Geochemical Investigation of the Madison Aquifer, Wind Cave National Park, South Dakota

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Abstract

Wind Cave, one of the most complex maze caves in the world, contains several underground lakes that are unique among caves in the southern Black Hills of South Dakota. Major ion chemistry, stable isotopes of water (^{18}O and ^{2}H) and geochemical modeling were used to investigate the origin and chemical evolution of water found in the underground lakes. Stable isotope and water chemistry data combined with water level data show that local recharge to underground lakes is the primary source of water. Flow is generally east and southeast from the park, following the dip of sedimentary units flanking the Black Hills uplift. Regional flow from the west mixes with local recharge south of the park, and mixing is evident in the stable isotope composition of spring discharge. A mixture of local recharge and regional flow from the west, combined with the process of dedolomitization, account for the water chemistry of large springs that discharge from the Madison aquifer in the Southern Black Hills.

Acknowledgements

Introduction

Wind Cave, located within Wind Cave National Park along the southeastern flank of the Black Hills of South Dakota, is recognized as one of the longest maze caves and as one of the oldest caves in the world (Palmer and Palmer, 2000). The park was originally established in 1903 to protect cave resources[1], but the enabling legislation was later revised to include protection of both surface and subsurface resources (16 U.S.C § 141).

Wind Cave is notable for its extensive, three dimensional complex maze of branching passages, its intricate calcite boxwork, and the distinctive helictite bushes that were first identified in Wind Cave. In addition, Wind Cave contains underground lakes with floating calcite rafts and a remarkable assemblage of speleothems and speleogens. Among the speleothems and speleogens that are of greatest public curiosity are various calcite and quartz crystals, flowstone, frostwork, popcorn, and rare gypsum flowers. In addition, Wind Cave represents one of the only known locations in the Black Hills where a cave intersects the water table of the regionally important Madison aquifer, and where water levels in Wind Cave correspond to water levels in nearby wells.

In 2006, the Southern Black Hills Water System filed a Future Use Water Permit application (No. 2580-2) to appropriate 1,474 acre-ft annually of groundwater from four well sites in the Madison aquifer in Custer and Fall River Counties. They also filed Water Permit Application 2585-2 to appropriate 1,600 acre-ft annually of groundwater from one well site in the Madison aquifer in Custer County. The National Park Service was concerned that drawdown produced by pumping wells in the vicinity of Wind Cave National Park would adversely impact the park's water rights and water-dependent resources.

Because of the close hydrologic connection between underground lakes and nearby wells, proposed development of the Madison aquifer has the potential to affect the underground water dependent features within Wind Cave. Understanding groundwater flow-paths in the Madison aquifer in the vicinity of the park will help resource managers make informed management decisions pertaining to both surface water and groundwater resources. Geochemical investigations can be used to identify the source and flow-path of water in an aquifer.

In 2007, an investigation of the geochemistry of the Madison aquifer, conducted by the U.S. Geological Survey and National Park Service, in cooperation with the Southern Black Hills Water System, was initiated to better understand the source and flow-path of water in the vicinity of Wind Cave National Park.

The chemical evolution of water within the Madison aquifer has been studied on a regional scale by Back and others (1983), Plummer and others (1990), Busby and others (1983 and 1991), and

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[1] An Act to set apart certain lands in the State of South Dakota as a public park to be known as the "Wind Cave National Park," approved January 9, 1903 (32 Stat. 765).

Naus and others (2001). Hayes (1999) evaluated sources of spring discharge at Cascade Springs, south of the town of Hot Springs, and Whalen (1994) evaluated flow-paths to both Cascade Springs and Beaver Creek Spring. Millen and Dickey (1987) reported that underground lake water was the result of direct meteoric recharge. Miller (1989) conducted a survey of the water chemistry of underground lakes in Wind Cave, and postulated that surface streams in the vicinity of the park were an unlikely source of water recharging the underground lakes. Alexander and others (1989) described the hydrology of both Wind and Jewel caves and conducted studies of water quality of drip sites within both caves. Tracer studies demonstrated that parking lot runoff was reaching some of the drip sites in Wind Cave, and high sodium and chloride concentrations in Beaver Creek and in several drip sites were associated with anthropogenic contamination. Despite these studies, the source of underground lake water and an understanding of flow paths in the vicinity of the park were not well known.

Purpose and Scope

The purpose of this report is to describe the results of an investigation that was initiated in 2007 to characterize the water chemistry and groundwater flow-paths of the Madison aquifer in the vicinity of the park. Water chemistry data sampled from various locations in an aquifer provide information about the movement of water from recharge areas where water first percolates into the aquifer to discharge areas where water discharges through springs or by wells drilled into the aquifer. The report includes a description of major ion chemistry, stable isotope chemistry, age of groundwater, and a discussion of both regional and local flow-paths.

Most of the data presented in this report were collected during 2007; however additional data from previous investigations was also reviewed (Back et al., 1983, Naus et al., 2001, Plummer et al., 1990, and Whalen, 1994). The objectives of the study were (a) to collect hydrochemical data for a comprehensive suite of springs, wells, and cave water fed by the Madison aquifer in the vicinity of Wind Cave National Park; (b) to test and refine existing regional geochemical models of the Madison aquifer and apply them to the southeastern Black Hills; and (c) to better understand the source of water found in the underground lakes in Wind Cave.

This report represents the first comprehensive study to evaluate the major ion chemistry and stable isotope composition of drip sites and underground lakes within Wind Cave, streams within the park, and wells and springs outside the park using a consistent methodology. The data collected as part of this study will allow us to better describe the different source areas and flow-paths of groundwater within the Madison aquifer in the vicinity of Wind Cave National Park. Information obtained as part of this study will help resource managers understand the potential effects of groundwater development of the Madison aquifer on the unique water dependent features found at Wind Cave National Park and make informed decisions regarding water resource development in the vicinity of Wind Cave.

Description of the Study Area

The Madison aquifer is part of a regional aquifer that underlies 120,000 square miles of the northern Great Plains in parts of Montana, South Dakota, North Dakota, and Wyoming. This report focuses on a part of the Madison aquifer that underlies the Black Hills of South Dakota near the Wyoming border. The Black Hills are a topographically distinct dome-shaped feature about 125 miles long and 60 miles across in western South Dakota. The Black Hills were formed

as the area was uplifted during the Laramide Orogeny, a period of mountain-building that occurred from about 70 to 40 million years ago. The approximate area of the Black Hills is represented by the generalized extent of the Inyan Kara Group (Figure 1).
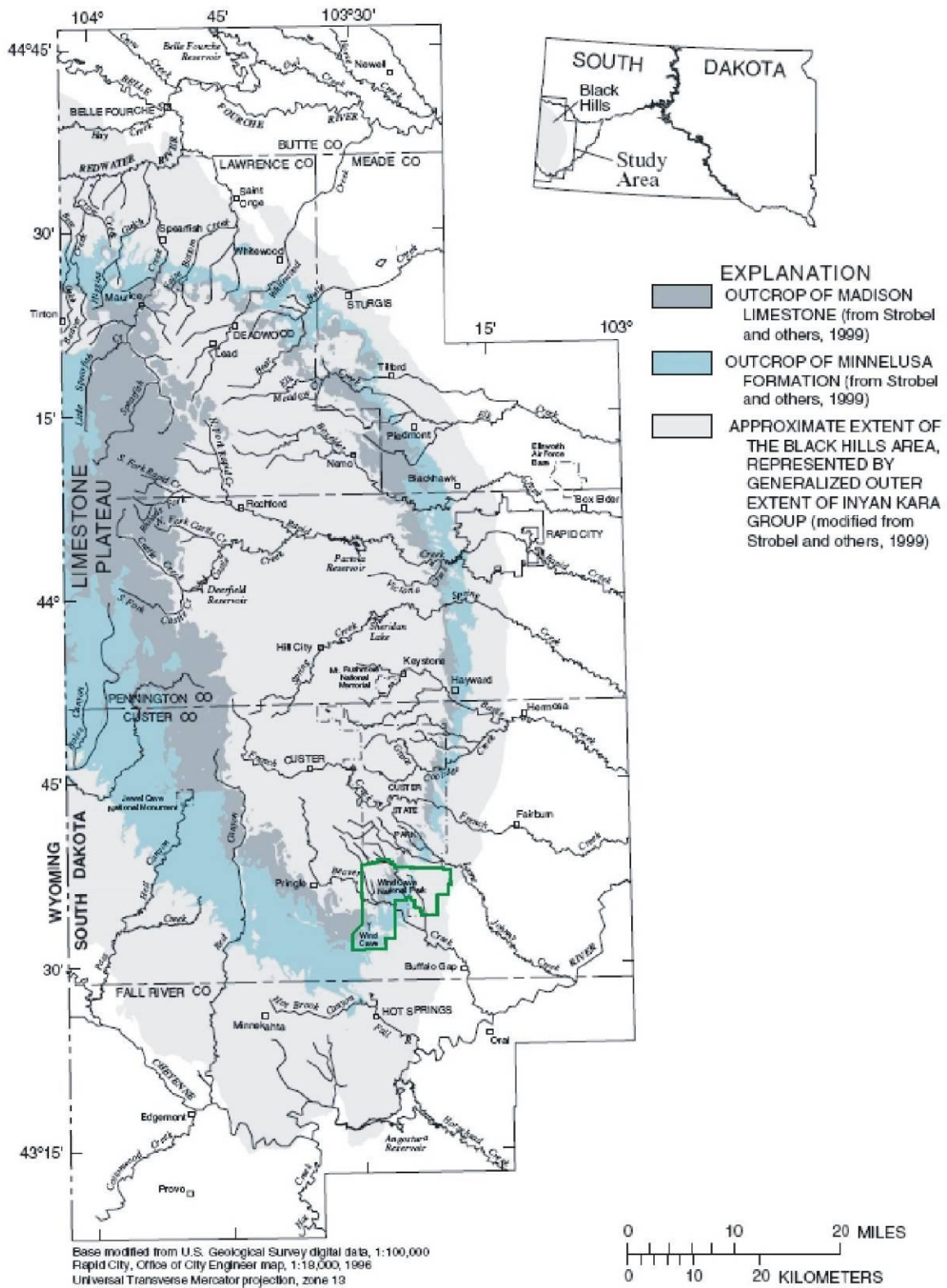
Figure 1. Location of Black Hills study area [Source: Naus et. al., 2001]. Wind Cave National Park boundary shown in green.

The study area is located in the general vicinity of Wind Cave National Park and the town of Hot Springs, South Dakota on the southeastern flank of the Black Hills. Wind Cave National Park encompasses about 28,000 acres of grasslands, pine forests, and stream-cut ravines on the southeastern flank of the Black Hills. Parts of Wind Cave extend below the water table in the regionally extensive Madison aquifer. Numerous underground lakes and pools of varying size have been identified within Wind Cave. Changes to the quality or quantity of water that infiltrates into Wind Cave or sustain the underground lakes and pools could affect the quality of the park's unique subsurface resources.

Southern Black Hills Geology

The oldest rocks in the study area are the Precambrian-age igneous and metamorphic rocks that are exposed in the crystalline core of the central Black Hills. A series of younger sedimentary rocks including limestones, sandstones, and shales are exposed in concentric rings that dip radially outwards from the uplifted central core (Figure 2). Sedimentary units that have been exposed through erosional processes include outcrops of the Ordovician-age Deadwood Formation, the Mississippian-age Madison Limestone, the Pennsylvanian and Permian-age Minnelusa Formation, and the Permian-age Minnekahta Limestone.

The topographically defined Black Hills and adjacent areas are underlain by two regionally important hydrogeologic units– the Madison Limestone and the overlying Minnelusa Formation. The Madison Limestone (also known as the Pahasapa Limestone), deposited as a marine carbonate, is composed of a massive light colored limestone that is locally dolomitic (Strobel and others, 1999) and is the primary aquifer in the Black Hills area and the focus of this study. The lower part of the Madison Limestone, combined with the Englewood Formation, forms a lower confining zone.

Karst is a type of landscape commonly associated with carbonate rocks that is characterized by closed depressions, disrupted or sinking streams, and caves and underground drainage systems. The development of these features is created by the dissolution of the bedrock. The upper part of the Madison Limestone was exposed at the surface for nearly 50 million years, and experienced significant karstification (Strobel and others, 1999). Several perennial streams lose all or much of their surface flow where they cross outcrops of the Madison Limestone. Numerous caves and fractures are found in the upper part of the formation that is now overlain by the Minnelusa Formation.

The Pennsylvanian and Permian Minnelusa Formation, which consists of sandstone, limestone, dolomite, and shale was deposited on top of the karstified Madison Limestone. In parts of the Black Hills, the Minnelusa Formation is characterized by thick beds of anhydrite. The anhydrite beds in the upper parts of the Minnelusa Formation have been removed by dissolution at or near outcrop areas (Redden and De Witt, 2008 and Braddock, 1963). The dissolution of anhydrite near outcrop areas has formed collapse features in overlying strata, such as the Mammoth Site in Hot Springs, South Dakota.

The thickness of the Madison Limestone ranges from zero in the northwest corner of the park where it has been eroded away, to about 275-375 feet thick in the southern and eastern parts of the park (Palmer and Palmer, 2000). The structure and stratigraphy of the Madison Limestone

limit the extent of cave passages (Horrocks and Szukalski, 2002). Wind Cave is found in the upper part of the Madison Limestone within zones of paleokarst and other dissolution features that were formed near land surface. Southeast and down-dip of the underground lakes in Wind Cave, the cave passages thin and eventually terminate. Lowering of water levels in this area could cause the lakes to go dry.

Recharge to the underground lakes likely occurs either as diffuse infiltration of precipitation or through streamflow loss zones, where the entire flow of a stream may disappear into the subsurface as the stream flows across outcrops of karstic rock, providing an important source of local recharge. Hortness and Driscoll (1998) estimated maximum streamflow losses of 10 ft^3/s for Highland Creek and 5 ft^3/s for Beaver Creek.

Natural discharge from the Madison aquifer occurs through several types of large springs. Rahn and Gries (1973) performed a reconnaissance of large springs in the Black Hills of South Dakota and determined that their origins are largely based on geologic controls. They proposed a spring classification system based on hydrogeologic position. The major springs found in the vicinity of the park were springs found at lower elevations near the margins of the aquifer where the Madison Limestone abuts relatively impermeable geologic formations, such as the Minnekahta-Spearfish or Minnelusa-Opeche contact (Rahn and Gries, 1973). Large springs in the vicinity of the park are Beaver Creek Spring, several springs within the town of Hot Springs such as Evan's Plunge and Hot Springs Intake Spring, and Cascade Springs located south of Hot Springs (Figure 3).

These large springs are found downgradient from streamflow loss zones (Naus and others, 2001). Beaver Creek Spring, located down-gradient of the Beaver Creek loss zone in the park, is the nearest major spring that discharges from the Madison aquifer. Mean annual spring discharge at Beaver Creek Spring was 9.6 cfs for the period from 1987 - 1996 (Carter and others, 2001).

