



Multivariate Analysis of Hydrochemical Data for Jewel Cave, Wind Cave, and Surrounding Areas

Natural Resource Report NPS/JECA/NRR—2019/1883



ON THE COVER

New Year's Lake, a subterranean lake in Jewel Cave at a depth of more than 700 feet below land surface.

NPS Photo

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Natural Resource Report NPS/JECA/NRR—2019/1883

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Abstract

Jewel Cave National Monument and Wind Cave National Park in South Dakota contain two of the six longest caves worldwide. These caves contain subterranean lakes that are important points of intersection between the water table of the Madison aquifer and the caves. During 2015 to 2017, several subterranean lakes were discovered in Jewel Cave, which previously was thought to be above the regional water table. The objectives of this study were to better understand the hydrology of the recently discovered subterranean lakes in Jewel Cave and to evaluate their relation or possible connection to similar lakes in Wind Cave. Both objectives align with National Park Service resource management purposes. Multivariate analysis, consisting of principal component analysis (PCA), cluster analysis, and end member mixing, was applied to hydrochemical data for 70 sites within and surrounding Jewel Cave and Wind Cave. Hydrochemical data consisted of the contents of major ions (Ca, Mg, Na, HCO₃, Cl, Si, SO₄), arsenic (As), strontium (Sr), uranium (U), stable isotopes of oxygen and hydrogen ($\delta^{18}\text{O}$, $\delta^2\text{H}$), radiogenic isotope ratios of strontium and uranium ($^{87}\text{Sr}/^{86}\text{Sr}$ and $^{234}\text{U}/^{238}\text{U}$), pH, and electrical conductivity (EC) in water samples. Five hydrogeologic domains were classified on the basis of PCA and cluster analysis for the area encompassing Jewel Cave and Wind Cave in the southern Black Hills. The Artesian 1 and Artesian 2 domains represent primarily artesian springs and surrounding groundwater, the East and West domains represent areas where Madison and Minnelusa aquifer rocks are at or near the land surface, and the Precambrian domain represents the Precambrian aquifer. Multivariate analysis indicates that the Jewel Cave area is part of the West domain and that Wind Cave is part of the East domain. End member mixing was applied to estimate that groundwater in the Jewel Cave area primarily was derived from the West domain and secondarily from the Precambrian domain. Jewel Cave and Wind Cave contain lakes that are well connected to regional groundwater flow in the Madison aquifer.

Acknowledgements

The study was conducted in cooperation between the National Park Service (NPS) and U.S. Geological Survey (USGS). The authors thank the two colleague reviewers and report production staff who helped improve this report in numerous ways.

Introduction

Jewel Cave National Monument and Wind Cave National Park contain two of the six longest caves worldwide (<http://www.caverbob.com/home.htm>), and because of numerous unique natural features, these lands were established to protect the caves (Figure 1). The National Park Service (NPS) manages both units to protect water-dependent biota and the natural water level fluctuations that support cave feature formation. In 2006, the NPS became aware of an application to withdraw groundwater near Wind Cave and began working toward protecting groundwater levels within the cave from withdrawals for rural water supply purposes. Wind Cave was formed within the Pahasapa Formation (regionally the Madison Limestone), which contains the regionally extensive Madison aquifer. In the southern Black Hills, groundwater in the Madison aquifer flows radially outward and then to the southeast (Figure 1). Wind Cave contains subterranean lakes that are considered by NPS to be unique and valuable natural resources. Much of the landscape and geomorphology surrounding Jewel and Wind Caves is characterized as a carbonate karst environment, with sinking streams and fast connections between surface water and groundwater, resulting in high vulnerability of groundwater to contamination.

Calcite Lake and Windy City Lake are two subterranean lakes in Wind Cave that merged into one lake sometime during 1999 or 2000 when their levels rose (Long and others, 2012). The merged lake commonly is referred to as Calcite Lake, but the name Windy City Lake is used in this report to be consistent with the USGS gauge (433302103281501) that was established for Windy City Lake. NPS continued to monitor levels for the merged lake after the USGS discontinued monitoring in 1999. Windy City Lake rises and declines concurrently with levels in nearby groundwater monitoring well Md7-11 that is open to the Madison aquifer (Long and others, 2012). The lake's surface is at an altitude similar to the estimated potentiometric surface altitude of this aquifer. These characteristics strongly suggest that the lake represents the aquifer's water table. As water levels in Windy City Lake and well Md7-11 increased in 1996 to the highest levels on record for that time, a new subterranean lake formed (What the Hell Lake), with a surface altitude also near the altitude of the potentiometric surface (Long and others, 2012). Fractures are prominent in the Madison aquifer (Palmer and Palmer, 1989), and it is likely that the rising groundwater levels flooded into a previously dry cave passage through fractures and other openings to form What the Hell Lake. Many other water bodies are present in the cave as well.

Until 2015, Jewel Cave was not known to contain subterranean lakes. Since then, several lakes, including Hourglass Lake, were discovered as cave explorers pushed into farther reaches of the cave. The similarity of altitudes of some of the subterranean lakes in Jewel Cave to the surrounding potentiometric surface suggests that these lakes represent groundwater in the regional aquifer, similarly to Windy City Lake. Therefore, Jewel Cave and Wind Cave likely contain lakes that are fully integrated with the regional flow system of the Madison aquifer, which means that regional groundwater can flow into and out of many of these lakes. The objectives of this study were to better understand the hydrology of the recently discovered lakes in Jewel Cave and how they may be related or connected to lakes in Wind Cave. The resulting increase in hydrologic understanding is useful for resource management at the parks.

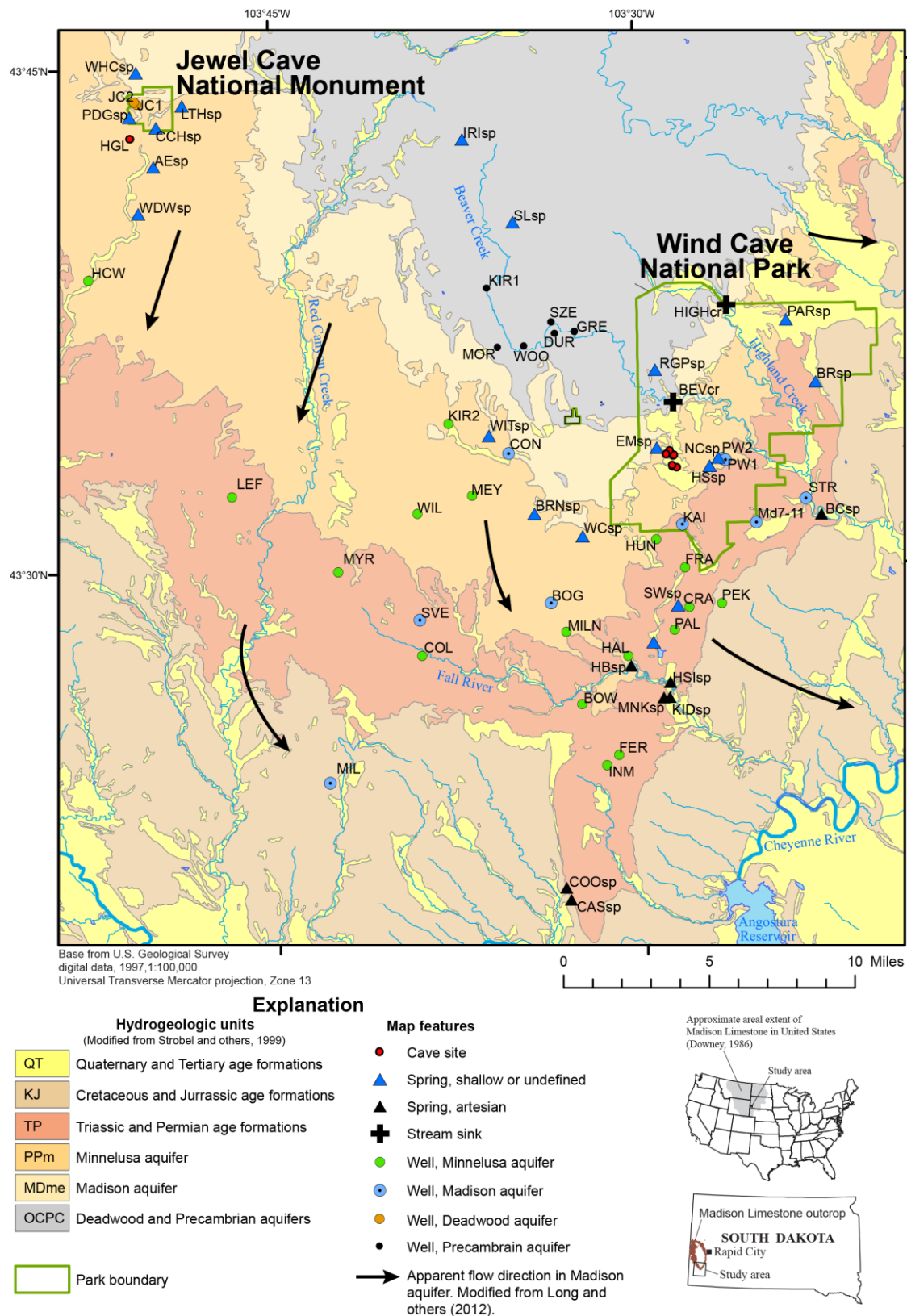


Figure 1. Study area and hydrogeologic units, with sites differentiated by site type.

Jewel Cave and Wind Cave are located in the southern part of the Black Hills of western South Dakota and eastern Wyoming (Figure 1). Hydrogeologic units are described in Table 1. Numerous hydrochemical groundwater and cave studies for the Black Hills include Back and others (1983), Bakalowicz and others (1987), Alexander and Davis (1989), Palmer and Palmer (1989), Plummer and others (1990), Ford and others (1993), Naus and others (2001), Heakin (2004), Back (2011), Long and others (2012), and Palmer and others (2016). Prior to the discovery of the lakes in Jewel Cave, Long and Valder (2011) evaluated regional hydrogeologic domains in relation to Wind Cave and the groundwater mixing of different sources of water. Much of the analysis described herein is a reanalysis of that described by Long and Valder (2011), except that water samples from within and surrounding Jewel Cave are included. The study by Long and Valder (2011) is referred to frequently in this report and, therefore, is abbreviated as WICA2011.

Table 1. Description of hydrogeologic units. Summarized from Strobel and others (1999) and Redden and DeWitt (2008).

