# Cannon River Wilderness Park Springs
# Water Analysis and Observation

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**Abstract**

An investigation was carried out to determine anion levels in spring water at seven different sites in the Cannon River Wilderness Park (CRWP), located in Rice County, Minnesota.  Water samples were analyzed for Fluoride, Chloride, Nitrate, Nitrite, Sulfate, Bromide, and Phosphorous content, and results were compared to maximum contaminant levels as determined by the EPA.  No anions were present above these levels, indicating that these springs in the CRWP are not a hazardous source of the contaminants listed above.

## Introduction

The Shakopee Aquifer overlies the Prairie du Chien-Jordan aquifer, which is the primary water supply for Rice county. It has a recharge rate of 0.27, meaning 27% of precipitation infiltrates the aquifer (Ruhl, *et. al.*, 2002). Previous studies by Carleton students have determined a recharge age of approximately 35 years for the Shakopee formation and a recharge age of approximately 65 years for the Jordan formation (James, *et. al.*, 2004). The Shakopee aquifer is the source of several springs in the Cannon River Wilderness Park (CRWP), located five miles south of Northfield, Minnesota. Much of the land surrounding the Cannon River watershed is used agriculturally. Nutrients such as Nitrate and Phosphate are typically applied in these areas as fertilizer. Runoff from fields has been shown to be a source of contamination in both the Cannon River watershed (Hendryx, *et. al.*, 2003) and in the groundwater in Rice County (James, *et. al.*, 2004).

This study is meant as a follow up and extension of the work done by previous Carleton students on the water chemistry of ground and spring water in CRWP. Samples were collected between three and four times from 7 sites within CRWP in October 2004. Field observations of temperature, clarity, salinity, and conductivity were taken. Samples were also analyzed for seven major anions, Fluoride, Chloride, Nitrate, Nitrite, Phosphate, Bromide, and Sulfate.

The purpose of this study is to see whether or not there has been measurable anthropogenic contamination of the groundwater in CRWP, specifically nutrient contamination resulting from penetration into the Shakopee aquifer of agricultural runoff.

**Methods**

Seven sites within CRWP were tested. Sites were located on an unnamed stream and on Fisk creek. Site 4 was the source of the unnamed stream; that is where water forming the unnamed stream first became visible on the surface. Sites 1 and 2 were springs along the unnamed stream. Site 3 was a small stream near the beginning of the trail. Site 6 was an area of still water at the source of Fisk Creek, site 7 was the first moving water visible at the source of Fisk Creek. Site 5 was a spring that entered Fisk Creek downstream from the creek's source (Figure 1).

