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PHREEQC MODELING AND GRAPHICAL ANALYSES OF FLINT RIDGE CAVE, AUSTIN, TRAVIS COUNTY, TEXAS

Prepared for
City of Austin
Austin Water, Wildlands Conservation Division
Balcones Canyonlands Preserve

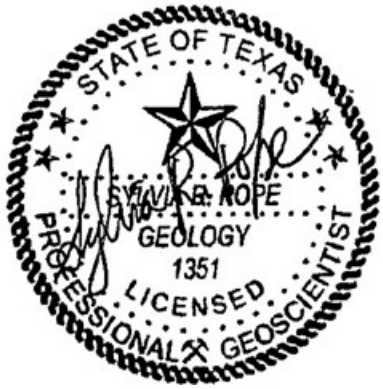
22 October 2021

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Abstract

Flint Ridge Cave is listed on the City of Austin and Travis County endangered species permit for the protection of karst invertebrate species and is managed by the City of Austin's Balcones Canyonlands Preserve Program. Completion of the construction of State Highway 45 Southwest proximal to the cave has altered the surface drainage basin of Flint Ridge Cave, which may affect the quantity and rate of flow and the water chemistry measured at monitored cave drips. This project was conducted to support interpretation of water chemistry data collected within the Flint Ridge Cave surface and subsurface drainage basin by the City of Austin or their contractors. Geochemical evaluation by PHREEQC modeling and graphical analyses is a component of ongoing efforts to characterize the geochemical composition of cave drips and pools, and of direct recharge surface water runoff sources. The data evaluated were collected between 26 February 2015 and 09 September 2020.

Water chemistry was examined during six time periods at two drip water sites and two pools along a flow path in the Flint Ridge Cave system near State Highway 45 Southwest. Water samples collected from the Balcony Room, Culvert Crawl Upper Pool, Culvert Crawl Lower Pool, and Drip Pit were used as spatial points along the flow path. PHREEQC (an acronym for a groundwater geochemistry software program that evaluates pH, redox potential, and equilibrium of a solution) was used to forward-model a serial dilution scenario where inflow is diluted geometrically from Balcony Room to Drip Pit. An additional scenario inverse-modeled water chemistry from Drip Pit to Balcony Room. Forward-modeling results suggest that equilibration of Drip Pit with celestite, dolomite, and calcite is a reasonable proxy for water chemistry evolution along the flow path following a precipitation event. Inverse-modeling results suggest that the water chemistry of Drip Pit can evolve from Balcony Room by dewatering and dissolution of celestite.

Graphical analyses of the primary ions collected from drips at the Balcony Room, Culvert Crawl Upper Pool, Culvert Crawl Lower Pool, and Drip Pit were conducted to evaluate similarities and to identify temporal trends that may reflect changes in surface and subsurface drainage patterns. Trilinear diagrams were created to evaluate geochemical composition at three groundwater discharge points and to compare the geochemical composition of these points to that of direct recharge sources. The results confirm a Ca-CO_3 type for discharge and recharge water and reveal slight differences, which is consistent with differences in rock-water interaction of discrete flow paths.

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Introduction

The Flint Ridge Cave PHREEQC modeling and geochemistry graphical analyses effort was conducted under the 2020-2021 contract extension for the Atmosphere Monitoring and Karst Studies in Balcones Canyonlands Preserve Caves contract initiated in August 2018 (Contract No. NA170000211). PHREEQC is an acronym for a groundwater geochemistry software program that calculates hydrochemical mineral speciation based on pH-REdox-Equilibrium and was originally written in C/C++ (Parkhurst et al. 2013). Data were provided by Balcones Canyonlands Preserve staff for this effort. The project area is limited to Flint Ridge Cave, located on City of Austin property in southwestern Travis County, Texas.

Flint Ridge Cave is listed on the City of Austin and Travis County endangered species permit and is managed by the City of Austin to maintain habitat for karst invertebrate species. The management of the cave is a component of the Balcones Canyonlands Conservation Plan, administered by the City of Austin and Travis County. The cave is located within the Recharge Zone of the Barton Springs segment of the Edwards Aquifer. Identifying water and nutrient flowpaths that sustain habitat in caves such as Flint Ridge Cave is an important part of the management plan.

Caves receive two types of groundwater recharge: 1) direct recharge, within the surface drainage basin via runoff into one or more entrances to the cave; and 2) indirect recharge, within the subsurface drainage basin via water infiltration through soil percolation or subsurface karst features, which enters the cave as drips and conduit flow. Geochemistry of water collected from cave drips, cave pools, and during direct recharge events was evaluated to differentiate flow paths or source waters throughout Flint Ridge Cave, as well as to identify trends observed in ion chemistry.

A conceptual diagram of the flow path was created to provide a framework to inform the selection of sample sites in Flint Ridge Cave for PHREEQC modeling input, as shown in Figure 1. The conceptual diagram is based upon the work of the City of Austin (Hauwert 2015) and 4CAVES Institute P.B.C. (2020), a contractor to the City of Austin. Four sites were selected to represent groundwater discharge: Balcony Room drip, Culvert Crawl Upper Pool, Culvert Crawl Lower Pool, and Drip Pit drip. Balcony Room drip is located in the upper portion of the cave within the Kirschberg Member of the Edwards Group, whereas Culvert Crawl Upper Pool, Culvert Crawl Lower Pool, and Drip Pit drip are located in the lower portion of the cave, within the Dolomitic Member of the Edwards Group (4CAVES Institute P.B.C. 2020). Groundwater seepage occurs at Culvert Crawl Upper and Lower Pools between runoff events and these sites receive direct recharge following runoff events.