Abbreviation	Aquifer name or general description	Formation name or hydrogeologic description	Geologic age
QT	Unconsolidated aquifers	Alluvium, colluvium, gravel, claystone, poorly indurated sandstone, conglomerate.	Quaternary, Tertiary
KJ	Aquifers and confining units	Undifferentiated shale, limestone, sandstone, conglomerate, siltstone, claystone, gypsum.	Cretaceous, Jurassic
TP	Aquifers and confining units	Spearfish Formation (shale with interbedded sandstone, siltstone, and gypsum), Minnekahta Limestone, Opeche Shale.	Triassic, Permian
PPm	Minnelusa aquifer	Minnesula Formation (interbedded sandstone, limestone, dolostone, and shale)	Permian, Pennsylvanian
MDme	Madison aquifer	Madison (Pahasapa) and Englewood Limestones – also contains dolostone	Mississippian, Devonian
OCPC	Precambrian and Deadwood aquifers	Deadwood Formation (glauconitic sandstone, shale, siltstone, and conglomerate), Precambrian rocks (fractured metamorphosed quartzite and metagraywacke with isolated areas of granite and pegmatite).	Ordovician, Cambrian, Precambrian

WICA2011 described multivariate analysis of hydrochemical data for 60 sites within and surrounding Wind Cave. These analyses consisted of principal component analysis, cluster analysis, and end member mixing, examples of which were described by Fritz and others (1976), Christophersen and Hooper (1992), Laaksoharju and others (1999), Suk and Lee (1999), Davis (2002), Carrera and others (2004), and Valder and others (2012). Additional data for 10 sites in the Jewel Cave area for samples collected in 2016 were combined with the WICA2011 data to characterize the hydrologic relation between Jewel Cave and Wind Cave. The analysis described herein is a repeat of the analysis described in WICA2011, except that all 70 sites for the Jewel Cave and Wind Cave areas were included (Appendix, Table 6). In addition, this report includes strontium

and uranium isotope data for both areas that previously were unavailable, and that have been used elsewhere as natural tracers of water sources and mixing (Paces and Wurster, 2014). Details, background, and assumptions for multivariate analyses applied in this study are described in WICA2011 and Valder and others (2012).

Data

For the 70 sites (60 previously sampled and 10 new; Appendix Table 6), hydrochemical data consisted of 12 variables: major ions (Ca, Mg, Na, Cl, Si, SO₄), alkalinity, arsenic (As), stable isotopes of oxygen and hydrogen ($\delta^{18}\text{O}$, $\delta^2\text{H}$), pH, and electrical conductivity (EC) measured in water samples. Table 2 lists new data that were not available for WICA2011 and were obtained from the National Water Information System (NWIS; <https://doi.org/10.5066/F7P55KJN>). Additional background information, including laboratory analytical methods, quality-control samples, and averaging of multiple samples at selected sites was described in WICA2011.

Total strontium (Sr) and uranium (U) concentrations and their radiogenic isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$ atomic ratios and $^{234}\text{U}/^{238}\text{U}$ activity ratios) were analyzed for 27 of the WICA2011 sites in a related study (Paces and others, 2013), as well as the 10 new sites for the Jewel Cave area (Table 3). These data were obtained following methods described in Paces and others (2015) and are available from NWIS.

Table 2. Hydrochemical data for samples collected in the Jewel Cave area in 2016. Data are available from the [National Water Information System](#). [µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; δ¹⁸O and δ²H (‰), stable isotopes of oxygen and hydrogen, respectfully, in reference to sea water].

Site name	Short name	Sample date (year-month-day)	pH	Electrical conductivity (EC), in µS/cm	Calcium (Ca), in mg/L	Magnesium (Mg), in mg/L	Sodium (Na), in mg/L	Chloride (Cl), in mg/L	Sulfate (SO ₄), in mg/L	Silica (Si), in mg/L	Arsenic (As), in µg/L	Alkalinity as calcium carbonate (CaCO ₃), in mg/L	δ ² H, in ‰	δ ¹⁸ O, in ‰
Hourglass Lake	HGL	2016-02-14	7.5	380	36.8	32.8	5.2	3.1	9.2	13.4	4.7	223	-110.42	-14.18
West Hell Canyon Spring	WHCsp	2016-05-09	7.45	529	63.4	36.7	2.0	1.2	5.2	10.5	1.6	299	-111.42	-14.67
Water Draw Spring	WDWsp	2016-05-11	7.53	524	56.0	36.9	6.7	6.5	13.8	13.6	5.7	275	-111.11	-14.25
Choke Cherry Spring	CCHsp	2016-05-09	8.05	594	47.4	58.1	6.3	4.9	20.0	11.1	6.6	318	-106.25	-13.39
Jewel Cave Well 1	JC1	2016-05-09	7.46	590	63.5	35.5	9.4	51.3	6.9	11.3	0.9	233	-107.33	-14.05
Jewel Cave Well 2	JC2	2016-05-09	7.51	499	59.4	35.3	2.5	1.9	4.7	11.6	1.9	281	-109.80	-14.43
Hell Canyon Well	HCW	2016-05-11	7.43	501	67.2	27.3	6.4	4.1	29.3	11.6	4.6	249	-113.65	-14.56
A&E Spring	AEsp	2016-05-11	7.8	614	46.3	58.5	10.0	6.6	24.0	12.7	9.1	327	-110.77	-14.09
Prairie Dog Spring	PDGsp	2016-05-11	7.52	1540	74.1	106*	98*	302*	29.3	13.0	9.6	348	-108.16	-13.91
Lithograph Spring	LTHsp	2016-05-09	7.5	670	70.8	54.7	5.1	4.0	19.9	14.7	5.0	368	-106.57	-13.82

* Suspected road salt contamination resulting in anomalously high value.

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Table 3. Concentrations and isotopic compositions for strontium and uranium dissolved in groundwater from sites associated with Wind Cave and Jewel Cave studies. Data were measured at the USGS radiogenic isotope lab in Denver, CO, and are available from the National Water Information System.[µS/cm, microsiemens per centimeter; strontium (Sr) and uranium (U) concentrations determined gravimetrically by isotope dilution and reported in nanograms per gram (ng/g); 95%-confidence uncertainties for Sr and U concentrations (not shown) are estimated to be smaller than 2% of the reported value and are largely dependent on the uncertainty of spike calibrations; ±2σ uncertainties for isotope ratios (shown in separate columns) include within-run counting statistics, estimates of error for blank subtraction and mass fractionation correction, and an external error determined from reproducibility of standards; --, not available].

Short name	Aquifer	Sample date (year-month-day)	pH	Electrical conductivity (EC), in µS/cm	Strontium (Sr), in ng/g	⁸⁷ Sr/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr ±2σ	Uranium (U), in ng/g	²³⁴ U/ ²³⁸ U	²³⁴ U/ ²³⁸ U ±2σ
HSIsp	Madison	2011-08-03	7.7	1060	–	0.713462	0.000010	5.78	1.807	0.004
KIDsp	Madison	2011-08-01	7.2	1580	–	0.711570	0.000010	6.26	1.731	0.004
KIDsp	Madison	2012-08-05	7.3	1510	3130	0.711570	0.000010	6.25	1.728	0.004
MNKsp	Madison	2012-08-05	7.2	1230	2340	0.713321	0.000010	6.05	1.721	0.004
HBsp	Minnelusa	2012-08-05	7.5	620	781	0.714811	0.000010	4.20	2.097	0.006
BCsp	Madison	2011-08-02	7.5	2000	–	0.708847	0.000010	7.55	1.813	0.004
CASsp	Madison	2011-08-01	7.0	2200	6570	0.708635	0.000008	5.33	1.879	0.004
COOsp	Madison	2011-08-01	7.5	1830	–	0.708644	0.000010	5.41	1.993	0.004
BRsp	Unknown	2012-08-03	8.2	3600	12700	0.707775	0.000010	9.04	1.443	0.003
CBsp	Unknown	2012-08-05	7.5	620	923	0.711002	0.000010	4.31	2.185	0.006

Table 3 (continued). Concentrations and isotopic compositions for strontium and uranium dissolved in groundwater from sites associated with Wind Cave and Jewel Cave studies. Data were measured at the USGS radiogenic isotope lab in Denver, CO, and are available from the National Water Information System.[$\mu\text{S}/\text{cm}$, microsiemens per centimeter; strontium (Sr) and uranium (U) concentrations determined gravimetrically by isotope dilution and reported in nanograms per gram (ng/g); 95%-confidence uncertainties for Sr and U concentrations (not shown) are estimated to be smaller than 2% of the reported value and are largely dependent on the uncertainty of spike calibrations; $\pm 2\sigma$ uncertainties for isotope ratios (shown in separate columns) include within-run counting statistics, estimates of error for blank subtraction and mass fractionation correction, and an external error determined from reproducibility of standards; --, not available].

	Short name	Aquifer	Sample date (year-month-day)	pH	Electrical	Strontium (Sr), in ng/g	⁸⁷ Sr/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr $\pm 2\sigma$	Uranium (U), in ng/g	²³⁴ U/ ²³⁸ U	²³⁴ U/ ²³⁸ U $\pm 2\sigma$
					conductivity (EC), in $\mu\text{S}/\text{cm}$						
✓	WCL	Madison	2011-08-18	–	–	–	0.715534	0.000008	4.35	1.806	0.004
	WCL	Madison	2015-06-05	7.8	316	795	0.715366	0.000011	4.09	1.785	0.005
	DP2	Madison	2015-06-05	8.1	390	321	0.711773	0.000009	1.46	1.406	0.012
	DP3	Madison	2015-06-05	8.0	268	421	0.712818	0.000008	1.14	1.158	0.004
	WTHL	Madison	2011-08-18	–	–	–	0.712470	0.000008	4.25	1.737	0.004
	WTHL	Madison	2012-08-04	8.1	400	238	0.712463	0.000010	4.27	1.742	0.004
	WTHL	Madison	2015-06-05	7.8	412	758	0.712496	0.000009	17.7	1.738	0.005
	HSsp	Minnelusa	2012-08-05	7.5	410	177	0.711578	0.000010	2.18	1.854	0.005
	NCsp	Minnelusa	2012-08-05	7.3	350	171	0.711486	0.000010	2.14	1.873	0.018
	PARsp	White River	2012-08-03	8.3	430	852	0.712083	0.000010	5.08	1.825	0.005
	BEVcr	Precambrian	2015-10-09	8.9	500	251	0.735269	0.000010	3.99	2.236	0.005
	HIGHcr	Precambrian	2012-08-03	8.2	280	169	0.736035	0.000010	3.23	2.360	0.012
	RGPsp	Precambrian	2012-08-03	7.2	330	212	0.738395	0.000010	2.41	2.675	0.009
	SLsp	Precambrian	2012-08-06	7.6	340	261	0.736435	0.000010	0.21	1.728	0.006
	JC1	Deadwood	2016-05-09	7.5	590	136	0.710792	0.000011	1.13	1.906	0.004
	JC2	Deadwood	2016-05-09	7.5	499	114	0.710891	0.000009	1.92	2.326	0.006
	HGL	Madison	2016-02-14	7.5	380	183	0.711354	0.000006	4.24	1.561	0.041
	WHCsp	Madison	2016-05-09	7.5	529	86	0.710743	0.000009	1.05	1.844	0.005
	AEsp	Minnelusa	2016-05-11	7.8	614	356	0.710466	0.000009	18.6	1.807	0.004
	CCHsp	Minnelusa	2016-05-09	8.1	594	303	0.710655	0.000100	8.95	1.726	0.004
	EMsp	Minnelusa	2012-08-05	7.3	590	235	0.711219	0.000010	3.24	1.591	0.005
	HCW	Minnelusa	2016-05-11	7.4	501	241	0.710426	0.000009	9.74	2.465	0.005
	LTHsp	Minnelusa	2016-05-09	7.5	670	193	0.710886	0.000009	4.89	1.902	0.005
	PDGsp	Minnelusa	2016-05-11	7.5	1540	372	0.710868	0.000009	19.1	1.678	0.004
	WDWsp	Minnelusa	2016-05-11	7.5	524	240	0.710930	0.000010	9.10	2.102	0.004

Table 3 (continued). Concentrations and isotopic compositions for strontium and uranium dissolved in groundwater from sites associated with Wind Cave and Jewel Cave studies. Data were measured at the USGS radiogenic isotope lab in Denver, CO, and are available from the National Water Information System.[μS/cm, microsiemens per centimeter; strontium (Sr) and uranium (U) concentrations determined gravimetrically by isotope dilution and reported in nanograms per gram (ng/g); 95%-confidence uncertainties for Sr and U concentrations (not shown) are estimated to be smaller than 2% of the reported value and are largely dependent on the uncertainty of spike calibrations; ±2σ uncertainties for isotope ratios (shown in separate columns) include within-run counting statistics, estimates of error for blank subtraction and mass fractionation correction, and an external error determined from reproducibility of standards; --, not available].