Discharge from the Madison aquifer to other formations may also occur. Hydraulic head is much higher in the Madison aquifer relative to the Minnelusa aquifer in the Hot Springs area and slightly higher in the vicinity of Cascade Springs (Naus and others, 2001). Hayes (1999), using geochemical modeling and mineralogical analyses, found that upward leakage from the Madison aquifer causes dissolution of anhydrite within the Minnelusa Formation, leading to solution-collapse breccia pipes and episodic turbidity events at Cascade Springs. Hayes (1999) noted that breccia pipes are uncommon in the lower Minnelusa Formation, but breccia layers and dikes were common, and these are probable pathways for the transmittal of upward leakage from the Madison aquifer.

Hydrologic Setting of Wind Cave

Most of the mapped portion of Wind Cave is located beneath two small drainages that combine to form Wind Cave Canyon, which eventually flows into Beaver Creek. Flow in this drainage is intermittent, with flood flows possible following large rain events. The area contributing to the drainage above Wind Cave is relatively small, encompassing less than four square miles. The elevation of the land surface ranges from about 3900 to 4100 feet above mean sea level (asl) in the drainage overlying Wind Cave.

The underground lakes in Wind Cave are located approximately 500 feet below land surface where Wind Cave intersects the water table (Figure 4). Surveys of wells and springs within and adjacent to the park were conducted July 2008 using high precision Global Positioning System survey equipment (Trimble GNSS R8 Dual-Frequency Geodetic Receiver). These surveys, coupled with surveys of cave passages, confirm that the lowest elevation lakes generally agree with the local potentiometric surface of the Madison aquifer. In 2007, the highest elevation lake (What the Hell Lake) was estimated to be located at 3,698 feet above mean sea level (asl), Rebel River was located at 3,667 feet asl and Calcite Lake was located at approximately 3,647 feet asl, in the deepest part of Wind Cave that is currently accessible. The elevation of Calcite Lake appears to reflect the potentiometric surface of the Madison aquifer in the area of the park. These estimates are more than 100 feet higher than previous estimates, which indicated that the lowest elevation lake was located at about 3,539 feet (Miller, 1989), but are consistent with recent surveys and water levels.

Water levels have fluctuated in the underground lakes over periods of several years. Windy City Lake rose 19 ft (5.8 m) between 1993 and 1999, then merged with Calcite Lake. The area now known as What the Hell Lake rose 7.2 feet (2.2 m) between June 1997 and July 1999. In July 1999 it suddenly rose four feet and flooded the route to the lower elevation lakes and 2 miles of surveyed cave. Since 2004, water levels in the accessible lakes have steadily declined about 4 feet. Calcite Lake levels appear to track water levels in nearby monitoring wells completed in the Madison aquifer.

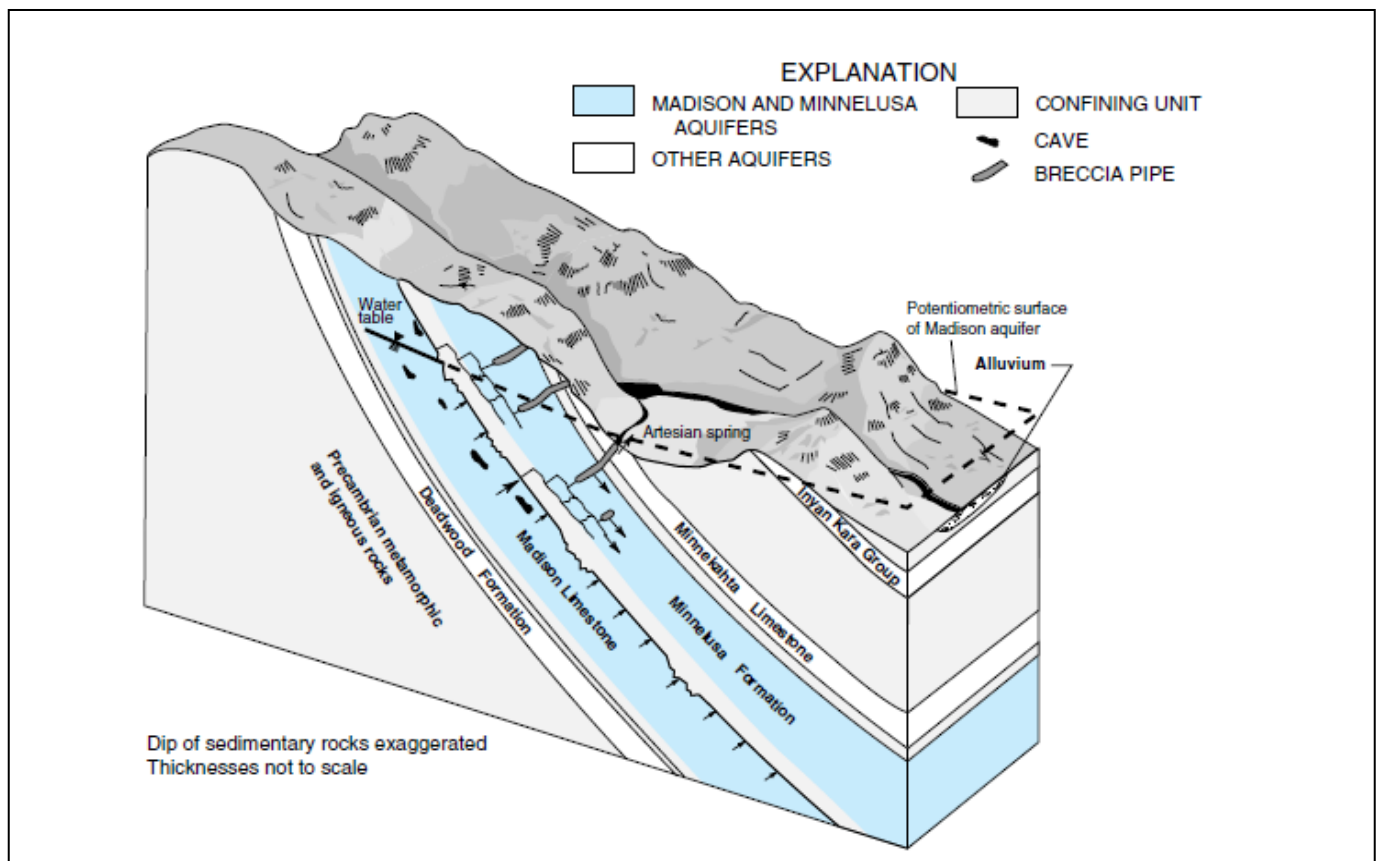**Figure 2.** Diagram of the hydrogeologic setting of the Black Hills area. Figure shows caves and breccia pipes which contribute to secondary porosity and may act as conduits for artesian springs.[Source: Naus et. al., 2001]
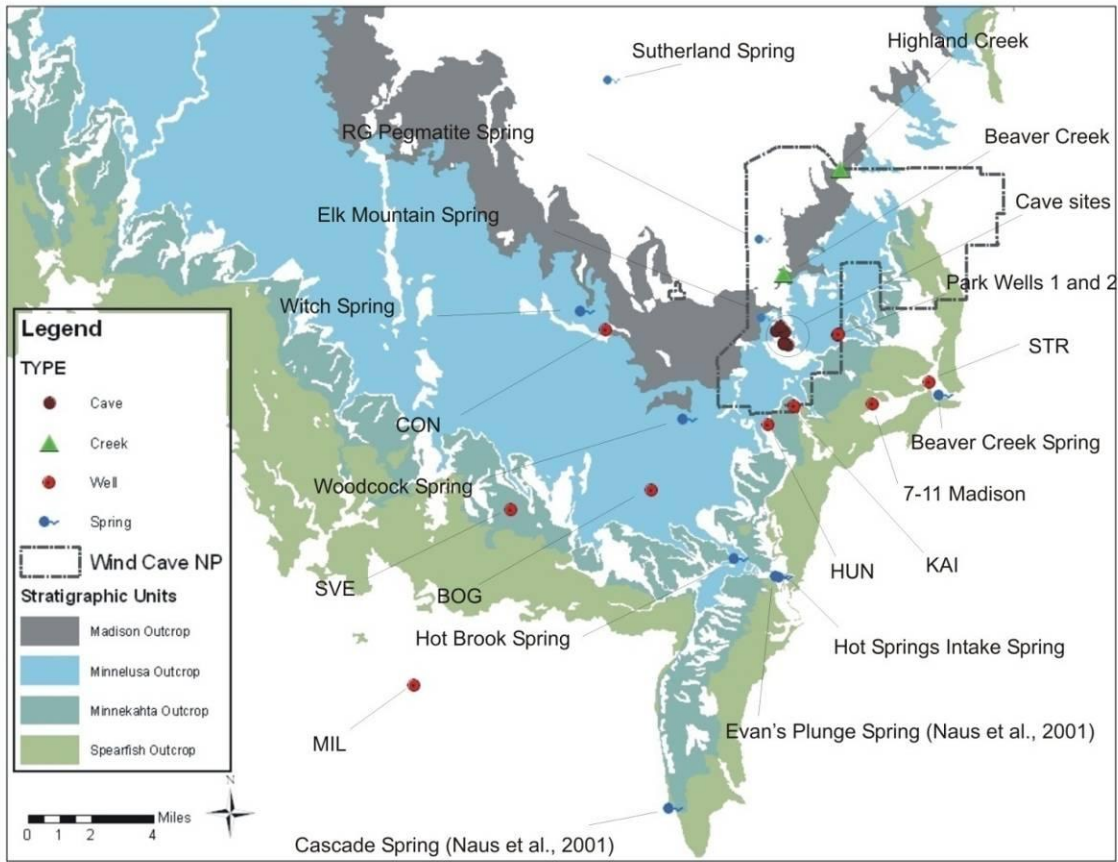
Figure 3. Site names and locations relative to outcrops of geologic units in the study area.
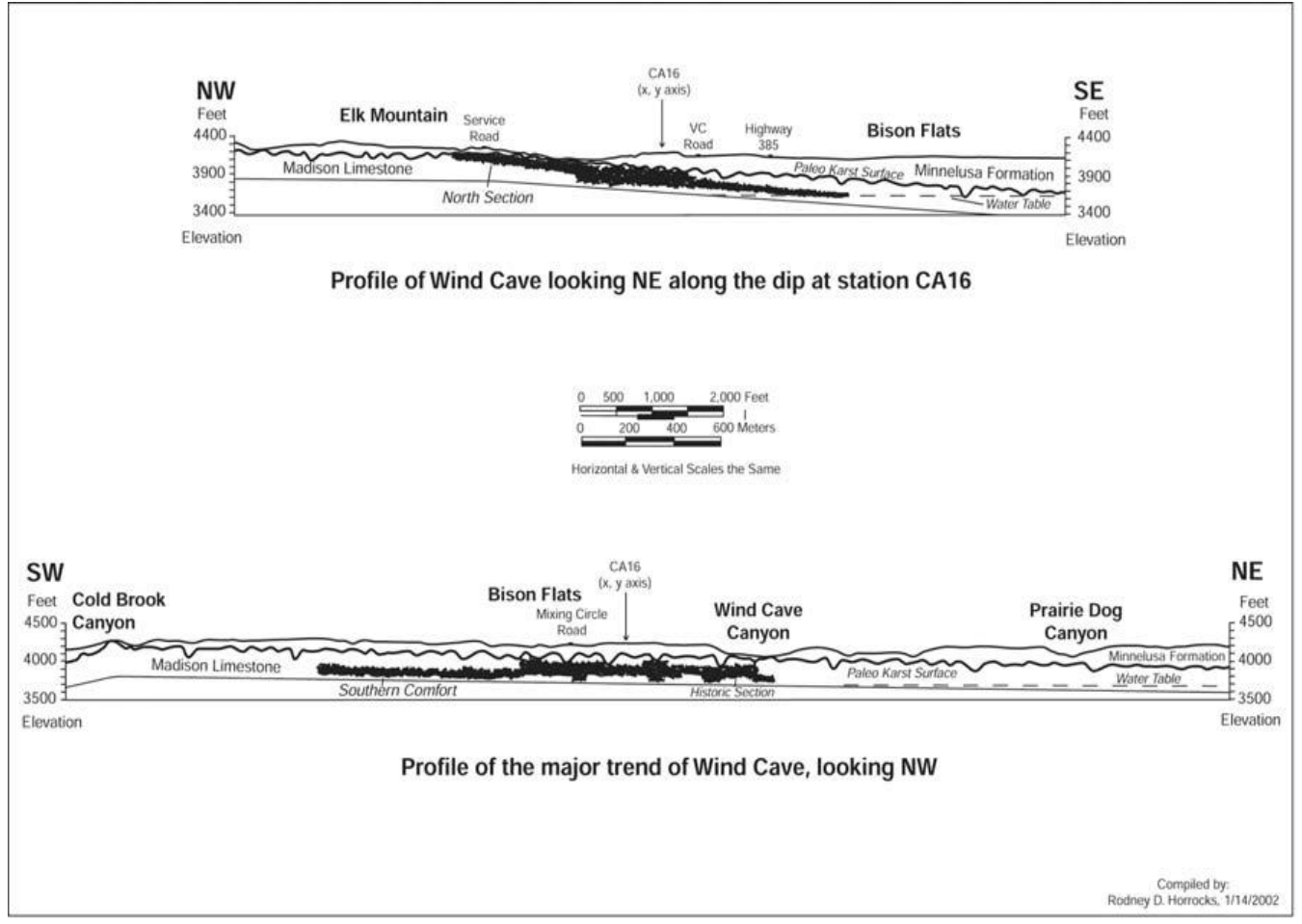
Figure 4. Profile of Wind Cave along the major trends of the cave. (Source: Horrocks and Szukalski, 2002].

Methods

The geochemical study for Wind Cave National Park relied on collecting groundwater, spring, stream and cave water samples and analyzing a wide variety of analytes. The selection of sampling sites and the purpose of different kinds of samples are described in the "Study Design" section. The sampling process and analytical methods are described in the "Field Sampling Protocols" section.

Study Design

Twenty-seven sample sites were sampled for fifteen parameters, two stable isotopes, three chlorofluorocarbons, and one radioactive isotope (Figure 5, Figure 6 and Table 1). Samples of stream water, cave water, spring discharge, and groundwater were collected during four sampling periods. The first group of samples were collected in March prior to spring runoff and consisted of a subset of sample sites in the vicinity of the park (HUN well, STR well, Beaver Creek Spring, Hot Springs Intake Spring, and Hot Brook Spring). The second group of samples was collected in June and included all twenty-seven sample sites. The third and fourth groups of samples were collected in July and September and consisted of a subset of sample sites, similar to the first sampling effort.

Sample sites were chosen to characterize local recharge to the Madison aquifer, water found in Wind Cave, groundwater in wells completed in the Madison aquifer, and discharge areas from the Madison aquifer. Local recharge to the aquifer was represented by headwater springs. Naus and others (2001) defined headwater springs as those springs located above streamflow loss zones. Springs noted as headwater springs in this study were sampled solely for stable isotopes to characterize the isotopic signature of local recharge and were not sampled for major ions. Drip water in Wind Cave was sampled to represent water that has infiltrated through the subsurface, whereas stream samples collected above streamflow loss zones in Highland Creek and Beaver Creek were sampled to represent water that infiltrates into the subsurface through loss zones in channels. Sites sampled for major ions were classified as local wells, cave sites (including both drip sites and underground lakes), regionally fed springs, regionally fed wells, and streams. Sites sampled for stable isotopes were classified as headwater springs, local wells, cave sites, regionally fed springs, regionally fed wells and streams. Locations of sites sampled in the vicinity of the park are shown in Figure 5 and sites within Wind Cave are shown on Figure 6.

