Advances in monitoring to understand flow paths in karst: comparison of historic and recent data from the Valley and Ridge of Pennsylvania

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Content

Abstract

We revisited seven karst springs studied in 1971 to examine how advances in monitoring techniques influence our understanding of spring flow paths and recharge. These springs in the Valley and Ridge of Pennsylvania offer a variety of spring discharge volumes and physical appearance (visible conduits at the discharge site versus fracture networks). We focused on temperature for a comparison between historic and recent trends because it is the least likely to differ in value due to updated measurement techniques. High resolution temperature data showed variations in storm responses (not observed with historic data) which distinguish among springs. We also used automatic samplers to track geochemical changes during storm events. Variations in CO_2 concentrations and Mg/Ca ratios provided indicators of fast and slow recharge and changes in flow paths over time. Some springs showed similar response from storm to storm and some varied. Rare earth elements (REEs) were analyzed in baseflow samples to evaluate their potential for distinguishing spring source rock along flow pathways. The REE grouped springs differently than their temperature and storm response geochemistry. This study showed that classification of karst springs varied depending on the parameter monitored. This variation further points out the complexity of karst flow paths and recharge. Multiple methods and long-

term monitoring are needed to interpret karst spring discharge and provide sampling schemes for source water protection.

Keywords: karst, temperature, stormwater sampling, REE

1. Background and Motivation

In 1971 Shuster and White [1] published a foundational study in karst hydrology. The classification system proposed by Shuster and White contrasted diffuse flow paths with water primarily flowing through the rock matrix and conduit flow paths with water primarily flowing through larger openings in the rock. This work established one of the earliest and most commonly used classification systems for karst springs. The Shuster and White study has been cited in hundreds of peer-reviewed papers since 1996 (data from SCOPUS), but the total citations to date more likely number in the thousands. The original work separated a group of fourteen Central Pennsylvania springs based on seasonal temperature behavior, saturation index with respect to calcite, hardness, and other water chemistry parameters collected on twice a month across a water year (1967-1968). While their spring flow classification system highlighted that springs occur along a continuum from diffuse- to conduit-dominated flow, many subsequent works neglected this fine distinction and instead focused on identifying springs as either one end-member or the other. Shuster and White's study was state of the art and innovative at its time of publication, but substantial subsequent advances, particularly in high-resolution monitoring of a wide variety of hydrologic parameters, encouraged us to return to some of Shuster and White's original springs in the Juniata and Penns Creek basins (Figure 1) with an eye to how we might interpret spring behavior with more frequent and wider-ranging data.

While Shuster and White's [1] classification system focused on flow, much subsequent work has examined the role of recharge in controlling spring behavior. Some of the newer data presented here are geared toward differentiating recharge-sourced behavior from flow-sourced behavior. Recharge is equally as complicated as flow in karst systems. Recharge can occur through swallets that act as point sources; through the soil zone as a diffuse source; or through weathered fractured bedrock and epikarst as a mix of diffuse and point sources (e.g., [2-5]). In addition to this potential mix of fast and slow recharge paths, the balance of karst recharge types can vary from storm to storm. Subsurface heterogeneity in the karst unsaturated zone poses problems in applications as diverse as basin delineation, paleoclimate reconstruction, and source area protection among others [6-9].

Some spring classification work has focused on temperature signals at springs to examine residence time and recharge. Luhmann et al. [10] found that recharge type and residence time could have effects on thermal signals due to the interaction of recharge water with bedrock as it flows through the fractures and conduits feeding the springs. Diffuse recharge led to muted or absent thermal fluctuations from storm events, and point source recharge (e.g., a sinking stream) led to a flashy response. Springs with delays in the signal or no temperature fluctuation were described as thermally effective which refers to long residence time in the matrix damping seasonal or storm signals. In contrast, springs with a seasonal shift in temperature had less interaction with the matrix and were described as thermally ineffective. The residence time of water in a karst aquifer can also vary between low flow and high flow (not storm-related) [11]. High resolution temperature monitoring at springs shows promise as a component of spring classification, but alone cannot illuminate both flow and recharge processes.

Many karst studies have focused on examining the geochemistry of springs and cave streams to characterize flow. Some studies used more traditional karst geochemistry signals like [Ca^{2+}] and [Mg^{2+}] to differentiate conduit from matrix flow (e.g., [12]) or to elucidate storm flow sources (e.g., [13]). Others examined oxygen and hydrogen isotopes to separate recharge and flow sources during single storm events [14-16] or used higher CO_2 outgassing rates as evidence of conduit flow [17-18]. Other researchers have used CO_2 and saturation index with respect to calcite (SI_C) in a variety of ways to examine questions of recharge and flow. Vesper and White [19] used CO_2 and SI_C during storm events at karst springs in Tennessee and Kentucky to develop conceptual models for recharge, while Hilberg et al. [20] applied similar relationships to differentiate among four recharge types reaching Central European Alpine springs. Liu et al. [13] used CO_2 and conductivity relationships to separate fracture and conduit flow where flooded fracture flow lead to higher CO_2 values sourced from soil gas and lower SI_C water as a result. Peyraube et al. [21] established that much of the dissolution of calcite occurs in the epikarst zone of a perched karstic aquifer in France as infiltrating water dissolves significant CO_2 leading to more aggressive water. Gulley et al. [22] tracked dissolution in eogenetic limestone caves to high CO_2 flux from the soil through fractures into the subsurface. Generally, substantial increases in CO_2 are attributed to fluxes through the soil and epikarst zones, and decreases in CO_2 values are linked to dilution from storm flow along fast recharge pathways.

Comparing ratios of isotopes and ions has also proven useful in characterizing karst flow and recharge. Musgrove and Banner [23] found $^{87}Sr/^{86}Sr$ was lower in carbonate rock than soil, and Barbieri et al. [24] used these differences in source trace elements along with hydrogen and oxygen isotopes to track changes in source water origin at spring discharges. Differences in Mg/Ca and Sr/Ca ratios have been used to track residence time in recharging drip waters, with higher values indicating longer water-rock interaction times [23, 25]. Caetano Bicalhlo et al. [26] also used Mg/Ca ratios in karst springs to indicate residence times. Toran and Reisch [27] extended these applications using Mg/Ca hysteresis patterns across storms to interpret flow, with higher Mg/Ca ratios indicating longer residence time water was reaching the spring.

Few studies in karst aquifers have used rare earth element (REE) concentrations to examine flow paths and source areas, but these approaches have been employed in porous media aquifers. REE are a group of metallic elements with atomic number between 57 and 71 plus Y (atomic number 39) found in association in ore deposits. Carbonate and clastic REE signatures do differ adequately [28] to shed light on source areas in geology similar to the Central Pennsylvania springs in this study. Johannesson and Xiaoping [29] found REE signatures in groundwater were associated with rock type, and Tang and Johannesson [30] identified variations in REEs along a flow path due to changing redox conditions and organic complexation. Johannesson et al. [31] observed variation in Ce concentrations and light to heavy REEs at four springs in Nevada. These differences were linked to the portion of carbonate rock in recharge areas. Tarbert and Vesper [32] measured an increase in REE concentrations after a large storm in one spring, along with enrichment in middle and heavier REEs (typically referring to elements heavier than 62 and 66, respectively). These studies show there may be opportunities to use REEs in delineating sources contributions or geochemical alterations along the flow path.

An efficient way to characterize flow and recharge in karst springs would be useful for a wide variety of applications including water supply from karst aquifers, source area protection, and contaminant transport, but current classification systems do not capture the variability of these systems adequately. To that end, we employed a variety of approaches using high-frequency logger data and storm samples to examine aspects of the Shuster and White classification system at some of their original springs. These additional data allowed us to address the following questions:

- Are historic and recent temperature trends similar?
- What do storm response and higher-frequency data reveal about the spring behavior not observed in twice monthly measurements?
- Is the classification of matrix- vs. conduit-dominated flow paths adequate to explain observed variations in springs?
- Are differences in recharge behavior revealed by geochemical responses?

We focused on temperature for a comparison between historic and recent trends because it is the least likely to differ in value due to updated measurement techniques and the historic precision was reported as 0.1^{o}C. In other words, using a thermometer in historic data collection is likely to produce the same value as a temperature sensor with data logger today. We focused on CO_2 concentrations and Mg/Ca ratios in the geochemical responses during storm events because of the information they provide on recharge and flow pathways. And we examined rare earth elements (REEs) at baseflow to evaluate their potential for distinguishing spring source rock along flow pathways.

2. Methods

2.1 Study Area

Shuster and White's original study included fourteen springs. All of the original springs were revisited for this study, and we selected seven for additional study to represent variation in discharge and flow types, including four in the Juniata basin and three in Penns Creek basin (Table 1, Figure 1). This region has a mean annual temperature of 10^{o}C and mean annual precipitation of 107 cm.

All fourteen springs are located within the large Nittany anticlinorium, a broad valley trending northeast in the Central Pennsylvania Valley and Ridge (Figure 1). Minor asymmetric folds generally parallel to the axis of Nittany Valley split the northeastern end of the valley into multiple valleys. The ridges surrounding the valleys are synclinal. Ridges throughout the area are topped with the Silurian Tuscarora quartzite (a pure quartz sandstone in this area). The Tuscarora is underlain by the Ordovician Juniata sandstones and shales, the Bald Eagle sandstone, and the Reedsville shale with the Tuscarora and Bald Eagle creating a double ridge and the Juniata creating the slope between. The Reedsville outcrops on the slopes reaching down into the Nittany Valley. Stratigraphically below the Reedsville is the thick sequence of Ordovician limestones and dolomites (up to 1000 m in the center of Nittany Valley) flooring the valleys which in turn are underlain by the Cambrian Gatesburg formation [1]. The springs in this study occur in the Ordovician limestones and dolomites.

Four of the seven springs were identified as primarily conduit flow by Shuster and White based on seasonal variation in ion concentrations and temperature (Arch, Tippery, Near Tippery and Elk Creek Rise/Smullton). Three of the springs were classified as diffuse flow based on higher and less variable ion concentrations along with lack of seasonal temperature variation (Birmingham Cave, Springhouse, and Weaver). Shuster and White used seasonal fluctuations in chemistry to compare behavior because visual features at the discharge point such as large conduits were not a good predictor of dominant flow paths (Figure 2). Because Shuster and White recognized the continuum from conduit- to diffuse-dominated flow, they noted that one of these diffuse flow springs (Weaver) had a mix of characteristics and could be transitional based on high ion concentrations and some seasonal variation. They also noted that high partial pressure of CO_2 in Weaver could be sourced from the recharge area, but in general their interpretations were focused on the flow path. They further noted that two adjacent springs only 75 m apart (Tippery and Near Tippery) had distinct chemical signatures, with higher Mg/Ca ratios and higher overall concentrations at Near Tippery. Elk Creek Rise is directly connected to Smullton Sinks, a series of karst windows upstream that expose the flow that ultimately reaches Elk Creek Rise 260 m down gradient. Over this short distance, the geochemical signature is not expected to change (as confirmed with temperature monitoring) and access was easier at Smullton. Monitoring was conducted at the sink closest to the rise.