Short name	Aquifer	Sample date (year-month-day)	pH	Electrical conductivity (EC), in μS/cm	Strontium (Sr), in ng/g	⁸⁷ Sr/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr ±2σ	Uranium (U), in ng/g	²³⁴ U/ ²³⁸ U	²³⁴ U/ ²³⁸ U ±2σ
WITsp	Minnelusa	2012-08-06	8.2	490	372	0.710695	0.000010	9.25	1.293	0.004
WCsp	Minnelusa	2012-08-05	7.3	620	346	0.710858	0.000010	4.81	1.622	0.004

Principal Component Analysis (PCA) and Cluster Analysis

WICA2011 classified five hydrogeologic domains on the basis of PCA and cluster analysis for the area encompassing Jewel Cave and Wind Cave in the southern Black Hills. Additionally, the domains could be described physiographically. The clusters were interpreted to be representative of five hydrogeologic domains, which were named as the East, West, Artesian 1, Artesian 2, and Precambrian domains.

Analysis with 70 sites and 12 variables

PCA and cluster analysis were applied to the 70 sites in the identical manner and with the same 12 variables that were applied in WICA2011. That report describes the details of the procedure, which are not repeated herein. The complete matrix of input values is given in the Appendix (Table 7). As in WICA2011, five clusters were specified for the cluster analysis of 70 sites, and with few exceptions, the original 60 sites were placed (by cluster analysis) in the same clusters as in WICA2011. The distribution of sites in the two-dimensional space of principal components 1 and 2 (PC1 and PC2) shows the five clusters (Figure 2).

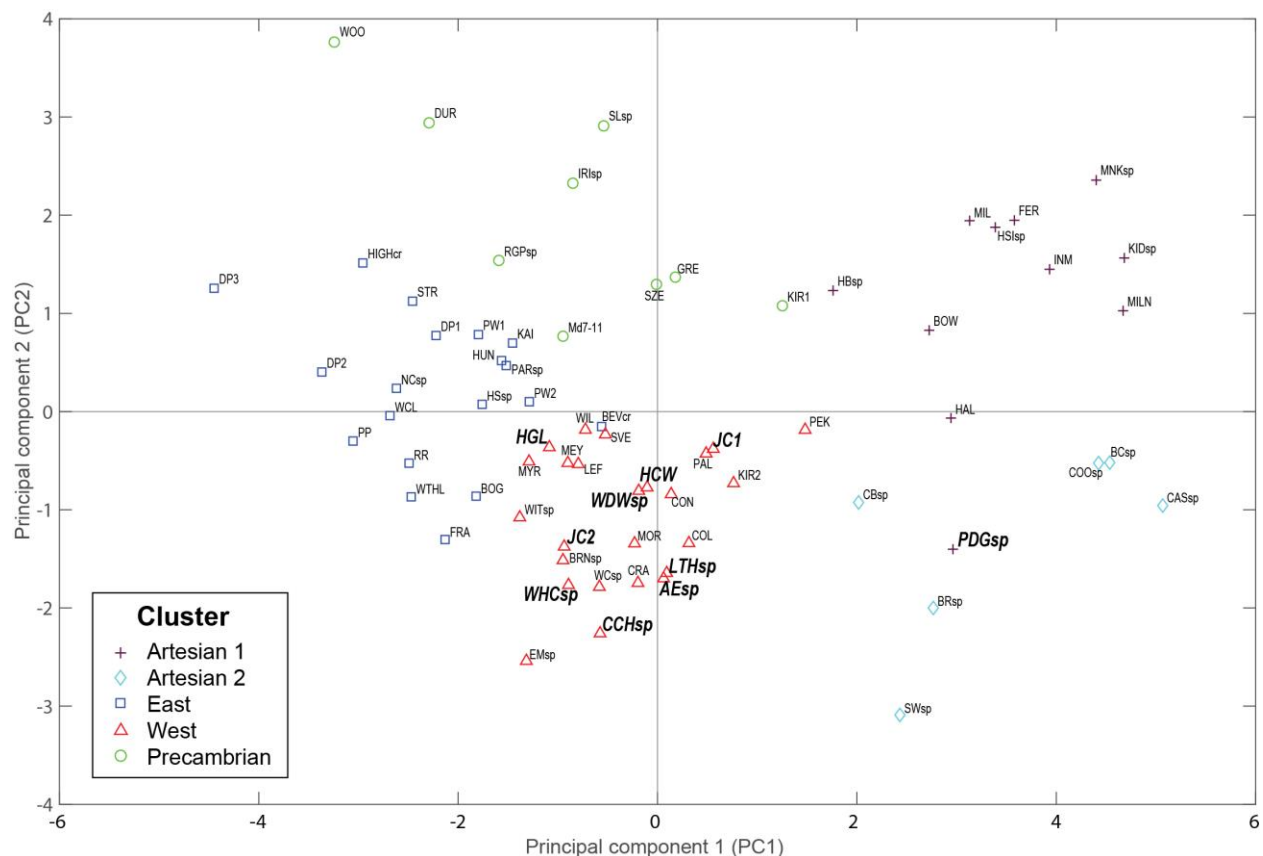


Figure 2. Scatter plot of score values for principal components 1 and 2 for 70 sites and 12 variables. Jewel Cave area sites are labeled in bold.

Nine of the ten Jewel Cave area sites were placed in the West cluster. Prairie Dog Spring (site PDGsp) was the only Jewel Cave area site that was not included in the West cluster, resulting from its unusually high concentrations of Mg, Na, Cl, and EC (Table 2). These variables were 2.5, 16.5, 32.5, and 2.8 times higher, respectively, than the averages for the other nine sites in the Jewel Cave area. Site PDGsp is located about 400 feet from U.S. Highway 16 in a small draw that drains away from the highway. Magnesium chloride (MgCl_2) and sodium chloride (NaCl) salts were applied to the highway during the winter prior to sampling (South Dakota Department of Transportation, 2016). Therefore, the unusual composition for PDGsp is attributed to road-salt contamination.

The separation of clusters along the PC axes is similar to WICA2011, where PC1 distinctly separates the Artesian clusters from the other three, and PC2 separates the Artesian 1 and 2 clusters from each other and also separates the East, West, and Precambrian clusters from each other, with partial overlap along this axis (Figure 2). In two-dimensional space (PC1 and PC2), the clusters are separated into five distinct regions, with little overlap. Combined, PC1 and PC2 explain 61 percent of the total variance of the dataset.

The two-dimensional space of PC1 and PC3 separates the clusters similarly, except there is more overlap for the East, West, and Precambrian clusters (Figure 3). Combined, PC1, PC2, and PC3 explain 74 percent of the total variance of the dataset. For the West cluster, the Jewel Cave area sites generally have the highest values on PC3, which indicates that PC3 represents hydrochemically distinct characteristics for the Jewel Cave area. Jewel Cave sites occupy a focused area in the two-dimensional space of PC1-PC3, unlike their wider scatter in PC1-PC2 space (compare Figure 2 and Figure 3). This result is interpreted to be further evidence that PC3 represents a unique characteristic of the Jewel Cave area. A cluster analysis using 6 clusters also was tested because of the possibility that the Jewel Cave area would form a separate sixth cluster; however, this analysis distributed the Jewel Cave area sites into multiple clusters and, overall, formed clusters that were not consistent with those obtained in WICA2011. Therefore, we consider the 6-cluster analysis to lack physical meaning and is not considered further.

Categorizing sites into clusters by cluster analysis was purely mathematical and was the primary guide in the final categorization into hydrogeologic domains (Figure 4). The cluster analysis (Figure 2, Figure 3) is consistent with the hydrogeologic domain classification, except for sites PDGsp, BEVcr, and HIGHcr. The probable contamination at site PDGsp was further evaluated by executing the PCA and cluster analysis again, except that the four variables affected by road salt (Mg, Na, Cl, and EC) were excluded. The result was that most of the sites (93%) were placed in the same clusters as previously, and all ten of the Jewel Cave area sites, including site PDGsp, were placed in the West cluster. Therefore, we classified site PDGsp in the West domain. The cluster analysis of 70 sites and 12 variables placed sites BEVcr and HIGHcr in the East cluster, as shown on Figure 2; however, we classified the sites into the Precambrian domain (Figure 4) after further analysis described in the next section.

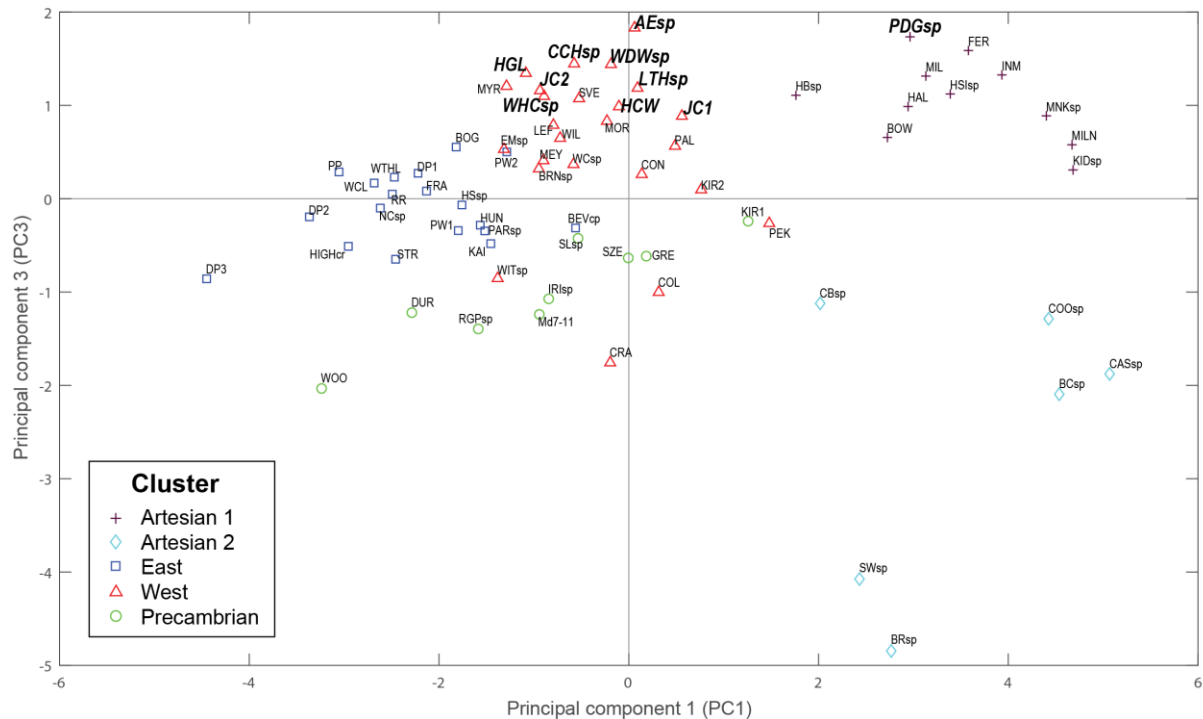


Figure 3. Scatter plot of score values for principal components 1 and 3 for 70 sites and 12 variables. Jewel Cave area sites are labeled in bold.