Samples were analyzed for field parameters (pH, specific conductance, dissolve oxygen and alkalinity) major ions (calcium, magnesium, potassium, silica, sodium, bicarbonate, chloride, sulfate, and nitrate plus nitrite), the trace metal arsenic, the stable isotopes of oxygen and hydrogen, the organic chlorine and fluorine containing compounds known as chlorofluorocarbons (CFCs) and tritium (Table 1).

Different chemical analyses provide different information about a water sample. Major anion and cation concentrations provide information about the minerals through which the water has flowed and may indicate possible contamination from anthropogenic activities. Stable isotopes of oxygen and hydrogen provide information about the geographic location of recharge and help distinguish between water recharged locally and water recharged at higher elevations or from some distance away. Anthropogenic tracers, such as chlorofluorocarbons (CFCs) and tritium,

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provide information about how long ago groundwater was recharged. Analysis of these constituents can be used to constrain conceptual models of the origin and flow-paths of groundwater.
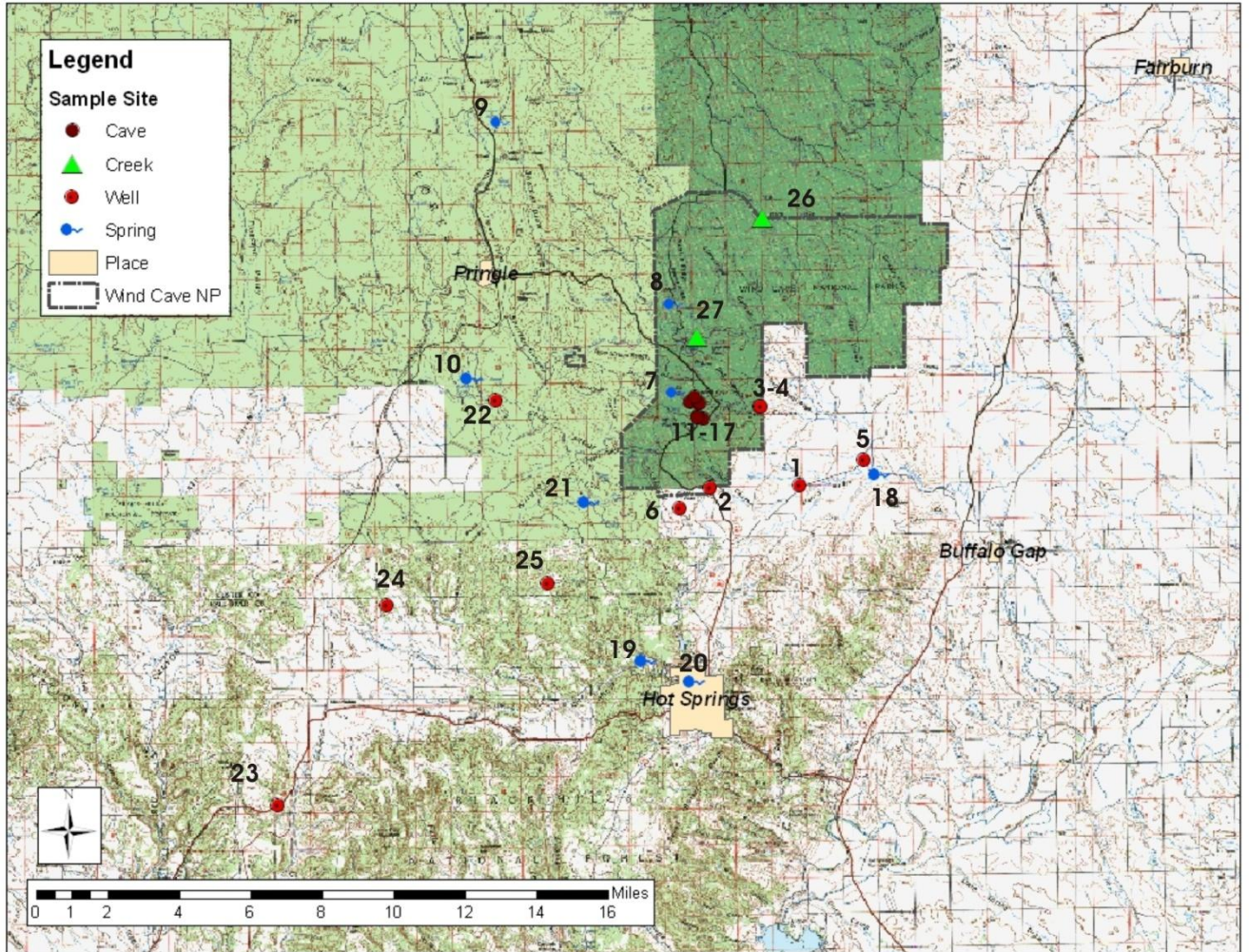
Figure 5. Site number and sample locations in the vicinity of Wind Cave National Park. Numbers correspond to Map ID numbers on Table 1.
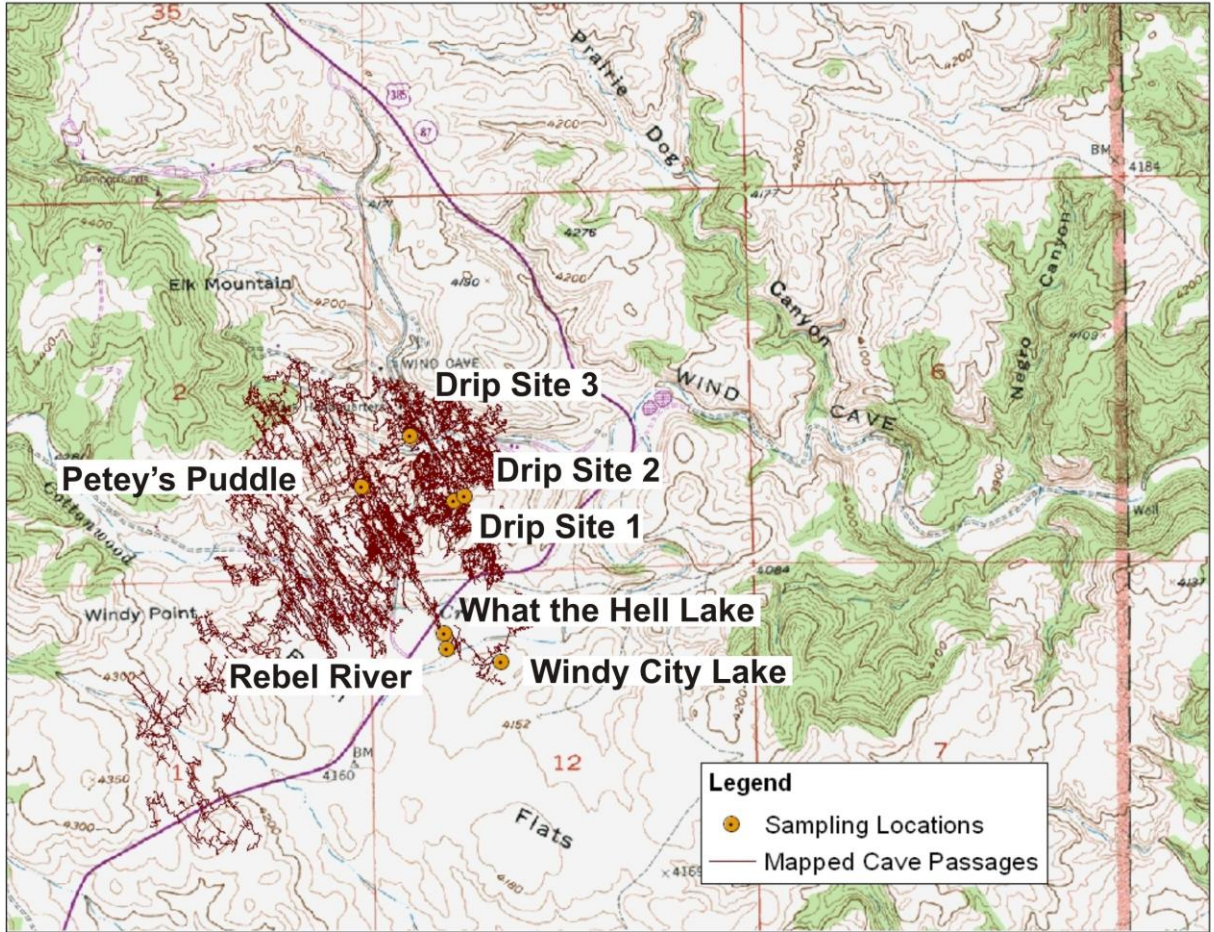
Figure 6. Location of sampling sites within Wind Cave. (Drip samples were collected from Room Draculum, WCTU Hall and the Caving Tour Drips).

Table 1. Parameters and Sites Sampled as part of the 2007 Geochemical Study.

Map ID	Station Number	Station Name	Field ID	Major Ions	Arsenic	Stable Isotopes	CFC	Tritium
			Local Wells					
1	433115103251401	7-11 MDSN (CU91A)	7-11 MDSN	x	x	x	x	x
2	433114103281601	Kaiser	KAI	x	x	x		
3	433311103263101	Park Well No. 1 (Headquarters Well)	Park Well 1	x	x	x		
4	433311103263102	Park Well No. 2 (New Well)	Park Well 2	x	x	x		
5	433150103230501	Streeter	STR	x	x	x	x	x
6	433034103284701	Strauss/Huntley	HUN	x	x	x	x	x
			Local Headwater Springs					
7	433333103291901	Elk Mountain Spring	Elk Mountain Spring			x		
8	433551103291901	RG Pegmatite Spring 1	RG Pegmatite Spring			x		
9	434020103350101	Sutherland Spring	Sutherland Spring			x		
10	433611103335801	Witch Spring	Witch Spring			x		
			Cave Sites					
11	433302103281507	Drip Site 1 (C53)	Drip Site 1	x	x	x		
12	433302103281508	Drip Site 2 (UD17)	Drip Site 2	x	x	x		
13	433302103281509	Drip Site 3 (NP38A)	Drip Site 3	x	x	x		x
14	433302103281504	Petey's Puddle (CC25C)	Petey's Puddle	x	x	x		
15	433302103281506	Rebel River (RD12)	Rebel River	x	x	x		
16	433302103281502	What the Hell Lake (JF83)	What the Hell Lake	x	x	x	x	x
17	433302103281501	Main Lake (JF901)	Windy City Lake	x	x	x		
			Regionally Fed Springs					
18	433128103223401	Beaver Creek Spring	Beaver Creek Spring	x	x	x	x	x
19	432703103302801	Hot Brook Spring	Hot Brook Spring	x	x	x	x	x
20	432632103285302	Hot Springs Intake Spring	Hot Springs Intake Spring	x	x	x		
21	433056103322201	Woodcock Spring	Woodcock Spring			x		
			Regionally Fed Wells					
22	433326103352001	Converse/Wahle	CON	x	x	x		
23	432340103421501	Miller/Simon	MIL	x	x	x		
24	432825103391201	Svenkeson/Marler	SVE	x	x	x		
25	432858103334201	Wood/Bogli	BOG	x	x	x	x	x
			Stream Sites					
26	433745103261900	HIGHLAND CR ABV MADISON	Highland Creek	x	x			
27	6402430	BEAVER CR NR PRINGLE, SD	Beaver Creek	x	x			x

The influence of parking lot runoff on cave drip was investigated from 2002 to 2003 (Heakin, 2004). Arsenic detected at a drip site known as Minnehaha Falls and in water quality samples from Park Well No. 2 has concerned resource managers at Wind Cave National Park. Park Well No. 2 was originally drilled as a replacement well for Park Well No. 1, but is not being used as a water supply due to the presence of arsenic and fluoride exceeding the Environmental Protection Agency (EPA) maximum contaminant levels (MCLs) for drinking water (10 µg/l for arsenic and 4 mg/l for fluoride). Arsenic ranged from 11.0 to 28 µg/l, and fluoride ranged from 4.40 to 5.37

mg/l in NPS Well No. 2 between 2001 and 2004. Arsenic in drinking water can impact human health and excess fluoride in drinking water has been associated with dental fluorosis, or mottling, of teeth. Both arsenic and fluoride may occur naturally in water. However, the use of inorganic pesticides containing arsenic and parking lot runoff have both been suggested as possible sources of arsenic in both cave and drip water. In order to address these concerns, arsenic was also included in the list of parameters sampled as part of this study.

Twenty four sites were sampled for major ions, arsenic and stable isotopes in June. A subset of five sites was also sampled for major ions, arsenic and stable isotopes in March, July and September. Four headwater springs, including two in the park, were only sampled for stable isotopes to characterize the isotopic signature of local precipitation. Seven wells, cave sites and springs were sampled for CFCs, and nine wells, cave sites and springs were sampled for tritium to obtain information on the residence time of water at various points in the aquifer.

Field Sampling Protocols

Samples were collected using standard methods and protocols of the United States Geologic Survey for water quality sampling (Wilde and others, 1998). Prior to sample collection, non-flowing wells were purged by withdrawing at least one well-volume of water. A closed flow-through cell was attached to the wellhead, and sampling began when temperature, pH and conductivity stabilized. Samples collected for common ion analyses were collected in three categories; raw unfiltered, filtered with 0.45 μm filter capsules and untreated, and filtered with 0.45 μm filter capsules and preserved with nitric acid.

Field measurements of pH, temperature, and specific conductance were made at each site and equipment was calibrated using standard pH and specific conductance solutions. Total carbonate alkalinity was measured in the field by titration as soon as possible following sample collection. After samples were collected, filtered and preserved, if applicable, they were shipped to the USGS National Water Quality Laboratory in Denver, CO for analysis. Stable isotope samples were analyzed by the USGS Reston Stable Isotope Laboratory in Reston, VA. CFC samples were analyzed by the USGS Reston Chlorofluorocarbon Laboratory in Reston, VA.

Quality assurance samples were collected and analyzed to provide assurance that field sampling techniques and laboratory analyses did not introduce bias or error into the results. Quality assurance samples consisted of blanks and duplicate samples. Blanks were collected by pumping high purity deionized water through the sampling equipment and processing in a manner identical to field samples. Duplicate samples were collected for at least 10% of the samples and analyzed concurrently with field samples.

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Geochemical Investigation

This section describes general information on the techniques used in this study to understand the origin, flow-path and groundwater age in the vicinity of the park. The section "Chemical Composition" includes a description of minerals controlling the chemical composition of the Madison aquifer, and a description of the geochemical techniques used to investigate the chemical reactions that occur between points of recharge and sample locations within the aquifer. The section "Isotope Composition" provides background information about stable isotopes and how they are used to provide information about areas of recharge and mixing between regional and local flow-paths. The two different techniques used to estimate the time since recharge occurred at a particular location in the aquifer are described in the section "Age Dating of Groundwater." Finally, the section "Geochemical Modeling" describes the use of a geochemical model to evaluate conceptual flow-paths.

Chemical Composition

The reaction between water, minerals and dissolved gases control the chemical composition of groundwater in an aquifer. The major reactive minerals in the Madison aquifer are calcite, dolomite and anhydrite, and the most important reaction that is occurring in the aquifer is the process of dedolomitization (Back and others, 1983; Plummer and others, 1990; and Busby and others, 1991). Dedolomitization is the process where dolomite dissolves and calcite precipitates in the presence of anhydrite or gypsum in a carbonate aquifer.