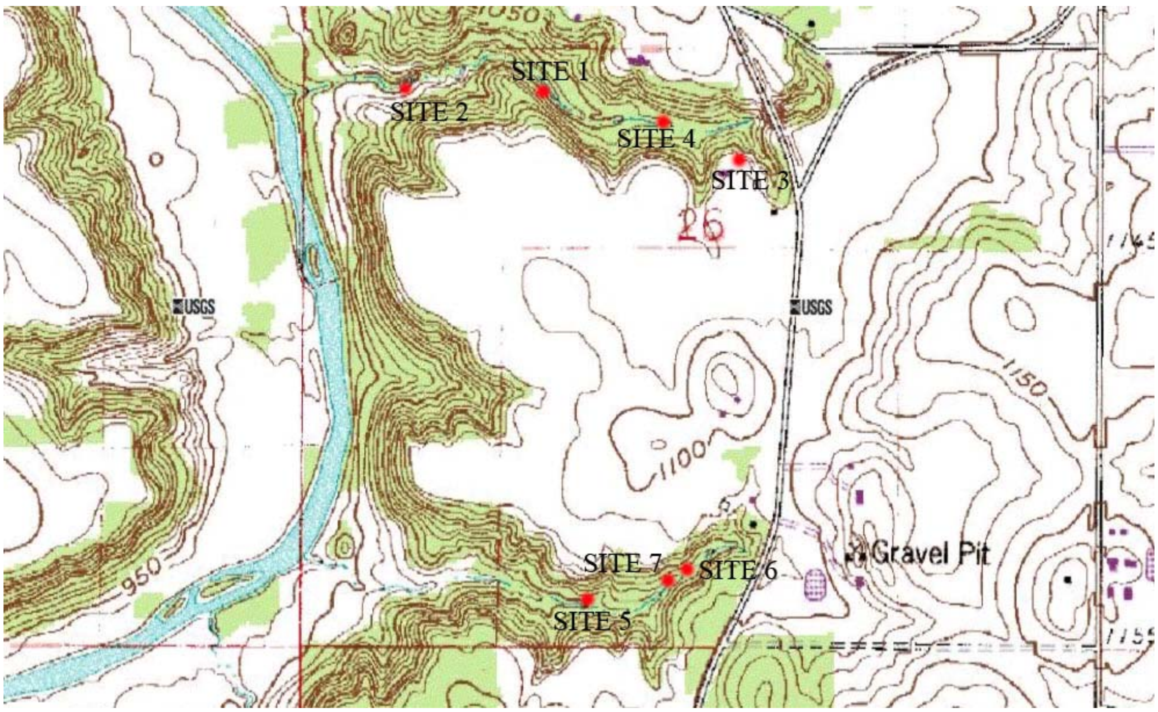


Figure 1: Topographical Map of the Cannon River Wilderness Park. Test sites are marked in red.

Conductivity, corrected conductivity, temperature, and salinity were measured on site using a YSI probe. Clarity was measured using a Secchi Tube. The measurements of Sites 1 and 2 were taken four times, one week apart, from October 5th to October 26th.

Site 3 was sampled on October 5$^{th}$ and 12$^{th}$, but subsequently dried up. The remaining sites were measured three times, on October 12$^{th}$, 19$^{th}$, and 26$^{th}$.

At each site, a water sample was taken in a plastic container that had previously been cleaned with deionized water. These were collected as near to the source of water as possible while avoiding disruption or collection of sediments. For Sites 2, 4, and 5, where metabolized iron was visibly present, samples of this iron on small rocks or leaves were also gathered in separate plastic containers. All samples were refrigerated as soon as possible.

Water samples were then analyzed for anions using Ion Chromatography. A water sample was injected into a stream of carbonate-bicarbonate eluant and passed through a series of ion exchangers. All samples were filtered through a 0.25 μm filter before being injected into the column. The filters were pre-rinsed with at least 30 ml of deionized water before filtering the sample to remove soluble salts on the filter. Samples were analyzed for the anions Fluoride, Chloride, Nitrate, Nitrite, Sulfate, Bromide, and Phosphorous.

Due to delays installing analysis equipment at the University of Minnesota, iron samples could not be analyzed.

## Results

### *Field Observations*

The water samples were consistently clear in all locations except for the still water at Site 6. Temperatures were stable at sites 1, 2, 3, and 5, ranging from between 8.6 °C to 9°C (Figure 2).