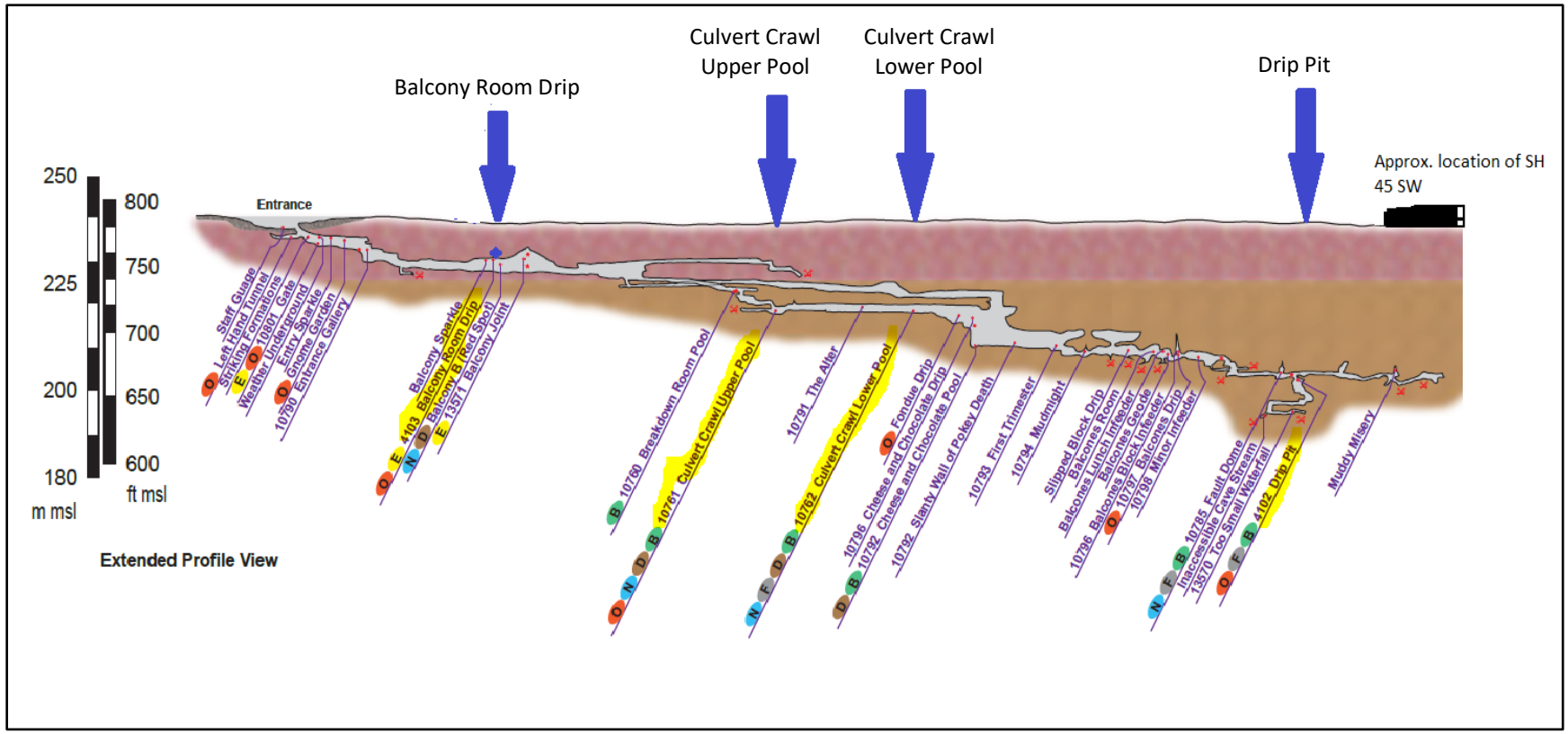


Figure 1. Conceptual diagram of Flint Ridge Cave, showing the profile view with drip and pool locations selected for this project. Figure modified from 4CAVES Institute P.B.C. (2020).

Methods

Data Evaluation

The City of Austin provided an Excel spreadsheet of water chemistry samples collected between 2015 and 2019 from Flint Ridge Cave and laboratory reports of additional data collected in 2020 (City of Austin, 2020a and 2020b). Data were reviewed for accuracy by calculating ion charge balances for each sample. If charge balances exceeded a value of 10% then they were excluded from the data set. Of these data, the 34 water samples provided in Table 1 were determined to be the most complete set of samples for the four study sites selected within Flint Ridge Cave. The time period examined ranges from 26 February 2015 to 08 June 2020 and represents six post-rainfall sampling events. While the number of samples is limited, it is the most complete representation of available data. It is important to note that the water chemistry of any natural system will have both temporal and spatial components. Points were chosen along the flow path in order of decreasing elevation to satisfy the latter requirement. Thus, the order of assumed inflow due to infiltration or percolation from a precipitation event is Balcony Room, Culvert Crawl Upper Pool, Culvert Crawl Lower Pool, and Drip Pit, as illustrated in Figure 1.

For this project, scientists examined alkalinity, bromide (Br), calcium (Ca), chloride (Cl), iron (Fe), potassium (K), magnesium (Mg), nitrogen (N), sodium (Na), strontium (Sr), and sulfate (S). Nitrogen is assumed to be in the form of nitrate and thus is N(V); sulfur is assumed to be in the form of sulfate and thus is S(VI). Alkalinity is assumed to be in the form of carbonate alkalinity and is reported where one mole of alkalinity is equivalent to 50.05 g (0.5 mol) of calcium carbonate ($CaC0_3$). Alkalinity speciation was done using the default PHREEQC parameters and the results were insensitive whether carbonate alkalinity or bicarbonate alkalinity was specified. Table 1 provides the sample data ion concentrations for this project.

For quality control purposes, the charge balance percentage as given by PHREEQC (Parkhurst et al. 2013) was used. All samples fell within an absolute range of less than 8%. The same data were used for a graphical comparison of primary ion concentrations.

The trilinear analyses data set includes three samples collected on 06 June 2020 from two cave drips and one pool within the cave and four samples collected on 09 September 2020 of post-rainfall runoff from four locations (Flint Ridge Cave Entrance, A Drainage, B Drainage, and C Drainage). Table 2 summarizes the data which is reported in millimoles (mM) and micromole (µM) units.

Table 1. Flint Ridge Cave geochemistry data. Note that concentrations are reported in millimole (mM) and micromole (µM) units depending on the constituent.