The hydrogeologic domains are spatially distributed into different physiographic regions consistent with WICA2011 (Figure 4). The East and West domains represent areas where the Madison and Minnelusa aquifer rocks are at or near the land surface and are located on the eastern and western sides of the Black Hills, respectively. The West domain is the most spatially extensive of the five domains, and the East and West domains generally are divided near the southern boundary of Wind Cave National Park. The Artesian 1 domain consists of artesian springs near the Fall River and proximal groundwater wells. The Artesian 2 domain consists of artesian springs farther from the Fall River, with an average water temperature about 7 degrees Celsius lower than that of the Artesian 1 domain (WICA2011). This might be the result of a deeper groundwater source or geothermal heating for the Artesian 1 domain. The Precambrian domain represents the Precambrian aquifer. Multivariate analyses distinguish the hydrochemistry of Jewel Cave from that of Wind Cave and indicate that both caves have compositions similar to the surrounding groundwater in each respective area.

Similarly to the case in Wind Cave, the subterranean lakes in Jewel Cave likely are connected hydraulically to regional groundwater flow in the Madison aquifer. Apparent groundwater flow directions (Long and others, 2012) indicate that groundwater is unlikely to flow directly from Jewel Cave to Wind Cave; it is more likely that groundwater flows from Jewel Cave toward the south and then east, passing miles south of Wind Cave (Figure 1). This interpretation is consistent with the finding that the division between the East and West domains is located to the south of Wind Cave. However, the two caves are hydraulically connected through the transfer of hydraulic head, because they are within a continuous groundwater system with no apparent physical barriers.

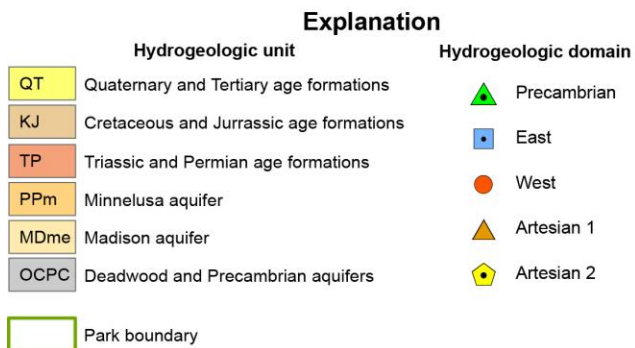
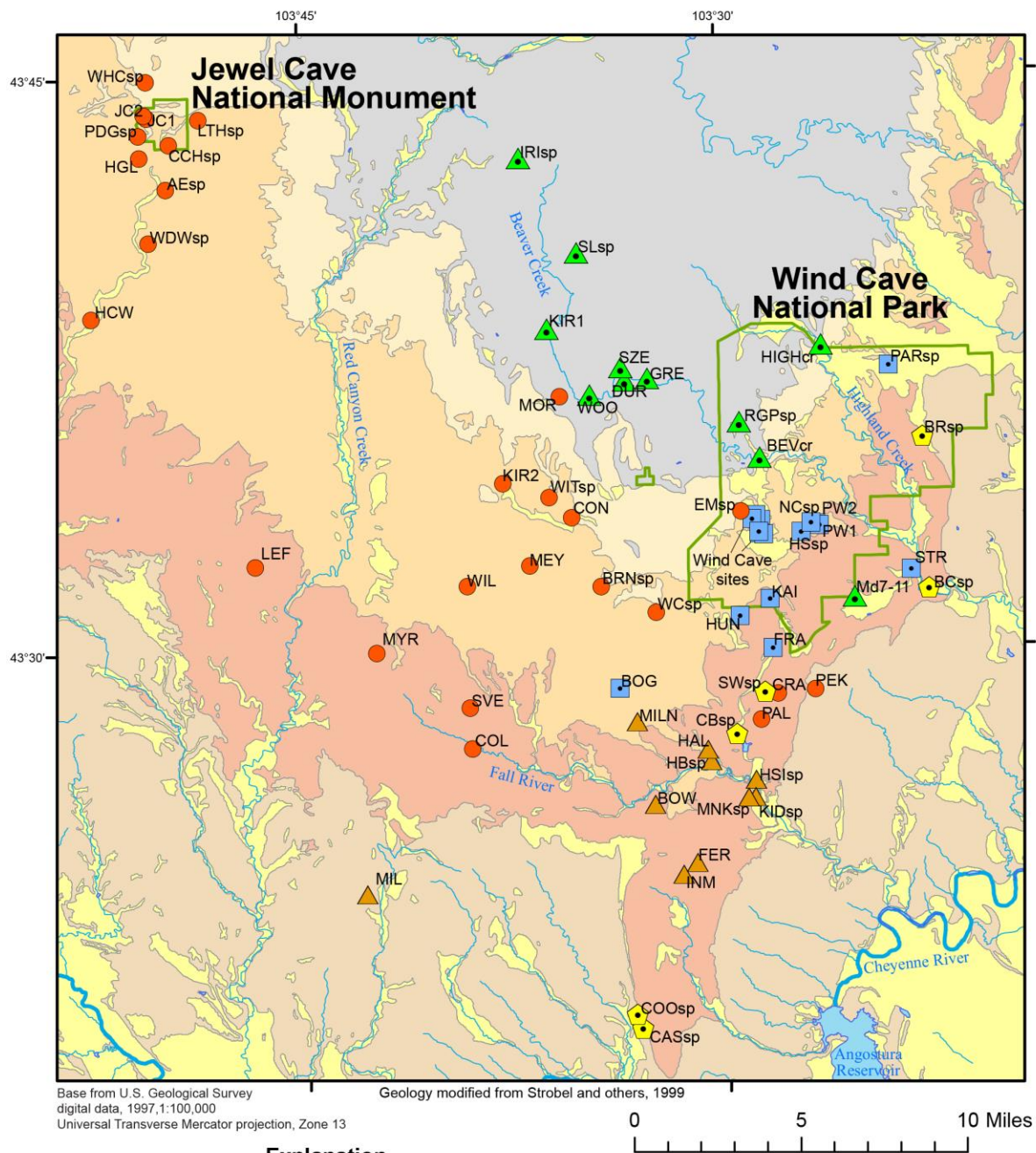


Figure 4. Study area, with sites differentiated by hydrogeologic domain.

Analysis of 33 sites and 15 variables

Principal component and cluster analyses were applied to the 33 sites for which strontium and uranium data were available. Both the $^{87}\text{Sr}/^{86}\text{Sr}$ atomic and $^{234}\text{U}/^{238}\text{U}$ activity ratios, as well as total U concentration were added to the previous 12 variables, for a total of 15 variables. Sr concentration was not included because data were not available for three of the sites (Table 3). The matrix of input values are in the Appendix (Table 8). Initially, five clusters were specified for the 33 sites; however, this resulted in clusters that were not consistent with the previous analysis of 70 sites, possibly because the number of sites was not large enough for meaningful separation into five clusters. A cluster analysis that considered four clusters resulted in clustering that was similar to results using 70 sites. In this case, Artesian 1 and 2 clusters were combined into a single Artesian cluster (Figure 5). This result is consistent with a four-cluster analysis described in WICA2011, where cluster analyses of two, three, four, five, and six clusters were tested. As for both the current analysis using 70 sites and for the WICA2011 analysis, the current analysis using 33 sites showed that PC1 separated the Artesian clusters from the other three clusters, and PC2 separated the Precambrian cluster from the East and West clusters. In two dimensional space (PC1-PC2) the four clusters are distinctly separated with little overlap (Figure 5). Combined, PC1 and PC2 explain 57 percent of the total variance of the dataset.

Sites BEVcr and HIGHcr are streams that sink into the Madison aquifer (Hortnes and Driscoll, 1998). In the analysis of 70 sites, these two sites were placed in the East cluster, whereas, in the analysis of 33 sites (Sr and U data included), the sites were placed in the Precambrian cluster (Figure 5). Highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values for sites BEVcr and HIGHcr (>0.735) are diagnostic of the interaction of water with Precambrian crystalline rocks. The two sites have $^{87}\text{Sr}/^{86}\text{Sr}$ values similar to those for groundwater discharging at sites RGPsp and SLsp (Figure 6A), which consistently were placed in the Precambrian cluster in the WICA2011 analyses. Therefore, Sr and U data influenced results of the PCA and cluster analysis to the degree that sites BEVcr and HIGHcr were placed in the Precambrian cluster rather than the East cluster. This result is reasonable because both streams drain Precambrian rocks, and further, these sites plot close to the Precambrian cluster in the analysis of 70 sites (Figure 2). Sites BEVcr and HIGHcr, therefore, were categorized into the Precambrian domain.

Similarly to the analysis of 70 sites and 12 variables, site PDGsp was included in the Artesian cluster (Figure 5) because of road salt contamination. However, $^{87}\text{Sr}/^{86}\text{Sr}$ values are not affected by road salt, and the site plots well within the range of the West domain sites on Figure 6B, further evidence that the site belongs in the West domain (Figure 4). Site WITsp was included in the West cluster in the analysis of 70 sites (Figure 2) and in the East cluster in the analysis of 33 sites (Figure 5). The final classification for site WITsp is with the West domain because it plots within the narrow range of $^{87}\text{Sr}/^{86}\text{Sr}$ values spanned by West domain sites (Figure 6B) and is located within the spatial extent of West domain sites (Figure 4).