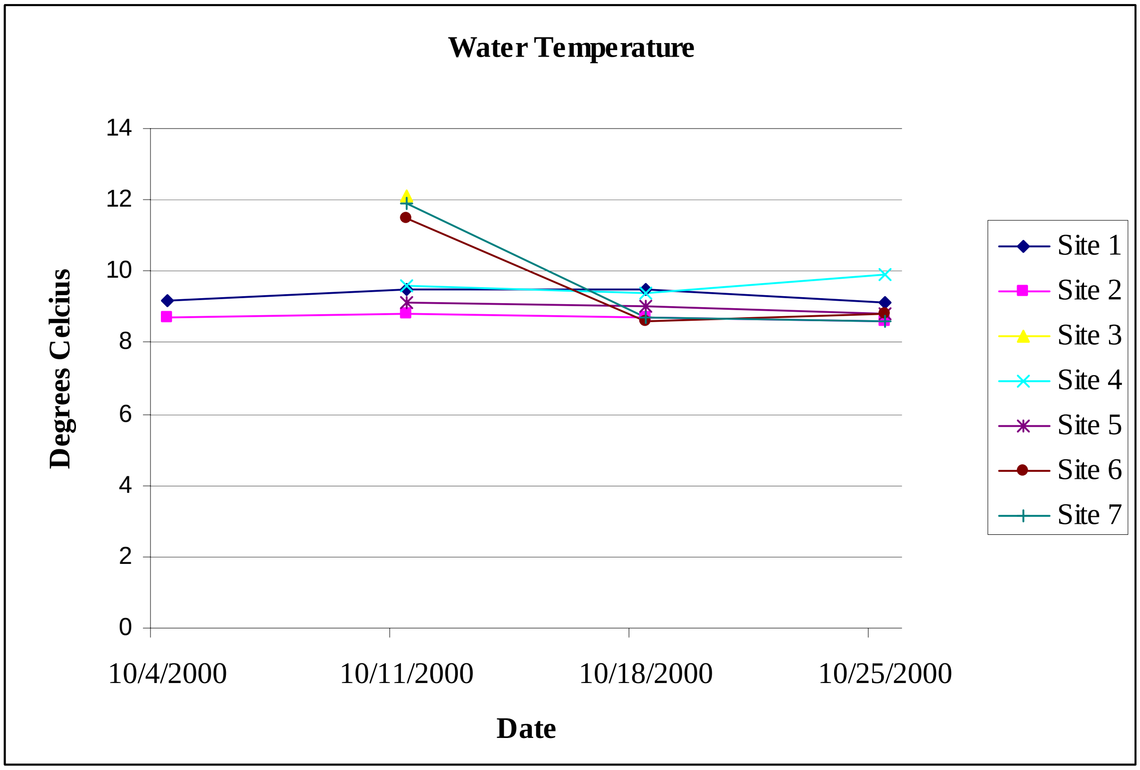


Figure 2: Temperature of Spring Water in Cannon River Wilderness Park

A substantial drop in temperature of approximately 3 °C at sites 6 and 7 was observed between 10/12 and 10/19; however from 10/19 to 10/26 the temperature at sites 6 and 7 remained stable, ranging from 8.6 °C to 8.8°C.

Conductivity ranged from 0.17 MS to 0.49 MS. Site 4 had the lowest observed conductivity, while the other sites showed greater conductivity. Adjusted conductivity ranged from 0.25 MS to 0.65 MS (Figure 3).

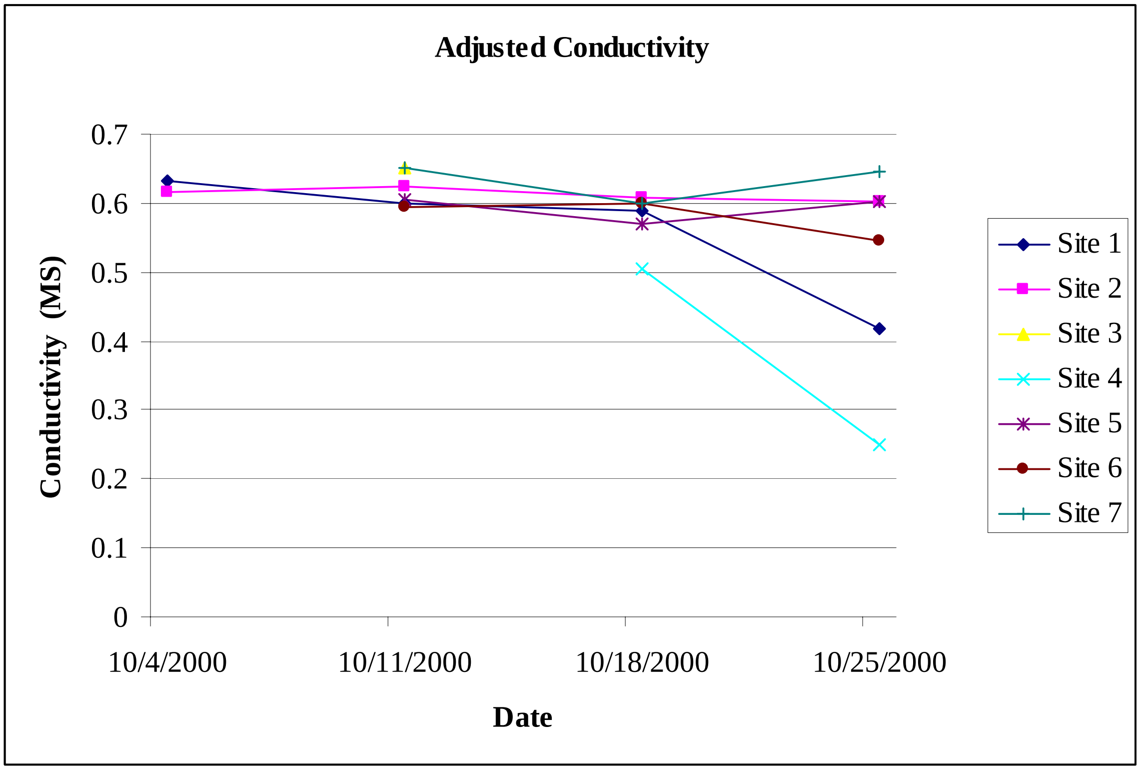


Figure 3: Adjusted Conductivity of Spring Water from CRWP

Again, the adjusted conductivity observed at site 4 on 10/26 is markedly different than the conductivity observed at other sites at the same date. The salinity at all times and locations was .3 parts per thousand, except for Site 4 (the source of the unnamed creek) on 10/12 (0.1 ppt) and on 10/19 (0.2 ppt) (Table 1).