2.2 Advanced Monitoring Techniques

Revisiting the springs studied in Shuster and White provided the opportunity to incorporate more recent monitoring techniques. While Shuster and White took twice a month measurements of temperature and water chemistry, we focused on several newer monitoring techniques which allowed us to capture storm responses in the springs. Here, we report on temperature sensors, automatic stormwater samplers, and rare earth element (REE) analysis. Additional sensors with data loggers and rain gauges were used to complement these methods.

We deployed temperature sensors for a year or more to collect data at 15-minute intervals, using a combination of Onset HOBO water level loggers, Onset Tidbit temperature loggers, and In-Situ water quality sondes (Figure 3). Most of the data reported here are from studies conducted in 2015-17, but Arch Spring was monitored in an earlier study in 2003 [33], and Smullton Sink (associated with Elk Creek Rise) was monitored from 2008-2016. For comparison with historic plots, only a single dataset was used, typically combining the available data from multiple years of the study. The historic data from 1967-68 were also combined and replotted to show January through December rather than chronologically since monitoring at most springs was initiated in March 1967.

ISCO automatic samplers, water level loggers (Onset HOBO or In Situ 9500 Trolls), and pH sensors were installed at five of the sites to collect data across storm events. In addition, a rain gauge was installed on site at the Tippery and Near Tippery Springs. The samplers were triggered by water level rise in the spring (Figure 4) or by rain gauges, and collected 24 samples at 30, 60, 180, or 240 minute intervals, depending on the programming sequence and average storm duration at the monitored spring. In some cases, the bottles were replaced to collect 48 samples to capture a long recession hydrograph. The samples were collected within a day to a week of the storm event, and preserved or analyzed promptly. The stability of the carbonate alkalinity in the samples collected in the stormwater sampler was tested by collecting a spring sample and comparing measurements of alkalinity at 1 day, 1 week, and 2 week intervals; based on the constancy in alkalinity over time, the holding period in the automatic samplers was confirmed as a minor source of error [34]. Alkalinity was measured by titration or Hanna colorimetric kits, anions by ion chromatograph (IC), and cations by IC, atomic adsorption (AA) or inductively coupled plasma optical emission spectrometry (ICP-OES). Sensors to measure pH were used to supplement the chemical data collected from automatic samplers using a combination of Manta pH loggers and In-Situ water quality sondes. These data were used to calculate CO_2 variation through storm events from carbonate alkalinity, temperature, and pH with the US Geological Survey PHREEQC code for chemical equilibrium modeling [35]. The stormwater samples were also analyzed for time series of Mg/Ca ratios to evaluate water/rock interaction. Based on analytical uncertainties, a change in the molar Mg/Ca ratio of 0.01 is a distinguishable change in signal.

In addition to stormwater sampling, we collected samples between storms and analyzed for REEs to complement major ion analysis. A single round of REE samples was collected in March 2016. Arch Spring was not sampled due to lack of access on the sampling date. The samples were field filtered into acid washed bottles, and acidified with high purity nitric acid. The samples were refrigerated until analysis using ICP-MS (Geosciences Lab, Canada). REE concentrations are normalized to a standard so that variations in concentration can be attributed to a process such as redox sensitive mobilization, rather than natural variability in concentrations. We used the North American Shale standard [36] which is commonly applied to water samples.

3. Results and Discussion

3.1 Temperature

The three springs with little seasonal variation showed considerable noise in the continuous data in the winter months, likely due to increased influence of air temperature. When the water in the spring pool became shallow, less than 12.4 cm deep at Springhouse Spring, the noise in temperature data became more pronounced (Figure 5). In the historic data, there was a hint of this influence in lower temperatures for a few points in the winter at Birmingham Cave Spring. Typically, however, when a thermometer is used to measure spring temperature (as was done in historic data collection), it will be placed where the water is deeper unlike a data logger which is tethered in place and always measures at the same location. In spring and summer, the temperatures were nearly constant at Springhouse and Birmingham Cave Springs, with no suggestion of air temperature influence at the discharge point.

The three springs that historically showed little or no seasonal variation in spring temperature, Weaver, Springhouse, and Birmingham Cave Springs, continued to have this pattern in recent data, although Weaver Spring showed a slight upward trend (1^{o}C) in August (Figures 6a-c). A smaller trend (perhaps 0.5^{o}C) was observed in the historic data, but the trend was more obvious when continuous data were available instead of twice monthly measurements. Because the increase was not observed until mid- to late-summer while air temperature rises in late spring and early summer, this response was a delayed seasonal response, which further supports the importance of diffuse flow (their original Shuster and White classification) in these spring waters. However, Weaver also displayed storm response in some seasons, suggesting rapid recharge transmitted to the spring mouth along fast flow paths. Springhouse and Birmingham Cave Springs did not exhibit this temperature storm response.

The four springs that previously showed a seasonal temperature response had similar response in recent data: Arch, Tippery, Near Tippery, and Smullton (Figures 6d-g). A temperature logger placed in Elk Creek Rise showed an identical signal to Smullton Sink for one month periods in the fall, winter, and spring which justified comparison of Smullton temperature data with historic Elk Creek Rise data. Storms tended to displace the logger in Elk Creek Rise, so a longer record was not available. The high frequency data revealed storm responses in addition to seasonal temperature changes for all of these springs, which provides further evidence of the rapid flow paths identified by Shuster and White. The storm response was more frequent at Smullton and Arch, two springs with larger discharge and mapped conduit systems. At Tippery (Figure 6e), there were more frequent storm responses than at Near Tippery (Figure 6f), further emphasizing the differences between these nearby springs. Near Tippery also showed a more gradual recession in temperature response.

One additional difference between historic and recent temperatures was that summer temperatures were 1-2^{o}C warmer for all of the springs in both Juniata and Penns basins. This temperature increase was observed both in springs with seasonal temperature variation and with little seasonal variation. Because winter temperatures and rising temperatures during the spring season matched well for locations with seasonal response, the late spring and summer temperature increase relative to 1967-1968 was not related to differences in monitoring techniques or locations. The summer warming trend was extended over multiple years (2008-2016) at Smullton Sink (Figure 6h), so it was not an anomaly for just one year. The mean air temperature for Pennsylvania has risen 1^{o}C since the original study year [37]. One hypothesis is that there was an increase in precipitation in late spring and early summer which would increase discharge and transmit the higher recharge temperature signal with more efficiency over part of the year. Modeling of temperature pulses in karst has shown that increased velocity and recharge lead to less damping of the input temperature signal [38-40]. Covington et al. [41] reported that the large influx of snowmelt (increase in discharge) created the largest observed temperature deviation (4^{o}C) at Tyson's Spring Cave in Minnesota across 15 months. Thus, low infiltration in the winter at these springs could have led to constant temperature compared to the historic monitoring period, while spring and summer rains increased discharge and led to less damping of the input signal and higher overall temperatures. Further evidence to support the transmission of higher temperatures during rain events appeared in the records for Tippery and Near Tippery, which showed lower overall temperatures in 2016 which had much lower annual precipitation (68 cm) and higher overall temperatures in 2017, which had higher precipitation (98 cm as of Nov 2017) (Figure 6e-f). However, at Smullton there was not a decrease in temperature in 2016; it may be that the higher discharge and faster flow paths at Smullton swamped the effects of annual variations in precipitation.

3.2 Changes in Mg/Ca Ratio and CO_2 During Storms

Variations in Mg/Ca ratios and CO_2 concentrations were observed during storm events at five of the springs monitored using ISCO-collected water samples. Three of these sampled springs showed seasonal variations in temperature while two had steady temperature signals. Mg/Ca ratio should decrease during storm events when rapidly flushing water with a lower ratio reaches the spring. CO_2 concentrations should decrease when direct, rapid infiltration occurs, but increase when recharge from soil water with high CO_2 concentrations reaches the spring or when concentrations recover to pre-storm levels. Comparing changes in these patterns can indicate the timing of different flow paths and recharge inputs across an event.

Weaver Spring (which had no seasonal temperature variation) showed a similar timing and response in Mg/Ca ratios and CO_2 concentrations. There was a sharp decline 0.5 to 1 day after the storm peak and a relatively rapid recovery (Figure 7). The same pattern was seen for a large storm and for small storms, although only the recession was captured for the large storm. The storm on 6/23/17 did not follow this pattern, but it was a small storm following a rain event two days earlier, and the discharge pattern differed from the other storms in that there was no recession. For this storm, the water level rose and remained high for 2 days, and the Mg/Ca ratios and CO_2 concentrations were variable across this time period.

At Springhouse Spring (which also had no seasonal temperature variation), the Mg/Ca variation was close to the detection limit and on the order of pre-storm variability (Figure 8). A period of non-storm data was included for comparison. This spring showed only a small water level rise (1-2 cm) for storm events. Neither the CO_2 concentration nor Mg/Ca ratio showed any pattern on the rising or falling limbs.

At Smullton Sink (which had seasonal temperature variation), five storm events including a double peak storm showed the Mg/Ca ratio began decreasing close to the peak and reached a low point about one half day later (Figure 9). For the double-peaked storm the Mg/Ca decrease began sooner suggesting the system was already flushed. For two storms where CO_2 was monitored, the CO_2 concentration also decreased after the peak, but more gradually than the Mg/Ca ratio, and did not recover to original CO_2 concentrations during the 3-4 days of recession monitoring. The change in Mg/Ca ratio was almost below detection for the smallest storm and larger for larger storms, but the CO_2 concentration change was not dependent on the size of the storm.

