 7.8 | 0.10 | 0.11 | < 0.05 | 0.12 | < 0.05 | < 0.05 |
| 0.4 | 4.3 | 15 | < 0.1 | < 0.1 | 1.2 | 0.16 | 1.9 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| 0.7 | 16 | 14 | 0.5 | < 0.1 | 1.2 | 0.57 | 2.5 | 0.15 | 0.11 | < 0.05 | 0.13 | < 0.05 | 0.05 |
| 0.6 | 23 | 17 | 0.1 | < 0.1 | 2.6 | 0.22 | 1.9 | 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| < 0.2 | 1.2 | 16 | 0.3 | < 0.1 | 0.8 | < 0.05 | 0.68 | 0.08 | < 0.05 | < 0.05 | 0.07 | < 0.05 | < 0.05 |
| 0.5 | 17 | 16 | 0.2 | < 0.1 | 1.6 | 0.14 | 1.9 | 0.05 | 0.08 | < 0.05 | 0.07 | < 0.05 | < 0.05 |
| 3.5 | 110 | 28 | 0.2 | < 0.1 | 4.6 | 3.8 | 7.8 | 0.07 | 0.08 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| 4.8 | 120 | 24 | 0.4 | < 0.1 | 3.8 | 6.2 | 13 | 0.13 | 0.10 | < 0.05 | 0.16 | < 0.05 | < 0.05 |
| 0.3 | 4.5 | 10 | 0.2 | 0.2 | 1.3 | 0.11 | 0.52 | 0.10 | 0.12 | < 0.05 | 0.12 | < 0.05 | < 0.05 |
| < 0.2 | 1.5 | 8.9 | 0.2 | < 0.1 | 0.6 | < 0.05 | 0.26 | 0.10 | 0.14 | < 0.05 | 0.12 | < 0.05 | < 0.05 |
| 2.1 | 69 | 14 | 0.2 | < 0.1 | 3.3 | 1.6 | 2.1 | 0.08 | 0.15 | < 0.05 | 0.10 | < 0.05 | < 0.05 |
| 8.9 | 300 | 28 | 0.1 | < 0.1 | 7.0 | 8.4 | 16 | < 0.05 | 0.10 | < 0.05 | 0.05 | < 0.05 | < 0.05 |

| Dy | Hf | W | Pb | Bi | Th | U |
|--------|--------|------|--------|------|--------|--------|
| ppb | ppb | ppb | ppb | ppb | ppb | ppb |
| 0.05 | 0.26 | 7.0 | < 0.05 | 0.08 | < 0.05 | 0.42 |
| < 0.05 | 0.24 | 64 | < 0.05 | 0.08 | < 0.05 | 0.26 |
| < 0.05 | < 0.05 | 4.5 | < 0.05 | 0.07 | < 0.05 | 1.1 |
| < 0.05 | 0.19 | 63 | < 0.05 | 0.08 | < 0.05 | 0.25 |
| 0.08 | < 0.05 | 5.6 | < 0.05 | 0.08 | < 0.05 | 0.55 |
| < 0.05 | < 0.05 | 0.26 | < 0.05 | 0.08 | < 0.05 | 0.56 |
| 0.07 | < 0.05 | 2.4 | 0.09 | 0.08 | < 0.05 | 0.34 |
| < 0.05 | < 0.05 | 0.14 | < 0.05 | 0.07 | < 0.05 | 0.08 |
| 0.06 | < 0.05 | 0.69 | < 0.05 | 0.08 | < 0.05 | 0.32 |
| < 0.05 | 0.86 | 37 | < 0.05 | 0.08 | 0.09 | 0.23 |
| < 0.05 | 0.11 | 0.73 | < 0.05 | 0.08 | < 0.05 | 0.04 |
| < 0.05 | < 0.05 | 5.8 | < 0.05 | 0.09 | < 0.05 | 0.19 |
| < 0.05 | < 0.05 | 1.1 | < 0.05 | 0.08 | < 0.05 | 0.15 |
| < 0.05 | < 0.05 | 0.33 | < 0.05 | 0.09 | < 0.05 | 0.36 |
| < 0.05 | < 0.05 | 3.0 | < 0.05 | 0.07 | < 0.05 | 0.22 |
| < 0.05 | 0.11 | 39 | < 0.05 | 0.08 | < 0.05 | 0.52 |
| < 0.05 | 0.15 | 55 | < 0.05 | 0.08 | < 0.05 | 0.22 |
| < 0.05 | < 0.05 | 3.5 | < 0.05 | 0.08 | < 0.05 | < 0.02 |
| < 0.05 | < 0.05 | 0.63 | < 0.05 | 0.08 | < 0.05 | < 0.02 |
| < 0.05 | 0.06 | 21 | < 0.05 | 0.09 | < 0.05 | 0.14 |
| < 0.05 | 0.25 | 97 | < 0.05 | 0.08 | < 0.05 | 0.12 |