| Date | 10/5/2004 | 10/12/2004 | 10/19/2004 | 10/26/2004 |
|---|---|---|---|---|
| Site 1 | 0.3 | 0.3 | 0.3 | 0.2 |
| Site 2 | 0.3 | 0.3 | 0.3 | 0.3 |
| Site 3 | n/a | 0.3 | n/a | n/a |
| Site 4 | n/a | 0.3 | 0.2 | 0.1 |
| Site 5 | n/a | 0.3 | 0.3 | 0.3 |
| Site 6 | n/a | 0.3 | 0.3 | 0.3 |
| Site 7 | n/a | 0.3 | 0.3 | 0.3 |

Table 1: Salinity content in parts per thousand

***Anions***

Fluoride was present in low concentrations in samples collected at sites 2, 3, 4, and 5, ranging from 0 to 0.17 mg/L (Table 2, Appendix). Fluoride was detected sporadically at these sites, appearing in about half the samples from sites 2,3, 4, and 5, and was not detected at all at sites 1, 6, and 7. The mean Fluoride content detected at each sight can be seen in Figure 4 (Appendix). Chloride was present at all sites, with concentrations ranging from 3.12 to 26.63 mg/L (Table 2). Mean Chloride levels can be seen in Figure 5. Nitrate was detected at varying concentrations at all sites, ranging from 0 to 16.03 mg/L (Table 2). Mean Nitrate levels for each site are shown in Figure 6 (Appendix). Sulfates were always present, ranging in concentration from 9.89 to 75.51 (Table 2). Mean sulfate levels can be seen in Figure 7 (Appendix). Phosphate was present in only 1 sample, which was collected at site 6, for which a concentration of 0.6 mg/L was obtained (Table 2).

**Discussion**

Fluoride is frequently added to municipal drinking water to encourage the development of strong teeth. At higher concentrations, Fluoride can cause bone tenderness and mottled teeth, although it is not associated with any specific health warning. For these reasons a maximum contamination level of 4 mg/L has been established (James *et. al.*, 2003; MPCA, 1999a). Fluoride data collected from the CRWP ranges from between 0.1 to .17 mg/L, well below harmful levels of contamination. The weathering of igneous rocks is the primary source of the Fluoride found in groundwater; however the weathering of limestone may also contribute. Minnesota Pollution Control

Agency (MPCA) tests indicate that anthropogenic sources of Fluoride are not significant (MPCA, 1999a).

No health warnings exist regarding the presence of Chloride in drinking water, however high concentrations can have an adverse effect on the taste of drinking water. For this reason a maximum concentration of 250 mg/L has been established. Chloride data from the CRWP exhibits a wide range, from 3.12 to 26.63 mg/L, however these levels are all well below the standards set by the MPCA. Common natural sources of Chloride include the weathering of halite. The most common anthropogenic source is road salt; other anthropogenic sources include fertilizers and industrial applications (James *et. al.,* 2003; MPCA, 1999a).

Sulfates can have a laxative effect and produce an unpleasant taste in drinking water, and so a maximum level of 500 mg/L has been set. Samples collected from CRWP showed a range from 9.89 to 75.51 mg/L, well below the level of maximum contamination. Sulfates result naturally from the weathering of Sulfur containing rocks in the aquifer such as pyrite. Common anthropogenic sources include fossil fuel combustion byproducts, fertilizers, and animal waste (James *et. al.,* 2003; MPCA, 1999b).

Nitrate concentrations found in the CRWP range from 0 to 16.03 mg/L. Samples collected at sites 3, 4, and 6 exceeded the limit of 10 mg/L of Nitrogen from Nitrate in drinking water determined by the EPA (EPA website, 10/2004). This figure is determined by the relative atomic weights of Nitrogen and Nitrate, such that dividing the concentration of Nitrate by 4.4 will give the Nitrogen concentration (Figure 8).