Tippery and Near Tippery Springs (which both had seasonal temperature variation) showed more complex stormwater response than the other springs. Three storms were sampled at both springs under wet and dry antecedent conditions (Figures 10-11). At both springs the Mg/Ca ratio tended to vary together with CO_2 concentration on the rising limb of the storm and deviated from each other on the falling limb of the storms. A double peak in the water level rise for a single sampling event did not change the trends on the recession, indicating that system flushing had occurred. The June storm was the most intense and had the largest variability (i.e., change in CO_2 concentration and Mg/Ca ratio over the course of the storm). At both sites chemograph variation and overall CO_2 concentration was lower for the May storm, which occurred a day after a previous storm. There was a large initial Mg/Ca peak in the May storm for the first sample on the rising limb at Tippery. This peak could represent flushing out of old water, but it is somewhat surprising given the previous storm which should have flushed out old, high Mg/Ca water. This peak was not observed for the June and July storms with dry antecedent conditions. Such variability may depend on the timing of the first sample collected which is difficult to control using a water level sensor for a trigger. Depending on the initial water level, sometimes the first sample can catch the beginning flush of low CO_2, low Mg/Ca stormwater and sometimes it is later. There was also a sharp increase in CO_2 concentration for the May storm at the peak of the hydrograph at Tippery. The May and July storms had similar intensities. The May storm occurred under wet antecedent conditions and the July storm under dry antecedent conditions, but the change in CO_2 concentrations were similar. The July storm showed less variability for the first storm pulse and a delayed drop in CO_2 concentration at Tippery Spring. The two springs showed more variability than the other springs during the storm hydrographs, but the patterns differed between the springs, with falling concentration occurring at one spring where rising concentrations occurred at the other. The variation in timing suggests differing flow path lengths for these two springs.

The patterns in these chemographs provided additional information about flow paths and recharge to suggest additional classifications of spring response. Weaver and Springhouse Springs were both originally classified as diffuse-flow dominated based on lack of seasonal temperature variations, higher concentrations of ions, and higher saturation indices with respect to calcite. Weaver was considered a mixed case because of slight variations in concentration seasonally. The behavior based on the chemographs differed in that Weaver showed variations in flow path contribution over the course of a storm. Because CO_2 concentrations and Mg/Ca values tracked together as they decreased and increased, Weaver showed evidence of fast flow from concentrated recharge leading to storm water dilution arriving at the spring early followed by a recovery to pre-storm values. Springhouse did not produce regular patterns in either Mg/Ca or CO_2, indicating the slow flow paths described by Shuster and White may be appropriate here. Springhouse also has smaller discharge and thus captures water from a smaller area.

Smullton, Tippery, and Near Tippery were originally classified as conduit-flow dominated based on seasonal temperature variations and lower concentrations of ions. Their chemographs differed from each other in that Smullton showed a regular pattern from storm to storm, but Tippery and Near Tippery varied from storm to storm and had more complex patterns of rising and falling concentrations within storms. Smullton showed an initial drop in Mg/Ca close to coincident with storm peak while CO_2 concentrations were high at the beginning of storms and decreased through a longer portion of the recession. This indicated combined recharge and flow paths effects appeared at the spring. Smullton has larger discharge than the Tippery and Near Tippery Springs. All three springs showed more variation in Mg/Ca ratios and CO_2 concentrations than did Weaver Spring, suggesting more complex flow patterns, in particular for Tippery and Near Tippery.

The differences in the chemographs at these springs point to variations in both source area and flow paths at different times (Figure 12). For Springhouse Spring, there was little variation over time. For Weaver, there was early dilution in both Mg/Ca ratios and CO_2 concentrations followed by increases, suggesting dilution from fast flow and recovery to pre-storm values later in the storm. At Smullton, the Mg/Ca ratios and CO_2 concentrations did not vary together, and soil water gas in the recharge area might have appeared early on in storms while later flow showed a decreasing CO_2 concentration from dilution. At Tippery and Near Tippery Springs there was variation in timing of the Mg/Ca ratios and CO_2 concentrations on the rising and falling limbs of the storm. On the rising limb, high Mg/Ca ratios and CO_2 concentrations suggested a nearby flow path that encountered soil gas or older water with higher CO_2 concentrations. Next the Mg/Ca ratio decreased while still maintaining higher CO_2 concentrations. Finally, higher Mg/Ca ratio without high CO_2 concentrations could indicate a more distant flow path. The complexity in flow paths at Tippery and Near Tippery Springs also was apparent in variations from storm to storm as different recharge areas contributed to discharge.

3.3 REE Concentrations

Rare earth elements (REEs) have not typically been used to classify karst springs, but provide an additional method of characterization of source areas or alteration along flow paths. REE concentrations are plotted together to show anomalies where one element is higher or lower than the other elements, indicating a positive or negative anomaly, respectively. Two REE anomalies associated with rock types and redox conditions along flow paths were observed in the seven springs analyzed: a negative cerium (Ce) anomaly and a negative europium (Eu) anomaly

A negative Ce anomaly was observed at Near Tippery, Weaver, and Springhouse (Figure 13a). This anomaly is associated with marine carbonates [42], so it can indicate contribution from matrix flow paths that would reflect more dissolution. In contrast, the Ce anomaly was weak at Birmingham Cave, Tippery, and Smullton (Figure 13b). Tippery and Near Tippery Springs once again showed distinct geochemical signatures from each other. Near Tippery likely receives more recharge from dolomite units than Tippery Spring, but Birmingham Cave Spring also discharges from a dolomite unit and did not have the Ce anomaly, so the signature was not linked to the rock type. The Ce anomaly was not associated with the classification based on temperature signatures either. One spring with seasonal variation in temperature had a Ce anomaly (Near Tippery), and one spring with no seasonal variation and no storm response had only a weak Ce anomaly (Birmingham Cave).

A slight decrease in Eu was also observed at two of the springs, Birmingham Cave and Springhouse. Both are springs with no seasonal temperature variation, but Weaver Spring did not have a negative Eu anomaly although it too was classified as having no seasonal temperature variation. Because Birmingham Cave and Springhouse exhibited differing Ce anomalies, the Eu signature was indicative of some other change along the flow path, possibly related to redox conditions since Eu is redox sensitive. A negative Eu anomaly has also been associated with shale signatures, so it could indicate recharge waters with more contact with soil.

Thus, the REE elements point out differences in flow contributions that are not marked by temperature variations or Mg/Ca patterns in storms. The Ce anomaly suggested differences in portion of matrix contributions and the Eu anomaly suggested differences in soil or redox conditions in the recharge area. These differences suggest that the portion of fast and slow flow paths is complex and varies among the different springs within the temperature groupings.

4. Conclusions

The classification proposed by Shuster and White [1] described two end members, conduit and diffuse flow springs, but was not intended to provide just two distinct categories for all springs. They recognized that there was a continuum between conduit and diffuse flow paths, but more data were needed to fully describe this continuum.

Additional monitoring methods have provided signatures to distinguish flow patterns and contributions from different recharge sources during rain events. A number of monitoring techniques are available now that were not available in the late 1960's, including high-frequency loggers and automatic samplers. These techniques in particular better characterize storm events, but additional chemical analyses such as REEs also characterize non-storm periods.

Based on the original end member classification, the seven springs in this study fell into two groups. Smullton, Tippery, Near Tippery and Arch Springs showed a higher component of conduit flow based on seasonal temperature response and lower ion concentrations. Weaver, Springhouse, and Birmingham Cave Springs showed a lower component of conduit flow based on lack of seasonal temperature response and higher ion concentrations. Additional data from continuous temperature monitoring created more gradations in this grouping, with Near Tippery Spring showing slightly less frequent stormwater response than Smullton, Tippery, and Arch Springs. At the other end, among the springs with less conduit flow contribution, Weaver Spring showed stormwater response overlain on the steady temperature pattern, while Springhouse and Birmingham Cave Springs did not, suggesting a gradation along this spectrum. Detailed sampling during storm events for five of the springs showed a different pattern among the springs. Tippery and Near Tippery Springs showed the greatest complexity in flow components, with variation both within and between storms and differing patterns for Mg/Ca ratios and CO_2 concentrations. Smullton and Weaver Springs tended to show a single decline in Mg/Ca ratio and CO_2 concentration, although Mg/Ca and CO_2 varied together at Weaver, but at different times at Smullton. Springhouse fell at the other end of the spectrum with low variation during storms, similar to variation observed during non-storm periods. REE concentrations measured during baseflow also showed significant variation from spring to spring. The Ce anomaly observed suggested less matrix interaction for Birmingham Cave, Tippery and Smullton Springs, and more matrix interaction for Near Tippery, Weaver, and Springhouse Springs. This pattern contrasted with the other measures of matrix interaction and may indicate variations in proportions of water-rock interactions or contrasts in the recharge area.

This study pointed out the importance of collecting data both before and during storm events to better characterize flow patterns. High-frequency data are an important component of such data collection efforts. If samples are collected at just one point in a storm, transport behavior may be misinterpreted because the storm signature is variable at most springs. This study showed that concentrations and source areas can potentially vary greatly depending on when the sample is collected. It can also be difficult to obtain samples across key parts of the storm because (a) changes can occur abruptly and (b) timing sample collection to observe such changes is challenging. Understanding the timing of different components is critical to understanding how to protect karst springs.

This study showed that classification of karst springs can vary depending on the component monitored (Figure 14). A classification scheme for karst waters may not be a continuum, but rather intersecting features that can form a mélange. This variation further points out that karst flow paths create a mixture of signals and that multiple methods and long-term monitoring are needed to interpret karst spring discharge.