Table 6. Background of trace metals (in ppb) in freshwater from Forstner and others, 1979 compared to the Soda Butte-Lamar Basin and Firehole-Gibbon Basin

| Metal | Background (Freshwater) | Soda Butte-Lamar Basins | Firehole and Gibbon Basins |
|-------|-------------------------|-------------------------|----------------------------|
| Ag | 0.3 | <0.05 | <0.05 |
| Al | <30 | 6 | 40 |
| As | 2 | 0.8 | 22.2 |
| Au | 0.01 | <0.01 | <0.01 |
| B | 10 | 17 | 128 |
| Ba | 10 | 16 | 3.2 |
| Be | 0.01 | <0.2 | 0.4 |
| Cd | 0.07 | <0.1 | <0.1 |
| Co | 0.05 | <0.5 | <0.5 |
| Cr | 0.5 | <1 | <1 |
| Cu | 1.8 | 0.5 | <0.5 |
| Fe | <30 | <20 | 43 |
| Li | 1 | 1.3 | 94 |
| Mn | <5 | 2.4 | 6.2 |
| Mo | 1 | 0.5 | 2.8 |
| Ni | 0.3 | <1 | <1 |
| Pb | 0.2 | <0.5 | <0.5 |
| Sb | 0.1 | <0.05 | 0.62 |
| Se | 0.1 | <5 | <5 |
| Sr | 50 | 78 | 8.9 |
| Sn | 0.03 | <1 | <1 |
| Ti | <1 | <2 | <2 |
| U | 0.5 | 0.09 | 0.19 |
| V | 0.9 | 2.2 | <1 |
| Zn | 10 | <0.5 | <0.5 |

mainly because of the input from the geothermal springs and geysers. These elements often occur in high concentrations in the thermal waters. High concentrations of As (up to 300 $\mu\text{g/l}$) and F (up to 9.3 mg/l) present in the Firehole and Gibbon basin is the most significant environmental problem associated with the stream waters. In addition, rare-earth elements (REE) La, Ce, and Nd are high in concentrations compared to average surface waters, probably due to input from the geothermal areas. RRE concentrations of Yellowstone springs were investigated by Lewis and others (1997). Of the major elements, Mg is low and K and Si concentrations are high, mainly because of the rhyolite composition rocks.

Comparison of the Two Areas

Composition of the rocks in the basin is a fundamental factor which determines the type of waters derived within a basin. The waters from the two study areas vary in chemistry and the means are compared in Table 7, along with average concentrations in freshwater (Table 6). The stream waters of the Soda Butte - Lamar basin are higher in concentrations of Ca, Mg, alkalinity, sulfate, Sr, V, and Cu as well as higher values of pH and conductivity compared to the Firehole and Gibbon basin (Tables 4 and 5). The reason for the higher concentrations of Ca, Mg, Sr, and alkalinity as well as higher values of pH is the occurrence of Paleozoic carbonate rocks within the basin. Carbonate rocks contain minerals such as calcite which is easily weathered and plays an important role in the evolution of water in a basin. Even though carbonate rocks are not abundant in the basin, they have a significant effect on the chemistry of the waters in the basin. Similarly, Drever and Hurcomb (1986) found that the most important reaction that neutralized acidity in the South Cascade Lake basin, Washington is weathering of calcite, which occurred only in trace amounts. The higher concentration of V is probably due to the presence of andesitic-composition rocks in the basin. Although Cu is low, the higher concentrations of Cu compared to Firehole - Lamar basin (maximum $<0.5 \mu\text{g/l}$), is probably due to the mineralization in upper Miller Creek. Cu concentrations reached a high of 4 $\mu\text{g/l}$ in upper Miller Creek and 2.6 $\mu\text{g/l}$ at Miller Creek at the junction with Soda Butte Creek.