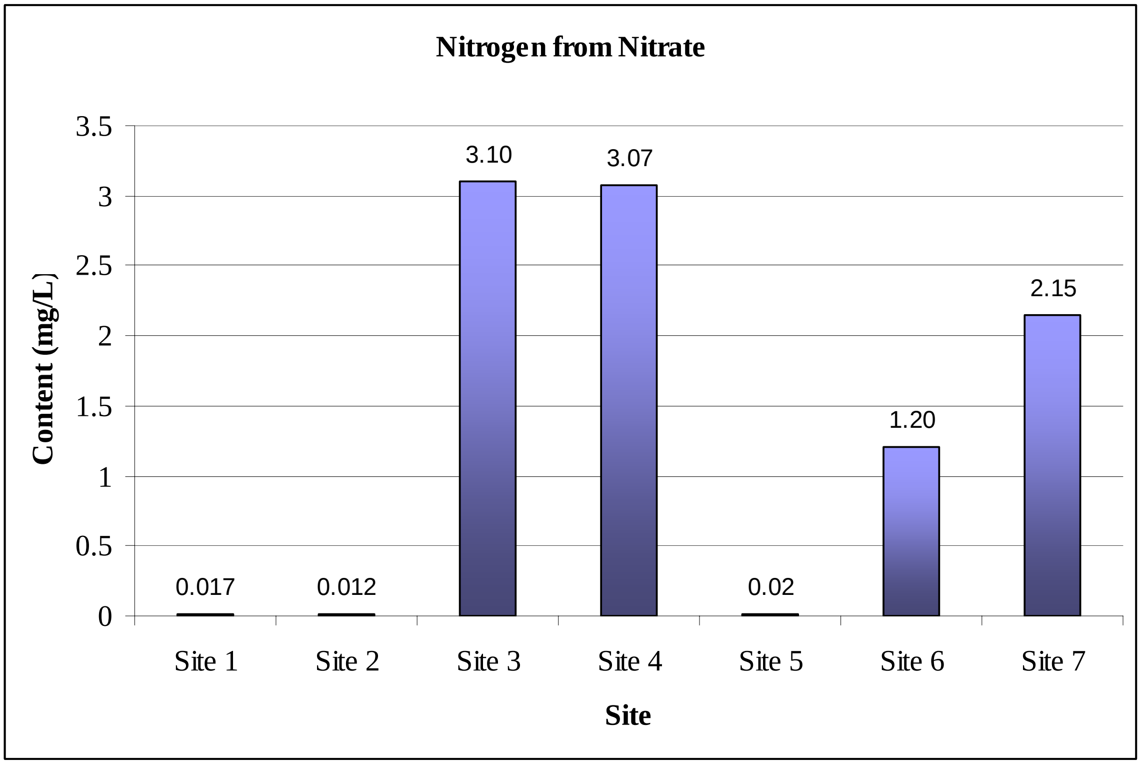


Figure 8: Mean Nitrogen from Nitrate in CRWP Springs

The major health risk associated with Nitrate is Methemoglobinemia, or Blue Baby Syndrome, which occurs when bacteria in the stomach convert Nitrate to Nitrite, which reduces the ability of the blood to carry oxygen. It is generally not a risk to children and adults over six months of age (James *et. al.*, 2003; MPCA, 1999a). No sites in the CRWP had Nitrogen from Nitrate levels that exceeded the EPA maximum contaminant level for drinking water. Nitrate is of particular concern because it is commonly used throughout the Rice County region as an ingredient in fertilizer (MPCA 1998).

Phosphate was present in only 1 of 19 total samples taken, at a low concentration. Due to small sample size further investigation was impossible.

**Conclusions**

Several improvements in methodology could have enhanced this study. Better calibration methods for the Ion Chromatograph, more effective labeling of samples, and a larger sample size would have produced more reliable data. Equipment malfunction, specifically difficulty calibrating the Ion Chromatograph, may have affected results.

Previous work by James *et. al.* (2003) found no Nitrate in the CRWP. That this study found levels of Nitrate up to 13.5 mg/L may indicate that anthropogenic Nitrate has just recently entered into the Shakopee aquifer. The Shakopee aquifer has a recharge rate of approximately 35 years, and overlies the Jordan aquifer, which has been shown to have a recharge age of approximately 65 years (James *et. al.,* 2003), and to be the principal water supply for Rice County (Ruhl, *et. al.*, 2002). Penetration of anthropogenic pollutants into the Shakopee aquifer may be a precursor to penetration by those pollutants into the Jordan aquifer, and eventually into the drinking water supply.

Further study could be enhanced by expanding the sample size and area of collection to include a larger region of the Shakopee Aquifer in and around Rice County. A study comparing seasonal variations in anion levels, especially Nitrate and Phosphorus, within the Shakopee Aquifer could be insightful into examining the extent of an agricultural anthropogenic effect on the groundwater. Using the time scale established by James *et. al.* (2003) it may be possible to develop a correlation between past fertilizer application and Nitrate levels in ground water.