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References

[1] Shuster ET, White WB (1971) Seasonal fluctuations in the chemistry of limestone springs: A possible means for characterizing carbonate aquifers. Journal of Hydrology 14: 93–128

[2] White WB (2002) Karst hydrology: Recent developments and open questions. Engineering Geology 65(2-3): 85-105

[3] Perrin J, Jeannin PY, Zwahlen F (2003) Epikarst storage in a karst aquifer: a conceptual model based on isotope data, Milandre test site, Switzerland. Journal of Hydrology 279(1-4): 106-124

[4] Aquilina L, Ladouche B, Dorfliger N (2006) Water storage and transport in the epikarst of karstic systems during high flow periods. Journal of Hydrology 327(3-4): 472-485

[5] Williams, P (2008) The role of the epikarst in karst and cave hydrogeology: a review. International Journal of Speleology 37(1): 1-10

[6] Hartmann A, Barberá JA, Lange J, Andreo B, Weiler M (2013) Progress in the hydrologic simulation of time variant recharge areas of karst systems–exemplified at a karst spring in Southern Spain. Advances in Water Resources 54: 149-160

[7] Hartmann A, Gleeson T, Wada Y, Wagener T (2017) Enhanced groundwater recharge rates and altered recharge sensitivity to climate variability through subsurface heterogeneity. PNAS 114(11): 2842-2847. doi:10.1073/pnas.1614941114

[8] Hartmann A, Baker A (2017) Modelling karst vadose zone hydrology and its relevance for paleoclimate reconstruction. Earth-Science Reviews 172: 178-192

[9] Ravbar N, Engelhardt I, Goldscheider N (2011) Anomalous behaviour of specific electrical conductivity at a karst spring induced by variable catchment boundaries: the case of the Podstenjšek spring, Slovenia. Hydrological Processes 25(13): 2130-2140

[10] Luhmann AJ, Covington MC, Peters AJ, Alexander SC, Anger CT, Green JA, Runkel AC, Alexander EC Jr. (2011) Classification of thermal patterns at karst springs and cave streams. Ground Water 49(3): 324–335

[11] Bailly-Comte V, Martin JB, Screaton EJ (2011) Time variant cross correlation to assess residence time of water and implication for hydraulics of a sink-rise karst system. Water Resources Research 47(5): W05547

[12] Dreiss SJ (1989) Regional scale transport in a karst aquifer. 1. Component separation of spring flow hydrographs. Water Resources Research 25: 117-125

[13] Liu Z, Groves C, Yuan D, Meiman J (2004) South China karst aquifer storm-scale hydrochemistry. Ground Water 42(4): 491-499

[14] Lakey B, Krothe NC (1996) Stable isotopic variation of storm discharge from a perennial karst spring. Water Resources Research 32: 721-731

[15] Fredrickson GC, Criss RE (1999) Isotope hydrology and residence times of the unimpounded Meramec River Basin, Missouri. Chemical Geology 157: 303-317

[16] Lee ES, Krothe NC (2001) A four-component mixing model for water in a karst terrain in south-central Indiana, USA; using solute concentration and stable isotopes as tracers. Chemical Geology 179(1-4): 129-143

[17] Jacobson RL, Langmuir D (1974) Controls on the quality variations of some carbonate spring waters. Journal of Hydrology 23: 247-265

[18] Toran L, Roman E (2006) Outgassing in a combined fracture and conduit karst aquifer near Lititz Spring, Pennsylvania. Geological Society of America Special Paper 404(23): 275-282

[19] Vesper DJ, White WB (2004), Storm pulse chemographs of saturation index and carbon dioxide pressure: Implications for shifting recharge sources during storm events in the karst aquifer at Fort Campbell, Kentucky/Tennessee, USA. Hydrogeology Journal 12:135-143

[20] Hilberg S, Brandstätter J, Glück D (2013) CO_2 partial pressure and calcite saturation in springs-useful data to identify recharge catchments in alpine hydrogeology. Environmental Science: Processes and Impacts 15(4): 823-832. doi:10.1039/C3EM30973H

[21] Peyraube N, Lastennet R, Denis A (2012) Geochemical evolution of groundwater in the unsaturated zone of a karstic massif, using the P_{CO2}-SI_C relationship. Journal of Hydrology 430-431: 13-24. doi.org/10.1016/j.jhydrol.2012.01.033

[22] Gulley J, Martin J, Moore P (2014) Vadose CO_2 gas drives dissolution at water tables in eogenetic karst aquifers more than mixing dissolution. Earth Surf Process Landforms 39: 1833–1846

[23] Musgrove M, Banner J (2004) Controls on the spatial and temporal variability of vadose dripwater geochemistry: Edwards Aquifer, central Texas. Geochimica et Cosmochimica Acta 68(5): 1007-1020

[24] Barbieri M, Boschetti T, Petitta MO, Tallini M (2005) Stable isotope (^{2}H, ^{18}O and $^{87}Sr/^{86}Sr$) and hydrochemistry monitoring for groundwater hydrodynamics analysis in a karst aquifer (Gran Sasso, Central Italy). Applied Geochemistry 20: 2063-2081

[25] Tatar E, Mihuca VG, Zambo L, Gasparics T, Zaray G (2004). Seasonal changes of fulvic acid, Ca and Mg concentrations of water samples collected above and in the Beke Cave of the Aggtelek karst system (Hungary). Applied Geochemistry 19(11): 1727-1733

[26] Caetano Bicalho C, Batiot-Guilhe C, Seidel JL, Van Exte S, Jourde H (2012) Geochemical evidence of water source characterization and hydrodynamic responses in a karst aquifer. Journal of Hydrology 450: 206-218

[27] Toran L, Reisch CE (2013) Using stormwater hysteresis to characterize karst spring discharge. Ground Water 51(4): 575-587

[28] Banner JL, Hanson GN, Meyers WJ (1988) Rare earth element and Nd isotopic variation in regionally extensive dolomites from the Burlington Keokuk Formation (Mississippian); implications for REE mobility during carbonate diagenesis. Journal of Sedimentary Petrology 58(3): 415-432

[29] Johannesson KH, Xiaoping Z (1997) Geochemistry of the rare earth elements in natural terrestrial waters: a review of what is currently known. Chinese Journal of Geochemistry 16(1): 20-42

[30] Tang J, Johannesson KH (2005) Rare earth element concentrations, speciation, and fractionation along groundwater flow paths: the Carrizo Sand (Texas) and Upper Floridan aquifers. In: Johannesson KH (ed) Rare Earth Elements in Groundwater Flow Systems, Springer, Netherlands, p 223-251

[31] Johannesson KH, Stetzenbach KJ, Hodge VF (1997) Rare earth elements as geochemical tracers of regional groundwater mixing. Geochimica et Cosmochimica Acta 61(17): 3605-3618

[32] Tarbert JA, Vesper DJ (2010) A preliminary evaluation of rare earth elements in karst spring water and their potential as indicators of water source. Presented at the Geological Society of America Northeastern and Southeastern Section Joint Meeting, 13-16 March, 2010, Abstracts with Programs 42(1): 192

[33] Herman EK, Toran L, White WB (2008) Threshold events in spring discharge: Evidence from sediment and continuous water level measurement. Journal of Hydrology 351(1–2): 98-106. doi:10.1016/j.jhydrol.2007.12.001.

[34] Barna JM (2017) Mg/Ca and P_{CO2} storm hysteresis as an indicator of flowpaths and recharge sources at two karst springs in Central Pennsylvania. Senior Honors Thesis, Bucknell University.

[35] Parkhurst, D L, Appelo, CAJ (1999) User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US Geological Survey Water Resources Investigation 99-4259

[36] Piper, DZ, Bau, M (2013) Normalized rare earth elements in water, sediments, and wine: identifying sources and environmental redox conditions. American Journal of Analytical Chemistry, 4(10): 69.

[37] National Oceanic and Atmospheric Administration (2017) https://www.ncdc.noaa.gov/temp-and-precip/state-temps/. Accessed September 2017

[38] Luhmann AJ, Covington MD, Myre JM, Perne M, Jones SW, Alexander EC Jr, Saar MO (2015) Thermal damping and retardation in karst conduits. Hydrology and Earth System Sciences 19(1): 137-157

[39] Brookfield AE, Macpherson GL, Covington MD (2017) Effects of changing meteoric precipitation patterns on groundwater temperature in karst environments. Ground Water 55(2): 227-236

[40] Burns ER, Zhu Y, Zhan H, Manga M, Williams CF, Ingebritsen SE, Dunham JB (2017) Thermal effect of climate change on groundwater-fed ecosystems. Water Resources Research 53: 3341–3351. doi:10.1002/2016WR020007

[41] Covington MD, Luhmann AJ, Gabrovšek F, Saar MO, Wicks CM (2011) Mechanisms of heat exchange between water and rock in karst conduits. Water Resources Research 47(10): *W10514.* doi: 10.1029/2011WR010683

[42] Henderson P (1984). Rare earth element geochemistry (Developments in geochemistry 2). Elsevier, Amsterdam

Table 1: Description of Shuster and White (S&W) springs revisited in this study. In column “S&W Class,” D indicates diffuse-dominated flow and C indicates conduit-dominated flow.

Spring Name	**S&W Class**	**Size l/s**	**Size cfs**	**Storm Sampling**
Juniata Basin				
Birmingham Cave	D	0.085 – 0.26	0.003-0.009	
Tippery	C	28 – 230	1-8	X
Near Tippery	C	28 – 110	1-4	X
Arch	C	280 – 11000	10-400	
Penns Basin				
Springhouse	D	14 – 85	0.5-3	X
Weaver	D	85 – 340	3-12	X
Elk Creek Rise/Smullton Sink	C	Elk: 140 - 5700	Elk: 5-200	X