Sample Date/Time	Site Name	Alkalinity (mM)	Br (µM)	Ca (mM)	Cl (mM)	Fe (µM)	K (mM)	Mg (mM)	N (mM)	Na (mM)	Sr (µM)	S (mM)
06/08/2020 11:42	Culvert Crawl Upper Pool	3.636	0.587	1.534	0.175	0.000	0.078	0.461	0.049	0.169	0.461	0.315
06/06/2020 12:00	Drip Pit	5.594	1.827	1.639	0.513	0.000	0.011	1.357	0.065	0.526	1.134	0.196
06/05/2020 12:01	Balcony Room	4.356	0.100	2.268	0.115	0.000	0.007	0.248	0.101	0.151	0.278	0.239
06/02/2020 11:27	Drip Pit	5.574	2.052	1.669	0.581	0.000	0.014	1.390	0.000	0.539	1.098	0.207
06/02/2020 10:02	Culvert Crawl Upper Pool	3.117	0.421	1.345	0.120	0.000	0.081	0.375	0.000	0.129	0.374	0.203
06/02/2020 09:37	Balcony Room	5.495	0.140	2.720	0.128	0.000	0.007	0.274	0.000	0.164	0.310	0.209
07/10/2017 11:20	Drip Pit	5.495	1.502	1.582	0.456	0.000	0.014	1.329	0.000	0.509	1.124	0.196
07/10/2017 09:25	Culvert Crawl Upper Pool	5.115	0.501	2.213	0.280	0.000	0.053	0.617	0.092	0.292	0.756	0.430
09/28/2016 17:07	Balcony Room	4.535	0.100	2.153	0.113	0.000	0.020	0.259	0.006	0.168	0.377	0.237
09/28/2016 13:02	Culvert Crawl Lower Pool	5.335	0.781	2.273	0.288	0.000	0.049	0.609	0.061	0.271	0.797	0.390
04/20/2016 18:02	Drip Pit	5.415	1.765	1.362	0.505	0.000	0.013	1.201	0.026	0.448	1.112	0.180
04/20/2016 16:22	Culvert Crawl Upper Pool	2.517	0.185	0.926	0.120	0.000	0.084	0.243	0.040	0.101	0.331	0.152
04/20/2016 15:57	Balcony Room	4.715	0.100	1.921	0.136	0.000	0.021	0.224	0.024	0.141	0.425	0.208
04/19/2016 20:00	Culvert Crawl Lower Pool	2.238	0.201	0.846	0.086	0.000	0.077	0.221	0.029	0.084	0.294	0.160
04/16/2016 20:00	Culvert Crawl Lower Pool	3.556	0.389	1.482	0.180	0.661	0.066	0.410	0.072	0.170	0.463	0.233
04/15/2016 11:37	Drip Pit	5.395	1.765	1.562	0.513	0.000	0.011	1.398	0.027	0.492	1.164	0.175
04/15/2016 10:37	Culvert Crawl Upper Pool	2.438	0.230	0.978	0.119	0.532	0.080	0.281	0.054	0.104	0.331	0.148

Table 1. (Continued) Flint Ridge Cave geochemistry data. Note that concentrations are reported in millimole (mM) and micromole (µM) units depending on the constituent.

Sample Date/Time	Site Name	Alkalinity (mM)	Br (µM)	Ca (mM)	Cl (mM)	Fe (µM)	K (mM)	Mg (mM)	N (mM)	Na (mM)	Sr (µM)	S (mM)
04/15/2016 10:27	Balcony Room	4.695	0.100	2.196	0.128	0.000	0.022	0.267	0.011	0.153	0.415	0.211
01/31/2016 15:22	Drip Pit	5.435	1.902	1.554	0.539	0.000	0.014	1.353	0.022	0.478	1.047	0.184
01/31/2016 13:52	Culvert Crawl Upper Pool	5.115	0.859	2.226	0.381	0.458	0.060	0.658	0.081	0.285	0.714	0.418
01/31/2016 13:12	Balcony Room	5.415	0.100	2.794	0.150	0.000	0.030	0.360	0.145	0.177	0.454	0.286
06/11/2015 12:07	Balcony Room	5.075	0.100	2.620	0.150	0.000	0.008	0.300	0.000	0.202	0.369	0.301
06/04/2015 11:22	Drip Pit	5.415	1.790	1.557	0.519	0.000	0.009	1.419	0.036	0.496	1.110	0.183
06/01/2015 10:47	Culvert Crawl Upper Pool	4.575	0.646	1.941	0.252	0.000	0.098	0.580	0.065	0.207	0.595	0.334
06/01/2015 10:27	Balcony Room	5.994	0.103	3.094	0.138	0.000	0.005	0.308	0.000	0.185	0.358	0.298
05/29/2015 13:12	Culvert Crawl Lower Pool	2.318	0.100	1.055	0.072	0.000	0.112	0.221	0.015	0.085	0.296	0.090
05/29/2015 12:07	Drip Pit	5.195	1.639	1.564	0.485	2.453	0.011	1.452	0.023	0.492	1.060	0.180
05/29/2015 10:37	Culvert Crawl Upper Pool	1.792	0.100	0.813	0.042	1.252	0.110	0.169	0.011	0.058	0.228	0.060
05/29/2015 10:27	Balcony Room	6.154	0.100	3.144	0.113	0.000	0.005	0.296	0.000	0.177	0.337	0.278
03/04/2015 00:22	Balcony Room	4.336	0.100	2.136	0.218	0.000	0.050	0.250	0.001	0.139	0.512	0.216
03/03/2015 23:02	Culvert Crawl Lower Pool	4.376	0.702	1.230	0.350	0.000	0.018	1.098	0.064	0.257	0.539	0.362
02/26/2015 11:18	Drip Pit	5.215	1.677	1.532	0.536	0.000	0.011	1.300	0.027	0.452	1.108	0.178
02/26/2015 10:12	Culvert Crawl Lower Pool	4.476	0.869	1.986	0.361	0.000	0.054	0.465	0.064	0.228	0.651	0.374
02/26/2015 10:08	Culvert Crawl Upper Pool	4.955	1.277	2.151	0.451	0.000	0.045	0.613	0.074	0.272	0.749	0.483

Table 2. Data used for trilinear analyses of cave drips and pool, and post-rainfall runoff samples.