CHEMICAL MODELING OF THE STREAM WATERS

To gain understanding of processes such as speciation of elements and identification of minerals that may control the concentration, mobility, and attenuation of elements in the stream waters, chemical modeling of the stream waters was carried out using PHREEQC (Parkhurst, 1995). The modeling program assumes mineral-solution equilibrium. For some chemical reactions, particularly with slow kinetics, this may not be the case. The dominant cations in the stream waters are mostly simple cations of Ca^{2+} , Na^+ , Mg^{2+} and K^+ or sulfate complexes CaSO_4^0 and MgSO_4^0 . The dominant anions are SO_4^{2-} , HCO_3^- , Cl^- , and F^- .

Saturation indexes were calculated for a suite of minerals to determine if concentrations

Table 7. Comparison of mean values for stream waters from Soda Butte-Lamar Basin and Firehole-Gibbon Basins. All means are geometric except for pH which is arithmetic mean

| Measurement | Soda Butte-Lamar Basin | Firehole and Gibbon Basins |
|--------------|------------------------|----------------------------|
| Temperature | 8.9 | 15.2 |
| pH | 8.24 | 7.71 |
| Conductivity | 171 | 161 |
| Ca | 18.2 | 5.5 |
| Mg | 5.2 | 0.60 |
| Na | 4.6 | 22.9 |
| K | 0.8 | 4 |
| Si | 6.8 | 29 |
| Alkalinity | 83 | 46 |
| Sulfate | 6.9 | 5.3 |
| Cl | 0.4 | 8.5 |
| F | <0.1 | 3.9 |
| B | 17 | 128 |
| Ba | 16 | 3.2 |
| Fe | <0.02 | 0.043 |
| Mn | 2.4 | 6.2 |
| Sr | 78 | 8.9 |
| V | 2.2 | <1 |
| Li | 1.3 | 94 |
| Be | <0.2 | 0.4 |
| Al | 6 | 47 |
| Cu | 0.5 | <0.5 |
| Zn | <0.5 | <0.5 |
| Pb | <0.05 | <0.05 |
| Ga | <0.5 | 1.2 |
| Ge | <0.2 | 0.7 |
| As | 0.8 | 22.2 |
| Rb | 1 | 21.6 |
| Y | <0.1 | 0.2 |
| Mo | 0.5 | 2.8 |
| Sb | <0.05 | 0.62 |
| Cs | <0.05 | 3.55 |
| La | <0.05 | 0.08 |
| Ce | <0.05 | 0.11 |
| Nd | <0.05 | 0.08 |
| W | <0.05 | 4.56 |
| Bi | 0.08 | 0.08 |
| U | 0.09 | 0.19 |

Temperature in degrees C, Conductivity in uS/cm, Ca, Mg, Na, K, Cl, SO4 in mg/L, Alkalinity in mg/L HCO3. All remaining species in ug/L.

of trace metals in water were controlled by mineral phases. The saturation index is a convenient means of expressing saturation states of minerals (Barnes and Clark, 1969 where:

$$SI = \log_{10} IAP/K_T.$$

In the expression, SI is the saturation index, IAP is the ion activity product, and K_T is the equilibrium constant of the dissolution reaction at the temperature in question. Mineral phases are supersaturated at $SI > 0$, saturated at $SI = 0$, and undersaturated at $SI < 0$.

Calcite is near saturation or supersaturated in 18 of the 27 stream waters from the Soda Butte-Lamar basin (Table 8, fig. 2). These sites include all stream waters from Soda Butte Creek and its tributaries from the north and Lost Creek. These waters are probably in contact with Paleozoic carbonate rocks, either on the surface and/or the subsurface. The carbonate rocks, although minor in surface occurrence, play a dominant role in the major element concentrations and the buffering of pH of these stream waters. In addition, 10 of these 18 waters are also near saturation or supersaturated with respect to dolomite (Table 8, fig 2). In contrast, all waters within the Firehole and Gibbon basin are undersaturated with respect to calcite and dolomite. The Paleozoic carbonate rocks in this study area were removed prior to and during the emplacement of the calderas.

The stream waters of Soda Butte and Lamar s are slightly undersaturated with respect to chalcedony. This is not the case in the Firehole and Gibbon basin, where all the stream waters are supersaturated with respect to chalcedony (Table 8). The concentration of dissolved silica in saturation with chalcedony increases with temperature. The waters from the geothermal areas contain silica concentrations which reflect these higher temperatures. These waters mix with the cooler stream waters. The mixed stream waters are initially supersaturated with respect to chalcedony (Table 8), but silica will precipitated from these waters with time.