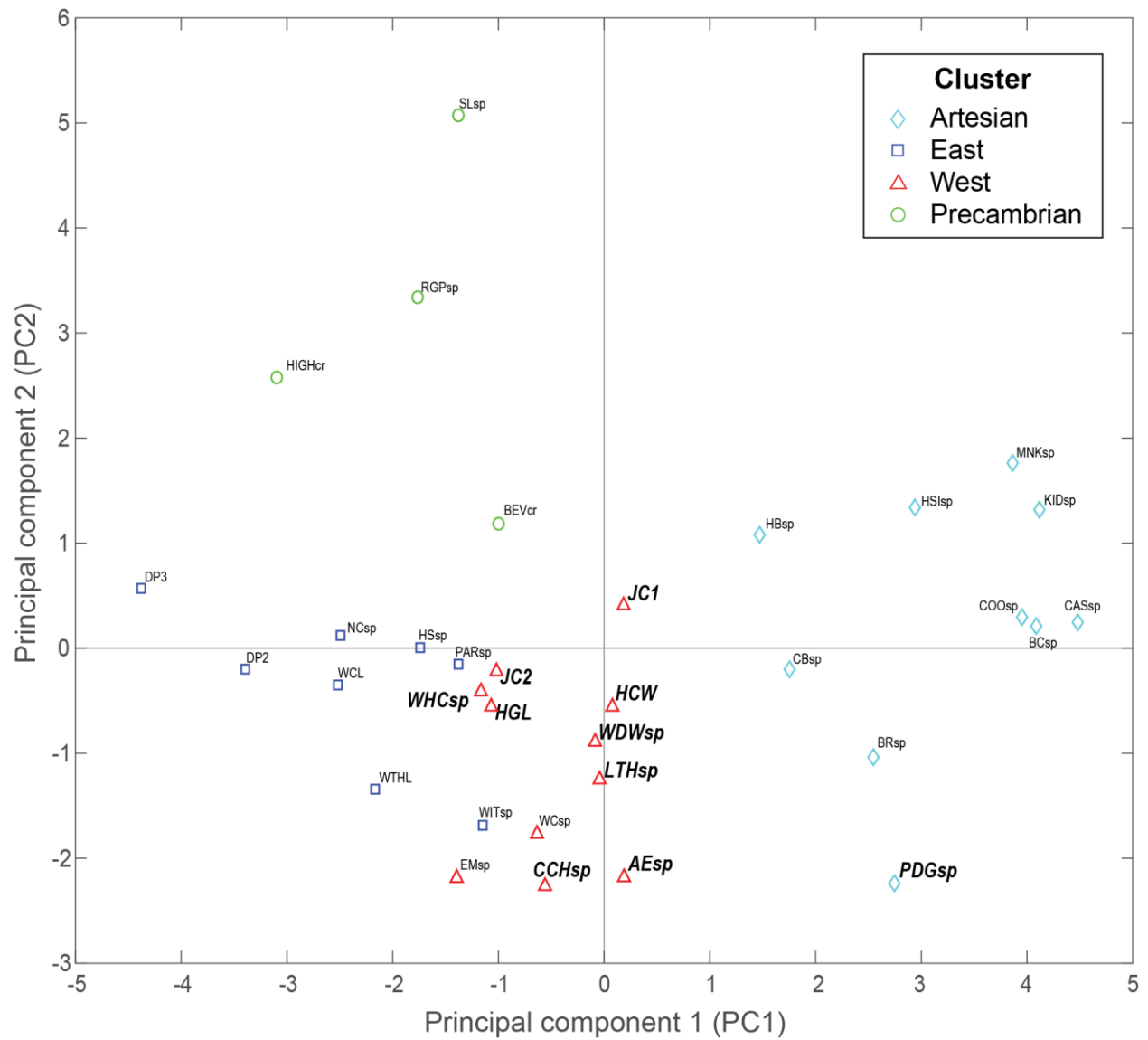


Figure 5. Scatter plot of score values for principal components 1 and 2 for 33 sites and 15 variables. Jewel Cave area sites are labeled in bold.

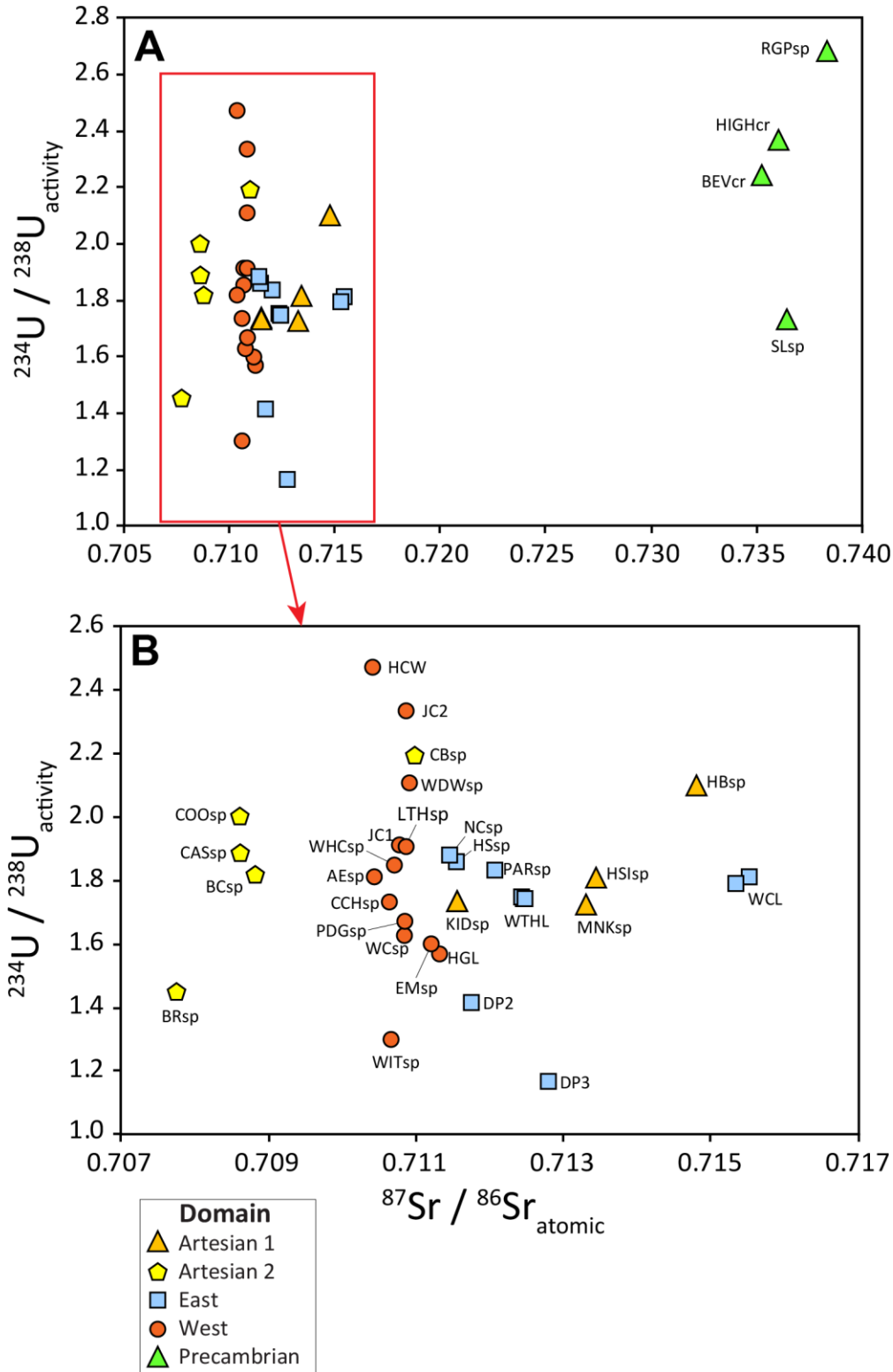


Figure 6. Bivariate plots of strontium and uranium isotope ratios showing (A) all samples and (B) samples having $^{87}\text{Sr}/^{86}\text{Sr}$ values less than 0.72, with labels. Data are given in Table 3.

The grouping of sites in Figure 6B generally is consistent with the cluster analysis of 33 sites (Figure 5). However, the separation of clusters mostly occurs along the $^{87}\text{Sr}/^{86}\text{Sr}$ axis, whereas, $^{234}\text{U}/^{238}\text{U}$ values do not distinguish the hydrogeologic domains (Figure 6). The Artesian 1 and 2 domains are clearly separated by $^{87}\text{Sr}/^{86}\text{Sr}$, and the West domain is within a narrow and unique range of $^{87}\text{Sr}/^{86}\text{Sr}$, with the exception of Cold Brook spring (CBsp; Figure 6B). Although CBsp was placed in the Artesian 2 cluster in all cluster analyses (Figure 2, Figure 3, Figure 5), the site plotted within the same $^{87}\text{Sr}/^{86}\text{Sr}$ range as the West domain sites and is separated from other Artesian 2 sites. Radiogenic isotopes do not distinguish the Artesian 1 and East domains, suggesting aquifer sources with similar Sr compositions or similar contributions from the Precambrian domain having much higher $^{87}\text{Sr}/^{86}\text{Sr}$ values.

Different chemical constituents used in this study have different properties for use as groundwater tracers. Using many constituents in combination adds value to the analyses. For example, the general consistency of the grouping of $^{87}\text{Sr}/^{86}\text{Sr}$ data shown on Figure 6B with multivariate analyses indicates the added value of $^{87}\text{Sr}/^{86}\text{Sr}$ data to understanding the hydrogeology of the study area. Exceptions to this consistency highlight the value of analyzing numerous hydrochemical constituents in combination. Stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) and Cl are conservative tracers in saturated groundwater, in that contact of groundwater with aquifer rock has little or no effect on these constituents (WICA2011). All other variables used in this analysis may be affected by mineral precipitation and dissolution, adsorption and desorption, and cation exchange. In many studies, the benefit of radiogenic isotopes as indicators of water type is that ratios of the heavy isotopes are negligibly affected by evaporation and transpiration in near-surface environments that can cause large changes in solute concentrations and the composition of light stable isotopes (i.e., $\delta^2\text{H}$ and $\delta^{18}\text{O}$; Paces and Wurster, 2014). Samples analyzed in this study, however, represent groundwater below the soil and root zone that is mostly unaffected by evaporation and transpiration or stream water sampled at locations where water is flowing rapidly into saturated parts of the aquifer.

End Member Mixing

This analysis assumes that each hydrogeologic domain primarily receives inflow from a water source that can be represented by a unique hydrochemical composition, which is referred to as an “end member.” Therefore, five end members were applied and were assumed to be mixed to varying degrees in the aquifer. The sources of the end members might originate within or outside of the study area, and we did not assume that any of the samples represent end members. The analysis allowed for all samples to be a mixture of multiple end members. Because the exact sources of water and the end member compositions were not known, these compositions had to be estimated, as described in WICA2011 and Valder and others (2012).

End member mixing was applied to 69 of the 70 sites in the identical manner and with the same 12 variables that were described in WICA2011. Site PDGsp was omitted from the analysis because of likely road salt contamination. The matrix of input values is given in the Appendix (Table 7). Most sites were assumed to be a possible mixture of all five end members; this assumption allowed for each hydrogeologic domain to be primarily influenced by a corresponding end member. As in WICA2011, we assumed that the three cave drip sites could not be influenced by the Artesian 1 and 2 end members. Most of the sites represented a mixture of multiple end members, and the average end member contribution for each hydrogeologic domain is shown in Table 4. For all hydrogeologic domains, except the East domain, the highest contribution was from its corresponding end member. The largest contribution to the East domain was from the Precambrian end member and secondarily from the East end member. This result is reasonable because a large source of recharge to the East domain is from sinking streams that drain Precambrian rocks (sites BEVcr and HIGHcr), and the largest contribution to these sites was from the Precambrian end member (Table 5). On the basis of the cluster analysis of 33 sites that included the added value of additional variables (Figure 5), the grouping of sites on Figure 6A, and results of end member mixing (Table 5), sites BEVcr and HIGHcr were reclassified from the East domain (WICA2011) into the Precambrian domain (Figure 4).

Table 4. Average end member mixing percentages by hydrogeologic domain.

Hydrogeologic domain	End-member (EM) contribution, in percent				
	Artesian 1 EM	Artesian 2 EM	East EM	West EM	Precambrian EM
Artesian 1	61*	5	7	16	11
Artesian 2	18	56*	8	11	8
East	2	3	32	22	39*
West	10	10	18	36*	26
Precambrian	0	1	6	4	88*

* Largest end-member contribution for each hydrogeologic domain, also shaded in gray.

The largest contribution to sites within the Jewel Cave area was dominantly from the West end member (Table 5). For sites within Wind Cave, the Precambrian end member was the primary contributor, and the East end member was the secondary contributor, which is consistent with results for East domain overall (Table 4).

The largest contribution to sites within the Jewel Cave area was dominantly from the West end member (Table 5). For sites within Wind Cave, the Precambrian end member was the primary contributor, and the East end member was the secondary contributor, which is consistent with results for East domain overall (Table 4).

Table 5. End member mixing percentages for selected sites.