Sample Date/Time	Site Name	Ca (meq)	Mg (meq)	K (meq)	Na (meq)	Na+K (meq)	Cl (meq)	SO4 (meq)	Alkalinity [as HCO_3] (meq)
06/02/2020 11:27	Drip Pit	3.338	2.781	0.014	0.539	0.553	0.580	0.138	5.58
06/02/2020 9:37	Balcony Room	5.439	0.547	0.007	0.164	0.172	0.128	0.139	5.5
06/02/2020 10:02	Culvert Crawl Upper Pool	2.690	0.749	0.081	0.129	0.210	0.120	0.135	3.12
09/09/2020 15:02	Flint Ridge Entrance	0.539	0.107	0.088	0.040	0.128	0.044	0.026	0.566
09/09/2020 15:02	Flint Ridge A Drainage	0.431	0.095	0.092	0.033	0.125	0.028	0.015	0.578
09/09/2020 15:02	Flint Ridge B Drainage	0.395	0.095	0.101	0.040	0.141	0.039	0.023	0.45
09/09/2020 15:02	Flint Ridge C Drainage	0.644	0.102	0.068	0.038	0.105	0.044	0.022	0.626

PHREEQC

Forward- and inverse-modeling of the Flint Ridge Cave system was performed using PHREEQC (Parkhurst et al. 2013). In each case, we assumed a starting pH of 7.2 (Pope 2021) and the default values for pE (value for the conventional negative log of the activity of the electron) and temperature were 4 and 25˚C, respectively.

Forward-modeling was examined as a geometrical serial dilution process. This method roughly approximates a titration and equilibration of small aliquots of incoming flow with larger amounts of pre-equilibrated water. Balcony Room waters are allowed to be in contact with calcite and do not constrain dissolution or precipitation. Similarly, Drip Pit is allowed to exchange with calcite, dolomite, and celestite without reaction direction constraints. The conserved mineral species are unreactive in the Flint Ridge Cave environment and essentially function as tracers for flow direction and indicators of dilution (precipitation event) or dewatering (dry conditions). This analysis was focused on dissolution/precipitation reactions and considered the mineral species present to be sources/sinks.

Inverse-modeling was performed assuming Drip Pit and Balcony Room as endpoints. Uncertainty constraints for all species were held at 0.5. Phases water (gas), carbon dioxide (gas), calcite, dolomite, and celestite. Charge balance was enforced on alkalinity, Ca, Cl, K, Mg, and S. No constraints were put on dissolution/precipitation as in the forward-modeling case. The models yielded by this method, in theory, indicate the reactions that occur from Drip Pit to Balcony Room. The models did not converge when Fe was included; therefore, it is not clear what mineral phases (e.g., goethite, Fe (III) hydroxide) could be present as sources and sinks. Due to the models not converging, Fe was eliminated from the solutions when inverse-modeling.

Graphical Analysis

Temporal trends in Ca versus Mg ion concentrations, as provided in Table 1, were plotted for the data set using a public version of visual data analytics application (Tableau 2021).

Trilinear Analysis

Comparison of major ion concentrations, as provided in Table 2, were plotted using a 2D and 3D graphing software program (Grapher 2021).

Results

PHREEQC Modeling

Water Samples collected 05 June 2020

Samples from 05 June 2020 were examined first to illustrate forward- and inverse-modeling results. Note that unity is assumed for water density, and thus interchanging molality and molarity.

Forward-modeling results for predicted endpoint at Drip Pit are:

Species	Molarity
Br^-	1.086e-06
Ca^{2+}	1.658e-03
Cl^-	3.294e-04
K^+	2.696e-05
Mg^{2+}	7.300e-04
N^{3-}	6.999e-05
Na^+	3.432e-04
S^{2-}	4.847e-04
Sr^{2+}	4.065e-04

From Table 1, the measured values for Drip Pit are:

Species	Molarity
Br^-	1.827e-06
Ca^{2+}	1.639e-03
Cl^-	5.130e-04
K^+	1.100e-05
Mg^{2+}	1.357e-03
N^{3-}	6.500e-05
Na^+	5.260e-04
S^{2-}	1.960e-04
Sr^{2+}	1.134e-06

Based on the order of magnitude between the modeled and measured values at this site, this model appears to be appropriate for all mineral species except for Sr, as the measured Sr value was 100 times lower than the modeled value. In this model, there was an intermediate step in Culvert Crawl Upper Pool where dilution occurs. Note that sulfate is reduced by a factor of 2. Thus, the results of this forward-model suggest good approximation for conservation of mineral species for those other than Sr and celestite.

Inverse-modeling of waters collected on 05 June 2020 suggest removal of water and precipitation or dissolution of celestite as water evolves from Balcony Room to Drip Pit. The solution fractions and phase mole transfers are shown immediately below:

Solution fractions:

	Molarity	Minimum	Maximum
Solution 1	1.487e+00	1.487e+00	2.168e+00
Solution 2	1.000e+00	1.000e+00	1.000e+00

Phase mole transfers:

	Molarity	Minimum	Maximum	Formula
H_20 (g)	-2.703e+01	-6.486e+01	-2.703e+01	H_2O
Celestite	7.207e-07	-3.386e-07	1.495e-06	$SrSO_4$

The computed endpoints for the 06 June 2020 samples are:

Solution 1: Balcony Room (06 June 2020)