Understanding the dedolomitization process relies in part on the use of saturation indices of minerals. The saturation index for a mineral is defined as the log of the ion activity product divided by the equilibrium constant for a mineral dissolution reaction (Appelo and Postma, 2005). In general terms, if the saturation index for a mineral is greater than zero, the mineral could precipitate from solution, but cannot dissolve; if the saturation index is less than zero, the mineral could dissolve but not precipitate; if the saturation index is equal to or near zero, the mineral is considered to be in equilibrium with the solution.

Busby and others (1983) and Naus and others (2001) noted that in the Madison aquifer, conditions consistent with dedolomitization are waters in equilibrium with calcite, undersaturated with respect to dolomite, and undersaturated with respect to anhydrite. Relatively dilute concentrations of water samples from recharge areas and the progression toward higher concentrations of calcium, magnesium and sulfate with lower values of pH in regionally fed wells and springs are evidence of dedolomitization in the study area.

Anhydrite is not known to be extensive in the Madison Limestone in the southern Black Hills, although it is found elsewhere in the Madison Limestone such as in North Dakota. It is abundant in the overlying Minnelusa Formation. Epstein (2005) noted that anhydrite is mostly absent in surface outcrops of the Minnelusa Formation because of dissolution by circulating groundwater, but it is found in abundance in the subsurface. As much as 235 feet of anhydrite was described in the upper part of the Minnelusa Formation in a log from Hell Canyon, which is on the southwestern flank of the Black Hills (Epstein, 2005).

Dissolution of anhydrite proceeds slowly down-dip resulting in a transition zone within the formation, up-gradient of which anhydrite is no longer present and down-gradient of which active dissolution is taking place (Figure 7). Water discharging from springs in these transition zones is characterized by
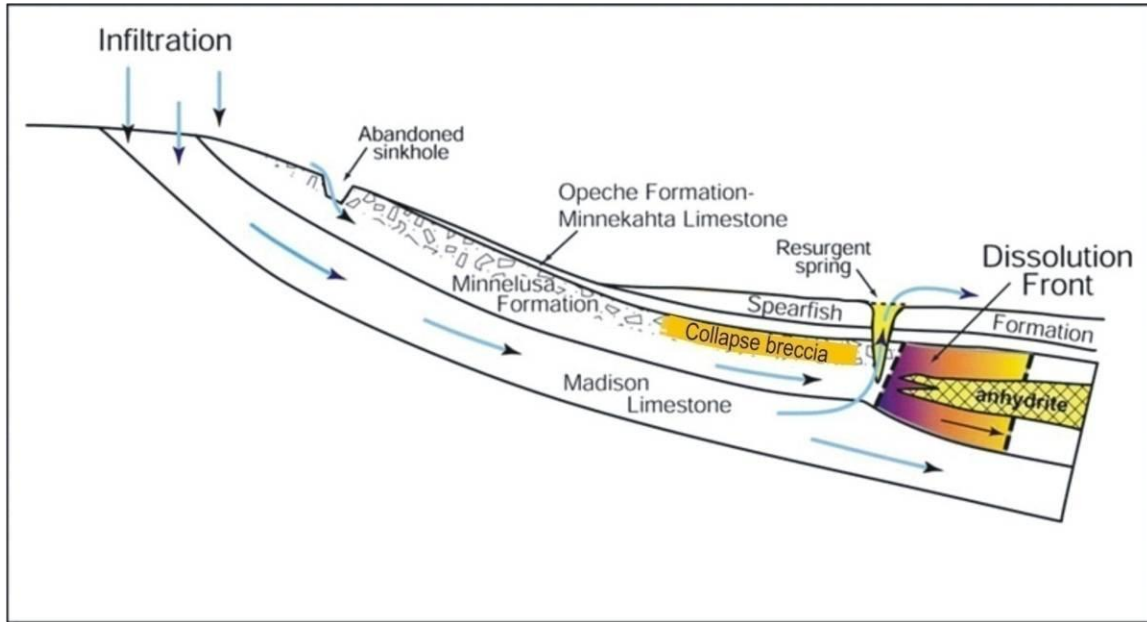
Figure 7. Dissolution of anhydrite in the Minnelusa Formation through interaction of water discharging from the Madison Limestone [Modified from Epstein, 2005].

higher concentrations of calcium and sulfate associated with the dissolving anhydrite. The higher calcium, magnesium and sulfate concentrations at Beaver Creek Spring and Cascade Springs are attributed to the process of dedolomitization (Back et al., 1983; Busby et al., 1983).

Isotope Composition

Stable isotopes of oxygen (^{18}O and ^{16}O) and hydrogen (^{2}H and ^{1}H) are used to evaluate recharge areas, flow-paths and mixing of waters from different areas. The radioisotope tritium, which is not stable, is used to evaluate groundwater age, and will be discussed in a subsequent section.

Isotopes are atoms of an element that have the same number of protons but different number of neutrons. The difference in the number of neutrons creates a slightly different mass in the various isotopes of an element. For example, an oxygen atom with a mass of 18 (denoted ^{18}O) has two more neutrons than the more common oxygen atom with a mass of 16 (^{16}O). Among the hydrogen isotopes, deuterium (denoted as D or ^{2}H) has one neutron and one proton. This is approximately twice the mass of protium (^{1}H), the more common atom of hydrogen with only one proton. Tritium (^{3}H) has 2 neutrons and one proton, or approximately three times the mass of protium.

Stable isotopes of hydrogen (D) and oxygen (^{18}O) may be used as tracers due to their mass difference and their relative abundance as water moves through the hydrologic cycle. Each water sample will have both ^{18}O and ^{16}O present, but the difference in the ratio of ^{18}O to ^{16}O in a water sample reflects the history of the air mass from which the water originally precipitated.

The stable isotopes of oxygen and hydrogen are reported using delta notation (δ), which compares the ratio of the heavy to light isotope in a sample to that of a reference standard. Delta values represent a difference in ratio, rather than an actual concentration. Delta values are reported as parts per thousand, or per mil (‰). For example, the isotope ratio of oxygen-18 in a water sample is written as follows:

$$\delta\ ^{18}O_{sample} = \frac{(^{18}O/^{16}O_{sample} - {}^{18}O/^{16}O_{standard})\ x\ 1000\ ‰\ _{VSMOW}}{^{18}O/^{16}O\ _{standard}}$$

where VSMOW stands for Vienna Standard Mean Ocean Water, the reference standard.

During phase changes from water vapor to precipitation, the ratio of heavy to light isotopes changes. As water vapor condenses, heavier isotopes (^{18}O and D) become more concentrated in the liquid phase, and lighter isotopes (^{16}O and ^{1}H) remain in the vapor phase. As the cloud mass loses more of the heavier isotope relative to the lighter isotope through rainfall, the delta value of the cloud mass becomes progressively more negative.

The more negative the reported value, the more depleted that sample is in the heavier isotope. The greater the positive reported value, the more enriched or concentrated that sample is in the heavier isotope. A sample with a δ value of -10 ‰ is depleted by 10 parts per thousand in the heavier isotope relative to the standard. A sample with a δ value of +10 ‰ is enriched by 10 parts per thousand in the heavier isotope relative to the standard.

Since the water molecule contains both oxygen and hydrogen atoms, a relationship exists between the concentration of $\delta^{18}O$ and δD values found in a water sample. When $\delta^{18}O$ and δ^2H values of precipitation samples collected from around the world are plotted together on an x-y plot, the data form a linear band that can be fitted with a linear equation, known as the global meteoric water line (Craig, 1961);

$$\delta D = 8 * \delta^{18}O + 10$$

Most precipitation from a local geographic area will have a distinct isotopic signature because it reflects the history of the air mass and the distance it has traveled. The isotopic composition of samples collected from wells and springs that are recharged locally will plot on a straight line (the local meteoric line) representing the variability in isotopic composition of local precipitation. The slopes of local meteoric water lines for areas within the continental United States generally plot slightly below but parallel to the global meteoric water line.

The difference in stable isotopic composition from north to south and west to east in the Black Hills serves as a natural tracer for groundwater flow paths. Several investigators have noted that δD and $\delta^{18}O$ in precipitation in the southeastern Black Hills are more positive than in the north or along the western flank due to lower elevations and warmer weather patterns from the south. Back and others (1983) and Naus and others (2001).

Age Dating Groundwater

The two groundwater dating techniques used in this study, tritium and CFCs, are tools used to determine whether recharge has occurred since about the 1950s. Each technique has certain advantages and disadvantages, but the use of both techniques is a means of validating the results.

Groundwater age is defined as the amount of time that has elapsed since the water first entered the aquifer (Kazemi and others, 2006). Alternatively, the groundwater residence time is the time it takes for a molecule of water to travel from the recharge area to the discharge area. It is important to recognize that the age estimated using an environmental tracer depends on how well the chemical substance is transported with the aqueous phase. The concentration of any chemical substance can be affected by chemical processes such as degradation, sorption or mixing. For this reason the reported ages are referred to as "apparent ages" or "model ages".

Groundwater age is generally classified as young, old and very old. Young groundwater generally refers to water ranging from less than a year to 50 or 60 years. Old groundwater ranges in age from about 60 to 50,000 years, and very old groundwater ranges in age from 50,000 to more than 100,000 years. The two techniques used in this study, chlorofluorocarbon and tritium, are environmental tracers that are used to determine whether or not there is young water present in the system.

The concept of groundwater age is particularly useful in understanding the renewability or replenishment of a groundwater system. Young groundwater is an indication of a groundwater system where rainfall actively recharges the system, whereas old groundwater indicates a system

that is not easily replenished and where groundwater pumping would likely result in groundwater mining.

Chloroflourocarbons

Chlorofluorocarbons (CFCs) are environmental tracers that are useful for estimating the date at which a parcel of groundwater recharged a groundwater system (IAEA, 2006). These compounds have been used in a wide variety of industrial and refrigerant applications and are now present in the atmosphere. The concentration of CFCs in the atmosphere is related to the amount of production of CFCs at that time. The age of groundwater at a particular location can be estimated by comparing concentrations in groundwater samples to historical atmospheric concentrations. Three compounds of CFCs that are used as tracers include CFC-12, CFC-11, and CFC-113. Examining all three of these tracers in conjunction with tritium can be helpful when characterizing groundwater mixtures. Because CFCs are dissolved gases, analytic results are expressed as parts per trillion by volume (pptv).

Use of CFCs as hydrologic tracers requires knowledge about the temperature of recharge and the elevation where recharge occurred. Temperature and elevation will affect the equilibrium solubility of a gas and are therefore needed to interpret the CFC data. This information is derived from dissolved gas data, such as nitrogen, argon and oxygen, which are analyzed from the sample at the time of the CFC analysis. If these data are not available, the estimated mean annual temperature may be substituted. Small changes in the above variables can significantly change the estimated age of the water sample.

The CFC laboratory in Reston, Virginia provides an estimated age of groundwater assuming piston flow. The piston flow model assumes that groundwater flows from recharge to discharge areas without exchanging water with confining layers. This assumption does not account for mixing scenarios that can occur in wells with large open intervals or from springs where multiple flow lines may converge. The modeled age that is reported assumes that the concentration of the CFC was not altered by transport processes from the point of entry to the measurement point in the aquifer.

In anoxic environments, CFC-11 degrades first, followed by CFC-113 and CFC-12. Under these conditions some or all of the model ages will appear older than they actually are. In the interpretation of CFC ages, the ages are considered reliable when all CFC tracers give similar model ages. If the model ages differ, CFC-12 has proved to be the most reliable tracer followed by CFC-113 and CFC-11.

Tritium

Tritium (^{3}H) is a short-lived radioisotope of hydrogen with a half-life of 12.43 years that is used to characterize the apparent age or residence time of groundwater. Nuclear testing during the 1950s and 1960s resulted in sharp increases in atmospheric tritium concentrations that have naturally declined since the testing was banned. Bomb-produced tritium can be used as a tracer in studying young groundwater to help determine flow rates and residence times. It can also be helpful in observing preferential flow paths and in investigating the mixing of waters. Tritium is reported in picocuries per liter, or tritium units (TU), where 1 TU = 3.2 pCi/l.

The large pulse of tritium that entered the hydrologic cycle in the 1960's can be used to establish the age of recent groundwater recharge. High levels of tritium (> approximately 30 TU) indicate water that was recharged during the late 1950's or early 1960's; moderate concentrations indicate water recharged during the past few decades; levels close to detection (approximately 1 TU) are likely old or very old groundwaters that have mixed with young groundwaters (Clark and Fritz, 1997).

Water pumped from a well or discharging from a spring is a mixture of waters from all the flow lines reaching the discharge point. Groundwater in karst aquifers flows through a complex network of pipe-like conduits, fractures, and other interconnected pore spaces. Conduit, intermediate and diffuse flow are three distinct components of karst aquifer flow. Water moving along these different flow lines will exhibit different ages. Wells and springs hydraulically connected to the various types of interconnected pore spaces will yield water with a distributed age.

Geochemical Modeling

Geochemical modeling using the computer program NETPATH (Plummer and others, 1994) was performed to evaluate groundwater flow paths in the vicinity of Wind Cave. NETPATH is used to determine geochemical reactions needed to account for a change in chemical composition along a flow path. NETPATH assumes that if the chemistry of the initial and final solutions are known, possible chemical reactions and the extent to which these reactions have occurred could be calculated based on mass-balance principles. NETPATH can also calculate mixing proportions of two or more initial waters to produce water at an endpoint along a flow path. NETPATH will find all plausible chemical reactions that could produce the final water. Constraints entered into the model include mineral phases encountered along the flow path. The greater the number of constraints used in the model, the fewer the number of plausible reactions found.

Model assumptions include the following:

1. The initial and final waters occur along a flow path and are hydraulically connected.
2. Dispersion and diffusion do not affect the solution chemistry.
3. Mineral phases used in the calculations are present.
4. The system was at steady state and the concentrations of the initial and final waters are not changing over time.

Results

The study results are reported in this section. Most data discussed in this report are from samples collected as part of this study. Results for two additional springs sampled by Naus and others (2001) in the vicinity of Hot Springs are also discussed in parts of the report (Evan's Plunge and Cascade Spring). All of the sites are assumed to be fed, at least in part, by the Madison aquifer.

Water Chemistry

This section describes the results of chemical analysis. Samples are classified as either local wells, cave sites, regionally fed springs, regionally fed wells, or streams. Headwater springs were not sampled for major ions since those in the vicinity of the park were not sourced in the Madison aquifer. Water chemistry data and corresponding Field IDs are reported by group in Table 2, and shown graphically in stiff diagrams in Figures 8, 9 and 10. The stiff diagrams use three parallel horizontal axes extending on both sides of a vertical zero axis. Concentrations of cations are plotted on each axis to the left of zero, and concentrations of anions are plotted on each axis to the right of zero. Concentrations are reported in milliequivalents per liter. The patterns produced in the diagrams are a distinctive method of showing water chemistry differences and similarities between samples.