**Acknowledgements**

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Web Sites

*http://www.epa.gov/ebtpages/water.html*, October 24, 2004

## Appendix

| site 1 | Fluoride | Chloride | Nitrate | Phosphate | Sulfate |
|---|---|---|---|---|---|
| 10/5/2004 | 0 | 10.943 | 0 | 0 | 75.5107 |
| 10/12/2004 | 0 | 10.8587 | 0.2187 | 0 | 74.3647 |
| | | | | | |
| site 2 | Fluoride | Chloride | Nitrate | Phosphate | Sulfate |
| 10/5/2004 | 0 | 4.6373 | 0 | 0 | 61.1559 |
| 10/12/2004 | 0 | 3.3136 | 0 | 0 | 57.9056 |
| 10/19/2004 | 0.1517 | 3.3119 | 0 | 0 | 56.7937 |
| 10/26/2004 | 0.1723 | 3.3548 | 0.2119 | 0 | 57.2644 |
| | | | | | |
| site 3 | Fluoride | Chloride | Nitrate | Phosphate | Sulfate |
| 10/5/2004 | 0.1575 | 26.6322 | 15.7687 | 0 | 17.8348 |
| 10/12/2004 | 0 | 25.1534 | 11.5021 | 0 | 18.2489 |
| | | | | | |
| site 4 | Fluoride | Chloride | Nitrate | Phosphate | Sulfate |
| 10/12/2004 | 0.0997 | 9.6493 | 9.9094 | 0 | 15.8053 |
| 10/19/2004 | 0 | 10.6406 | 16.0305 | 0 | 16.3813 |
| 10/26/2004 | 0 | 10.2972 | 14.6202 | 0 | 15.8842 |
| | | | | | |
| site 5 | Fluoride | Chloride | Nitrate | Phosphate | Sulfate |
| 10/12/2004 | 0 | 5.6376 | 0.2606 | 0 | 53.3509 |
| 10/19/2004 | 0.1728 | 5.0926 | 0 | 0 | 53.8257 |
| 10/26/2004 | 0 | 4.9905 | 0 | 0 | 53.0345 |
| | | | | | |
| site 6 | Fluoride | Chloride | Nitrate | Phosphate | Sulfate |
| 10/12/2004 | 0 | 10.0262 | 10.3212 | 0 | 15.2635 |
| 10/19/2004 | 0 | 3.9343 | 2.7781 | 0.5997 | 9.8891 |
| 10/26/2004 | 0 | 4.5416 | 2.7538 | 0 | 11.3547 |
| | | | | | |
| site 7 | Fluoride | Chloride | Nitrate | Phosphate | Sulfate |
| 10/12/2004 | 0 | 10.6498 | 9.436 | 0 | 22.0717 |
| 10/26/2004 | 0 | 10.4804 | 9.4994 | 0 | 23.8412 |