	Input		Delta		Input+Delta
pH	7.200e+00	+	0.000e+00	=	7.200e+00
Alkalinity	4.357e-03	+	-6.922e-04	=	3.665e-03
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	4.896e-03	+	0.000e+00	=	4.896e-03
Ca	2.269e-03	+	-6.145e-04	=	1.654e-03
Cl	1.151e-04	+	5.756e-05	=	1.727e-04
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00
K	7.214e-06	+	0.000e+00	=	7.214e-06
Mg	2.477e-04	+	5.669e-05	=	3.044e-04
O(0)	0.000e+00	+	0.000e+00	=	0.000e+00
S(-2)	0.000e+00	+	0.000e+00	=	0.000e+00
S(6)	7.966e-05	+	-3.617e-05	=	4.349e-05
Sr	2.786e-07	+	0.000e+00	=	2.786e-07

Solution 2: Drip Pit (06 June 2020)

	Input		Delta		Input+Delta
pH	7.200e+00	+	0.000e+00	=	7.200e+00
Alkalinity	5.597e-03	+	-1.468e-04	=	5.450e-03
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	6.288e-03	+	9.927e-04	=	7.281e-03
Ca	1.640e-03	+	8.199e-04	=	2.460e-03
Cl	5.136e-04	+	-2.568e-04	=	2.568e-04
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00
K	1.131e-05	+	-5.804e-07	=	1.073e-05
Mg	9.053e-04	+	-4.526e-04	=	4.526e-04
O(0)	0.000e+00	+	0.000e+00	=	0.000e+00
S(-2)	0.000e+00	+	0.000e+00	=	0.000e+00
S(6)	6.540e-05	+	0.000e+00	=	6.540e-05
Sr	1.135e-06	+	0.000e+00	=	1.135e-06

Based on the model, it is possible to evolve the Drip Pit results from samples collected at Balcony Room with the phases present. In this case, the predominant reaction is dissolution of celestite and the concentration of Balcony Room (dewatering). The concentration ratio is about 1.5, where 1.5 L of Balcony Room water yields 1 L of Drip Pit water with the observed chemistry and dissolves celestite. Dissolution is the expected reaction as indicated by the 10 times increase in Sr seen at Drip Pit in this case. Additionally, these results imply a source of sulfate.

<u>Water Samples collected 29 May 2015</u>

The same exercise as above has been completed for water samples collected on 29 May 2015. Forward- and inverse-models were compared with measured water sample values.

Forward-modeling results for predicted endpoint at Drip Pit are:

Species	Molarity
Br^-	8.701e-07
Ca^{2+}	1.559e-03
Cl^-	2.800e-04
Fe^{2+}	1.384e-06
K^+	4.761e-05
Mg^{2+}	7.604e-04
N^{3-}	1.660e-05
Na^+	2.965e-04
S^{2-}	4.667e-04
Sr^{2+}	4.157e-04

From Table 1, the measured values for Drip Pit are:

Species	Molarity
Br^-	1.639e-06
Ca^{2+}	1.564e-03
Cl^-	4.850e-05
Fe^{2+}	2.543e-06
K^+	1.100e-05
Mg^{2+}	1.452e-03
N^{3-}	2.300e-05
Na^+	4.920e-04
S^{2-}	1.800e-05
Sr^{2+}	1.060e-06

Again, the order of magnitude between the modeled and measured values are not consistent for the Sr ion concentrations, and in this case, S also presents a similar issue. Iron appears to be conserved, although no Fe-containing phases for sources/sinks were input into the model. As with the water samples collected 06 June 2020, the mixture model produced a solution that is too dilute in Sr and S.

Inverse-modeling of waters collected on 29 May 2015 yields one converged model. Here, the model does not suggest dewatering but dissolution of celestite does occur as water evolves from Balcony Room to Drip Pit. The solution fractions and phase mole transfers are shown immediately below:

Solution fractions:

	Molarity	Minimum	Maximum
Solution 1	1.000e+00	1.000e+00	1.000e+00
Solution 2	1.000e+00	1.000e+00	1.000e+00

Phase mole transfers:

	Molarity	Minimum	Maximum	Formula
Celestite	7.238e-07	-3.243e-07	1.772e-06	$SrSO_4$

The computed endpoints for the 29 May 2015 samples are:

Solution 1: Balcony Room (29 May 2015)

	Input		Delta		Input+Delta
pH	7.200e+00	+	0.000e+00	=	7.200e+00
Alkalinity	6.157e-03	+	-9.599e-04	=	5.197e-03
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	6.900e-03	+	-1.067e-03	=	5.834e-03
Ca	3.145e-03	+	-7.921e-04	=	2.353e-03
Cl	1.134e-04	+	7.893e-06	=	1.213e-04
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00
K	4.503e-06	+	0.000e+00	=	4.503e-06
Mg	2.963e-04	+	6.684e-05	=	3.631e-04
O(0)	0.000e+00	+	0.000e+00	=	0.000e+00
S(-2)	0.000e+00	+	0.000e+00	=	0.000e+00
S(6)	9.269e-05	+	-3.322e-05	=	5.947e-05
Sr	3.368e-07	+	0.000e+00	=	3.368e-07

Solution 2: Drip Pit (29 May 2015)

	Input		Delta		Input+Delta
pH	7.200e+00	+	0.000e+00	=	7.200e+00
Alkalinity	5.197e-03	+	0.000e+00	=	5.197e-03
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	5.834e-03	+	0.000e+00	=	5.834e-03
Ca	1.565e-03	+	7.881e-04	=	2.353e-03
Cl	4.853e-04	+	-3.640e-04	=	1.213e-04
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00
K	1.064e-05	+	-6.140e-06	=	4.503e-06
Mg	1.453e-03	+	-1.089e-03	=	3.631e-04
O(0)	0.000e+00	+	0.000e+00	=	0.000e+00
S(-2)	0.000e+00	+	0.000e+00	=	0.000e+00
S(6)	6.019e-05	+	0.000e+00	=	6.019e-05
Sr	1.061e-06	+	0.000e+00	=	1.061e-06

Forward-modeling with equilibration phases calcite (Balcony Room) and calcite, celestite, and dolomite (Drip Pit) illustrates that conserves species are unreactive and are conserved as inflow dilutes runoff, enters the cave system, and terminates at Drip Pit. Strontium and S concentrations are measurably higher than predicted by a serial dilution model.