Streams

Water samples collected from streams within the park are relatively dilute and dominated by calcium magnesium bicarbonate (Table 2). Beaver Creek contains higher levels of nearly all ions, including chloride, when compared to Highland Creek, drip sites, and underground lakes. Chloride concentration in Beaver Creek was 14.3 mg/l, whereas concentrations in four underground lakes ranged from 3.0 to 4.5 mg/l, and concentrations in Highland Creek ranged from 2.9 to 3.06 mg/l. The higher concentration of chloride in Beaver Creek suggests that it is unlikely that water from Beaver Creek contributes directly to the underground lakes.

Cave Sites

Water sampled from within Wind Cave is remarkably dilute and is also dominated by calcium-magnesium bicarbonate. The pH of underground lakes in Wind Cave ranged from 7.8 and 8.1 and drip sites ranged from 8.1 to 8.4. Underground lake water was oversaturated with respect to calcite, as demonstrated by the thin calcite rafts that form on the surface of quiescent lakes. The greatest concentrations of arsenic sampled during this study were found in drip sites, with values ranging from 25.2 to 34.2 µg/l, which is greater than the EPA MCL of 10 µg/l. Nitrite plus nitrate was also higher in water sampled from Wind Cave than anywhere else in the study, except for the CON well, although values were well below the EPA MCL.

Locally Recharged Groundwater

The chemical composition of groundwater generally evolves from relatively dilute in areas of recharge to higher concentrations in discharge areas. The distinction between locally recharged groundwater and regionally fed groundwater is largely based on isotopic composition, which is dicussed in the "Isotope Chemistry" section. Groundwater sampled in this study includes water recharged locally in the vicinity of the park, water that flows easterly along the southern margin of the Black Hills from recharge areas on the western flank, and water that is a mixture of the two. The pH of locally recharged groundwater ranged from 6.8 to 7.7 at the STR Well, with most values between 7.1 and 7.3. Specific conductance ranged from 327 to 435 µS/cm in local wells,

Regionally Fed Groundwater

The pH of regionally fed groundwater ranged from 7.3 at the MIL well to 7.8 at the BOG well, with most values equal to 7.7. Specific conductance ranged from 455 to 743 µS/cm in regional wells. Except for the BOG well, calcium, magnesium and carbonate concentrations were generally greater in samples from wells sampled along a regional flow path than in locally recharged wells, likely due to a longer residence time in the aquifer. Sodium and chloride were both higher in the MIL well than other regionally fed wells sampled as part of this study.

Regionally Fed Springs

Higher sodium and chloride concentrations are evident in Hot Brook Spring, Hot Springs Intake Spring and one well west of Hot Springs (MIL well). Chloride ranged from 45.4 at Hot Brook Spring, to 48 at the MIL well, and 97.5 mg/l at the Hot Brook Intake Spring. Chloride values reported by Naus and others (2001) were 110 mg/l at Evan's Plunge and 47 mg/l for Cascade Spring. The chloride values reported for Beaver Creek Spring (33.1 mg/l) and Cascade Spring (47 mg/l) lie midway between values reported for local wells and the higher concentrations reported in the Hot Springs area at Evan's Plunge Spring and the Hot Springs Intake Spring. Both Beaver Creek Spring and Cascade Spring show much greater concentrations of calcium and sulfate than any other samples in this study (Figure 10).

Park Well No. 2

Water from Park Well No. 2 does not resemble any other water sampled as part of this study. The well is considered to be completed in the Madison Limestone. However, water sampled from Park Well No. 2 is classified as sodium-bicarbonate type water. The difference in chemistry is due to greater concentrations of sodium, bicarbonate and chloride and a lesser concentration of calcium compared to nearby wells. The presence of higher concentrations of sodium in Park Well No. 2 is likely due to the exchange of Ca^{2+} for Na^+ as water percolates through clay rich sediments. These data suggest that Park Well No. 2 is likely drilled through a clay layer or lens within the Madison Limestone. Clay minerals have been found in minor amounts in the Madison Limestone (Busby et al., 1991) and in cave-fill and breccia sediment (Hayes, 1999). The exchange of one ion for another is called ion exchange, and it is common when groundwater flows through a clay-bearing aquifer. Calcium ion becomes adsorbed by clay minerals in exchange for sodium ion, which is released to groundwater. This exchange causes the calcium concentration to decrease and the sodium concentration to increase.

Table 2. Water Chemistry Results for the 2007 Wind Cave Study.

Station ID	Field ID	Date	DO	pH, field	Spec. Cond., field	ANC	Ca
			(mg/l)	(std. units)	(µS/cm)	(mg/l as CaCO$_3$)	(mg/l)
Local Wells							
433115103251401	7-11 MDSN	4/20/2007	4	7.3	403	170	40.4
433115103251401	7-11 MDSN	4/20/2007	4	7.3	403		40.1
433114103281601	KAI	7/9/2007	6.8	7.1	435	188	51.4
433114103281601	KAI	7/9/2007					51.6
433114103281601	KAI	9/26/2007	8.4	7.1	413	188	50.8
433311103263101	Park Well 1	5/24/2007	7.5	7.3	385	178	46.2
433311103263102	Park Well 2	5/24/2007	3.9	7.7	586	223	24.3
433150103230501	STR	3/14/2007	6.7	7.7	327		39
433150103230501	STR	4/17/2007	7.4	7.5	343	157	39.8
433150103230501	STR	7/10/2007		7.3	356	142	
433150103230501	STR	9/26/2007	0.5	6.8	342	158	40
433034103284701	HUN	3/14/2007	7.3	7.5	400		48.2
433034103284701	HUN	4/17/2007		7.3	419	190	50.5
433034103284701	HUN	9/27/2007	8	7.2	409	192	51
Cave Sites							
433302103281507	Drip Site 1 (C53)	4/27/2007	9.5	8.3	385	139	35.4
433302103281508	Drip Site 2 (UD17)	4/25/2007	9.6	8.4	339	157	45.7
433302103281509	Drip Site 3 (NP38A)	4/25/2007	9.7	8.4	252	120	37.2
433302103281504	Petey's Puddle (CC25C)	4/27/2007	9.4	8.1	331	157	34.4
433302103281506	Rebel River (RD12)	4/18/2007		7.8	435	182	43.2
433302103281502	What the Hell Lake (JF83)	4/18/2007		7.8	427	211	47.4
433302103281501	Windy City Lake	4/18/2007		8	335	149	35.7
Regionally Fed Springs							
433128103223401	Beaver Cr Spring	3/14/2007	4.8	7.3	2260		460
433128103223401	Beaver Cr Spring	4/17/2007	6.2	7.1	2390	179	443
433128103223401	Beaver Cr Spring	7/10/2007		7	2450	177	446
433128103223401	Beaver Cr Spring	9/26/2007	5.2	6.9	2350	177	478
432703103302801	Hot Brook Spring	3/15/2007	6.8	7.3	683		63.9
432703103302801	Hot Brook Spring	4/20/2007	6.9	7	700	208	64.5
432703103302801	Hot Brook Spring	4/20/2007	6.9	7	700		65.4
432703103302801	Hot Brook Spring	7/9/2007	5.2	7.1	718	206	
432703103302801	Hot Brook Spring	9/27/2007	7.7	7.2	669		66.3
432703103302801	Hot Brook Spring	9/27/2007	7.3	7.1	672	211	65.4
432632103285302	Hot Springs Intake Spr	3/15/2007	5	7.3	1020		87.5
432632103285302	Hot Springs Intake Spr	4/17/2007	5.4	7.2	1030	198	89.2
432632103285302	Hot Springs Intake Spr	7/9/2007	5.7	7	1040	198	
432632103285302	Hot Springs Intake Spr	9/27/2007	5.5	6.8	1050	204	94.1
Regionally Fed Wells							
433326103352001	CON	4/23/2007	8.6	7.7	579	240	65.4
433326103352001	CON	4/23/2007	8.6	7.7	579		66.5
432340103421501	MIL	4/23/2007	3.9	7.3	743	212	77.8
432825103391201	SVE	4/23/2007	8.4	7.7	455	231	53
432858103334201	BOG	4/26/2007	8.4	7.8	466	217	44.7
Streams							
433745103261900	Highland Cr ab MDSN	3/15/2007	10.4	8.8	286		38.9
433745103261900	Highland Cr ab MDSN	4/26/2007	10.2	9.2	288	131	41.3
433745103261900	Highland Cr ab MDSN	7/9/2007	2.8	8	315	138	
433745103261900	Highland Cr ab MDSN	9/26/2007	7.4	8.1	321	138	42
6402430	Beaver Cr ab MDSN	4/16/2007		8.1	538	196	68.2

Table 2 (continued).

Station ID	Field ID	Date	Mg	K	Na	HCO₃	Cl
			(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
Local Wells							
433115103251401	7-11 MDSN	4/20/2007	19.6	3.27	16.4	206	5.95
433115103251401	7-11 MDSN	4/20/2007	19.1	3.28	16.3		5.96
433114103281601	KAI	7/9/2007	18.5	2.92	9.74	229	5.74
433114103281601	KAI	7/9/2007	18.5	2.95	9.68		5.75
433114103281601	KAI	9/26/2007	18.4	3.06	9.86	228	5.52
433311103263101	Park Well 1	5/24/2007	15.9	2.94	12.8	217	5.1
433311103263102	Park Well 2	5/24/2007	13.5	3.37	91.8	270	20.2
433150103230501	STR	3/14/2007	13.8	2.44	9.08		2.48
433150103230501	STR	4/17/2007	14.1	2.35	9.32	190	2.55
433150103230501	STR	7/10/2007				172	
433150103230501	STR	9/26/2007	14.1	2.45	9.38	192	2.47
433034103284701	HUN	3/14/2007	17.1	2.98	9.57		5.88
433034103284701	HUN	4/17/2007	18.1	2.98	10.1	230	5.97
433034103284701	HUN	9/27/2007	17.6	3.03	10	233	5.75
Cave Sites							
433302103281507	Drip Site 1 (C53)	4/27/2007	16.9	4.48	12.6	167	13.2
433302103281508	Drip Site 2 (UD17)	4/25/2007	13	3.8	4.29	188	3.88
433302103281509	Drip Site 3 (NP38A)	4/25/2007	8.19	2.81	0.97	144	1.27
433302103281504	Petey's Puddle (CC25C)	4/27/2007	19.8	2	4.47	189	3.07
433302103281506	Rebel River (RD12)	4/18/2007	25.1	1.65	4.86	221	2.96
433302103281502	What the Hell Lake (JF83)	4/18/2007	27.1	1.71	5.08	255	3.02
433302103281501	Windy City Lake	4/18/2007	19.4	2.28	7.67	180	4.46
Regionally Fed Springs							
433128103223401	Beaver Cr Spring	3/14/2007	76.8	5.18	29.2		32.5
433128103223401	Beaver Cr Spring	4/17/2007	73.3	4.69	27.4	217	32.9
433128103223401	Beaver Cr Spring	7/10/2007	77.3	5.35	30.5	215	33.8
433128103223401	Beaver Cr Spring	9/26/2007	79.4	5.34	30.8	215	33.1
432703103302801	Hot Brook Spring	3/15/2007	24.7	5.19	36		45.6
432703103302801	Hot Brook Spring	4/20/2007	25.3	5.15	36.9	253	45.5
432703103302801	Hot Brook Spring	4/20/2007	25.8	5.27	37.2		45.4
432703103302801	Hot Brook Spring	7/9/2007				251	
432703103302801	Hot Brook Spring	9/27/2007	25.7	5.25	38.4		45.1
432703103302801	Hot Brook Spring	9/27/2007	25.4	5.28	36.8	256	45
432632103285302	Hot Springs Intake Spr	3/15/2007	28	8.31	70		97.5
432632103285302	Hot Springs Intake Spr	4/17/2007	29.1	8.34	71.9	240	99.1
432632103285302	Hot Springs Intake Spr	7/9/2007				241	
432632103285302	Hot Springs Intake Spr	9/27/2007	30.1	8.76	74.4	248	94
Regionally Fed Wells							
433326103352001	CON	4/23/2007	29.9	4.13	10.8	292	8.1
433326103352001	CON	4/23/2007	30.3	4.25	10.9		7.95
432340103421501	MIL	4/23/2007	26.6	5.5	37.5	257	48
432825103391201	SVE	4/23/2007	26.8	1.96	4.67	281	1.86
432858103334201	BOG	4/26/2007	29.9	1.97	6.29	262	2.63
Streams							
433745103261900	Highland Cr ab MDSN	3/15/2007	7.25	2.09	7.93		3.06
433745103261900	Highland Cr ab MDSN	4/26/2007	7.46	1.86	8.24	146	3.01
433745103261900	Highland Cr ab MDSN	7/9/2007				163	
433745103261900	Highland Cr ab MDSN	9/26/2007	7.89	2.14	8.42	166	2.9
6402430	Beaver Cr ab MDSN	4/16/2007	21.7	4.45	13.7	236	14.3

Table 2 (continued).

| Station ID	Field ID	Date	SO4	NO$_2$ + NO$_3$	As	Mn	Si
			(mg/l)	(mg/l as N)	(µg/l)	(µg/l)	(mg/l)
Local Wells							
433115103251401	7-11 MDSN	4/20/2007	23.5	0.31	0.28	86.3	12.8
433115103251401	7-11 MDSN	4/20/2007	23.5	0.313	0.25	84.9	12.3
433114103281601	KAI	7/9/2007	16.4	0.616	6.8	0.9	16.3
433114103281601	KAI	7/9/2007	16.3	0.618	6.6	0.9	16.2
433114103281601	KAI	9/26/2007	16.4	0.626	7.1	0.8	14.9
433311103263101	Park Well 1	5/24/2007	17.9	0.569	8.5	0.2	16.1
433311103263102	Park Well 2	5/24/2007	43.8	0.21	26.7	1.6	11.1
433150103230501	STR	3/14/2007	11.2	0.511	8.9	0.2	16.3
433150103230501	STR	4/17/2007	11	0.52	8.5	0.1	16.4
433150103230501	STR	7/10/2007					
433150103230501	STR	9/26/2007	11.3	0.513	8.9	0.2	15.8
433034103284701	HUN	3/14/2007	17.3	0.589	7.9	0.3	15.5
433034103284701	HUN	4/17/2007	17.2	0.608	7.7	0.5	15.4
433034103284701	HUN	9/27/2007	17	0.596	7.4	1.1	15
Cave Sites							
433302103281507	Drip Site 1 (C53)	4/27/2007	21.3	1.36	34.2	0.2	17.6
433302103281508	Drip Site 2 (UD17)	4/25/2007	10.7	1.55	29.3	0.2	17.5
433302103281509	Drip Site 3 (NP38A)	4/25/2007	7.44	0.455	25.2	0.2	19.3
433302103281504	Petey's Puddle (CC25C)	4/27/2007	6.62	0.959	13.1	0.2	12.6
433302103281506	Rebel River (RD12)	4/18/2007	6.76	1.29	12.6	0.2	13.4
433302103281502	What the Hell Lake (JF83)	4/18/2007	6.91	1.32	12.8	0.2	13.2
433302103281501	Windy City Lake	4/18/2007	9.17	2.38	16.4	0.6	13.9
Regionally Fed Springs							
433128103223401	Beaver Cr Spring	3/14/2007	1280	0.409	2.1	0.6	16
433128103223401	Beaver Cr Spring	4/17/2007	1290	0.39	2.1	0.5	14.9
433128103223401	Beaver Cr Spring	7/10/2007	1290		1.7	0.2	16.5
433128103223401	Beaver Cr Spring	9/26/2007	1280	0.391	2	0.6	14.3
432703103302801	Hot Brook Spring	3/15/2007	69.3	0.431	6.6	0.2	18.2
432703103302801	Hot Brook Spring	4/20/2007	67.5	0.417	7.2	0.2	18.1
432703103302801	Hot Brook Spring	4/20/2007	67.4	0.423	7.2	0.2	18.4
432703103302801	Hot Brook Spring	7/9/2007					
432703103302801	Hot Brook Spring	9/27/2007	68.1	0.429	6.6	0.2	17.1
432703103302801	Hot Brook Spring	9/27/2007	67.8	0.43	6.3	0.2	16.8
432632103285302	Hot Springs Intake Spr	3/15/2007	167	0.45	5.8	0.2	23.8
432632103285302	Hot Springs Intake Spr	4/17/2007	168	0.456	5.7	0.2	22.7
432632103285302	Hot Springs Intake Spr	7/9/2007					
432632103285302	Hot Springs Intake Spr	9/27/2007	174	0.489	5.8	0.2	21.9
Regionally Fed Wells							
433326103352001	CON	4/23/2007	28.9	2.24	6.4	1.6	12.6
433326103352001	CON	4/23/2007	28.3	2.24	6.4	1.4	13.1
432340103421501	MIL	4/23/2007	110	0.112	0.99	38.6	22.1
432825103391201	SVE	4/23/2007	8.61	0.451	3.9	0.6	12.6
432858103334201	BOG	4/26/2007	10.5	1.29	15.8	0.3	12.7
Streams							
433745103261900	Highland Cr ab MDSN	3/15/2007	14.5	0.27	3.3	2.1	19.2
433745103261900	Highland Cr ab MDSN	4/26/2007	14.6	0.161	3	1.8	17.4
433745103261900	Highland Cr ab MDSN	7/9/2007					
433745103261900	Highland Cr ab MDSN	9/26/2007	15	0.111	2.4	2.1	19.4
6402430	Beaver Cr ab MDSN	4/16/2007	39.7	0.013	3.7	5.1	14.8