Table 2: Date specific anion content in spring water from CRWP

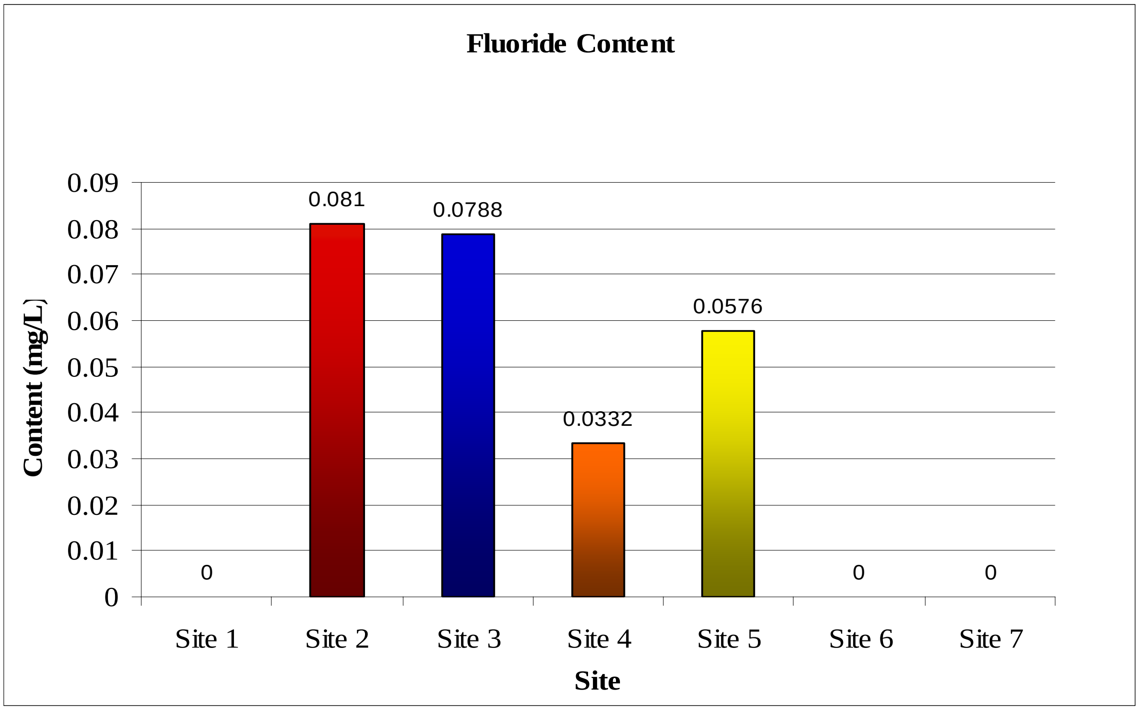


Figure 4: Average Fluoride Content of Spring Water from CRWP

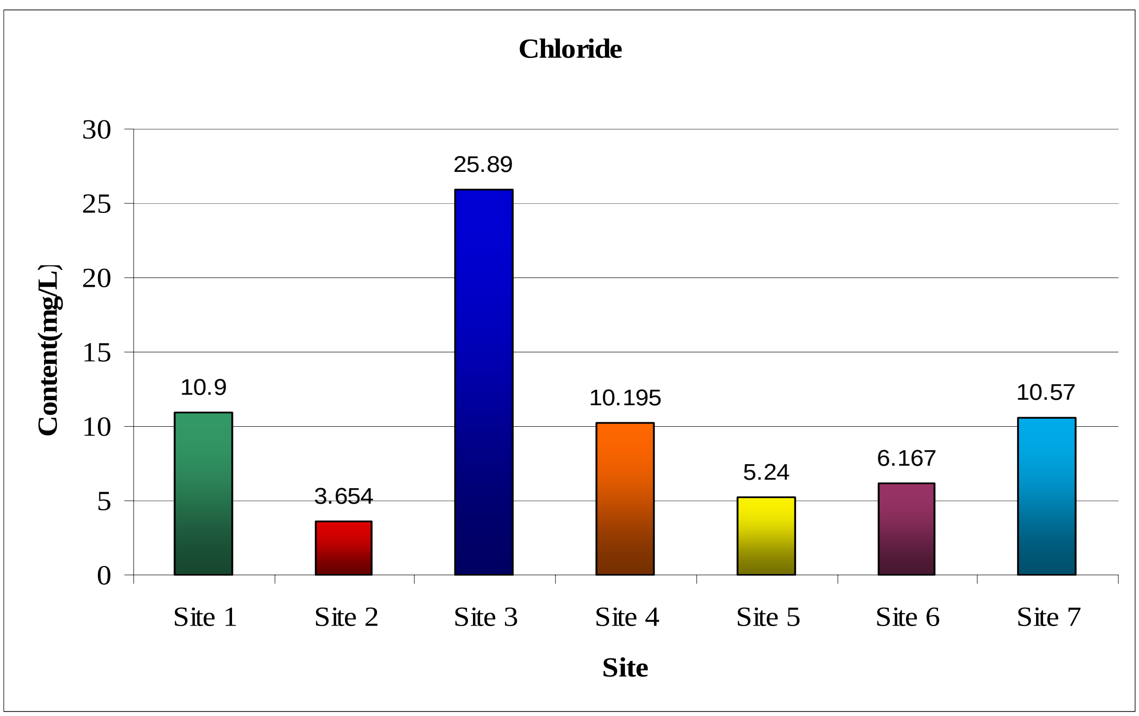