Site area	Site name	Short name	Site type	End-member (EM) contribution, in percent				
				Artesian 1 EM	Artesian 2 EM	East EM	West EM	Precambrian EM
Sites in the Jewel Cave area	Hourglass Lake	HGL	Subterranean lake	15	6	15	41*	23
	West Hell Canyon Spring	WHCsp	Spring	13	11	12	49*	15
	Water Draw Spring	WDWsp	Spring	16	8	15	43*	17
	Choke Cherry Spring	CCHsp	Spring	9	15	22	47*	8
	Jewel Cave Well 1	JC1	Well	22	8	16	33*	20
	Jewel Cave Well 2	JC2	Well	13	10	13	46*	19
	Hell Canyon Well	HCW	Well	18	8	14	46*	15
	A&E Spring	AEsp	Spring	16	13	20	49*	2
	Lithograph Spring	LTHsp	Spring	9	13	14	44*	20
	Average	—	—	15	10	16	44*	15
Sites inside Wind Cave	Drip site 1	DP1	Cave drip	0	0	42*	25	33
	Drip site 2	DP2	Cave drip	0	0	44*	18	38
	Drip site 3	DP3	Cave drip	0	0	39	13	49*
	Petey's Puddle	PP	Subterranean lake	2	5	33	27	34*

* Largest end-member contribution for each hydrogeologic domain, also shaded in gray

Table 5 (continued). End member mixing percentages for selected sites.

Site area	Site name	Short name	Site type	End-member (EM) contribution, in percent				
				Artesian 1 EM	Artesian 2 EM	East EM	West EM	Precambrian EM
Sinking streams	Rebel River	RR	Subterranean lake	0	6	31	25	37*
	Windy City Lake	WCL	Subterranean lake	2	4	34*	25	34*
	What the Hell Lake	WTHL	Subterranean lake	0	7	32	28	33*
	Average	–	–	1	3	36	23	37*
	Beaver Creek Sink	BEVcr	Sinking stream	2	7	25	17	49*
	Highland Creek sink	HIGHcr	Sinking stream	0	1	24	11	64*

* Largest end-member contribution for each hydrogeologic domain, also shaded in gray

Discussion and Limitations

Overall, results are consistent with those of WICA2011 and do not change any major conclusions of that study. With few exceptions, sites were classified into the same hydrogeologic domains as in the previous study. The two main exceptions were for sites BEVcr and HIGHcr, which were reclassified from the East domain into the Precambrian domain (Table 6). The largest contributing end member for most sites is consistent with WICA2011.

The mixing percentages estimated in this report are useful for furthering the understanding of groundwater flow and the mixing characteristics of different aquifers and different zones within aquifers. End member mixing confirms that cluster analysis, in combination with PCA, was effective in identifying different hydrogeologic domains because results were mutually consistent between methods. However, the accuracy of end member mixing is dependent on many simplifying assumptions that introduce error. One assumption was that all samples were a possible mixture of five different sources of groundwater, or end members. In a general sense, each end member represented one of the five hydrogeologic domains. Another limitation and source of error is that the hydrochemical composition of end members is unknown and must be estimated. An end member composition could differ from all samples in that domain and might represent regional flow from outside of the study area. Although we assumed all samples were a mixture of only five end members, the samples might be mixed from a much larger number of end members. Finally, mineral precipitation and dissolution, adsorption and desorption, and cation exchange occurs for most the variables, but these were neglected in end member mixing. The conservative constituents $\delta^2\text{H}$, $\delta^{18}\text{O}$, and Cl were weighted more heavily in end member mixing, as described in WICA2011, to compensate for this limitation.

Conclusions

Jewel Cave and Wind Cave contain several lakes that are well connected to regional groundwater flow in the Madison aquifer. Five hydrogeologic domains were classified on the basis of multivariate analysis for the area encompassing Jewel Cave and Wind Cave. The Artesian 1 and Artesian 2 domains represent primarily artesian springs and surrounding groundwater, the East and West domains represent the Madison and Minnelusa aquifers on the eastern and western sides, respectively, of the southern Black Hills, and the Precambrian domain represents the Precambrian aquifer. Multivariate analysis distinguished the hydrochemistry of Jewel Cave from that of Wind Cave and indicates that water in both caves has compositions similar to the surrounding groundwater in each respective area. Jewel Cave and Wind are within the West and East domains, respectively, and have distinctly different hydrochemical signatures. For four of the domains, the largest contribution was from the end member corresponding to that domain. For the East domain overall, the largest contribution was from the Precambrian domain. The Precambrian domain also was the largest contributor for four of the seven sites inside of Wind Cave. These results are reasonable because a large source of recharge to the East domain is from sinking streams that drain Precambrian rocks. Results of end member mixing indicate that the largest contribution to samples from the Jewel Cave area was dominantly from the West domain end member. Groundwater from Jewel Cave and surrounding area probably flows to the southeast toward the southern extent of the Black Hills as it passes to the south of Wind Cave, rather than into Wind Cave.

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Appendix

Sites sampled and included in this study are described in Table 6. The complete matrices of input values for principal component analysis, cluster analysis, and end member mixing are provided in Table 7 for 70 sites and 12 variables and in Table 8 for 33 sites and 15 variables.

Table 6. Description of sampled sites.

Site name	Short site name	Description	Hydrogeologic domain	Source aquifer	Station number
Hot Springs Intake Spring	HSIsP	Artesian spring	Artesian 1	Madison ^b	432632103285302
Kidney Spring	KIDsp	Artesian spring	Artesian 1	Madison ^b	432605103285401
Minnekahta Spring	MNKsp	Artesian spring	Artesian 1	Madison ^b	432605103290901
Hot Brook Spring	HBsp	Artesian spring	Artesian 1	Minnelusa ^a	432703103302801
MIL well	MIL	Well	Artesian 1	Madison	432340103421501
BOW well	BOW	Well	Artesian 1	Minnelusa	432555103323201
FER well	FER	Well	Artesian 1	Minnelusa	432437103305701
HAL well	HAL	Well	Artesian 1	Minnelusa	432720103303701
INM well	INM	Well	Artesian 1	Minnelusa	432332103314801
MILN well	MILN	Well	Artesian 1	Minnelusa	432806103330801
Beaver Creek Spring	BCsp	Artesian spring	Artesian 2	Madison ^b	433128103223401
Cascade Spring	CASsp	Artesian spring	Artesian 2	Madison ^b	432006103330501
Cool Spring	COOsp	Artesian spring	Artesian 2	Madison ^b	432028103331601
Boland Ridge Spring	BRsp	Spring	Artesian 2	Unknown ^c	433525103224401

^aAssumed to flow primarily from Minnelusa aquifer but could include water from other aquifers.

^bAssumed to flow primarily from Madison aquifer but could include water from other aquifers.

^cPossibly artesian flowing from Madison or Minnelusa aquifer or both.

Table 6 (continued). Description of sampled sites.

Site name	Short site name	Description	Hydrogeologic domain	Source aquifer	Station number
Cold Brook Spring	CBsp	Spring	Artesian 2	Unknown ^c	432744103293401
Southwest Spring	SWsp	Spring	Artesian 2	Unknown ^c	432849103283201
Drip site 1	DP1	Wind Cave drip	East	Madison	433302103281507
Drip site 2	DP2	Wind Cave drip	East	Madison	433302103281508
Drip site 3	DP3	Wind Cave drip	East	Madison	433302103281509
Petey's Puddle	PP	Wind Cave water body	East	Madison	433302103281504
Rebel River	RR	Wind Cave water body	East	Madison	433302103281506
What the Hell Lake	WTHL	Wind Cave water body	East	Madison	433302103281502
Windy City Lake	WCL	Wind Cave water body	East	Madison	433302103281501
Horse Shelter Spring	HSsp	Shallow spring	East	Minnelusa ^a	433258103270801
Negro Canyon Spring	NCsp	Shallow spring	East	Minnelusa ^a	433312103264701
Parker Spring	PARsp	Shallow spring	East	White River	433717103235401
BOG well	BOG	Well	East	Madison	432858103334201
KAI well	KAI	Well	East	Madison	433114103281601
Park well 1	PW1	Well	East	Madison	433311103263101
Park well 2	PW2	Well	East	Madison	433311103263102

^aAssumed to flow primarily from Minnelusa aquifer but could include water from other aquifers.

^bAssumed to flow primarily from Madison aquifer but could include water from other aquifers.

^cPossibly artesian flowing from Madison or Minnelusa aquifer or both.

Table 6 (continued). Description of sampled sites.

Site name	Short site name	Description	Hydrogeologic domain	Source aquifer	Station number
STR well	STR	Well	East	Madison	433150103230501
FRA well	FRA	Well	East	Minnelusa	432958103281401
HUN well	HUN	Well	East	Minnelusa	433034103284701
Irish Spring	IRIsP	Shallow spring	Precambrian	Precambrian	434249103370401
Reeves Gulch Pegmatite Spring	RGPsp	Shallow spring	Precambrian	Precambrian	433551103291901
Southerland Spring	SLsp	Shallow spring	Precambrian	Precambrian	434020103350101
Beaver Creek Sink	BEVcr	Stream sink	Precambrian	Precambrian	6402430
Highland Creek sink	HIGHcr	Stream sink	Precambrian	Precambrian	433745103261900
Md7-11 well	Md7-11	Well	Precambrian	Madison	433115103251401
DUR well	DUR	Well	Precambrian	Precambrian	433658103332301
GRE well	GRE	Well	Precambrian	Precambrian	433701103323401
KIR1 well	KIR1	Well	Precambrian	Precambrian	433821103360901
SZE well	SZE	Well	Precambrian	Precambrian	433718103333101
WOO well	WOO	Well	Precambrian	Precambrian	433636103343901
Hourglass Lake	HGL	Jewel Cave water body	West	Madison	434258103504201
A&E Spring	AEsp	Shallow spring	West	Minnelusa ^a	434207103494601
Brown Spring	BRNsp	Shallow spring	West	Minnelusa ^a	433137103342101

^aAssumed to flow primarily from Minnelusa aquifer but could include water from other aquifers.

^bAssumed to flow primarily from Madison aquifer but could include water from other aquifers.

^cPossibly artesian flowing from Madison or Minnelusa aquifer or both.

Table 6 (continued). Description of sampled sites.

Site name	Short site name	Description	Hydrogeologic domain	Source aquifer	Station number
Choke Cherry Spring	CCHsp	Shallow spring	West	Minnelusa ^a	434319103493701
Elk Mountain Spring	EMsp	Shallow spring	West	Minnelusa ^a	433332103291801
Lithograph Spring	LTHsp	Shallow spring	West	Minnelusa ^a	434356103483101
Prairie Dog Spring	PDGsp	Shallow spring	West	Minnelusa ^a	434335103504401
Water Draw Spring	WDWsp	Shallow spring	West	Minnelusa ^a	434045103502301
West Hell Canyon Spring	WHCsp	Shallow spring	West	Minnelusa ^a	434458103503001
Witch Spring	WITsp	Shallow spring	West	Minnelusa ^a	433611103335801
Woodcock Spring	WCsp	Shallow spring	West	Minnelusa ^a	433056103322201
Jewel Cave Well 1	JC1	Well	West	Deadwood	434402103502301
Jewel Cave Well 2	JC2	Well	West	Deadwood	434406103503301
CON well	CON	Well	West	Madison	433326103352001
SVE well	SVE	Well	West	Madison	432825103391201
COL well	COL	Well	West	Minnelusa	432727103390201
CRA well	CRA	Well	West	Minnelusa	432846103280501
Hell Canyon Well	HCW	Well	West	Minnelusa	433846103523001
KIR2 well	KIR2	Well	West	Minnelusa	433420103374901
LEF well	LEF	Well	West	Minnelusa	433215103464401
MEY well	MEY	Well	West	Minnelusa	433215103365801

^aAssumed to flow primarily from Minnelusa aquifer but could include water from other aquifers.