28
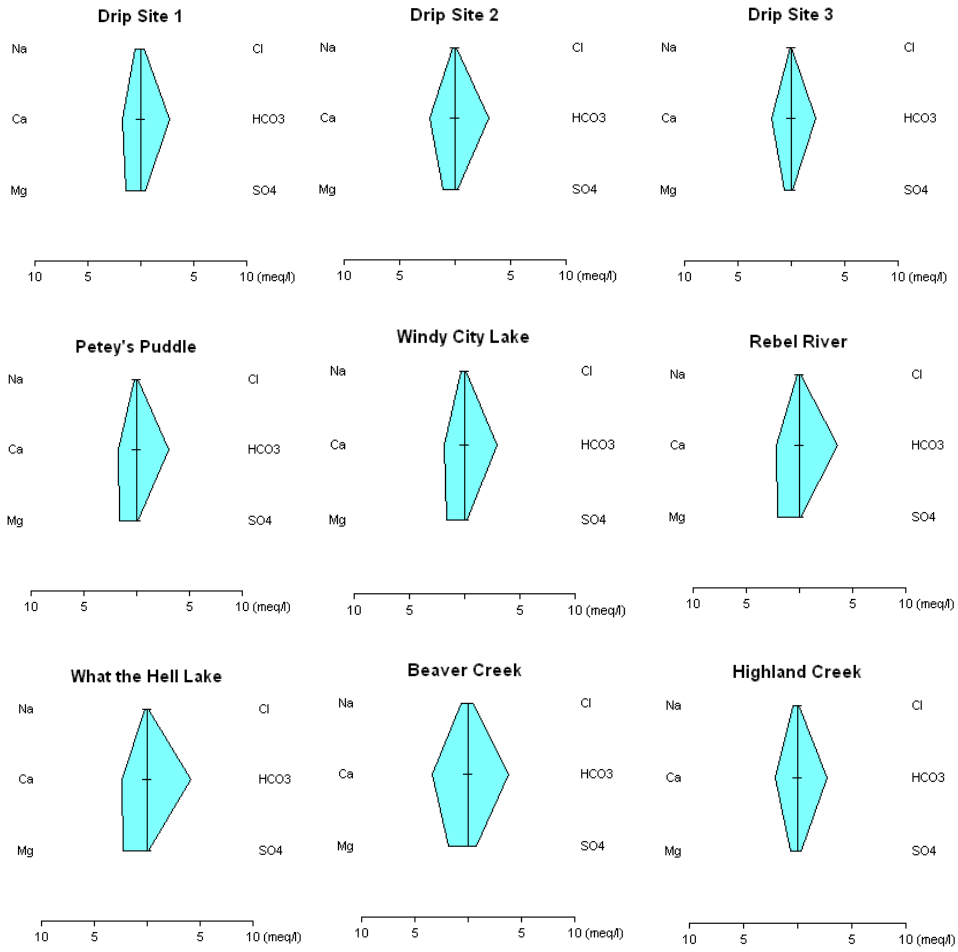
Figure 8. Stiff Diagrams of Cave and Stream Samples.
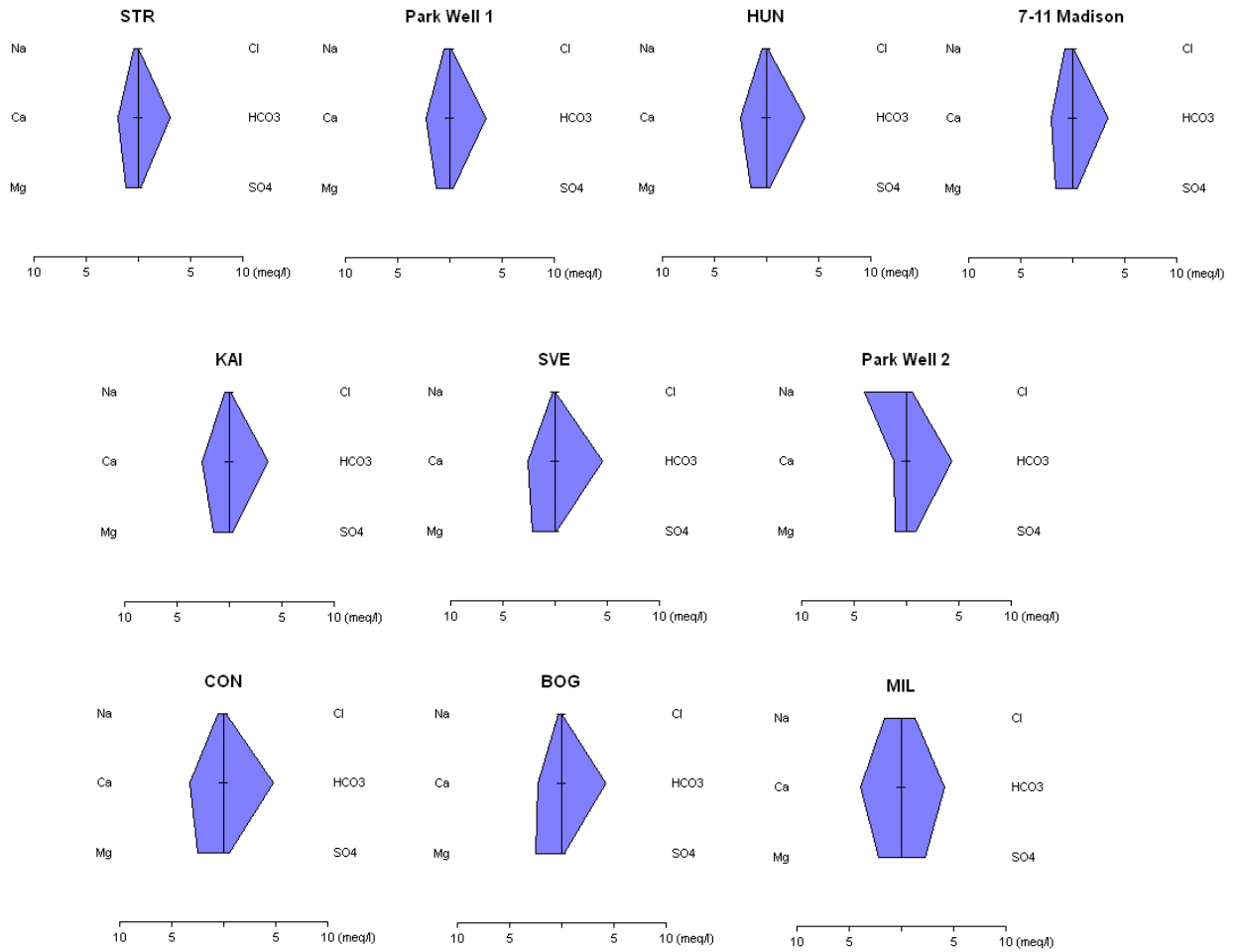
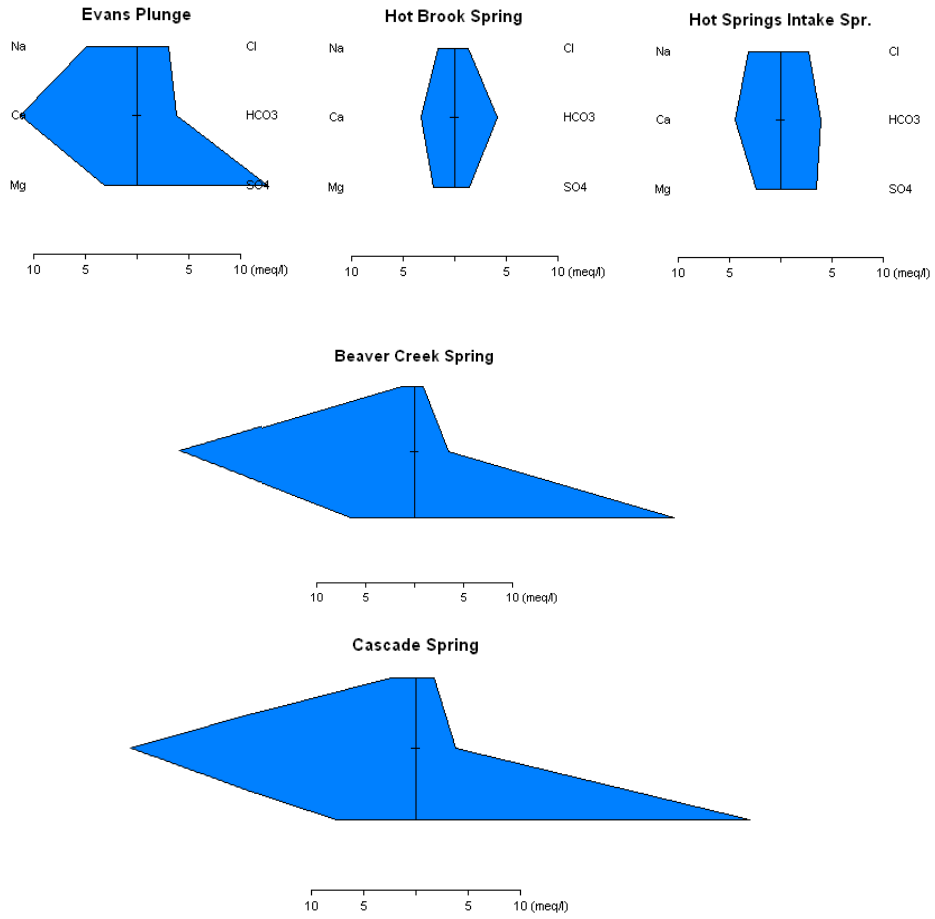**Figure 9. Stiff Diagram of Well Samples.**

Figure 10. Stiff Diagrams of Regionally Fed Springs.

Arsenic

Arsenic was found at relatively high concentrations in Park Well No. 2, in drip sites in Wind Cave, in the BOG well, and in underground lake water. The highest concentration was observed at Drip Site No. 1, with slightly lower values at Drip Site No. 2. Williamson and Carter (2001) reported arsenic concentrations that were greater than 10 μg/l in several streams and wells within the Black Hills. Although elevated arsenic concentrations in the Black Hills are associated with mining activities, arsenic is also naturally occurring within the central Precambrian core of the Black Hills. In their study of the water quality characteristics of groundwater and surface water of the Black Hills, Williamson and Carter (2001) noted that the highest concentrations of arsenic in groundwater were found in the Minnelusa Formation in the southern and eastern Black Hills.

Williamson and Hayes (2000), investigating mineralogic controls on arsenic solubility in Lawrence County, South Dakota, found a connection between pH, concentrations of calcite and dissolved arsenic concentrations. They noted that higher dissolved arsenic concentrations in streams occurred in areas where pH was above 8.0, and iron concentrations were relatively low in bed sediments. In drainages where the Madison Limestone was present, and the calcite saturation index was above zero, higher pH levels were associated with higher concentrations of dissolved arsenic.

Heakin (2004) evaluated the water quality of Cold Spring Creek, Highland Creek and Beaver Creek as they flow into the park. Arsenic concentrations were highest in Cold Spring Creek, followed by Highland Creek and then Beaver Creek. However, none of the stream samples were as high as those found in Wind Cave. The pH and calcite saturation index in Wind Cave appear to be suitable for arsenic mobilization. It is possible that the arsenic concentrations in Wind Cave originate from the overlying Minnelusa Formation, but further investigation is warranted.

Stable Isotope Composition

This section describes the results of isotopic analysis, which are reported by group and corresponding Field IDs in Table 3. A map of sample sites with associated δD values are shown on Figure 11. The δD and $\delta^{18}O$ values reported for samples from this study generally plot slightly below the global meteoric water line (Figure 12), as a result of the general meteoric conditions in the southern Black Hills. Water samples that plot significantly below (or to the right of) the meteoric water line indicate the effects of evaporation. The sample for Witch Spring was collected from a concrete cistern with no visibly moving water and its position to the right of the local meteoric water line indicates secondary fractionation due to evaporation. None of the other samples appear to be affected by secondary fractionation. Where secondary fractionation has not occurred, deuterium and oxygen-18 are well correlated. Therefore, only δD values are reported in the following sections.

Headwater Springs

Four headwater springs were sampled for stable isotopes to characterize the isotopic composition of local recharge. These four springs, two located within the park and two outside the park, all have relatively small catchments. The δD values for these springs ranged from -91.16 to -93.83 per mil.

Streams

Two streams were sampled at locations within the park, Beaver Creek and Highland Creek. The δD values ranged from -87.1 to -90.12 per mil. These values are consistent with values from an earlier study for French Creek (-89.1 and -89.8 per mil) located north of the park, but more positive than values reported for Beaver Creek (-91.9 and -92.4 per mil) from a site upstream of the park near Pringle (Naus and others, 2001). The difference is likely due to a relatively smaller drainage area and higher catchment elevation near Pringle than at the sample site in the park.

Cave Sites

Underground lakes were slightly more negative in isotopic values (both δD and $\delta^{18}O$) than local streams, while drip sites were slightly more positive (Table 3). Underground lakes had δD values ranging from
-90.14 to -91.50 per mil, which is close to the mean value calculated for local wells (-90.13 per mil, n= 10). Two of the three drip sites were more positive than headwater springs, local wells or streams in this study, although values fall parallel to the meteoric water line. Based on isotopic values, the source of water to underground lakes is likely local recharge. This finding is consistent with the results of the earlier work conducted by Millen and Dickey (1987), which found that the underground lakes were the result of direct meteoric recharge.