Figures

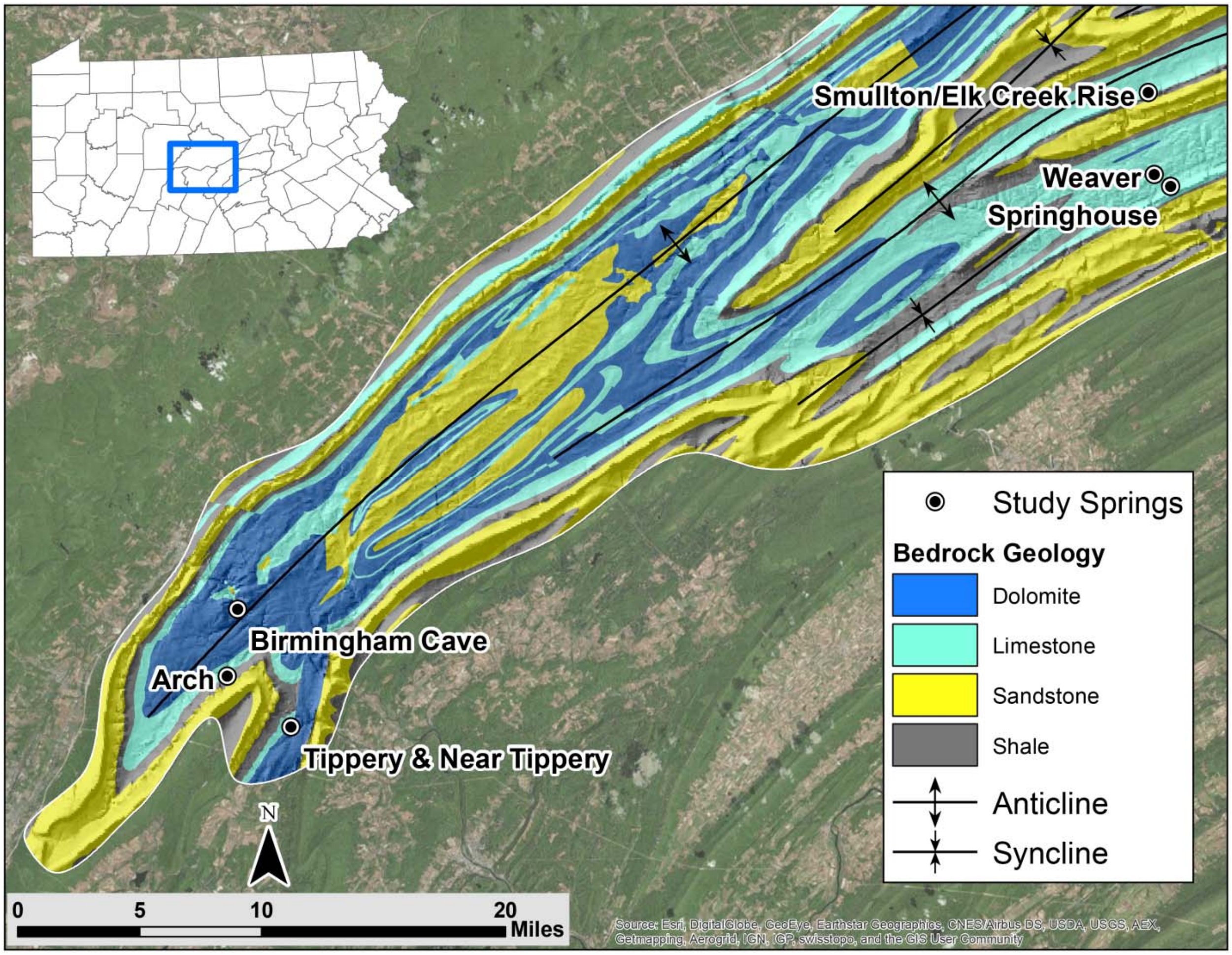

Figure 1: Seven springs from Shuster and White [1] revisited in this study. The original set included 14 springs. Geologic structure overlain on aerial photograph of the study area. Location map for the state of Pennsylvania U.S.A. shown as inset.

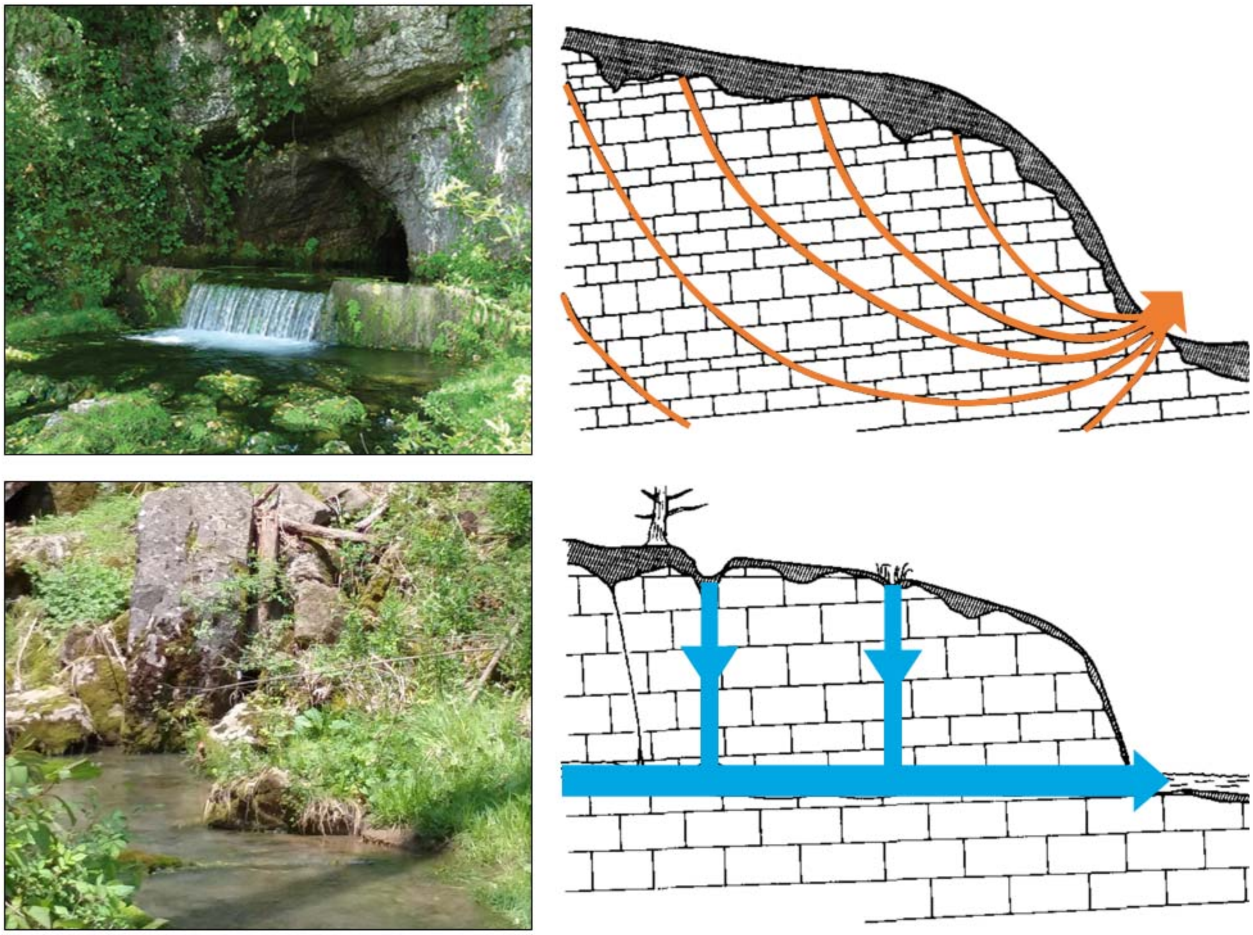

Figure 2: The classification system proposed by Shuster and White [1] contrasted diffuse flow paths with water primarily flowing through the rock matrix and conduit flow paths with water primarily flowing through larger openings in the rock, although the system recognized a continuum between these end members. The authors found that the discharge point of the springs did not provide a visual cue to the spring network. Weaver Spring (top) had characteristics of diffuse flow and an open conduit at the discharge point. Tippery Spring (bottom) discharged from a fracture network, but showed characteristics of conduit flow. Discharge diagram after Shuster and White [1].

Figure 3: Example of loggers used in recent monitoring. (A) Multiport logger with pH, conductivity, temperature, and water level sensors. (B) Temperature logger attached to a stake. (C) Data download.

Figure 4: Automatic ISCO stormwater sampler with 24 one-liter bottles used to collected stormwater discharge at the springs. Inset shows water level trigger and pump tubing intake.

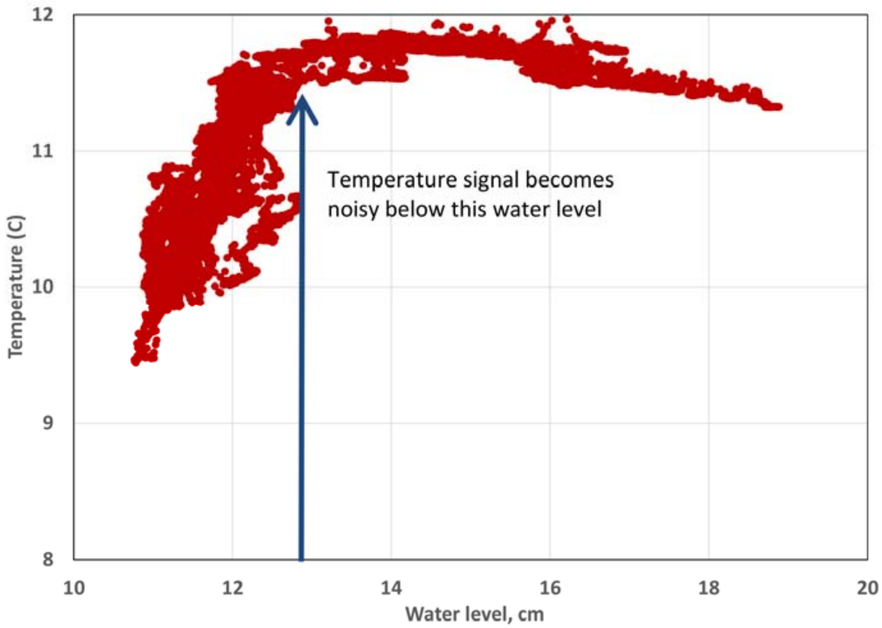

Figure 5: For springs with little seasonal change, water depth affected the temperature logger signal. The water level versus temperature plot at Springhouse showed the depth when the signal was stable (above 12.4 cm) and when the signal was noisy (below 12.4 cm). When the water was shallow in cold months, water temperature was affected by air temperature and the data became noisy. However, the upper end of the temperature signal matched the baseflow spring temperature.