Stream waters from the Soda Butte-Lamar basin are all undersaturated with respect to albite (Table 8). This is not the case of waters from the Firehole-Gibbon basin where 10 of the waters are supersaturated with respect to albite (Table 8). The geothermal waters in the Firehole-Gibbon basin are higher in concentrations of Na and silica (White and others, 1988 and Thompson and Yadav, 1979). As stated earlier, the stream waters in the Firehole-Gibbon basin are all supersaturated with respect to chalcedony. These higher concentrations of silica and Na from the geothermal areas cause albite to be supersaturated in ten of the stream waters. With time, silica precipitates as chalcedony, and the stream waters will no longer be supersaturated with respect to albite.

The stream waters from Soda Butte-Lamar basin are all undersaturated with respect to fluorite (Table 8), suggesting the lack of a fluorine-rich source from either rocks or a geothermal source in this study area. Within the Firehole-Gibbon basin, several stream waters (Sites Y48, Y28, Y29, and Y31) are saturated or near saturation with respect to fluorite (Table 8 and fig. 3). The high concentrations of fluoride is probably due to geothermal input, particularly from Lower

Table 8. Saturation indexes of stream waters from Yellowstone National Park and vicinity

| Site No. | Albite | Calcite | Dolomite | Chalcedoney | Fluorite | Talc |
|------------------------|--------|---------|----------|-------------|----------|-------|
| Soda Butte-Lamar Basin | | | | | | |
| Y01 | -4.54 | 0.45 | 0.22 | -0.41 | -5.22 | -1.01 |
| Y02 | -4.85 | 0.45 | 0.24 | -0.42 | -5.26 | -0.8 |
| Y03 | -4.96 | -0.02 | -0.8 | -0.52 | -5.36 | -2.41 |
| Y04 | -5.23 | 0.06 | -0.63 | -0.62 | -5.41 | -4.18 |
| Y05 | -4.86 | -0.01 | -0.48 | -0.55 | -5.48 | -1.66 |
| Y06 | -3.66 | 0 | -0.54 | -0.3 | -5.47 | -0.86 |
| Y07 | -2.34 | -1.19 | -2.98 | -0.15 | -5.69 | -4.93 |
| Y08 | -2.55 | -0.84 | -2.28 | -0.12 | -5.55 | -3.93 |
| Y09 | -3.59 | 0.31 | 0.2 | -0.32 | -5.34 | -0.29 |
| Y10 | -3.81 | 0.1 | -0.4 | -0.31 | -5.32 | -1.23 |
| Y11 | -1.95 | -1.51 | -3.45 | -0.13 | -5.9 | -5.28 |
| Y12 | -3.76 | 0.16 | -0.26 | -0.31 | -5.37 | -0.71 |
| Y13 | -4 | 0.49 | 0.51 | -0.3 | -5.34 | 0.91 |
| Y14 | -3.65 | 0.58 | 0.73 | -0.26 | -5.36 | 1.7 |
| Y15 | -4.05 | 0.69 | 0.99 | -0.26 | -5.39 | 2.45 |
| Y16 | -2.06 | -1.23 | -2.63 | 0.13 | -5.495 | -2.01 |
| Y17 | -3.66 | 0.3 | 0.3 | -0.14 | -3.11 | 0.5 |
| Y18 | -1.3 | -0.71 | -1.6 | -0.03 | -2.59 | -0.87 |
| Y19 | -3.7 | 0.38 | 0.43 | -0.09 | -3.14 | 2.06 |
| Y20 | -3.59 | 0.09 | -0.27 | -0.13 | -3.08 | -0.42 |
| Y21 | -1.62 | 0.09 | -0.16 | 0 | -2.59 | 0.97 |
| Y22 | -1.97 | 0.5 | 0.67 | -0.07 | -2.61 | 3.22 |
| Y23 | -1.48 | -1.55 | -3.29 | -0.11 | -1.94 | -4.46 |
| Y24 | -1.43 | -1.82 | -3.82 | -0.09 | -1.94 | -5.87 |
| Y25 | -2.21 | -1.06 | -2.44 | 0.07 | -1.94 | -1.02 |
| Y26 | -2.5 | 0.51 | 0.7 | 0.06 | -1.8 | 3.45 |
| Y27 | -1.56 | -0.95 | -2.11 | -0.11 | -1.85 | -1.52 |
| Firehole-Gibbon Basin | | | | | | |
| Y28 | 1.32 | -1.06 | -2.88 | 0.52 | -0.1 | -2.66 |
| Y29 | 1.16 | -0.81 | -2.48 | 0.53 | -0.16 | -1.81 |
| Y30 | 0.59 | -1.35 | -3.35 | 0.45 | -0.53 | -5.46 |
| Y31 | 0.93 | -0.54 | -1.89 | 0.5 | -0.2 | 0.02 |
| Y32 | 0.93 | -1.1 | -2.77 | 0.39 | -0.65 | -2.59 |
| Y33 | -0.44 | -1.06 | -2.62 | 0.31 | -0.55 | -1.58 |
| Y34 | 0.17 | -1.73 | -3.96 | 0.31 | -0.96 | -5.62 |
| Y35 | -2.87 | -2.44 | -5.47 | 0.08 | -1.25 | -9.44 |
| Y36 | -0.5 | -1.85 | -4.38 | 0.32 | -0.96 | -5.98 |
| Y37 | 0.22 | -1.14 | -3.26 | 0.42 | -0.54 | -2.97 |
| Y38 | -1.02 | -1.43 | -4.02 | 0.35 | -0.27 | -3.91 |
| Y39 | -1.17 | -2.49 | -5.94 | 0.28 | -1.26 | -8.33 |
| Y40 | -0.99 | -1.5 | -3.61 | 0.34 | -0.73 | -3.09 |
| Y41 | -0.91 | -1.99 | -4.95 | 0.33 | -0.98 | -4.83 |
| Y42 | -0.76 | -1.16 | -3.16 | 0.31 | -0.76 | -1.96 |
| Y43 | -0.17 | -0.55 | -1.94 | 0.37 | -0.58 | 0.83 |
| Y44 | -0.03 | -0.77 | -2.31 | 0.31 | -0.81 | 0.28 |
| Y45 | -1.26 | -1.82 | -4.28 | 0.23 | -0.93 | -4.83 |
| Y46 | -1.51 | -2 | -4.65 | 0.19 | -1.18 | -5.36 |
| Y47 | -0.01 | -1.43 | -3.6 | 0.42 | -0.5 | -4.26 |
| Y48 | 0.87 | -0.98 | -2.72 | 0.52 | 0 | -2.93 |