Deuterium values reported by Millen and Dickey (1987) are 10 per mil more positive than those reported as part of the current study. When the three samples from the 1980s are plotted on a graph with the meteoric water line, they clearly plot above the meteoric water line (Figure 12). Increased fractionation between water and minerals may result in waters that plot above the meteoric water line (Clark and Fritz, 1997). However, it is more likely that the difference is due to different laboratory analytic methods or a different reference standard than is in current use today. These historic δD values are much more positive than any samples reported for the Black Hills area (Naus et al., 2001). Therefore, care should be taken in interpreting the δD values from the earlier report.

Locally Recharged Groundwater

The isotopic values of local wells generally reflect the volume-weighted mean of annual precipitation (Clark and Fritz, 1997). The variation in isotopic values that normally occur within individual storms, between storms of different air mass trajectories, and due to seasonal effects are dampened in groundwater sampled in local recharge areas. The range in isotopic values found in local wells encompasses the range in isotopic values from headwater springs and streams (Table 3), and reflect the isotopic value of local recharge. The δD for local wells ranged from -87.14 to -93.28 per mil.

Regionally Fed Groundwater

The δD value of the MIL well (-124.95 per mil) is more negative than values in local wells, streams and cave sites in the park, and springs in the vicinity of Hot Springs. The MIL well has an isotopic signature that is similar to values reported at higher elevations along the western flank of the Black Hills (Naus et al., 2001and Plummer et al., 1990) and likely represents regional flow from the west. The δD value reported for the CON, BOG and SVE wells ranged from -98.6 to -114.46 per mil. These values are more negative than local recharge but not as negative as the MIL well and indicate mixing between local recharge and regional flow from the west.

Regionally Fed Springs

A wide range in δD values was observed in regionally fed springs. The δD values for springs in the Hot Springs area (-112.82 to -120.13 per mil) are more negative than local springs and streams, indicating the influence of regional flow from the west. The δD values observed at Beaver Creek Spring (-109.67 to -110.23) are also more negative than locally recharged groundwater and therefore must also represent a mixture of both regional flow from the west and local recharge. Differences in values between Beaver Creek Spring and springs in the Hot Springs area are due to different mixing proportions of regional and local recharge.

The isotopic value of Woodcock Spring (-97.6) is noteworthy because of its location just southwest of the park boundary and southwest of Wind Cave. Woodcock Spring is located within a drainage that cuts through the Minnelusa Formation. It is not clear whether water discharging at Woodcock Spring is solely derived from the Minnelusa aquifer, or is a mixture of water from both the Minnelusa and Madison aquifers. Naus and others (2001) examined interactions between the Minnelusa and Madison aquifers using hydraulic and geochemical information for well pairs and artesian springs but did not find conclusive evidence of extensive mixing between aquifers. However, mixing between the two aquifers in the southern Black Hills warrants additional examination. What is clear is that the isotopic value of Woodcock Spring indicates a mixture of local recharge with water recharged at higher elevations. The isotopic composition of Woodcock Spring is more negative than water found in Wind Cave. Assuming that the isotopic value of Woodcock Spring represents a mixture of local recharge and regional flow from the west, it does not appear that regional flow from the west contributes directly to water found in the underground lakes or local wells.

Table 3. Stable Isotopic Results for the 2007 Wind Cave Study.

| Station ID	Field ID	Date	Deuterium	Oxygen-18
Local Wells				
433115103251401	7-11 MDSN	4/20/2007	-89.72	-11.98
433115103251401	7-11 MDSN	4/20/2007	-90.64	-11.93
433311103263101	Park Well 1	5/24/2007	-89.9	-12.01
433311103263102	Park Well 2	5/24/2007	-87.14	-11.88
433150103230501	STR	3/14/2007	-89.28	-11.86
433150103230501	STR	7/10/2007	-88.49	-11.84
433034103284701	HUN	3/14/2007	-90.37	-12.17
433034103284701	HUN	4/17/2007	-92.36	-12.23
433114103281601	KAI	7/9/2007	-90.14	-12.24
433114103281601	KAI	7/9/2007	-93.28	-12.28
Local Headwater Springs				
433333103291901	Elk Mountain Spring	4/26/2007	-93.83	-12.33
433551103291901	RG Pegmatite Spring 1	4/26/2007	-92.22	-12.32
434020103350101	Sutherland Spring	4/27/2007	-91.16	-12.58
433611103335801	Witch Spring	4/26/2007	-92.43	-11.64
Cave Sites				
433302103281507	Drip Site 1	4/27/2007	-90.86	-12.42
433302103281508	Drip Site 2	4/25/2007	-85.12	-11.69
433302103281509	Drip Site 3	4/25/2007	-84.37	-11.61
433302103281504	Petey's Puddle	4/27/2007	-91.5	-12.25
433302103281506	Rebel River	4/18/2007	-90.67	-12.12
433302103281502	What the Hell Lake	4/18/2007	-90.14	-12.11
433302103281501	Windy City Lake	4/18/2007	-90.51	-12.15
Regionally Fed Springs				
433128103223401	Beaver Creek Spring	3/14/2007	-109.67	-14.42
433128103223401	Beaver Creek Spring	7/10/2007	-110.23	-14.41
432703103302801	Hot Brook Spring	3/15/2007	-112.82	-15.05
432703103302801	Hot Brook Spring	4/20/2007	-113.22	-15.07
432703103302801	Hot Brook Spring	4/20/2007	-113.32	-15.11
432703103302801	Hot Brook Spring	7/9/2007	-114.49	-15.08
432632103285302	Hot Springs Intake Spring	3/15/2007	-119.76	-16.02
432632103285302	Hot Springs Intake Spring	4/17/2007	-120.03	-16.13
432632103285302	Hot Springs Intake Spring	7/9/2007	-120.13	-15.97
433056103322201	Woodcock Spring	4/26/2007	-97.6	-12.76
Regionally Fed Wells				
432858103334201	BOG	4/26/2007	-99.03	-12.9
433326103352001	CON	4/23/2007	-98.6	-12.86
433326103352001	CON	4/23/2007	-99.33	-12.82
432825103391201	SVE	4/23/2007	-114.46	-15.14
432340103421501	MIL	4/23/2007	-124.95	-16.64
Streams				
433745103261900	Highland Creek	3/15/2007	-87.57	-11.95
433745103261900	Highland Creek	4/26/2007	-87.73	-11.9
433745103261900	Highland Creek	7/9/2007	-87.1	-11.78
6402430	Beaver Creek	4/16/2007	-90.12	-11.92
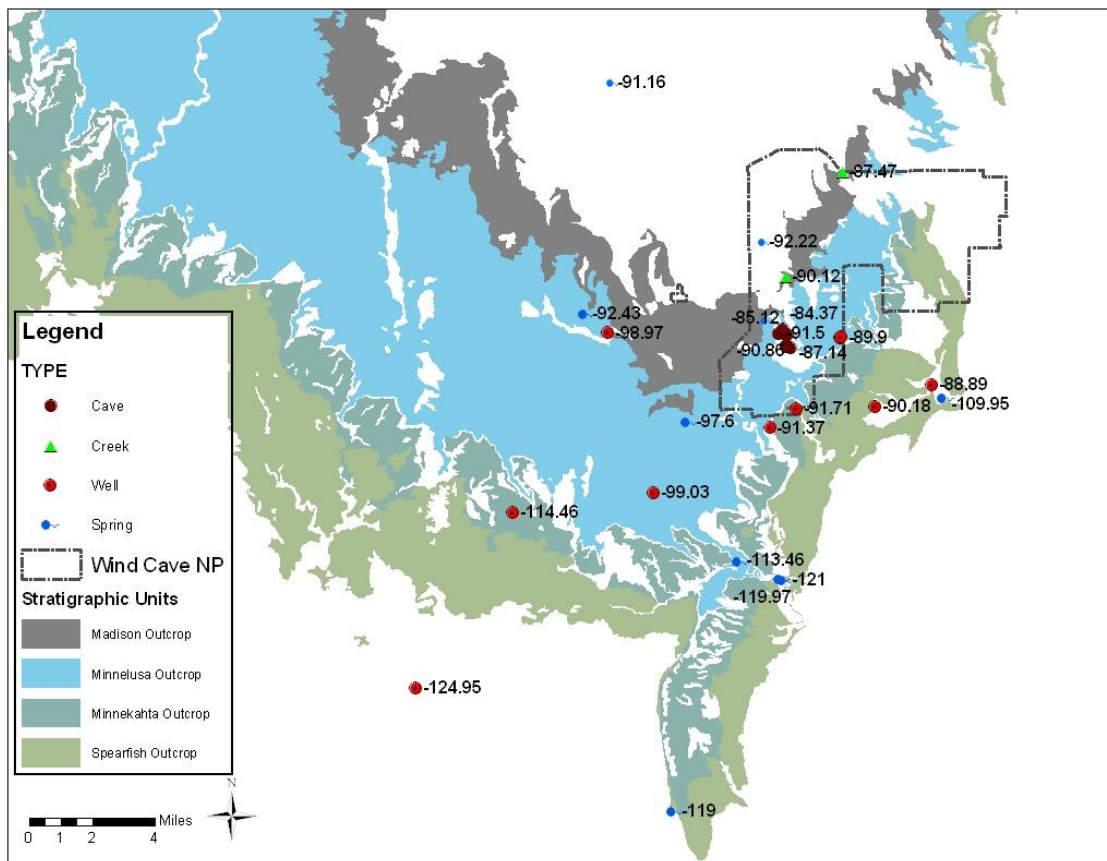
Figure 11. Deuterium values (in per mil) of springs, streams, cave waters and groundwater from the Madison aquifer in the vicinity of Wind Cave National Park.
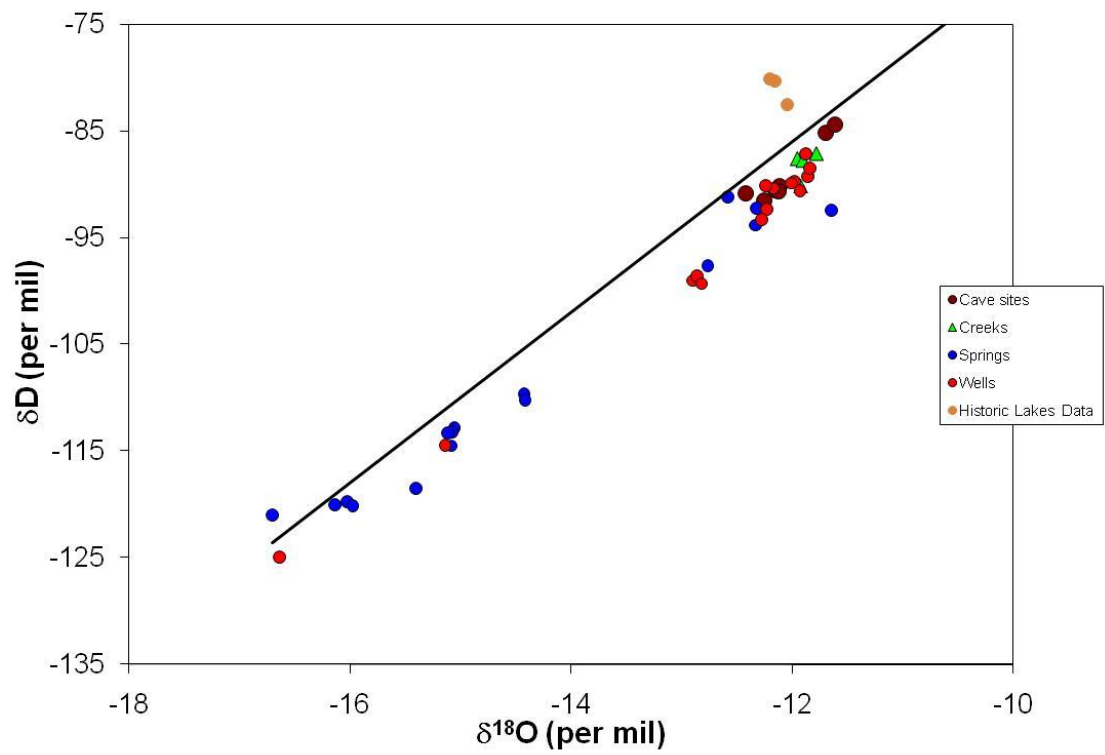
Figure 12. Isotopic values reported in this study and from Millen and Dickey (1987), plotted with the meteoric water line.

Groundwater Age

The apparent age of groundwater determined using CFC concentrations are reported in Table 4. Tritium data are reported in Table 5. Groundwater age estimates are generally more limited using tritium than CFCs.

All samples analyzed for both CFCs and tritium indicate the presence of some fraction of young water, except for the BOG well and the 7-11 Madison well. Low concentrations of tritium in the BOG well support the concept that recharge occurring in the higher elevation areas on the western part of the Black Hills must travel a substantial distance within the aquifer prior to reaching a point of discharge. However, CFC data suggest possible recharge during the 1970's. The piston flow model assumed in interpreting age data may not be appropriate at this location.

There are two possible explanations for the older apparent age estimates for the 7-11 Madison well. In contrast to the other wells sampled in this study, the 7-11 Madison well is an observation well and is not pumped on a regular basis. Wells that are pumped regularly are generally considered to provide a more representative age sample of the aquifer. The fact that the well is not pumped regularly, and the possibility that the well is located in a part of the aquifer where flow occurs predominantly through smaller and less well connected pore spaces could account for the older apparent age of water in this well.

A second possibility is that the CFC concentrations have been degraded in this well. High concentrations of manganese and lower dissolved oxygen in this well indicate that oxygen is being consumed and manganese released in the vicinity of the well, which is common under anoxic conditions. In addition, methane was detected in the sample analyzed for CFCs, which is an indication of low oxygen. Under conditions of low oxygen, CFC concentrations may be degraded and may falsely indicate an older residence time.

The apparent age of water in the underground lakes appears to be related to recharge during the mid to late 1980s. The CFC concentrations indicate a recharge date between 1983 and 1987, and tritium concentrations indicate at least some portion of modern water. Two local wells (STR and HUN), located just outside the park, have water with an apparent age from the 1970's. CFC data for local wells and underground lakes are in general agreement with tritium data reported in this study (Table 5), and reported from an earlier investigation (Naus et al., 2001). The variability observed among local wells and water sampled from Wind Cave reflects the variability in mixing conditions and the heterogeneity of the aquifer.

Age data for water discharging at Hot Brook Spring and Beaver Creek Spring are more difficult to interpret. The low but measureable concentrations at the two springs support the concept that artesian springs tend to develop near preferential flow paths and likely represent water converging from a number of flowlines. Water discharging from these springs is likely a mixture of both modern and sub-modern water.

Table 4. Results of CFC Model Ages from the 2007 Study.

Well Name	CFC Model Dates Based on Piston Flow			Remarks
	CFC-11	CFC-12	CFC-113	
7-11 MDSN	1956.0	1947.0	1953.0	Mid to late 1940's. Trace CH4.
Beaver Creek Spring	1965.5	1966.5	1976.5	Mid 1960's. Possible mixture.
Hot Brook Springs	1968.0	1968.0	1976.5	Mid to late 1960's. Possible mixture
HUN Well	1976.0	1978.0	1983.5	Mid to late 1970's Possible mixture
STR Well	1971.0	1971.0	1977.5	Early 1970's Possible mixture
What the Hell Lake	1983.0	1987.0	1987.0	Mid to late 1980's.
BOG Well	1971.5	1972.0	1980.0	Early 1970's Possible mixture.