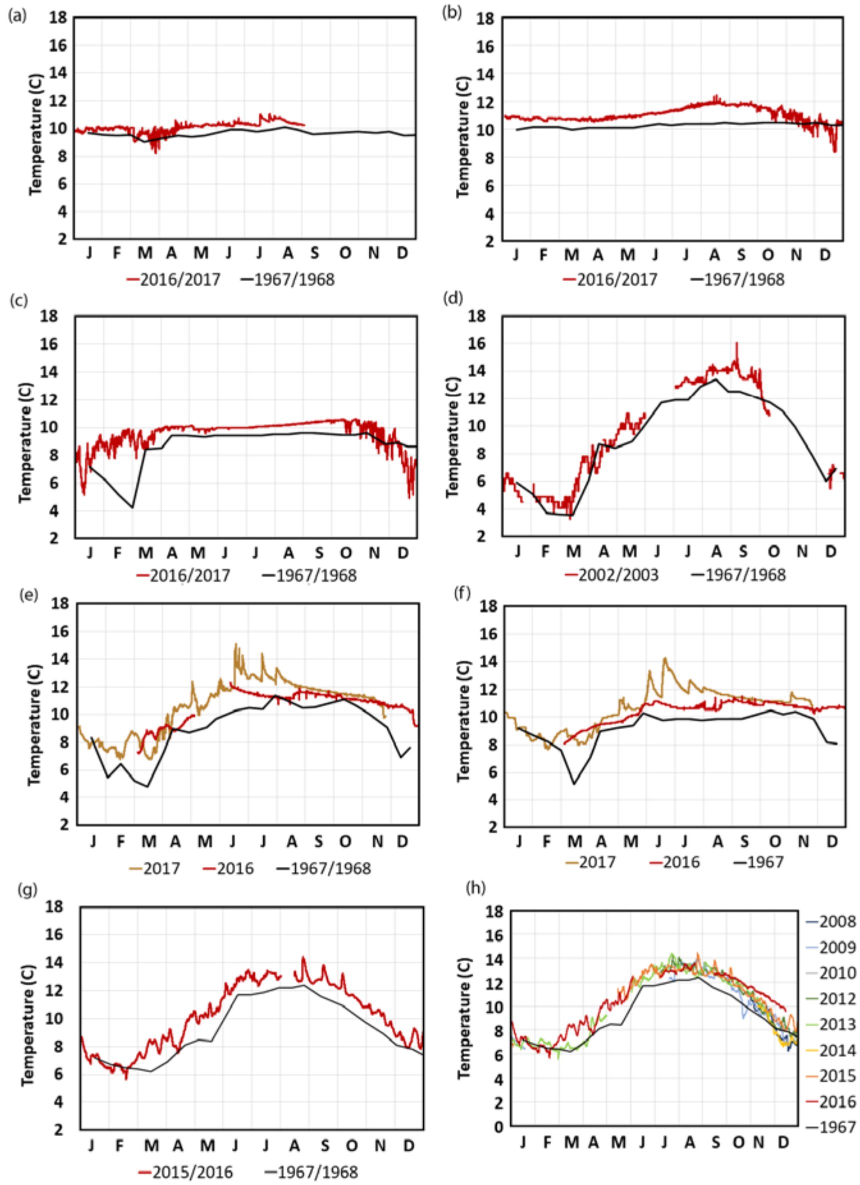

Figure 6: Temperature from 15-min logger data in 2016/2017 compared to historic temperatures measured twice a month in 1967/1968 as reported in Shuster and White [1]. For (a) Weaver Spring, (b) Springhouse Spring and (c) Birmingham Cave Spring the temperatures are primarily steady, indicating a thermally effective spring. Springhouse Spring showed a slightly delayed season response and Weaver Spring showed some storm response in the high resolution data, and all three of these springs showed noisy data in cold months. At (d) Arch Spring, (e) Tippery Spring, (f) Near Tippery Spring and (g) Smullton Sink the high resolution data showed that the seasonal response was overlain by storm responses, indicating a thermally ineffective spring with rapid recharge. At Tippery and Near Tippery there was less frequent storm response in 2016 which was a drier year than 2017 and the storm response at Near Tippery was less frequent and with longer recessions that at Tippery. (h) Smullton Sink response for 2008-2016 (partial and complete) showed that the higher summer temperatures relative to historic temperatures occurred in multiple years, and was not a deviation for a single annual cycle.

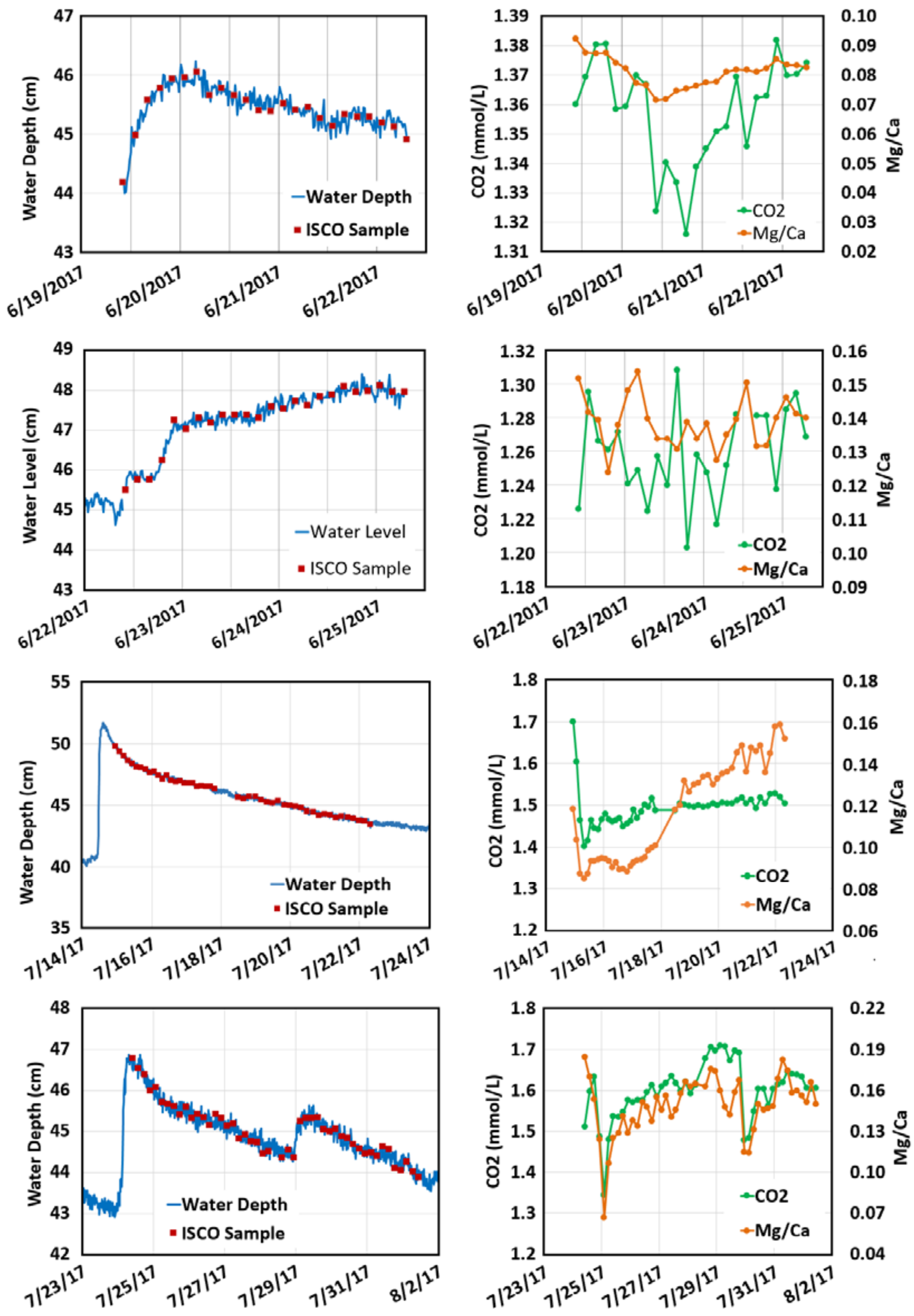

Figure 7: Chemographs of CO_2 concentration and Mg/Ca ratio for storms at Weaver Spring. Similar decline and recovery was observed for both except for the storm starting on 6/20/17 with no recession.

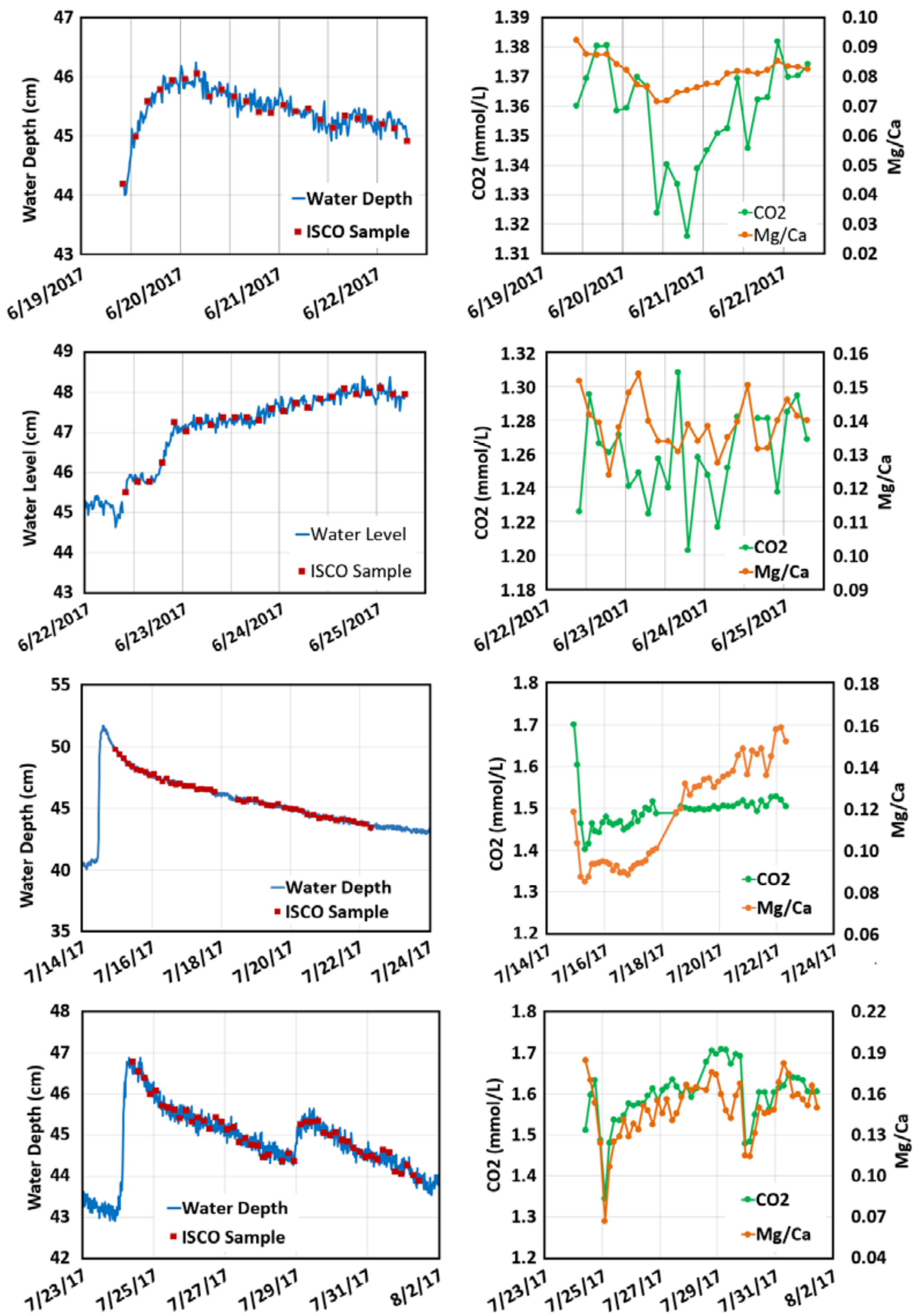

Figure 8: Chemographs of CO_2 concentration and Mg/Ca ratio for storms at Springhouse Spring. The decline in Mg/Ca ratio around the detection limit as shown in the non-storm data for July 2017. The storm on 5/28/17 showed a decline in CO_2 concentration on the recession, but this was not observed in other storms. Most storms showed slight concentrations changes across the storm event, and no alignment of CO_2 concentration and Mg/Ca ratio.