Geyser basin. Thompson (1979) also found high fluoride concentrations in the upper Madison River system.

Conclusion and Summary

Temperature, pH, conductivity, and the concentrations of 64 elements were determined on 48 stream water samples collected from the Soda Butte-Lamar basin and the Firehole-Gibbon basin within and adjacent to Yellowstone National Park. Because of the low sensitivity of the ICP-MS analyses, these results provide a geochemical baseline for a wide range of elements, many documented for the first time. Stream water chemistry is sensitive to changes in the environment, therefore these results can be used to compare with future stream water chemistry, to determine if any change has taken place.

Based on the chemistry of the stream waters from the two study areas, the composition of the rocks is a major factor in evolution of the waters within the basin. Within the Firehole-Gibbon basin, input from geothermal areas is also a major factor in the chemical composition of waters in this basin. High concentrations of As (up to 300 $\mu\text{g/l}$) and F (up to 9.3 mg/l) are present in the Firehole and Gibbon basin, which is the most significant environmental problem associated with the stream waters.

The concentrations of Cu and Zn in Miller Creek which drains the mined area are 4 $\mu\text{g/l}$ and 1.3 $\mu\text{g/l}$, respectively at site Y04 in upper Miller Creek and 2.6 $\mu\text{g/l}$ and 1.6 $\mu\text{g/l}$ at site Y03, on Miller Creek above the junction with Soda Butte Creek. The old mine workings in the upper part of Miller Creek appears to have minimal effect of the stream water chemistry of Soda Butte Creek at this time of year. At sites Y02 and Y03 along Soda Butte Creek below the mine tailings and above Cooke City, maximum concentrations of Cu and Zn are less than 1 $\mu\text{g/l}$. The mine tailings along Soda Butte Creek, above Cooke City, appears to have no effect on the water chemistry of Soda Butte Creek at this time of year.

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