Inverse-modeling was constrained to the same phases present as for forward-modeling. In each case presented, celestite dissolution is identified as a reaction that occurs during the evolution of waters from the Balcony Room to Drip Pit drip site. In one scenario (05 June 2020), the model suggests that dewatering (water outgassing, to be precise) accompanies celestite dissolution. The

second scenario (29 May 2015) suggests that just dissolution of celestite occurs, with no indication of simultaneous dewatering. Iron was not present in sufficient quantities due to the lack of Fe-containing mineral phases for sources and sinks.

Graphical Analyses

Cave drip water in carbonate host rock typically is dominated by Ca and bicarbonate ion concentrations. Plotting the ratio of Ca to Mg ion concentrations may reveal potential differences in source water inputs to cave drips (Musgrove et al. 2004). A comparison plot of the Ca to Mg (Ca/Mg) ion concentrations for Balcony Room drip, Culvert Crawl Upper Pool, Culvert Crawl Lower Pool, and Drip Pit is provided as Figure 2. These data clusters indicate differences between Balcony Room drip and Drip Pit Ca/Mg ratios may be attributed to rock-water interaction with the host rock. Balcony Room drip has lower concentrations of Mg, as indicated by the blue trend line in Figure 2. Drip Pit has higher concentrations of Mg, shown as the green trend line in Figure 2, that may be explained by greater abundance of Mg within strata of the Dolomitic member of the Edwards Group. Culvert Crawl Upper Pool samples have a trend that lies between the two end member cave drips and may represent a transition from Ca-enriched groundwater discharging from the Kirschberg member of the Edwards Group, such as the Balcony Room drip, or mixing of Ca-enriched groundwater with direct recharge water. This graphical representation of samples collected over a five-year period may include a temporal component that has not been evaluated with this project.

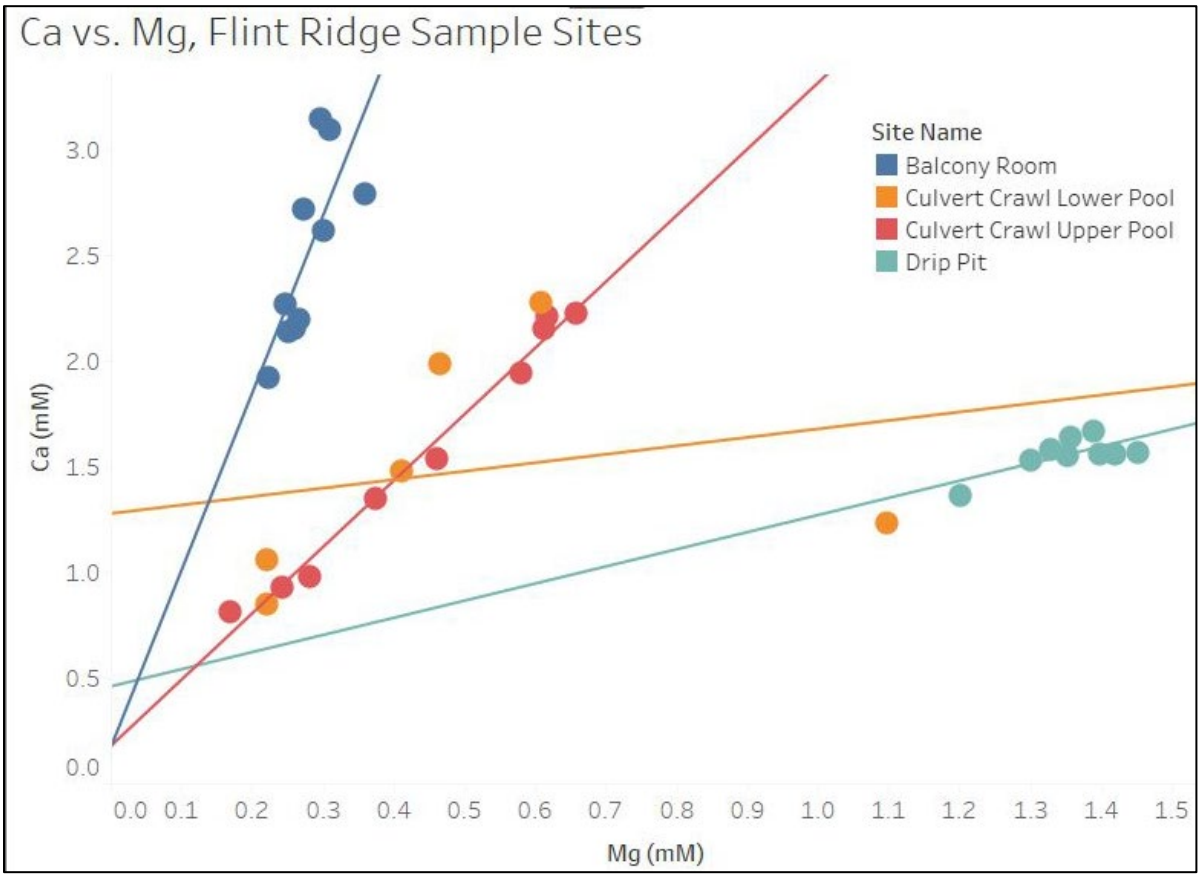


Figure 2. Comparison plot of Ca/Mg concentrations from the Flint Ridge Cave sample sites.

Trilinear Analyses

Trilinear diagrams were developed to assist in the interpretation of geochemical constituents of water (Piper 1953). They are a visual tool that can be used classify hydrochemical facies of water, such as $CaCO_3$, by depicting the relative abundance of major cations and anions. For this project, trilinear plots were used to compare the major ion components of samples collected on 06 June 2020. Figure 3 is a trilinear plot based on three sites within Flint Ridge Cave: Balcony Room, Drip Pit, and Culvert Crawl Upper Pool. Figure 3 indicates that these water samples are calcium-bicarbonate-type, and that Drip Pit has a greater percentage of Mg.