Figure 5: Average Chloride Content of Spring Water from CRWP

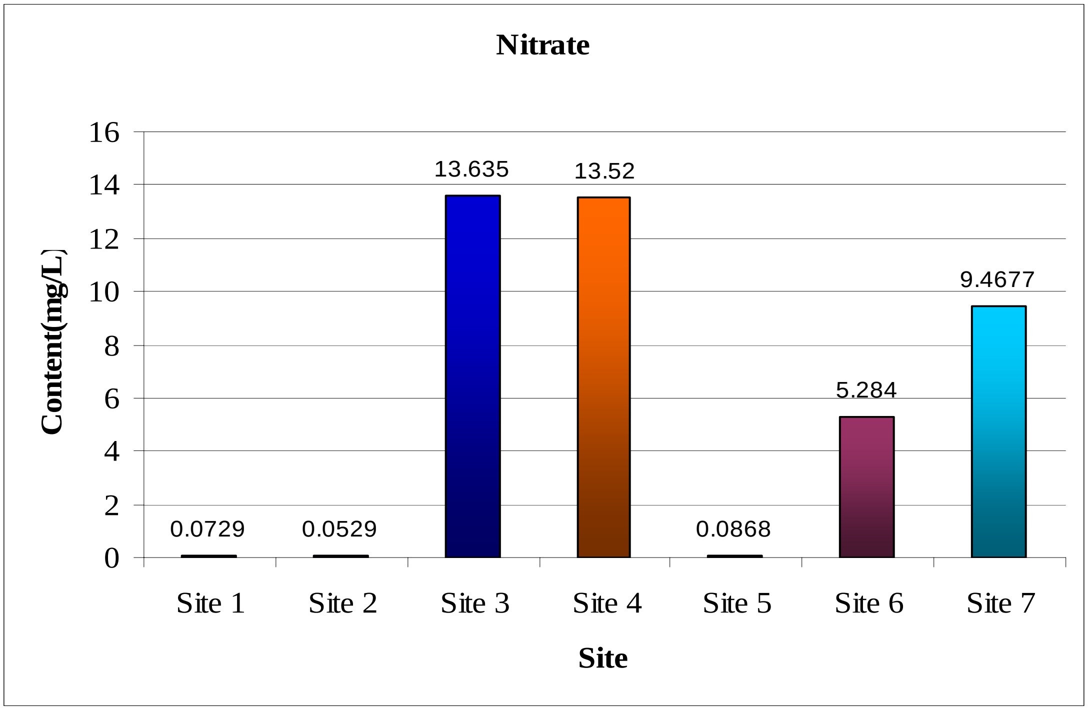


Figure 6: Average Nitrate Content in Spring Water from CRWP

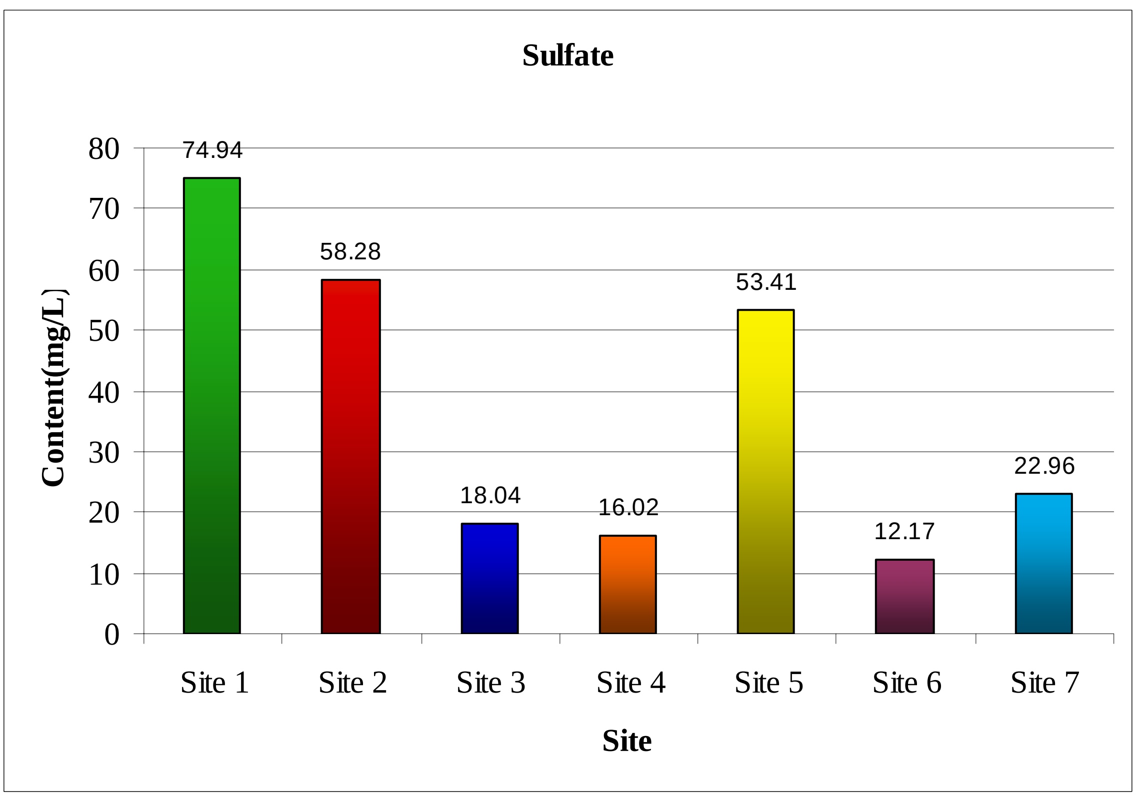


Figure 7: Average Sulfate Content of Spring Water from CRWP