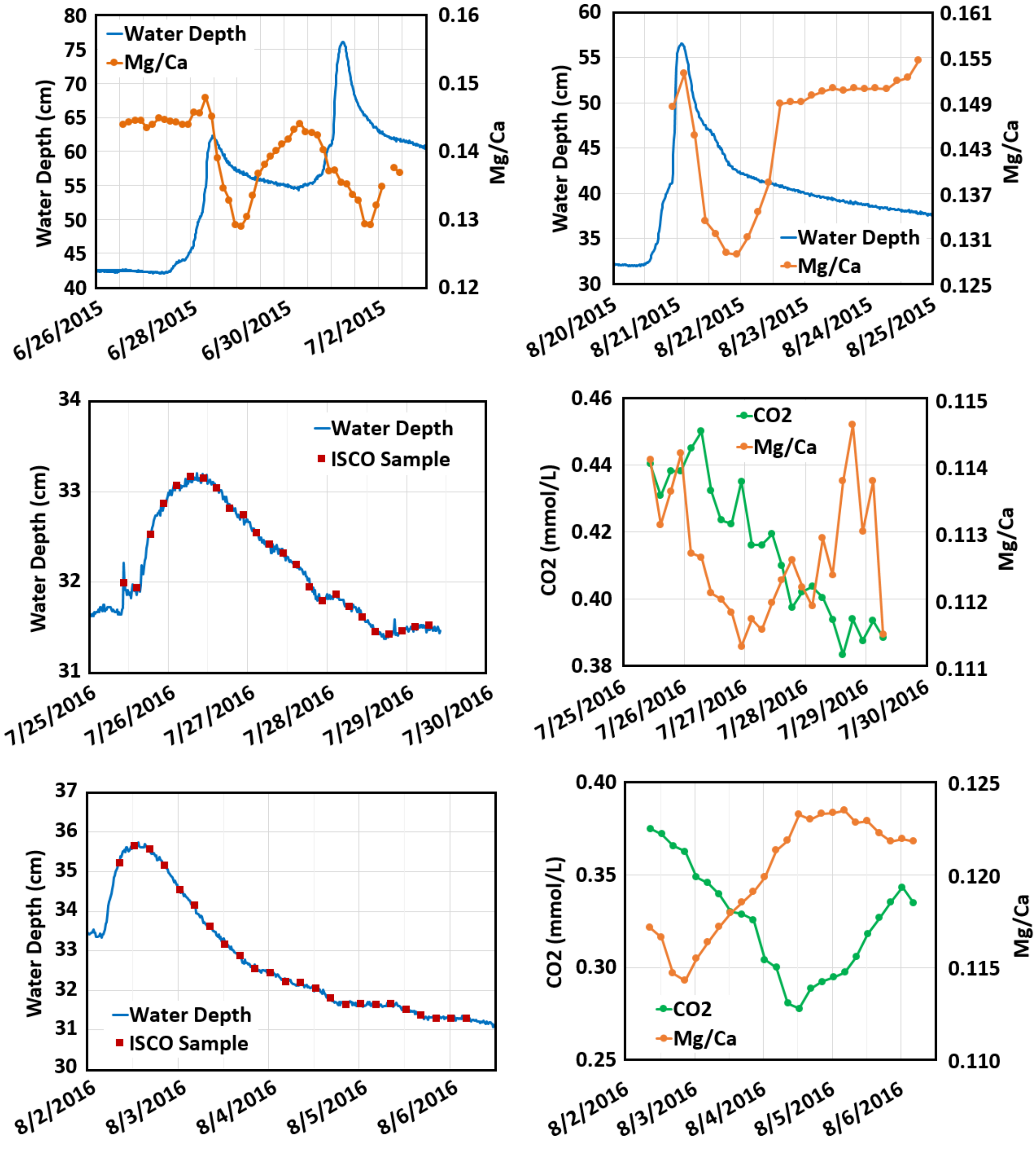

Figure 9: Chemographs of CO_2 concentration and Mg/Ca ratio for storms at Smullton Sink. Only Mg/Ca ratio data were available for storms in 2015. There was a decline in Mg/Ca ratio 0.5 to 1 day after the storm peak, even for the back to back storms on 6/28/15 and 7/1/15. The CO_2 concentrations recorded in the 2016 storms also declined in the storm recession, but more gradually than the Mg/Ca ratio. The patterns were repeated for both small and large storms even when the Mg/Ca ratio decline was close to the detection limit.

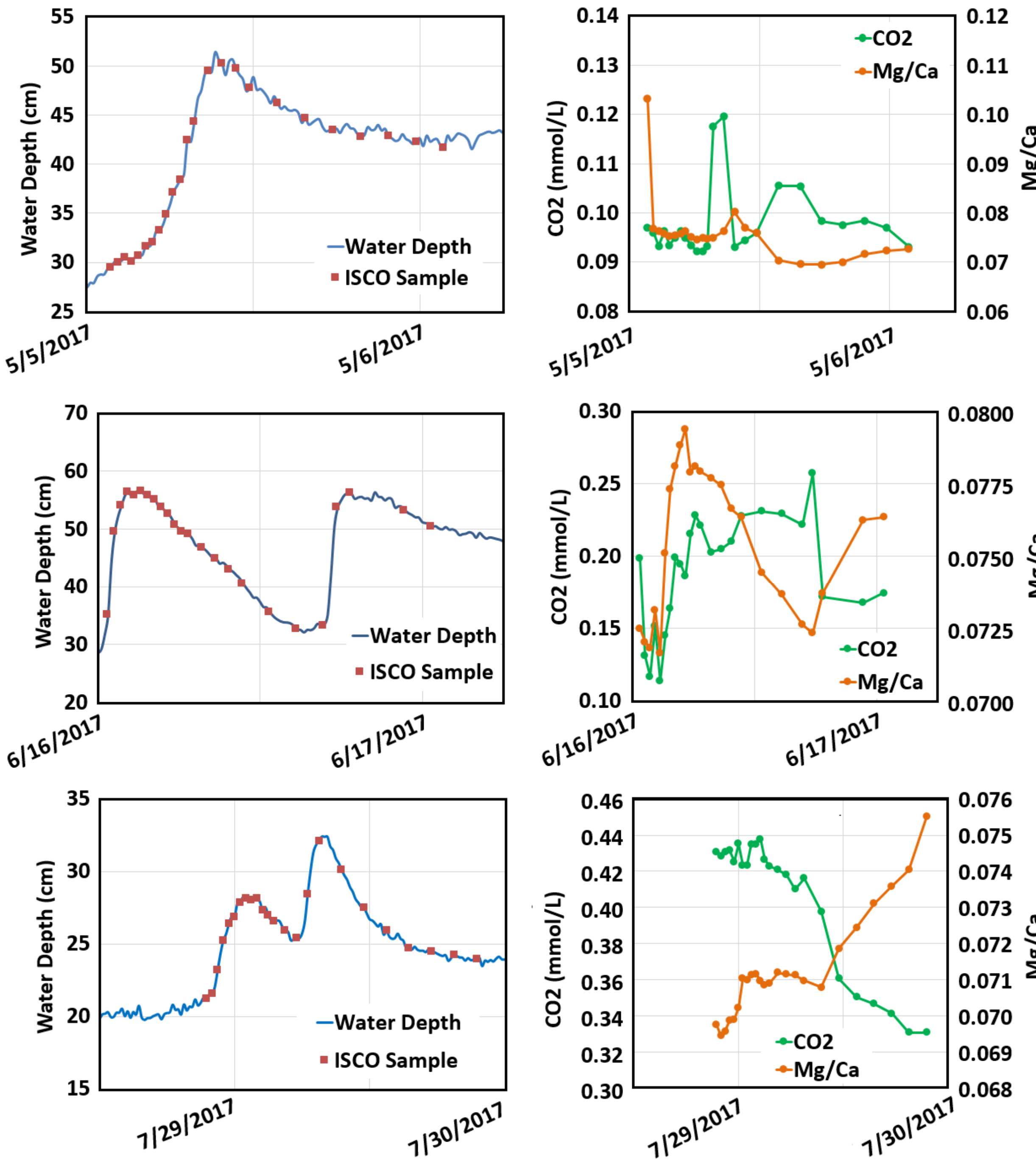

Figure 10: Chemographs of CO_2 concentration and Mg/Ca ratio for storms at Tippery Spring. On the rising limb the CO_2 concentration and Mg/Ca ratio tended to decrease and increase together, but on the recession the CO_2 concentration increased when the Mg/Ca ratio decreased.