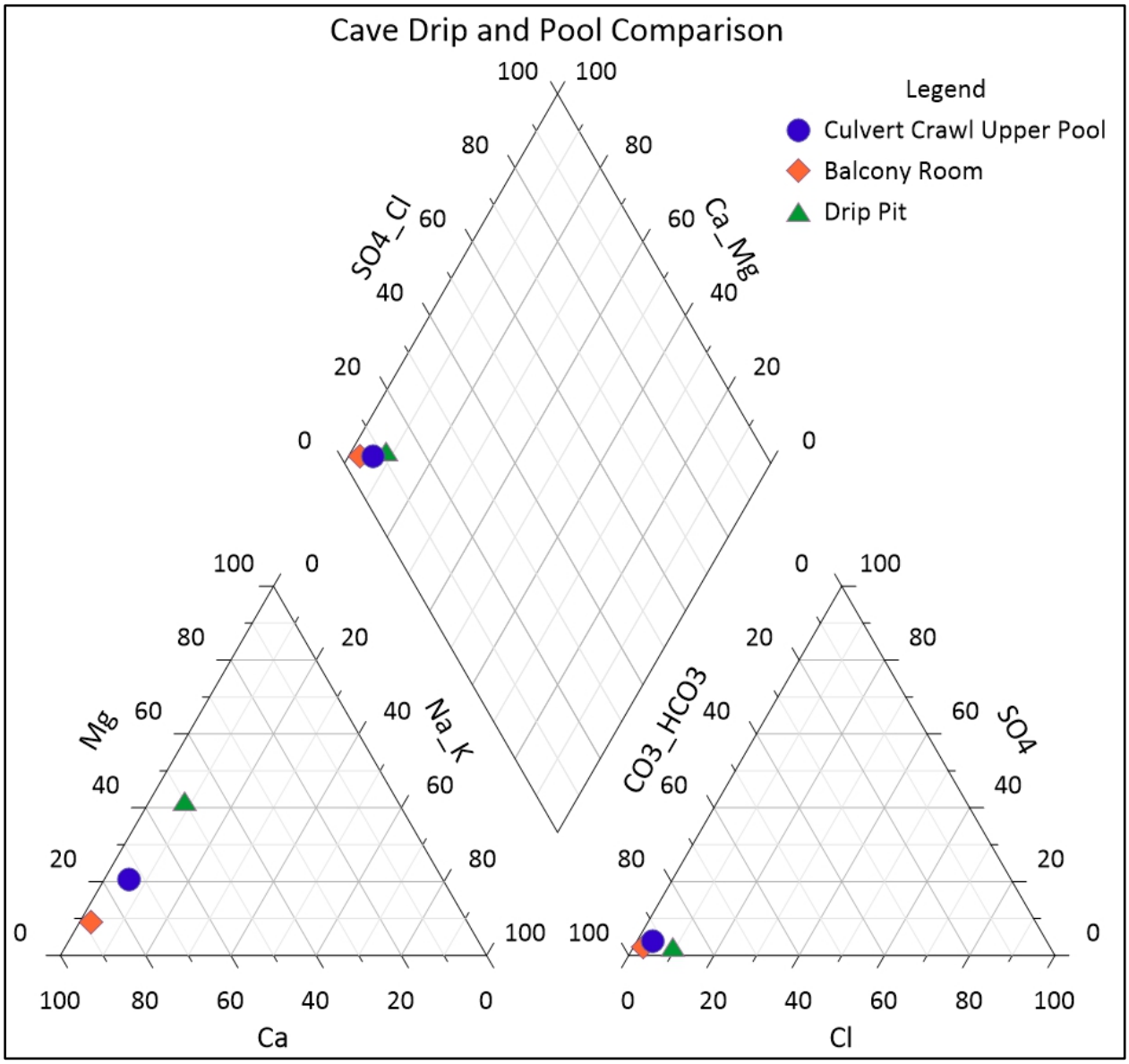


Figure 3. Trilinear Plot of Flint Ridge Cave drips and pool.

Figure 4 is a trilinear plot that compares the major ion chemistry of Balcony Room drip, Drip Pit, and Culvert Crawl Upper Pool of 06 June 2020 to runoff samples collected 09 September 2020 at the Flint Ridge Cave entrance, from Flint Ridge A Drainage, Flint Ridge B Drainage, and Flint Ridge

C Drainage. Samples representing the same post-rainfall runoff and drip water event were not collected in 2020. All samples are within a calcium bicarbonate hydrochemical facies. The runoff samples are enriched with Na plus K, relative to the drip water samples. The relative abundance is attributed to contact with surface terrain sources of Na and K as post-rainfall runoff enters the Flint Ridge Cave surface drainage basin.

The trilinear plots indicate that rock-water interaction in different geological units results in a difference in the relative abundance of Ca and Mg in drip water chemistry. Comparison of drip water composition and that of direct recharge runoff samples indicate that rock-water interaction is dilute with respect to Ca and Mg and enriched with respect to Na and K.