Table 5. Estimated Age of Groundwater Using Tritium.

Site Name	Tritium		Tritium Estimated Age
	(pCi/L)	TU	
7-11 MDSN well	1.2	<0.5	Sub-Modern
Beaver Creek	50.2	16	Modern water
Drip Site 3 (NP38A)	29.4	9.2	Modern water
Beaver Creek Spring	4.5	1.4	Mixture
Hot Brook Springs	3.8	1.2	Mixture
HUN well	26.9	8.4	Modern water
STR well	16.6	5.2	Modern water
What the Hell Lake (cave)	15.7	4.9	Modern water
BOG well	1.6	0.5	Sub-Modern

Note: <0.8 TU   **Sub-modern**
        0.8 - 4 TU   **Mixture**
        5-15 TU   **Modern**
        15-30 TU   **Bomb tritium**
        (Source: Clark and Fritz, 1997)

Sources of Water to Underground Lakes

Three possible sources of water recharging the underground lakes were considered, including direct infiltration of precipitation, streamflow losses, and regional groundwater flow through the Madison aquifer.

Millen and Dickey (1987) thought that underground lake water was the result of direct meteoric recharge, or rainwater. Rainfall infiltrating into the unsaturated zone and eventually into the cave system through relatively small pore spaces is represented by water collected at the drip sites within the cave. Drip sites contain a range of chloride values that bracket those of the underground lake water. However, silica concentrations are greater in drip sites than in underground lake water, likely reflecting the longer residence time in contact with silica containing minerals in the unsaturated zone.

The isotopic values of the drip sites were generally more positive than the isotopic values of the underground lakes. Based on the relatively slow drip rate, more positive isotopic signatures, and higher concentrations of silica, it seems unlikely that the slow process of infiltration represented by the drip sites is a primary source of water found in the underground lakes and streams within the cave system. However, episodic recharge that occurs primarily during peak flow events in streams and flows through fractures and conduits could recharge the underground lakes. Water that infiltrates rapidly during peak flow events or particularly wet winters could account for the lower silica concentrations and slightly more negative isotopic values found in the underground lakes.

The streamflow loss zone where Beaver Creek crosses the Madison Limestone has been suggested as a possible source of recharge to the underground lakes in Wind Cave. Alexander and others (1989) thought that the source of underground lake water could be diluted water from Beaver Creek. Analysis of samples collected from Beaver Creek shows that the concentrations of nearly all major ions are greater in Beaver Creek than in the underground lakes. In particular, Beaver Creek contains higher concentrations of chloride when compared to underground lake water. The higher concentrations of chloride and other ions in Beaver Creek are likely due to anthropogenic activities in the Beaver Creek watershed, which extends several miles upstream of the park. Although hydrologic connection was demonstrated between the Beaver Creek loss zone and NPS Park Well No. 1 through tracer studies (Alexander et al., 1989), it does not seem likely that it directly recharges the underground lakes.

In contrast, the water chemistry of Highland Creek, which is north of Beaver Creek and further from the cave system, more closely resembles water found in the cave system than does Beaver Creek. Silica concentrations are higher in Highland Creek compared to the underground lakes, likely reflecting longer contact time with silica containing minerals in sediments in the Highland Creek watershed. Although Highland Creek is too far from the cave system to be the main source of recharge, it may be more representative of local recharge that has been unaffected by anthropogenic activities and may more closely represent the chemical composition of local recharge.

The third possible source of underground lake water is regional flow in the Madison aquifer. Although the chemistry observed at the SVE and BOG wells are not that different from the

underground lakes, the isotopic signatures are much more negative. The isotopic signature of regional groundwater flowing from west to east along the southern margin of the Black Hills is represented by the MIL well (δD of -124.95 per mil), while underground lake water exhibited δD values ranging from -90.14 to -91.5 per mil. The similarity between isotopic values found in local headwater springs and underground lake water, and the much more negative values found in regional flow from the west, suggest that regional flow is not a likely source of water found in the underground lakes. The BOG and SVE wells are likely a mixture of local recharge and regional flow from the west.

Geochemical Modeling

The stable isotope data for the underground lakes indicates that the lake water must be locally recharged, since the isotopic values are much more positive than regional flow from the west. Modeling regional groundwater mixing with local recharge was attempted using NETPATH to verify this conclusion. NETPATH was run with a minimal number of constraints, but as expected, no plausible models could be found using local recharge mixing with regional groundwater. Constraints included stable isotopes, calcium and magnesium. Mineral phases of calcite and dolomite were included as reactants. Alternatively, a plausible model was found using rainwater as the initial water reacting with calcite and dolomite to produce the underground lake water as the final water.

NETPATH was used to evaluate a groundwater flow path between the underground lakes and Beaver Creek Spring. Mixing with isotopically more negative water from the west was required to find a satisfactory model. Recharge from the west, represented by the MIL well, was assumed to mix with underground lake water to produce the water observed at Beaver Creek Spring. The modeling was performed to first test whether this flow path and mixing was possible geochemically, and if so, to determine the simplest water/mineral reactions that could explain the observed change in concentrations of major ions along this flow path.

Two suitable models were found that satisfied both geochemical and isotopic constraints and confirmed that this mixing model was possible. Calcium, magnesium, carbon, sodium, sulfur, and chloride were used as constraints in the geochemical model. Approximately 42-45 % of local recharge was mixed with 55-58% of regional flow to produce the water at Beaver Creek Spring. Both models required calcite precipitation, which lowers the pH, and anhydrite dissolution, which releases both calcium and sulfate into solution, consistent with the process of dedolomitization.

Whalen (1994) used geochemical modeling to show that water with a chemical composition similar to Hot Brook Spring water reacting with dolomite and anhydrite could produce the water at Cascade Spring. Hayes (1999) refined the earlier geochemical model developed by Whalen (1994) and determined that Hot Brook Spring water and accompanying dissolution of anhydrite and dolomite from the overlying Minnelusa Formation was the only plausible source of water discharging at Cascade Spring. A similar process was suggested at Beaver Creek Spring (Whalen, 1994).

Conceptually, the geochemical modeling suggests that in the vicinity of Wind Cave, local recharge infiltrates through the Madison Limestone and into the underground lakes. Water flows

down-dip through the Madison aquifer from the outcrop area in the vicinity of the park to areas south and southeast of the park where the aquifer thins and is confined beneath overlying sedimentary units. Water flowing through the regional Madison aquifer from the west around the southern margin of the Black Hills mixes with local recharge down gradient of the park and is forced upward where it discharges at large artesian springs, such as Beaver Creek Spring (Figure 13). A similar reaction path is likely at Cascade Spring, albeit with less local recharge contributing to the final water.
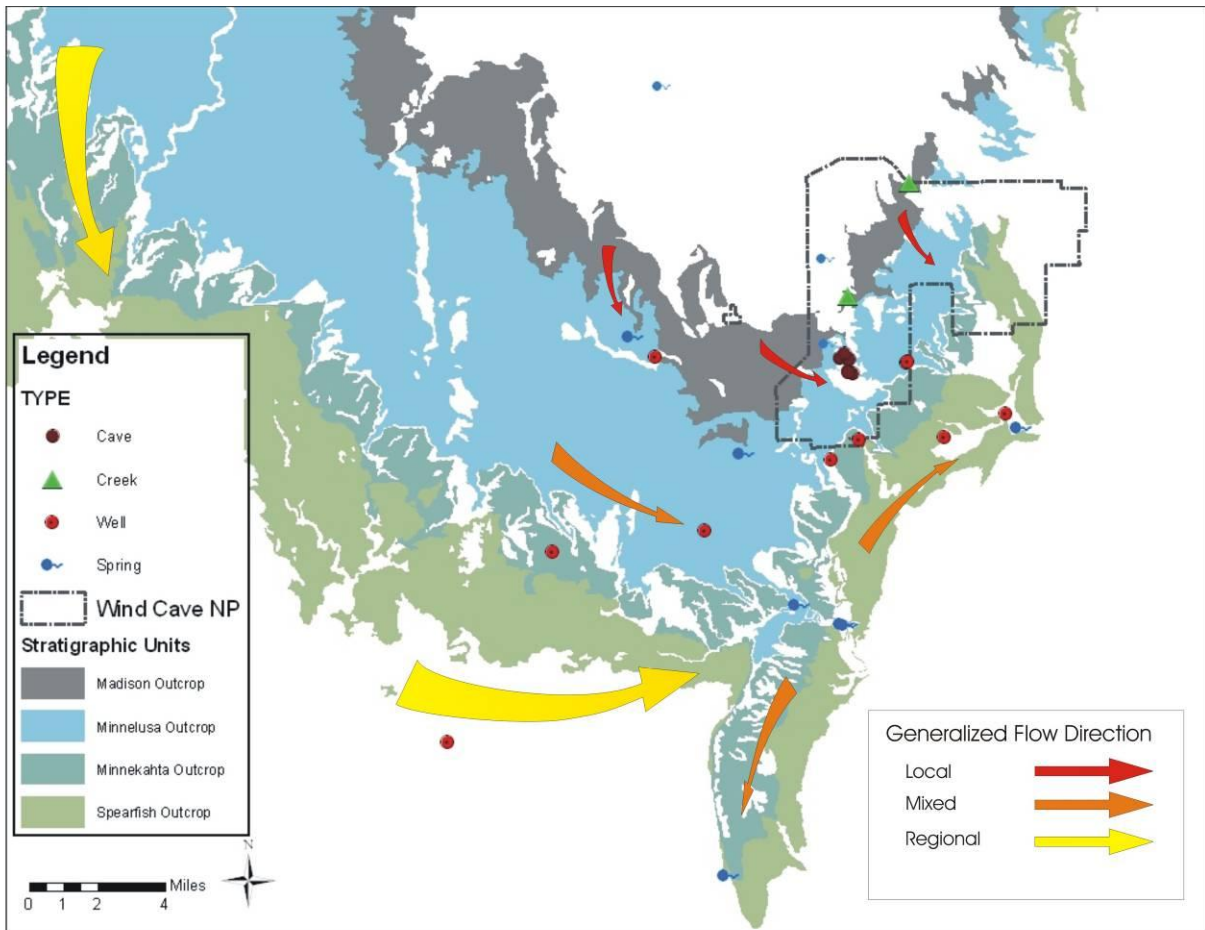
Figure 13. Groundwater flow-paths in the study area.

Discussion of Results

In general, measured values of pH decrease in a down-gradient direction, with the highest values observed in creeks sampled above the Madison outcrop and in drip sites, and the lowest values observed in flowing wells and artesian springs near areas of discharge. Values of pH ranged from a high of 9.2 sampled at Highland Creek to a low of 6.8 sampled at Beaver Creek Spring.

The calcite saturation index, a measure of calcium concentration and the ability of a solution to dissolve or precipitate calcite, also decreases in a down-gradient direction. It is greatest in streams flowing into the park, followed by drip sites, then underground lake waters and finally local wells outside the park. The calcite saturation index ranged from +0.9 in Highland Creek above the streamflow loss zone, to -0.3 in local wells outside the park, reflecting oversaturation in upland areas and undersaturation in wells outside the park. The trend in calcite saturation index and pH is a consequence of calcite precipitation, which releases hydrogen ions as calcium and bicarbonate combine to form calcite.

The trends in pH and calcite saturation index reflect a set of reactions that must occur to satisfy thermodynamic controls on the aquifer. This is the commonly observed "major ion evolution sequence" (Freeze and Cherry, 1979), first described by Chebotarev (1955). A trend in water composition is expected in sedimentary basins, where groundwater moves from an area of active groundwater recharge with low dissolved solids concentration and bicarbonate as the dominant anion, to an area with less active recharge and sulfate as the dominant anion, and eventually to an area where little active groundwater recharge occurs and highly soluble minerals are present with chloride as the dominant anion.

The dramatic change in water chemistry over a short distance from local wells such as the STR well to Beaver Creek Spring suggests a relatively abrupt change in the thermodynamics of the system. The water chemistry of Beaver Creek Spring is likely controlled by the process of dedolomitization as water in the Madison aquifer comes in contact with anhydrite or gypsum in overlying formations. The isotopic composition of Beaver Creek Spring requires a mixture of isotopically negative water flowing from the west mixing with more positive local recharge to account for the isotopic signature of spring discharge. A similar process is likely occurring at Cascade Spring, with less mixing from local recharge.

Wells sampled as part of this study represent a range of conditions in the aquifer. The MIL well represents regional flow from the western flank of the Black Hills. The BOG well, although similar in chemistry to the underground lakes, is isotopically more negative and appears to be much older when compared to underground lakes and wells closer to the park. Beaver Creek Spring and springs in the Hot Springs area show evidence of mixing between local recharge and regional flow, with dissolution of anhydrite contributing to their chemical composition. Large variation in chemistry over relatively small distances between wells and springs indicates complexity in the flow system, most likely associated with structural controls.

Groundwater age dating based on CFC modeling shows that underground lake water has an apparent age that is slightly younger than groundwater found in wells just outside the park, such as the STR and HUN wells. This supports the conceptual understanding that the lakes are likely

closer to areas of recharge than the wells outside the park, and therefore exhibit slightly younger water.

Arsenic was found at relatively high concentrations at all of the sites sampled within Wind Cave and at Park Well No. 2. It is suspected that the high concentrations are associated with a high pH which allows arsenic to become mobile in water. It is likely that the arsenic is from a naturally occurring source, although additional study is warranted.

Conclusion

Major ion and stable isotope data collected during 2007 were used to evaluate possible sources of water to underground lakes and flow paths in the vicinity of Wind Cave National Park. The major ion chemistry of water found in the underground lakes is consistent with infiltration of local rainfall through well connected pores or fractures. Local recharge infiltrates through the Madison Limestone and into the underground lakes. Water flows down-dip through the Madison aquifer from the outcrop area in the vicinity of the park to areas south and southeast of the park where the aquifer thins and is confined beneath overlying sedimentary units. Water flowing through the regional Madison aquifer from the west around the southern margin of the Black Hills mixes with local recharge down gradient of the park and is forced upward where it discharges at Beaver Creek Spring.

The chemical and isotopic composition of water in the underground lakes is similar to water found in local wells completed in the Madison aquifer. Differences in chemical composition between local wells, such as the Streeter Well, and Beaver Creek Spring are likely due to minerals that water flowing to the spring interacts with as it flows upward through overlying formations. Dissolution of dolomite and precipitation of calcite as water comes in contact with gypsum or anhydrite in overlying formations can account for the difference in chemical composition between Streeter Well and Beaver Creek Spring. The more negative isotopic value of Beaver Creek Spring indicates mixing with regional flow in the Madison aquifer that is not evident in local wells or the underground lakes.

Further investigation of recharge mechanisms contributing to underground lake levels during episodic peak flow events is warranted. Periodic monitoring of stable isotopes of precipitation and lake water, combined with periodic monitoring of water chemistry and water levels in the lakes could identify isotopic and chemical variations associated with episodic recharge.

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