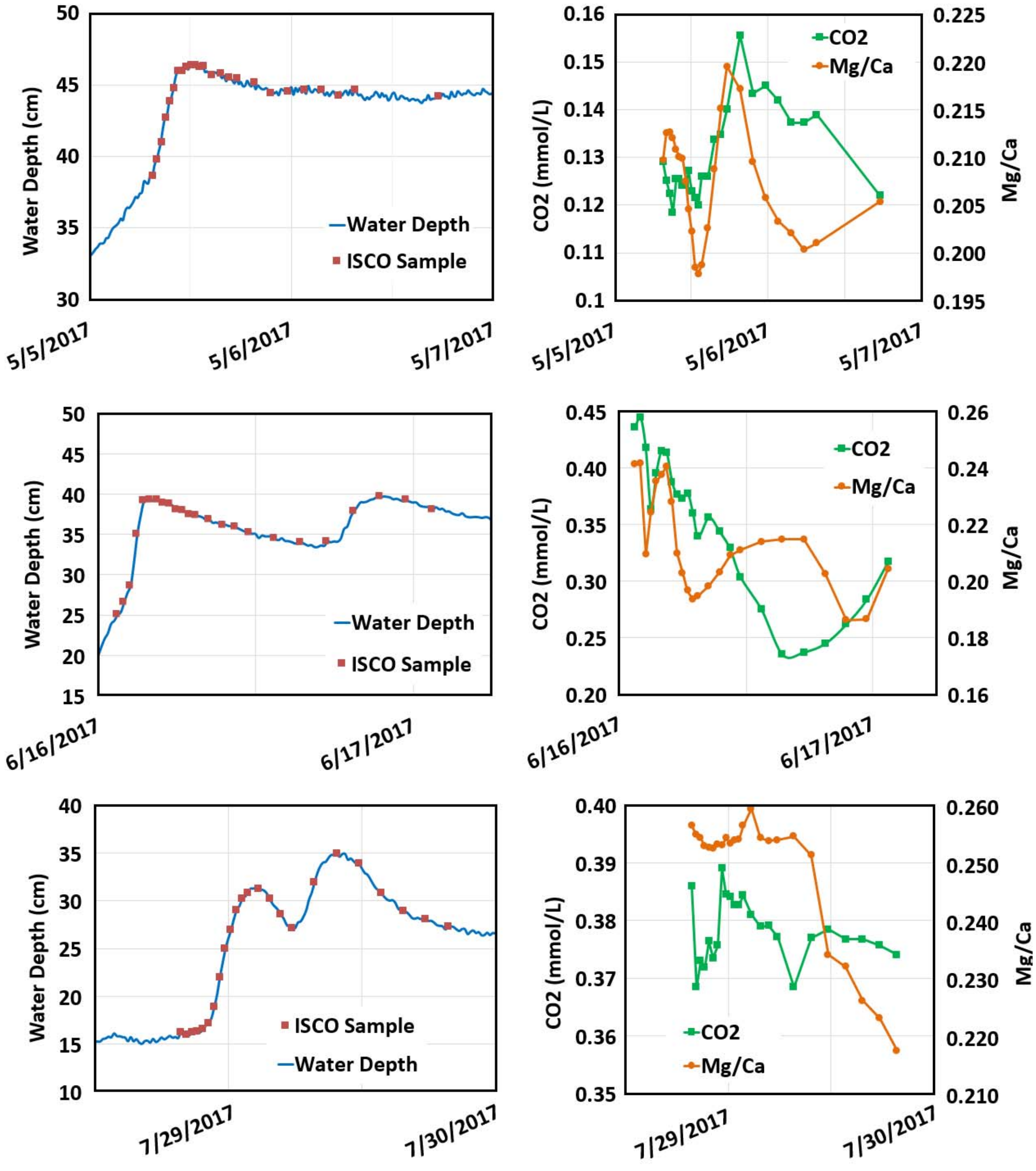

Figure 11: Chemographs for CO_2 concentration and Mg/Ca ratio for storms at Near Tippery Spring. On the rising limb the CO_2 concentration and Mg/Ca ratio tended to decrease and increase together, but on the recession the CO_2 concentration increased when the Mg/Ca ratio decreased.

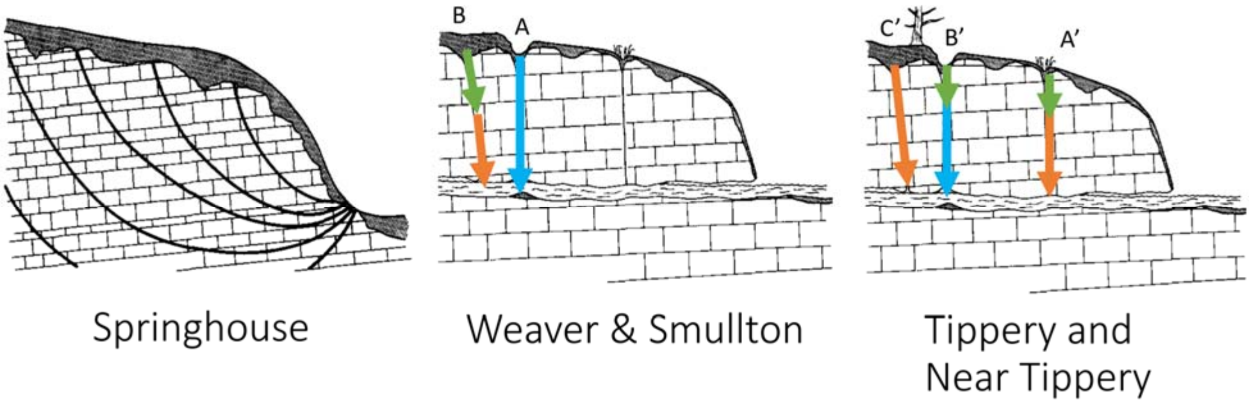

Figure 12: Schematic explaining three different patterns in storm sample chemographs from the five springs. (Flow diagram after Shuster and White [1]). Orange arrows represent sources with high Mg/Ca ratio, green arrows represent sources with high CO_2 concentration, and blue arrows represent dilution. Springhouse Spring showed no distinct pattern in the chemograph during storms, indicating diffuse flow paths as originally proposed by Shuster and White. Smullton Sink and Weaver Spring showed a decrease in the Mg/Ca ratio and CO_2 concentrations due to A: dilute stormwater at the beginning of recession. This was followed by B: an increase in the Mg/Ca ratio and CO_2 concentrations due to recharge of high CO_2 soil water and slower flow paths during recovery. Tippery and Near Tippery Springs showed more complex patterns with A': an initial recharge of stormwater flushing soil gas and slower flow paths. Next there was B': continued high CO_2 soil water flushing with fast flow that decreased the Mg/Ca ratio. This was followed by C': a slower flow path that increased the Mg/Ca without high CO_2 soil water recharge.

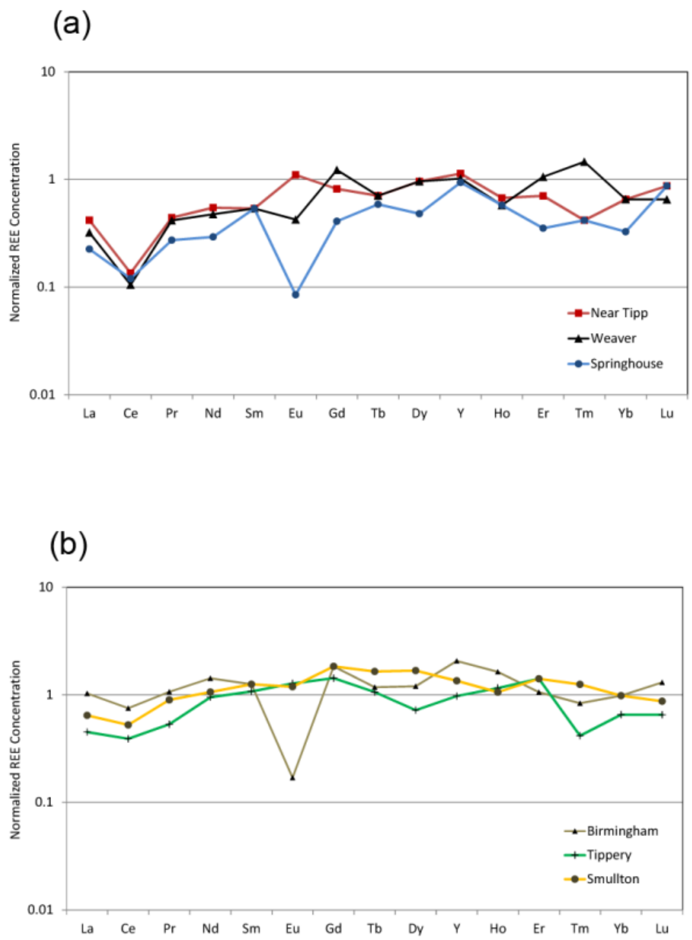

Figure 13 (a) Normalized REE concentrations showed a strong Ce anomaly for Near Tippery, Weaver, and Springhouse Springs. (b) Normalized REE concentrations showed a weak Ce anomaly for Tippery, Birmingham Cave, and Smullton Sink.

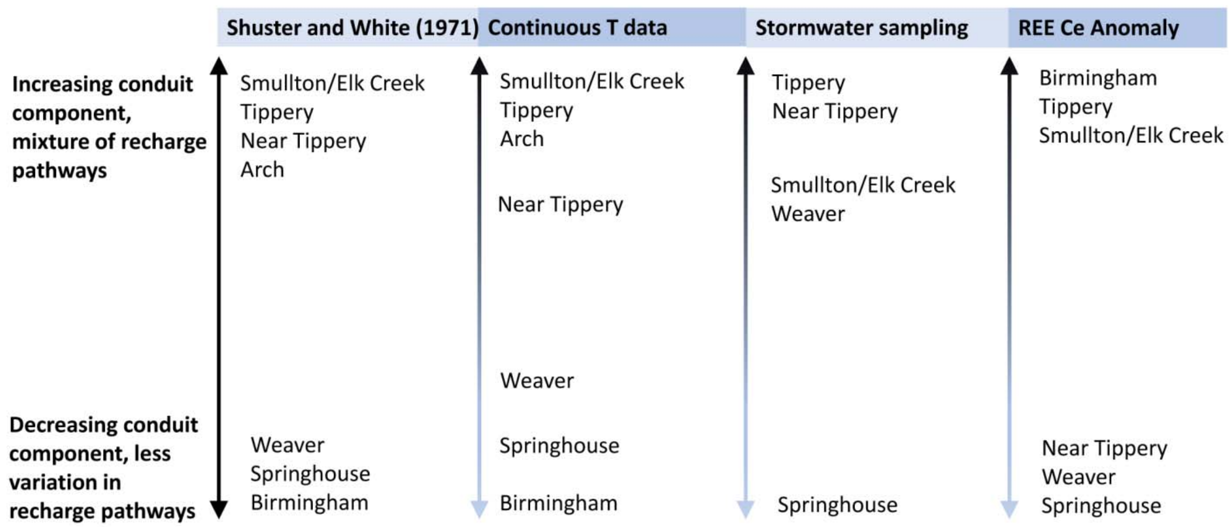

Figure 14: Alternate classifications systems for spring discharge. The older end member classification was based on data collected twice a month. With high resolution temperature data, more gradations can be seen in spring behavior; Near Tippery Spring had less prominent storm response than Arch and Smullton. Weaver, Springhouse, and Birmingham Cave Springs were distinguished by occasional storm response indicating some fast flow paths (Weaver) and a slight seasonal temperature response with a delay indicating less thermal equilibrium with the matrix (Springhouse). The stormwater sampling showed different distinctions between springs, with both Tippery and Near Tippery showing the most variation in pathways. Smullton Sink and Weaver Spring showed variation in CO_2 and Mg/Ca during storms, while Springhouse Spring did not have a regular variation in storm chemographs. The Ce anomaly grouped the springs differently, with Birmingham Cave, Near Tippery, and Smullton showing a weak Ce anomaly and Near Tippery, Weaver, and Springhouse Springs showing a strong Ce anomaly. Different groupings indicate that classification of karst springs can vary depending on the component monitored.