^bAssumed to flow primarily from Madison aquifer but could include water from other aquifers.

^cPossibly artesian flowing from Madison or Minnelusa aquifer or both.

Table 6 (continued). Description of sampled sites.

Site name	Short site name	Description	Hydrogeologic domain	Source aquifer	Station number
MYR well	MYR	Well	West	Minnelusa	433003103420701
PAL well	PAL	Well	West	Minnelusa	432806103284101
PEK well	PEK	Well	West	Minnelusa	432852103264401
WIL well	WIL	Well	West	Minnelusa	433141103390901
MOR well	MOR	Well	West	Precambrian	433635103354301

^aAssumed to flow primarily from Minnelusa aquifer but could include water from other aquifers.

^bAssumed to flow primarily from Madison aquifer but could include water from other aquifers.

^cPossibly artesian flowing from Madison or Minnelusa aquifer or both.

Table 7. Input values for principal component analysis, cluster analysis, and end member mixing of 70 sites. Values represent averages if multiple values were available for a site. Data were obtained from the [National Water Information System](#). [µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; δ¹⁸O and δ²H (‰), stable isotopes of oxygen and hydrogen, respectfully, in reference to sea water].

Short site name	Activity of hydrogen ion	Electrical conductivity (EC), in µS/cm	Calcium (Ca), in mg/L	Magnesium (Mg), in mg/L	Sodium (Na), in mg/L	Alkalinity as calcium carbonate (CaCO ₃), in mg/L	Chloride (Cl), in mg/L	Silica (Si), in mg/L	Sulfate (SO ₄), in mg/L	Arsenic (As), in µg/L	δ ² H, in ‰	δ ¹⁸ O, in ‰
BEVcr	1.21E-08	553.3	72.8	23.7	13.6	277.5	20.8	16.1	46.6	4.1	-89.77	-11.81
CASp	1.00E-07	2560.0	558.0	83.6	27.8	231.3	29.3	13.7	1550	1.2	-116.62	-15.09
COOsp	1.26E-07	1960.0	327.0	75.3	30.3	235.2	33.1	14.5	975.0	2.3	-115.99	-15.01
INM	3.98E-08	1190.0	110.0	37.9	83.1	254.9	119.0	23.9	247.0	4.4	-124.82	-16.22
MIL	6.48E-08	736.5	79.4	26.6	37.1	258.2	48.2	23.2	104.2	0.7	-126.33	-16.59
FER	2.00E-08	1100.0	97.5	29.4	86.6	224.5	123.0	27.5	207.0	5.6	-125.48	-16.26
BOW	5.01E-08	890.0	99.8	33.9	39.1	253.2	48.6	18.1	198.0	3.3	-116.73	-15.28
KIDsp	1.00E-07	1580.0	182.0	38.9	81.8	219.3	117.0	22.4	478.0	3.5	-125.10	-16.31
MNKsp	2.00E-07	1300.0	123.0	32.9	90.8	237.8	125.0	27.4	275.0	5.2	-126.55	-16.44
HSIsp	8.70E-08	1034.0	91.8	29.3	71.5	244.9	97.3	23.6	173.2	5.4	-120.86	-15.98
HBsp	7.44E-08	696.6	65.5	25.3	36.5	256.1	45.3	18.1	68.4	6.4	-114.06	-15.06
HAL	3.16E-08	985.0	112.0	38.5	46.1	295.4	67.3	14.4	210.0	4.0	-118.27	-15.40
COL	6.31E-08	760.0	99.2	41.5	6.5	272.4	2.8	11.1	201.0	4.5	-100.71	-13.08
CBsp	1.00E-07	1130.0	168.0	49.2	15.1	286.1	19.6	12.8	388.0	5.6	-101.38	-13.28
PAL	1.00E-07	582.0	62.4	29.6	13.1	270.2	15.9	10.3	61.4	10.6	-109.31	-14.30
MILN	1.00E-07	1490.0	179.0	52.6	75.1	295.2	99.2	24.0	433.0	3.2	-122.30	-15.91
SVE	1.33E-07	453.3	51.9	26.2	4.5	287.4	1.9	12.1	8.8	3.9	-115.32	-15.15

Table 7 (continued). Input values for principal component analysis, cluster analysis, and end member mixing of 70 sites. Values represent averages if multiple values were available for a site. Data were obtained from the [National Water Information System](#). [$\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (‰), stable isotopes of oxygen and hydrogen, respectfully, in reference to sea water].

Short site name	Activity of hydrogen ion	Electrical	Calcium (Ca), in mg/L	Magnesium (Mg), in mg/L	Sodium (Na), in mg/L	Alkalinity	Chloride (Cl), in mg/L	Silica (Si), in mg/L	Sulfate	Arsenic (As), in µg/L	δ ² H, in ‰	δ ¹⁸ O, in ‰
		conductivity (EC), in µS/cm				as calcium carbonate (CaCO ₃), in mg/L			(SO ₄), in mg/L			
CRA	3.98E-08	809.0	101.0	46.9	9.8	209.6	2.7	9.0	276.0	10.1	-93.15	-12.27
SWsp	3.98E-08	2500.0	502.0	107.0	6.8	209.3	5.1	8.5	1540	1.1	-90.76	-11.83
PEK	1.00E-07	786.0	90.6	37.8	19.5	247.7	16.0	12.5	198.0	6.1	-106.99	-14.16
BOG	2.37E-08	455.0	43.0	29.5	6.3	262.4	2.4	12.3	10.3	13.0	-98.14	-12.80
FRA	1.26E-08	434.0	47.2	21.3	15.1	241.5	3.3	9.0	32.9	37.1	-91.79	-12.08
MYR	3.16E-08	444.0	59.0	20.2	5.3	273.8	2.8	12.7	13.5	24.6	-108.65	-14.14
HUN	4.87E-08	410.5	50.2	17.7	9.8	234.9	5.8	15.3	17.4	7.4	-91.50	-12.20
WCsp	7.94E-08	689.0	67.8	53.9	5.3	468.9	3.8	13.9	19.5	12.0	-95.22	-12.40
KAI	7.94E-08	424.0	51.1	18.5	9.8	228.5	5.6	15.6	16.4	7.0	-90.86	-12.24
Md7-11	5.01E-08	403.0	40.4	19.6	16.4	206.0	6.0	12.8	23.5	0.3	-89.72	-11.98
BCsp	1.11E-07	2337.5	460.8	77.0	29.5	218.4	33.4	15.7	1290	1.8	-109.24	-14.33
BRNsp	7.94E-08	568.0	59.0	42.2	5.9	359.4	3.6	11.4	20.5	16.9	-97.65	-12.73
WIL	6.31E-08	479.0	53.0	29.8	8.1	268.1	7.1	14.0	22.7	18.7	-103.65	-13.32
STR	5.71E-08	339.6	39.9	14.1	9.2	188.8	2.5	16.5	11.2	8.7	-88.27	-11.84
MEY	3.98E-08	495.0	55.8	30.9	6.7	271.2	9.3	13.4	29.0	18.5	-99.29	-12.88
LEF	3.16E-08	467.0	48.0	26.1	9.7	272.5	3.3	11.9	21.5	6.5	-105.84	-13.81
HSsp	7.94E-08	575.0	72.8	11.8	4.0	269.7	3.6	14.1	9.8	19.5	-95.87	-12.63

Table 7 (continued). Input values for principal component analysis, cluster analysis, and end member mixing of 70 sites. Values represent averages if multiple values were available for a site. Data were obtained from the [National Water Information System](#). [$\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (‰), stable isotopes of oxygen and hydrogen, respectfully, in reference to sea water].

Short site name	Activity of hydrogen ion	Electrical conductivity (EC), in $\mu\text{S}/\text{cm}$	Calcium (Ca), in mg/L	Magnesium (Mg), in mg/L	Sodium (Na), in mg/L	Alkalinity as calcium carbonate (CaCO_3), in mg/L	Chloride (Cl), in mg/L	Silica (Si), in mg/L	Sulfate (SO_4), in mg/L	Arsenic (As), in $\mu\text{g}/\text{L}$	$\delta^2\text{H}$, in ‰	$\delta^{18}\text{O}$, in ‰
WCL	1.00E-08	348.5	35.8	19.5	7.4	187.9	4.3	13.1	9.4	14.6	-91.03	-12.12
WTHL	1.35E-08	419.0	45.4	25.6	4.9	248.0	3.0	12.6	7.2	12.7	-91.30	-12.11
PP	7.94E-09	331.0	34.4	19.8	4.5	189.0	3.1	12.6	6.6	13.1	-91.50	-12.25
RR	1.58E-08	435.0	43.2	25.1	4.9	221.0	3.0	13.4	6.8	12.6	-90.67	-12.12
DP1	1.04E-08	366.5	34.6	18.0	10.4	171.8	10.2	16.8	22.0	33.3	-90.61	-12.29
DP2	7.88E-09	311.3	47.7	13.1	4.3	196.0	3.7	17.6	10.7	28.2	-83.74	-11.51
DP3	2.14E-08	285.3	37.7	8.1	1.0	148.1	1.2	19.4	7.4	24.8	-84.02	-11.57
PW1	4.09E-08	384.5	46.2	15.6	12.5	220.9	5.2	16.1	18.1	8.7	-89.95	-11.98
PW2	1.79E-08	564.5	25.8	13.6	85.2	270.4	18.8	11.3	41.1	24.9	-87.70	-11.86
NCsp	6.31E-08	409.0	75.0	6.5	2.9	255.6	2.4	12.3	7.1	16.9	-95.56	-12.55
CON	4.15E-08	666.0	75.9	33.5	12.6	338.3	12.8	12.8	31.6	5.0	-99.34	-12.94
EMsp	3.98E-08	656.0	47.9	61.8	3.1	436.0	2.0	11.2	20.4	15.3	-95.55	-12.48
KIR2	6.61E-08	771.0	107.0	30.9	13.4	387.0	41.1	12.9	24.1	3.0	-96.97	-12.83
BRsp	6.31E-08	2900.0	594.0	149.0	16.9	163.4	3.2	13.8	1940	2.2	-86.57	-11.11
RGPsp	3.16E-07	372.0	55.3	11.9	6.7	222.5	1.9	17.1	19.7	2.0	-89.53	-12.16
WITsp	6.31E-08	528.0	55.4	23.4	10.2	271.9	5.3	8.7	24.4	4.5	-90.90	-11.62
MOR	9.12E-08	774.0	47.3	78.2	14.1	517.2	8.1	18.8	22.1	35.2	-91.77	-11.95

Table 7 (continued). Input values for principal component analysis, cluster analysis, and end member mixing of 70 sites. Values represent averages if multiple values were available for a site. Data were obtained from the [National Water Information System](#). [$\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (‰), stable isotopes of oxygen and hydrogen, respectfully, in reference to sea water].