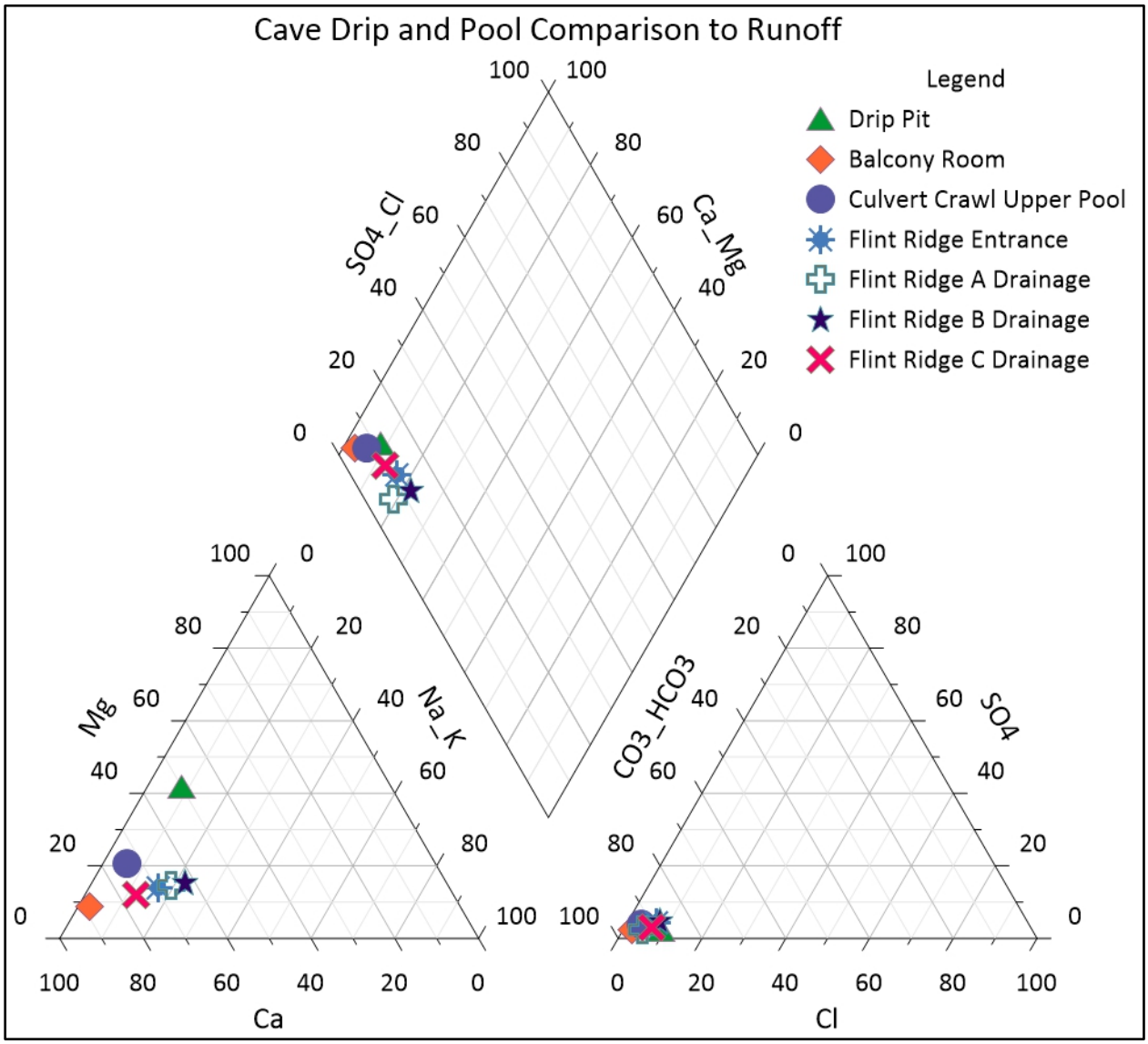


Figure 4. Trilinear plot of Flint Ridge Cave samples compared to direct recharge runoff ion concentrations.

Discussion

PHREEQC

Twelve data points were identified from 2015 to 2017 and 2020 for examination with PHREEQC mixing and inverse-modeling. Data from a maximum of four spatial locations in Flint Ridge Cave (Balcony Room, Culvert Crawl Upper Pool, Culvert Crawl Lower Pool, and Drip Pit) are available for only three points in time. A serial dilution mixing model was used to simulate forward- and reverse-reactions to identify the putative reactions that may occur after a rainfall event along a flowpath within the cave system. Data were verifiably quantified by charge balance to within at most 8% (one case) and less than 5% (all other cases).

Forward-modeling with equilibration phases of calcite-calcite (Balcony Room) and calcite-celestite-dolomite (Drip Pit) illustrates that conserved mineral species are unreactive and are conserved as inflow dilutes runoff, enters the cave system, and terminates at Drip Pit. Sr and S concentrations are measurably higher than predicted by a serial dilution model.

Inverse-modeling was constrained to the same phases present as for forward-modeling. In each case presented, celestite dissolution is identified as a reaction that occurs during the evolution of waters from Balcony Room to Drip Pit drip. In one scenario (05 June 2020), the model suggests that dewatering (water outgassing, to be precise) accompanies celestite dissolution. The second scenario (29 May 2015) suggests that just dissolution of celestite occurs, with no indication of simultaneous dewatering. Iron was not present in sufficient quantities due to the lack of Fe-containing mineral phases for sources and sinks.

There appears to be a consistent and identifiable relationship between celestite dissolution and S and Sr concentrations in Balcony Room and Drip Pit, irrespective of residence time or contact with the Culvert Crawl segment of the flow path. Further studies should include phases which can serve as iron sources or sinks.

Graphical Analyses

Graphical analyses using a standard 2-dimensional graph of Ca/Mg concentration ratios and a trilinear diagram indicate a strong host-rock influence on Mg concentrations in the Drip Pit sample site (Figure 2 and Figure 3). As mentioned, this is likely a product of water-rock interactions and could be indicative of different flow paths for the Balcony Room drip and the Drip Pit sample sites as they travel through different members of the Edwards Group. A similar relationship is depicted in the trilinear plot (Figure 3) of samples collected 06 June 2020 from Balcony Room drip, Drip Pit, and Culvert Crawl Upper Pool. Hydrochemical differences between drip water and surface runoff ion concentrations, shown in Figure 4, indicate that drip water chemistry is distinct from surface runoff chemistry within the Flint Ridge Cave drainage basin. Future application of graphical analyses may be used to identify trends in ion concentrations that correlate to observations of changes within the surface drainage basin, or in cave drip flow rate, or other physical changes observed at cave drips.

PHREEQC modeling was conducted to evaluate groundwater discharge flowpaths to four sample sites within the Flint Ridge Cave. Future applications of modeling may be used to identify mineral speciation relationships tested for other cave drip locations within Flint Ridge Cave or other caves. The graphical analyses complement the findings of the PHREEQC model results for Ca and Mg speciation. Future application of graphical analyses may be used to explore other hydrochemical species or ion differences for other cave drip locations within Flint Ridge Cave or other caves.

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