Short site name	Activity of hydrogen ion	Electrical conductivity (EC), in $\mu\text{S}/\text{cm}$	Calcium (Ca), in mg/L	Magnesium (Mg), in mg/L	Sodium (Na), in mg/L	Alkalinity as calcium carbonate (CaCO_3), in mg/L	Chloride (Cl), in mg/L	Silica (Si), in mg/L	Sulfate (SO_4), in mg/L	Arsenic (As), in $\mu\text{g}/\text{L}$	$\delta^2\text{H}$, in ‰	$\delta^{18}\text{O}$, in ‰
WOO	3.39E-07	196.0	24.8	7.1	5.0	75.8	4.6	17.3	27.1	12.7	-87.36	-11.99
DUR	2.14E-07	299.0	43.1	7.6	6.7	158.2	3.8	22.9	14.4	5.7	-87.81	-12.00
GRE	9.33E-08	564.0	75.9	18.2	17.7	253.3	28.8	19.7	36.7	2.6	-92.66	-12.38
PARsp	6.31E-08	607.0	61.8	18.4	11.5	313.9	5.2	21.0	8.4	11.1	-87.82	-11.10
SZE	1.02E-07	523.0	77.0	15.9	11.7	264.6	15.1	19.4	40.5	1.9	-94.23	-12.63
HIGHcr	4.16E-09	298.0	41.2	7.6	8.4	148.4	3.3	18.3	14.4	3.2	-87.60	-11.85
KIR1	1.26E-07	718.0	88.3	24.0	24.8	307.1	53.8	19.3	40.6	1.8	-97.82	-12.84
SLsp	3.31E-07	319.0	44.8	8.5	5.6	149.7	3.1	17.3	26.7	0.8	-111.76	-14.91
IRIsp	2.00E-07	508.0	46.9	12.6	13.8	190.0	10.5	21.2	19.2	2.7	-90.73	-12.06
HGL	3.16E-08	380.0	36.8	32.8	5.2	271.9	3.1	13.4	9.2	4.7	-110.42	-14.18
WHCsp	3.55E-08	529.0	63.4	36.7	2.0	364.6	1.2	10.5	5.2	1.6	-111.42	-14.67
WDWsp	2.95E-08	524.0	56.0	36.9	6.7	335.3	6.5	13.6	13.8	5.7	-111.11	-14.25
CCHsp	8.91E-09	594.0	47.4	58.1	6.3	387.7	4.9	11.1	20.0	6.6	-106.25	-13.39
JC1	3.47E-08	590.0	63.5	35.5	9.4	284.1	51.3	11.3	6.9	0.9	-107.33	-14.05
JC2	3.09E-08	499.0	59.4	35.3	2.5	342.6	1.9	11.6	4.7	1.9	-109.80	-14.43
HCW	3.72E-08	501.0	67.2	27.3	6.4	303.6	4.1	11.6	29.3	4.6	-113.65	-14.56
AEsp	1.58E-08	614.0	46.3	58.5	10.0	398.7	6.6	12.7	24.0	9.1	-110.77	-14.09

Table 7 (continued). Input values for principal component analysis, cluster analysis, and end member mixing of 70 sites. Values represent averages if multiple values were available for a site. Data were obtained from the [National Water Information System](#). [$\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (‰), stable isotopes of oxygen and hydrogen, respectfully, in reference to sea water].

Short site name	Activity of hydrogen ion	Electrical conductivity (EC), in $\mu\text{S}/\text{cm}$	Calcium (Ca), in mg/L	Magnesium (Mg), in mg/L	Sodium (Na), in mg/L	Alkalinity as calcium carbonate (CaCO_3), in mg/L	Chloride (Cl), in mg/L	Silica (Si), in mg/L	Sulfate (SO_4), in mg/L	Arsenic (As), in $\mu\text{g}/\text{L}$	$\delta^2\text{H}$, in ‰	$\delta^{18}\text{O}$, in ‰
PDGsp	3.02E-08	1540.0	74.1	106.0	98.0	424.3	302.0	13.0	29.3	9.6	-108.16	-13.91
LTHsp	3.16E-08	670.0	70.8	54.7	5.1	448.7	4.0	14.7	19.9	5.0	-106.57	-13.82

Table 8. Input values for principal component analysis and cluster analysis of 33 sites. Values represent averages if multiple values were available for a site. Data were obtained from the National Water Information System (<https://doi.org/10.5066/F7P55KJN>). [$\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (‰), stable isotopes of oxygen and hydrogen, respectfully, in reference to sea water; Sr, strontium; U, uranium; ng/g , nanograms per gram].

Site name	Activity of hydrogen ion	Electrical conductivity (EC), in $\mu\text{S}/\text{cm}$	Calcium (Ca), in mg/L	Magnesium, (Mg), in mg/L	Sodium (Na), in mg/L	Alkalinity as calcium carbonate (CaCO_3), in mg/L	Chloride (Cl), in mg/L	Silica (Si), in mg/L	Sulfate (SO_4), in mg/L	Arsenic (As), in $\mu\text{g}/\text{L}$	$\delta^2\text{H}$, in ‰	$\delta^{18}\text{O}$, in ‰	$^{87}\text{Sr}/^{86}\text{Sr}_{\text{atomic}}$	$^{234}\text{U}/^{238}\text{U}_{\text{activity}}$	Uranium (U), in ng/g
AEsp	1.58E-08	614	46.3	58.5	10.0	398.7	6.6	12.7	24.0	9.1	-110.8	-14.1	0.710466	1.807	18.60
BCsp	1.11E-07	2338	460.8	77.0	29.5	218.4	33.4	15.7	1290.0	1.8	-109.2	-14.3	0.708847	1.813	7.55
BEVcr	1.21E-08	553	72.8	23.7	13.6	277.5	20.8	16.1	46.6	4.1	-89.8	-11.8	0.735269	2.236	3.99
BRsp	6.31E-08	2900	594.0	149.0	16.9	163.3	3.2	13.8	1940.0	2.2	-86.6	-11.1	0.707775	1.443	9.04
CASsp	1.00E-07	2560	558.0	83.6	27.8	231.3	29.3	13.7	1550.0	1.2	-116.6	-15.1	0.708635	1.879	5.33
CBsp	1.00E-07	1130	168.0	49.2	15.1	286.1	19.6	12.8	388.0	5.6	-101.4	-13.3	0.711002	2.185	4.31
CCHsp	8.91E-09	594	47.4	58.1	6.3	387.7	4.9	11.1	20.0	6.6	-106.3	-13.4	0.710655	1.726	8.95
COOsp	1.26E-07	1960	327.0	75.3	30.3	235.2	33.1	14.5	975.0	2.3	-116.0	-15.0	0.708644	1.993	5.41
DP2	7.88E-09	311	47.7	13.1	4.3	196.0	3.7	17.6	10.7	28.2	-83.7	-11.5	0.711773	1.406	1.46
DP3	2.14E-08	285	37.7	8.1	1.0	148.1	1.2	19.4	7.4	24.8	-84.0	-11.6	0.712818	1.158	1.14
EMsp	3.98E-08	656	47.9	61.8	3.1	436.0	2.0	11.2	20.4	15.3	-95.6	-12.5	0.711219	1.591	3.24
HBsp	7.44E-08	697	65.5	25.3	36.5	256.1	45.3	18.1	68.4	6.4	-114.1	-15.1	0.714811	2.097	4.20
HCW	3.72E-08	501	67.2	27.3	6.4	303.6	4.1	11.6	29.3	4.6	-113.7	-14.6	0.710426	2.465	9.74
HGL	3.16E-08	380	36.8	32.8	5.2	271.9	3.1	13.4	9.2	4.7	-110.4	-14.2	0.711355	1.561	4.20
HIGHcr	4.16E-09	298	41.2	7.6	8.4	148.4	3.3	18.3	14.4	3.2	-87.6	-11.8	0.736035	2.360	3.23
HSIsp	8.70E-08	1034	91.8	29.3	71.5	244.9	97.3	23.6	173.2	5.4	-120.9	-16.0	0.713462	1.807	5.78
HSsp	7.94E-08	575	72.8	11.8	4.0	269.7	3.6	14.1	9.8	19.5	-95.9	-12.6	0.711578	1.854	2.18
JC1	3.47E-08	590	63.5	35.5	9.4	284.1	51.3	11.3	6.9	0.9	-107.3	-14.1	0.710792	1.906	1.13
JC2	3.09E-08	499	59.4	35.3	2.5	342.6	1.9	11.6	4.7	1.9	-109.8	-14.4	0.710891	2.326	1.92
KIDsp	1.00E-07	1580	182.0	38.9	81.8	219.3	117.0	22.4	478.0	3.5	-125.1	-16.3	0.711570	1.729	6.26
LTHsp	3.16E-08	670	70.8	54.7	5.1	448.7	4.0	14.7	19.9	5.0	-106.6	-13.8	0.710886	1.902	4.89
MNKsp	2.00E-07	1300	123.0	32.9	90.8	237.8	125.0	27.4	275.0	5.2	-126.6	-16.4	0.713321	1.721	6.05
NCsp	6.31E-08	409	75.0	6.5	2.9	255.6	2.4	12.3	7.1	16.9	-95.6	-12.6	0.711486	1.873	2.14
PARsp	6.31E-08	607	61.8	18.4	11.5	313.9	5.2	21.0	8.4	11.1	-87.8	-11.1	0.712083	1.825	5.08
PDGsp	3.02E-08	1540	74.1	106.0	98.0	424.3	302.0	13.0	29.3	9.6	-108.2	-13.9	0.710868	1.678	19.10
RGPsp	3.16E-07	372	55.3	11.9	6.7	222.5	1.9	17.1	19.7	2.0	-89.5	-12.2	0.738395	2.675	2.41

Table 8. Input values for principal component analysis and cluster analysis of 33 sites. Values represent averages if multiple values were available for a site. Data were obtained from the National Water Information System (<https://doi.org/10.5066/F7P55KJN>). [$\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (‰), stable isotopes of oxygen and hydrogen, respectfully, in reference to sea water; Sr, strontium; U, uranium; ng/g , nanograms per gram].

Site name	Activity of hydrogen ion	Electrical conductivity (EC), in $\mu\text{S}/\text{cm}$	Calcium (Ca), in mg/L	Magnesium, (Mg), in mg/L	Sodium (Na), in mg/L	Alkalinity as calcium carbonate (CaCO_3), in mg/L	Chloride (Cl), in mg/L	Silica (Si), in mg/L	Sulfate (SO_4), in mg/L	Arsenic (As), in $\mu\text{g}/\text{L}$	$\delta^2\text{H}$, in ‰	$\delta^{18}\text{O}$, in ‰	$^{87}\text{Sr}/^{86}\text{Sr}_{\text{atomic}}$	$^{234}\text{U}/^{238}\text{U}_{\text{activity}}$	Uranium (U), in ng/g
SLsp	3.31E-07	319	44.8	8.5	5.6	149.6	3.1	17.3	26.7	0.8	-111.8	-14.9	0.736435	1.728	0.21
WCL	1.00E-08	349	35.8	19.5	7.4	187.9	4.3	13.1	9.4	14.6	-91.0	-12.1	0.715450	1.796	4.22
WCsp	7.94E-08	689	67.8	53.9	5.3	468.9	3.8	13.9	19.5	12.0	-95.2	-12.4	0.710858	1.622	4.81
WDWsp	2.95E-08	524	56.0	36.9	6.7	335.3	6.5	13.6	13.8	5.7	-111.1	-14.3	0.710930	2.102	9.10
WHCsp	3.55E-08	529	63.4	36.7	2.0	364.5	1.2	10.5	5.2	1.6	-111.4	-14.7	0.710743	1.844	1.05
WITsp	6.31E-08	528	55.4	23.4	10.2	271.9	5.3	8.7	24.4	4.5	-90.9	-11.6	0.710695	1.293	9.25
WTHL	1.35E-08	419	45.4	25.6	4.9	248.0	3.0	12.6	7.2	12.7	-91.3	-12.1	0.712476	1.739	8.75

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